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# THEORETICAL AND EXPERIMENTAL STUDIES OF ESR SPIN HAMILTONIAN PARAMETERS OF TRANSITION METAL OXOHALO COMPLEXES

By

K. K. Sunil

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#### ABSTRACT

# THEORETICAL AND EXPERIMENTAL STUDIES OF ESR SPIN HAMILTONIAN PARAMETERS OF TRANSITION METAL OXOHALO COMPLEXES

By

#### K. K. Sunil

A detailed study of the electronic structure of a series of d<sup>1</sup> transition metal oxohalo complexes  $[MOX_n]^{m-}$ , where M = V, Nb, Cr, Mo, W and X = F, Cl, Br (n = 4,5), has been carried out by the self-consistent field multiplescattering Xa (SCF-MS-Xa) method. The results of the study provide values of the d-d transition energies, and also give some understanding of the similarities and differences in bonding characteristics, of the penta- and hexacoordinated complexes. The g and hyperfine interaction (A) tensor components were computed using the SCF-MS-Xa wavefunctions and values of spin-orbit coupling constants and  $< r^{-3} >$  values computed for the appropriate valence configuration of the atoms in the molecule using atomic Xa wavefunctions. Comparison with the g and A tensor components of  $[CrOCl_4]^{1-}$  computed using extended Hückel wavefunctions shows the importance of using good quality wavefunctions in estimating spin-Hamiltonian parameters as well as the need to estimate the required spin orbit coupling constants and  $\langle r^{-3} \rangle$  values in a nonempirical manner. The various factors which determine the magnitudes and signs of the ESR spin-Hamiltonian parameters of transition metal oxohalo complexes are also discussed.

In this thesis, the results of ESR studies of three pentacoordinated d<sup>1</sup> transition metal oxohalo complexes are also discussed. The single-crystal ESR spectra of  $[VOF_4]^{2-}$  and  $[MoOF_4]^{1-}$  were studied in single crystals of  $(NH_4)_2SbF_5$  and  $[MoOCl_4]^{1-}$  in single crystals of  $(NH_4)_2SbCl_5$ . The spin-Hamiltonian parameters are compared with those of the corresponding hexacoordinated species. TO MY PARENTS

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iii

#### TABLE OF CONTENTS

Chapter	Page
LIST OF	TABLES
LIST OF	FIGURES
CHAPTER	I - INTRODUCTION 1
CHAPTER	II - AN INTRODUCTION TO THE THEORY OF ESR SPECTRA 4
Α.	Spin Hamiltonians 7
•	1. $\mathcal{H}_{LS}$ : Spin-Orbit Interaction 7
	2. $\mathcal{K}_{Z}$ : Zeeman Interaction 9
	3. $\mathcal{H}_{SI}$ : Electron Spin-Nuclear Spin Interaction
	4. $\mathcal{H}_{LI}$ : Nuclear Spin-Orbit Inter-
	action
	5. $\mathcal{K}_{SS}$ : Electron Dipole Interaction 11
	6. $\mathcal{H}_Q$ : Nuclear Quadrupole Interaction 11
Β.	Experimental Methods for Obtaining the Spin-Hamiltonian Parameters 14
Chapter	II - References
CHAPTER	III - THEORY OF g AND HYPERFINE INTERACTION TENSORS
Α.	Theory of the g Tensor
В.	Theory of the Hyperfine Interaction (A) 24
С.	Evaluation of g and A Tensor Components

Chapter

Chapter	III - References	30
CHAPTER	IV - AN INTRODUCTION TO THE SELF- CONSISTENT FIELD MULTIPLE SCATTERING $X_{\alpha}$ THEORY	31
Α.	Hartree-Fock Equations and the Xa Approximation	32
в.	Determination of a in the Xa Method	42
с.	Interpretation of $X_{\alpha}$ Eigenvalues and Slater Transition States	44
D.	Multiple Scattering SCF Method	49
	1. Muffin-tin Approximation	50
	2. Secular Equations	53
	3. The Self-consistent Potential Field	64
	4. Overlapping-Sphere Model	68
	5. Evaluation of One-electron Properties	70
Chapter	IV - References	75
CHAPTER	V - ELECTRONIC STRUCTURE AND ESR	
	PARAMETERS OF $[CrOCl_4]^{\perp}$	77
Α.	Introduction	77
в.	Methods	78
С.	Technical Details	83
D.	Electronic Structure of [CrOC1 <sub>4</sub> ] <sup>1-</sup>	87
E.	Theory of g and Hyperfine Inter- action Tensors	92

Page

## Chapter

## Page

G.	Conclusions	14
Chapter	V - References	15
CHAPTER	VI - AN SCF-MS-Xa STUDY OF a <sup>1</sup> TRANSITION METAL OXOHALO	
	COMPLEXES	L 8
Α.	Introduction	18
в.	Methods	20
	(i) The SCF-MS-Xa Method	20
	(ii) Computational Details	22
с.	Electronic Structure	26
D.	Electronic Excitation Energies 13	39
E.	Evaluation of g and Hyperfine	
	Interaction Tensor Components 14	14
F.	Conclusion 15	57
Chapter	VI - References	59
CHAPTER	VII - ESR STUDY OF [VOF4] <sup>2-</sup> , [MOOF4] <sup>1-</sup>	
	and $[MoOCl_{4}]^{1-}$	52
Α.	Experimental	54
в.	Results	56
	1. Tetrafluoro Complexes of Oxo-	
	vanadium(IV) and $Oxomolybdenum(V)$ 16	56
	2. Tetrachlorooxomolybdate(V) Ion 18	\$7
С.	Discussion	96
Chapter	VII - References	)4
APPENDIZ	ХА 20	)7

LIST OF TABLES

#### Table

## Page

#### Chapter V

1	Geometry, sphere radii and	
	α values	2
2	Extended Hückel parameters and	
	basis functions 85	5
3	One-electron eigenfunctions	
	and eigenvalues 86	5
4	Chromium-oxygen bonding in some	
	oxochromium compounds 88	}
5	Charge distribution in some oxo-	
	chromium compounds 89	)
6	Electronic transition energies	
	from EHT and SCF-MS-X $\alpha$ calculations 90	)
7	Chromium spin orbit coupling	
	constants (3d) and $\langle r^{-3} \rangle^{3d}$ values 103	3
8	ESR parameters of $[CrOCl_4]^{1-}$ 107	,
9	Estimated chromium spin-orbit	
	coupling constants $(\lambda^{3d})$ and	
	<r<sup>-3&gt;<sup>3d</sup> 108</r<sup>	}
10	Extended Hückel results for g and A	
	tensor components	)

#### Table

## Chapter VI

1	Geometrical data for $[MOX_n]^{m-1}$
	complexes
2	Sphere radii (R), $\alpha$ values and
	virial ratios for $[MOX_n]^{m-}$ com-
	plexes
3	Molecular orbitals of $[VOF_4]^{2-}$ 127
4	Molecular orbitals of $[VOC1_4]^{2-}$ 128
5	Molecular orbitals of $[VOF_5]^{3-}$ 129
6	Molecular orbitals of $[VOCI_5]^{3-}$ 130
7	Charge distribution in $[MOX_n]^{m-1}$
	complexes
8	Electron distribution in the
	metal orbitals of $[MOX_n]^{m-1}$
	complexes
9	Electronic transition (d-d)
	energies (cm <sup>-1</sup> ) in [MOX <sub>n</sub> ] <sup>m-</sup>
	complexes
10	Computed values of $\lambda_{M}^{nd}$ ,
	$< r^{-3} >_{M}^{nd}$ and $P_{M}^{nd}$ 149
11	Computed values of g
	$g_{j}$ for $[MOX_n]^{m-}$ complexes
12	Computed values of $A_{  }$ and $A_{ }$ for
	$[MOX_n]^{m-}$

#### Table

## Page

## Chapter VII

1	Single-crystal ESR parameters
	of $[VOF_4]^{2-}$
2	Single-crystal ESR parameters
	of $[MoOF_4]^{1-}$
3	Single crystal ESR parameters
	of $[MoOCl_4]^{1-}$ 194
4	Molecular orbital coefficients
	for molybdenyl complexes
5	Molecular orbital coefficients
	for vanadyl complexes
6	Spin Hamiltonian parameters for
	vanadyl complexes
7	Spin Hamiltonian parameters for
	molybdenyl complexes

## Appendix A

1	Molecular	orbitals	of	[CrOF4] <sup>1-</sup> .	•	•	•	•	207
2	Molecular	orbital o	of [	[croc1 <sub>5</sub> ] <sup>2-</sup> .	•	•	•	•	208
3	Molecular	orbitals	of	[CrOF <sub>5</sub> ] <sup>2-</sup> .	•	•	•	•	209
4	Molecular	orbitals	of	[MoOF <sub>4</sub> ] <sup>1-</sup> .	•	•	•	•	210
5	Molecular	orbitals	of	[MoOC14] <sup>1-</sup>	•	•	•	•	211
6	Molecular	orbitals	of	[MoOBr <sub>4</sub> ] <sup>1-</sup>	•	•	•	•	212
7	Molecular	orbitals	of	[MoOF <sub>5</sub> ] <sup>2-</sup> .	•	•	•	•	213
8	Molecular	orbitals	of	[MoOC1 <sub>5</sub> ] <sup>2-</sup>	•	•	•	•	214

9	Molecular	orbitals	of	[NbOF <sub>4</sub> ] <sup>1-</sup> .	•	•	•	•	215
10	Molecular	orbitals	of	[WOF4] <sup>1-</sup> .	•	•	•	•	216
11	Molecular	Orbitals	of	[woc1 <sub>4</sub> ] <sup>1-</sup> .	•	•	•	•	217

LIST OF FIGURES

Page

#### Chapter IV

Figure

1	Partitic	on of	space	for	a	tr	i-						
	atomic m	olecu	le	• •	•	•	•••	•	•	•	•	•	51

#### Chapter V

1	Coordinate system for $[CrOCl_4]^{1-}$ 96
2	Plot of spin orbit coupling
	constant $(\lambda_{Cr}^{3d})$ versus charge
	on chromium (Q <sub>Cr</sub> ) 109
3	Plot of spin orbit coupling
	constant $(\lambda_{Cr}^{3d})$ versus $\langle r^{-3} \rangle_{Cr}^{3d}$ 110

#### Chapter VI

1	Percentage d contribution to M-O			
	$\sigma$ and $\pi$ bonds in MO <sup>n+</sup> and [MOX <sub>m</sub> ] <sup>n-</sup>			
	where $M = V$ , Cr, Mo, $X = F$ , Cl and			
	m = 4 and 5			
2	Plot of electronic transition			
	(d-d) energies for [MOX <sub>5</sub> ] <sup>n-</sup> where			
	M = V, Cr, Mo and $X = F$ , Cl 140			

## Figure

3	Plot of electronic transition
	energies for $[MOX_4]^{n-}$ where
	M = V, Cr, Mo, W and X =
	F, Cl
4	Plot of electronic transition
	energies for $[MOX_4]^{n-}$ where
	M = Mo, W and X = F, Cl, Br 142
Chapter V	II
l	Crystal structure of $(NH_4)_2SbF_5$
	with internuclear distances given
	in Ångstrom units
2	Coordinate system for the
	analysis of g and A tensors of
	pentacoordinated transition
	metal oxohalo complexes 167
3	Variation of g with the magnetic
	field in the ab plane for $[VOF_4]^{2-}$
	in $(NH_4)_2SbF_5$
4	Variation of A with the magnetic
	field in the ab plane for $[VOF_4]^{2-}$
	in $(NH_4)_2SbF_5$
5	Variation of g with the magnetic
	field in the bc plane for $[VOF_4]^{2-}$
	in $(NH_4)_2SbF_5$

.

Page

.

6	Variation of A with the magnetic
	field in the bc plane for $[VOF_4]^{2-}$
	in $(NH_4)_2SbF_5$
7	ESR spectrum of polycrystalline
	sample of $[VOF_4]^2$ in $(NH_4)_2SbF_5$
	at room temperature
8	Simulated ESR spectrum of poly-
	crystalline sample of $[VOF_4]^{2-}$ in
	(NH <sub>4</sub> ) <sub>2</sub> SbF <sub>5</sub>
9	Variation of g with magnetic field
	in the bc plane for $[MoOF_4]^{1-}$ in
	(NH <sub>4</sub> ) <sub>2</sub> SbF <sub>5</sub>
10	Variation of g with magnetic field
	in the ab plane for $[MoOF_4]^{1-}$ in
	(NH <sub>4</sub> ) <sub>2</sub> SbF <sub>5</sub>
11	ESR spectrum of $[MOOF_4]^{1-}$ in
	$(NH_4)_2 SbF_5$ for $\theta = 0^\circ$ and
	$\phi = 0^{\circ} \dots \dots$
12	ESR spectrum of $[MoOF_4]^{\perp}$ in
	$(NH_4)_2SbF_5$ for $\theta = 90^\circ$ and
	$\phi = 0^{\circ} \text{ or } 90^{\circ} \dots \dots \dots \dots \dots \dots \dots \dots \dots 182$
13	ESR spectrum of polycrystalline
	sample of $[MoOF_4]^{-}$ in $(NH_4)_2SbF_5$
	at 77°K185

Page

14	Crystal structure of $(NH_4)_2SbCl_5$
	with internuclear distance given
	in Ångstrom
16	Variation of g with magnetic
	field in the bc* plane for $[MoOCl_4]^{1-}$
	in $(NH_4)_2$ SbCl <sub>5</sub>
17	Variation of g with magnetic field
	in the ab plane for $[MoOCl_4]^{1-}$ in
	(NH <sub>4</sub> ) <sub>2</sub> SbCl <sub>5</sub> 190
18	Variation of A with magnetic field
	in the ab plane for $[MoOCl_4]^{1-}$ in
	(NH <sub>4</sub> ) <sub>2</sub> SbCl <sub>5</sub> 191
19	Variation of A with magnetic field
	in the bc* plane for $[MoOCl_4]^{1-}$ in
	(NH <sub>4</sub> ) <sub>2</sub> SbCl <sub>5</sub> 192
20	Variation of A with magnetic field
	in the ac* plane for $[MoOCl_4]^{1-}$
	in $(NH_4)_2$ SbCl <sub>5</sub>

#### CHAPTER I

#### INTRODUCTION

The nature of bonding in molecules has been an active area of study since the early days of chemistry and will continue to be so, since more and more powerful experimental and theoretical techniques are being developed. The ultimate goal of all spectroscopic studies is to understand the basic forces that hold atoms together in the form of molecules, ions and radicals and to explain the observed trends in physical and chemical properties. The main aim of the various theoretical models of molecular electronic structure theory is essentially the same.

Among the numerous spectroscopic techniques available to study the basic features of bonding in transition metal complexes, electron spin resonance spectroscopy is considered to be one of the most powerful. The analysis of electron spin resonance spectra provides valuable information concerning molecular symmetry, spin distribution and the nature of the ground and low lying excited states. Hence the electron spin resonance parameters which depend on the details of molecular electronic structure are interpreted in terms of the molecular orbitals

of the system.

A detailed study of the electronic structure of a series of d<sup>1</sup> transition metal oxohalo complexes [MOX\_]<sup>m-</sup>, where M = V, Nb, Cr, Mo, W and X = F, Cl, Br (n = 4,5), has been carried out by the self consistent field multiple scattering  $X^{\alpha}$  (SCF-MS-X $^{\alpha}$ ) method. The electronic structure studies were carried out in the SCF-MS-Xa model primarily because it allows an approximately quantitative description of the electronic structure of systems with a large number of electrons. The results of the study provide values of the d-d transition energies, and also give some understanding of the similarities and differences in bonding characteristics, of the penta- and hexa coordinated complexes. The g and hyperfine interaction (A) tensor components were computed using the SCF-MS-Xa wavefunctions and values of spin-orbit coupling constants and  $\langle r^{-3} \rangle$  values computed for the appropriate valence configuration of the atoms in the molecule using atomic Xa wavefunctions. Comparison with the g and A tensor components of  $[CrOCl_{\downarrow}]^{1-}$  computed using extended Hückel wavefunctions shows the importance of using good quality wavefunctions in estimating spin-Hamiltonian parameters as well as the need to estimate the required spin orbit coupling constants and  $\langle r^{-3} \rangle$  values in a nonempirical manner. The various factors which determine the matnitudes and signs of the ESR spin Hamiltonian

parameters of transition metal oxohalo complexes are also discussed.

In this thesis, ESR spectra of three penta coordinated  $d^{1}$  transition metal oxohalo complexes are discussed. The single-crystal ESR spectra of  $[VOF_{4}]^{2-}$  and  $[MoOF_{4}]^{1-}$  in single-crystals of  $(NH_{4})_{2}SbCl_{5}$ . The spin-Hamiltonian parameters are compared with those of the corresponding hexacoordinated species.

#### CHAPTER II

# AN INTRODUCTION TO THE THEORY OF

#### ESR SPECTRA

An electron has a spin angular momentum of one-half which, in the absence of a magnetic field gives rise to a doubly-degenerate spin energy level. The degeneracy of the spin states is removed by a magnetic field and the energy separation  $\Delta E$ , of the two states is then given by

$$\Delta E = hv = g\beta B, \qquad (1)$$

where h is Planck's constant, v is the frequency of the electromagnetic radiation required to induce a transition between these two energy states, g = 2.0023 is a constant for a free electron and B is the magnitude of the applied magnetic field. An unpaired electron in a molecule or ion which moves in the force field of nuclei possess orbital angular momentum in addition to the spin angular momentum. The interaction between the orbital and spin angular momenta of the electron, which is referred to as spin-orbit interaction, makes a

contribution to the g value, thus making 'g' a characteristic property of the molecule or ion containing the unpaired electron<sup>1</sup>.

The spin angular momentum of an electron interacts with the nuclear magnetic moment giving rise to hyperfine structure in the ESR spectra of molecules or ions containing nuclei with nonzero nuclear spin. An electron interacting with a nucleus of spin angular momentum I gives rise to (2I+1) lines in the ESR spectrum. The hyperfine coupling constant can be measured from the spacing between the lines. The measured values of g and of the hyperfine coupling constants provide valuable information concerning the molecular symmetry, symmetry of the orbital containing the unpaired electron, the spin distribution and the nature of bonding.

The analysis and interpretation of ESR spectra are customarily done in terms of a spin Hamiltonian<sup>2</sup>, since the spectral transitions arise from induced changes in the spin state of the system. The spin Hamiltonian arises from the replacement of the complete Hamiltonian<sup>1</sup> by an effective Hamiltonian which includes the applied magnetic field, the spin operators and a set of parameters which characterize the ESR spectra. The expressions for the magnetic energy levels of the system can be worked out in terms of these ESR parameters. The analysis of an ESR spectrum thus reduces to the specification

of the appropriate values of the parameters which appear in the spin Hamiltonian for the system and the interpretation of the spectrum is concerned with understanding the magnitudes and signs of the parameters in terms of the molecular electronic structure of the system.

There are many surveys of the transition metal ESR literature<sup>3-6</sup>. The use of molecular orbital theory to interpret ESR results has been reviewed by McGarvey<sup>1</sup>, Konig<sup>7</sup>, and Kuska and Rogers<sup>8</sup>. There are two reviews by Kuska and Rogers<sup>9,10</sup> with emphasis on first row transition metal complexes. A review by Goodman and Raynor<sup>11</sup> gives comprehensive coverage of the d<sup>1</sup> to d<sup>9</sup> ions for the entire transition metal series. Recently Kohin<sup>12</sup> has reviewed ESR studies of vanadyl ion in crystalline solids. In addition to these the current literature is reviewed in the annual reports of the Chemical Society<sup>13</sup>, in the series "Spectroscopic properties of Inorganic and Organometallic Compounds"<sup>14</sup> and in the journal "Magnetic Resonance Reviews"<sup>15</sup>.

There is also a large number of books on ESR. The books by Carrington and McLachlan<sup>16</sup> and by Slichter<sup>17</sup> give complete introduction to magnetic resonance while those by Atherton<sup>18</sup>, Orton<sup>19</sup>, Pake<sup>20</sup> and Wertz and Bolton<sup>21</sup> deal with only ESR. A comprehensive account of the ESR of transition metal ions is given in the book by Abragam and Bleaney<sup>22</sup> and a detailed mathematical account of the

theory of transition metal ions is available in the book by Griffith<sup>23</sup>. Books dealing with experimental techniques include those by Poole<sup>24</sup> and by Alger<sup>25</sup>.

#### A. Spin Hamiltonians

For a molecule with fixed nuclei (Born-Oppenheimer approximation), the general Hamiltonian<sup>1</sup> which takes into account all the magnetic and electric interactions that arise in ESR spectroscopy can be written as

$$\hat{\boldsymbol{\mu}} = -\frac{\hbar^2}{2m} \sum_{i} \nabla_{i}^2 + \nabla + \boldsymbol{\mu}_{LS} + \boldsymbol{\mu}_{Z} + \boldsymbol{\mu}_{SI} + \boldsymbol{\mu}_{LI} + \boldsymbol{\mu}_{SS} + \boldsymbol{\mu}_{Q}$$
(2)

where the first term is the kinetic energy operator for the electrons and V is the electrostatic potential which includes both attractive potentials between electrons and nuclei and repulsive potentials between electrons. The remaining terms in the Hamiltonian are discussed below:

# 1. JC\_LS: Spin-Orbit Interaction<sup>23</sup>

The spin-orbit interaction is a relativistic effect arising from interaction between the spin magnetic moment of the electron and the magnetic field produced by the motion of the nucleus. In relativistic quantum theory this interaction is represented as

$$\mathcal{H}_{LS} = \frac{e\hbar^2}{2m^2c^2} \{\vec{E} \times [\vec{p} + \frac{e}{C} \vec{A}]\} \cdot S , \qquad (3)$$

where  $\vec{E}$  is the electric field in which the electron moves,  $\vec{p}$  is the linear momentum operator for the electron,  $\vec{S}$ is the spin-angular momentum operator in units of  $\vec{n}$ , and  $\vec{A}$  is the vector potential for any magnetic field present. In most cases the term involving  $\vec{A}$  is neglected, owing to its small magnitude. Since the electric field is spherically symmetric for a single ion or atom,

$$\mathcal{L}_{LS} = \left(\frac{e\hbar^2}{2m^2c^2}\right) \frac{E(\mathbf{r})}{\mathbf{r}} \vec{L} \cdot \vec{S} = \xi(\mathbf{r}) \vec{L} \cdot \vec{S} , \qquad (4)$$

where  $\vec{L}$  is the orbital angular momentum of the electron in units of  $\vec{n}$ . For the case of an atom in a molecule, where there is more than one center of the electric field, it is customary to assume that the spin-orbit interaction can be written as

$$\mathcal{H}_{LS} = \sum_{i} \{ \sum_{K} \xi_{K}(r_{iK}) \vec{k}_{iK} \} \cdot \vec{s}_{i}, \qquad (5)$$

where  $r_{iK}$  is the distance of electron i from nucleus K,  $\vec{t}_{iK}$  is the orbital angular momentum operator for electron i centered at nucleus K and  $\vec{S}_i$  is the spin angular momentum operator for the electron i. Equation (5) is based on the assumption that the main contribution to  $\mathcal{H}_{LS}$  comes from the region close to the nucleus, since  $\xi(r)$  varies as  $\langle r^{-3} \rangle$ , and that near the nucleus the electric field can be regarded as approximately spherical.

#### 2. <u>*H*</u><sub>7</sub>: Zeeman Interaction

The interaction between the magnetic field and the spin and orbital angular momentum is called the Zeeman interaction. This interaction is represented by the following term in the Hamiltonian

$$\mathcal{F}_{\mathbf{Z}} = g_{\mathbf{e}} \beta_{\mathbf{e}} \vec{\mathbf{B}} \cdot \vec{\mathbf{S}} + \beta_{\mathbf{e}} \vec{\mathbf{B}} \cdot \vec{\mathbf{L}} - g_{\mathbf{N}} \beta_{\mathbf{N}} \vec{\mathbf{B}} \cdot \vec{\mathbf{I}} , \qquad (6)$$

where  $g_e$  is the free electron g value,  $\beta_e$  is the electronic Bohr magneton,  $\vec{B}$  is the magnetic field,  $g_N$  the nuclear g factor and  $\beta_N$  the nuclear Bohr magneton.

# 3. $\mathcal{H}_{SI}$ : Electron Spin-Nuclear Spin Interaction

This interaction which is called the hyperfine interaction can be written as

$$\mathcal{\mathcal{H}}_{SI} = g_{e}g_{N}\beta_{e}\beta_{N} \sum_{i,K} [3(\vec{s}_{i}\cdot\vec{r}_{iK})(\vec{t}_{K}\cdot\vec{r}_{iK}) - r_{iK}^{2}(\vec{s}_{i}\cdot\vec{t}_{K})]r_{iK}^{-5}$$

$$+ \frac{8\pi}{3} g_{e}g_{N}\beta_{e}\beta_{N} \sum_{i,K} \delta(r_{iK})\vec{t}_{K}\cdot\vec{s}_{i}, \qquad (7)$$

where  $\boldsymbol{g}_N$  is the nuclear g value,  $\boldsymbol{\beta}_N$  the nuclear Bohr magneton and  $\vec{r}_{iK}$  the vector connecting electron i with nucleus K. The summation index i represents the summation over all electrons in the system and for K the summation is over all the nuclei with nonzero nuclear spin. In Equation (7)  $\delta(r_{iK})$  is the Dirac delta function which, when integrated with the wavefunction, gives the value of the wavefunction at  $r_{iK} = 0$ . The two terms in Equation (7) are the two limiting forms of the same interaction. The first term represents the dipole-dipole interaction for two dipoles that are not too close to each other. It is the proper form of  $\mathcal{H}_{ST}$  for electrons in p,d, and f orbitals which have nodes at the nucleus. The second term, which is referred to as the contact term in the hyperfine interaction, represents the interaction between the nucleus and an electron which has a finite probability density at the nucleus.

# 4. $\mathcal{H}_{LI}$ : Nuclear Spin-Orbit Interaction

$$\mathcal{H}_{LI} = g_e g_N \beta_e \beta_N \sum_{i,K} r_{iK}^{-3} (\vec{\ell}_{iK} \cdot \vec{I}_K)$$
(8)

This term is important only in that it gives a second order contribution to the hyperfine interaction by allowing the nuclear spin and electron spin to couple indirectly through the orbital angular momentum. 5.  $\mathcal{H}_{SS}$ : Electron Dipole Interaction

This interaction gives rise to the zero field or the spin-spin splitting, in the ESR spectra and arises from a dipole-dipole type interaction between the electrons.

$$\mathcal{H}_{SS} = g_{e}^{2} \beta_{e}^{2} \sum_{j,K} [r_{jK}^{2}(\vec{s}_{j} \cdot \vec{s}_{K}) - 3(\vec{s}_{j} \cdot \vec{r}_{jK})(\vec{s}_{K} \cdot \vec{r}_{jK})]r_{jK}^{-5}$$
(9)

where  $r_{jK}$  is the distance between two electrons. This interaction arises only for systems with more than one unpaired electron.

# 6. <u>H\_Q</u>: Nuclear Quadrupole Interaction

If the nucleus has a quadrupole moment Q, there is an electrostatic interaction between the electrons and the nuclear quadrupole. This interaction is represented by the following term in the Hamiltonian

$$\mathcal{H}_{Q} = \sum_{i,K} [e^{2}Q_{K}/2I_{K}(2I_{K}-1)][r_{iK}^{2}I_{K}(I_{K}+1) - 3(\dot{r}_{iK}\cdot\dot{I}_{K})^{2}]r_{iK}^{-5},$$
(10)

where  ${\tt Q}_{\tt K}$  is the electric quadrupole moment of nucleus K.

Some small terms have not been included in the total Hamiltonian (Equation (2)) since these terms were not found necessary to account for the observed ESR spectra. The terms so neglected are the nuclear spin-spin coupling term and the nuclear chemical shift term. For systems with only one unpaired electron, including those which are the subject of this thesis, the electron-dipole interactions do not make any contribution and the nuclear Zeeman interaction and the nuclear quadrupole interaction have been found to be generally negligible. Hence these interactions will not be considered further.

The complete Hamiltonian for a system with one unpaired electron, where the nuclear Zeeman and nuclear quadrupole interactions make negligible contributions, can be written as

$$\mathcal{H} = \mathcal{H}_{O} + \mathcal{H}_{LS} + \mathcal{H}_{Z} + \mathcal{H}_{SI} + \mathcal{H}_{LI} , \qquad (11)$$

where

$$\mathcal{FC}_{o} = -\frac{\hbar^{2}}{2m}\sum_{i}\nabla_{i}^{2} + V \qquad (12)$$

$$\mathcal{H}_{Z}^{i} = g_{e}\beta_{e}\vec{B} \cdot \vec{S} + \beta_{e}\vec{B} \cdot \vec{L}$$
(13)

and the remaining terms in Equation (11) are defined in Equations (5), (7) and (8). If  $\psi_N^0$  is the ground state electronic wavefunction, i.e.,

$$\mathcal{F}_{O}\psi_{N}^{O} = E_{N}^{O}\psi_{N}^{O} , \qquad (14)$$

then the wavefunction corrected to first order for the spin-orbit interaction gives rise to a pair of Kramer's doublets<sup>26</sup> as shown below

$$|+\rangle = |\psi_{N}\alpha\rangle = |\psi_{N}^{\circ}\alpha\rangle + \sum_{K \neq N} |\psi_{K}^{\circ}\rangle \frac{\langle\psi_{K}^{\circ}| \mathcal{I}C_{LS} |\psi_{N}^{\circ}\alpha\rangle}{E_{N}^{\circ} - E_{K}^{\circ}}$$
$$|-\rangle = |\psi_{N}\beta\rangle = |\psi_{N}^{\circ}\beta\rangle + \sum_{K \neq N} |\psi_{K}^{\circ}\rangle \frac{\langle\psi_{K}^{\circ}| \mathcal{I}C_{LS} |\psi_{N}^{\circ}\beta\rangle}{E_{N}^{\circ} - E_{K}^{\circ}}, \quad (15)$$

These first-order spin-orbit corrected wavefunctions |+> and |->, are not eigenfunctions of the spin angular momentum operator  $\hat{S}$ . Now we define a fictitious spin angular momentum operator  $\hat{S}$ , the components of which are defined to act on the states |+> and |-> in exactly the same way as the true spin operators act on the spin functions  $|\alpha>$  and  $|\beta>$ ; that is

$$\hat{s}_{Z} |+> = \frac{1}{2} |+>, \quad \hat{s}_{X} |+> = \frac{1}{2} |->$$

$$\hat{s}_{Z} |-> = -\frac{1}{2} |->, \quad \hat{s}_{Y} |+> = \frac{1}{2} |->$$
(16)

and so on. Then the total Hamiltonian can be rewritten in terms of only the spin (fictitious) operators and the magnetic field as follows

$$\mathcal{F} = \beta \hat{B} \cdot \hat{\hat{g}} \cdot \hat{\hat{g}} + \sum_{K} \hat{\hat{g}} \cdot \hat{\hat{g}}_{K} + \sum_{K} \hat{\hat{g}}_{K} \cdot \hat{h}_{K}$$
(17)

where  $\hat{g}$  and  $\hat{A}$  are the g and hyperfine interaction tensors, respectively. The Hamiltonian of Equation (17) is the ESR spin Hamiltonian for a system containing only one unpaired electron. The spin Hamiltonian is an artificial but useful concept which has become the crossroad for the path followed by the experimentalists and the theoreticians. Experimentally, the spin Hamiltonian and the parameters which define it, are determined from the ESR spectra, whereas, theoretically, the parameters are computed from the wavefunction<sup>1</sup>.

# B. Experimental Methods for Obtaining the Spin-Hamiltonian Parameters

Electron spin resonance measurements are usually made on magnetically dilute samples. Measurements made with pure paramagnetic samples are less informative because of exchange broadening of the lines. Magnetic dilution is usually done in solution by preparing a dilute solution of the material in a suitable solvent. In the solid state it is accomplished by doping the paramagnetic sample to an extent of about 1% in a diamagnetic solid.

For the transition metal oxohalo complexes studied here the spin-Hamiltonian is

$$\hat{\mathcal{F}} = g_{\parallel} |_{\beta_{e}} B_{Z} \hat{S}_{Z} + g_{\perp} \beta_{e} (B_{X} \hat{S}_{X} + B_{y} \hat{S}_{y})$$

$$+ A_{\parallel}^{M} \hat{I}_{z} \hat{S}_{z} + A_{\perp}^{M} (I_{x} S_{x} + I_{y} S_{y})$$

$$g_{\parallel} = g_{zz}, \quad g_{\perp} = g_{xx} = g_{yy}, \quad A_{\parallel}^{M} = A_{zz}^{M} \& A_{\perp}^{M} = A_{xx}^{M} = A_{yy}^{M},$$

where only the interaction between the unpaired electron and the metal atom is included and  $S_i$ ,  $I_i$ , i = x,y,z are the components of the electron and nuclear spin operators, respectively.

The principal components  $(g_{||}, g_{\perp}, A_{||}^{M}, A_{\perp}^{M})$  of both the g and the hyperfine interaction (A) tensors can be obtained from single crystal studies. In Schonland's method<sup>27</sup> of determining the principal components of g and A tensors, ESR spectra should be obtained for rotations of the crystal about three orthogonal axes. The need to obtain spectra for rotations about three orthogonal axes is only a limitation of Schonland's method. The method of Waller and Rogers<sup>28</sup> for the general case of rotations about any three axes can be used to determine the principal components of both the g and A tensors. Even though it is difficult, the principal components of g and A tensors can be obtained from powder and frozen solution samples with fairly good accuracy<sup>29</sup>. The spectra of powder and frozen solution

samples can be simulated to facilitate the analysis and to obtain accurate values for the spin Hamiltonian parameters. The ESR spectra of low viscosity solution samples provide only the average values of g and A tensors because of the rapid molecular motions. These average values of g and A are related to their principal components by the equations

$$g = \frac{1}{3} (g_{xx} + g_{yy} + g_{zz})$$
$$A = \frac{1}{3} (A_{xx} + A_{yy} + A_{zz}).$$

Since the dipolar part of the hyperfine interaction tensor is traceless, the measured hyperfine coupling constant from solution spectra is equal to the Fermi contact coupling constant. REFERENCES
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#### CHAPTER III

#### THEORY OF g AND HYPERFINE INTERACTION TENSORS

The theory of g values and hyperfine interactions in the electron spin resonance spectra of transition metal complexes is based on the perturbation theory treatment of Abragam and  $Pryce^1$  for the crystal field model, later modified to include covalency effects. The general subject of the interpretation of spin Hamiltonian parameters has been discussed in detail by McWeeny<sup>2-4</sup> and the theory of g values and hyperfine interaction has been the subject of detailed reviews<sup>5-7</sup>. So in this chapter only outlines of the theories are given to show the dependence of g and hyperfine interaction tensor components on the molecular electronic structure of the system.

#### A. Theory of the g Tensor

The electronic Zeeman interaction term in the spin Hamiltonian which accounts for the observed g value is

$$\hat{\mathcal{F}} = \beta \hat{B} \cdot \hat{g} \cdot \hat{S} , \qquad (1)$$

where  $\hat{g}$  is the g tensor, which can be isotropic or anisotropic depending upon the system. If the g value calculated from the g tensor (average of the principal components of the g tensor) differs from the free electron value of 2.0023, then  $\hat{S}$  cannot possibly represent the true spins. The experimental g value deviates considerably from the free electron value. Hence the spin operator  $\hat{S}$  in Equation (1) should be replaced by a fictitious spin operator  $\hat{S}$  as shown in Chapter I.

The spin and orbital angular momenta interact with the magnetic field as given in the complete Hamiltonian (Chapter I). Hence the actual total electronic Zeeman interaction is given by

$$\hat{\mathcal{F}} = \beta_{e}(\hat{L} + g_{e}\hat{S}) \cdot \hat{B}$$
 (2)

Since the electronic Zeeman interaction of Equations (1) and (2) represents the same interaction, we have

$$\beta_{e}(\hat{L} + g_{e}\hat{S}) \cdot \hat{B} = \beta_{e}\hat{B} \cdot \hat{g} \cdot \hat{S}, \qquad (3)$$

where  $\hat{S}$  is the so called fictitious spin angular momentum operator.

For a molecule with a single unpaired electron (spin  $\alpha$ ) in an orbitally nondegenerate ground state the Zeeman interaction energy is given by

$$E_{\alpha} = \langle \psi_{0} \alpha | \hat{L}_{z} + g_{e} \hat{S}_{z} | \psi_{0} \alpha \rangle \beta_{e} B$$
$$= \beta_{e} B \langle \psi_{0} | \hat{L}_{z} | \psi_{0} \rangle + g_{e} \beta_{e} B \langle \alpha | \hat{S}_{z} | \alpha \rangle$$
$$= \beta_{e} B \langle L_{z} \rangle + \frac{1}{2} g_{e} \beta_{e} B^{'}; \quad \langle L_{z} \rangle = 0$$

where  $\psi_0$  is the molecular orbital containing the unpaired electron. A similar calculation for the state  $\psi_0\beta$  gives

$$E_{\beta} = \beta_{e}B < L_{z} > -\frac{1}{2}g_{e}\beta_{e}B; \quad  = 0$$
$$E_{\alpha} - E_{\beta} = g_{e}\beta_{e}B = h\nu .$$

From this one concludes that the g value should always be equal to the free electron g value which is contradictory to the experimental observation.

The shift in the g value from  $g_e = 2.0023$  is attributed to the fact that the electron possesses orbital angular momentum in addition to the spin angular momentum. The odd electron can acquire orbital angular momentum via the spin-orbit interaction. The ground state wavefunctions  $|\Psi_0^{\alpha}\rangle$  and  $|\Psi_0^{\beta}\rangle$ , corrected for the spin-orbit interactions through first order in the perturbation, takes the following form:

$$|+>=|\psi_{0}\alpha> - \frac{1}{2}\sum_{n\neq 0}\frac{\langle\psi_{n}|\xi(r)\hat{L}_{z}|\psi_{0}\rangle}{E_{n}-E_{0}}|\psi_{n}\alpha> - \frac{1}{2}\sum_{n\neq 0}\frac{\langle\psi_{n}|\xi(r)\hat{L}_{+}|\psi_{0}\rangle}{E_{n}-E_{0}}|\psi_{n}\beta>$$
(14)  
$$|-> = |\psi_{0}\beta> + \frac{1}{2}\sum_{n\neq 0}\frac{\langle\psi_{n}|\xi(r)\hat{L}_{z}|\psi_{0}\rangle}{E_{n}-E_{0}}|\psi_{n}\beta> - \frac{1}{2}\sum_{n\neq 0}\frac{\langle\psi_{n}|\xi(r)\hat{L}_{-}|\psi_{0}\rangle}{E_{n}-E_{0}}|\psi_{n}\alpha>$$

where the summation index n refers to all the excited single particle states,  $E_n$  are the energies of the excited single particle states labelled n, and  $\xi(r)$  the spin-orbit coupling operator. The two states obtained by correcting for the spin-orbit interaction are no longer eigenstates of the true spin operator  $\hat{S}$ . Now we define the fictitious spin operator  $\hat{S}$  as an operator, the components of which act on the states  $|+\rangle$  and  $|-\rangle$  in exactly the same way as the components of the true spin operator  $\hat{S}$  act on the spin functions  $|\alpha\rangle$  and  $|\beta\rangle$ , <u>i.e.</u>,

$$\hat{s}_{z}|+> = \frac{1}{2}|+> \quad \hat{s}_{x}|+> = \frac{1}{2}|->$$
$$\hat{s}_{z}|-> = -\frac{1}{2}|-> \quad \hat{s}_{y}|+> = \frac{1}{2}|->$$

In a magnetic field directed along the z-axis the spin Hamiltonian for the Zeeman interaction takes the form

$$\hat{\mathcal{H}} = \beta_{e} \hat{B}(g_{xz} \hat{S}_{x} + g_{yz} \hat{S}_{y} + g_{zz} \hat{S}_{z})$$

and Equation (3) can be written as follows:

$$\beta_{e}(\hat{L}_{z}+g_{e}\hat{S}_{z})B = \beta_{e}B(g_{xz}\hat{S}_{x}+g_{yz}\hat{S}_{y}+g_{zz}\hat{S}_{z})$$
(5)

Using the expression for |+> of Equation (4), evaluating the matrix element

$$<+|\beta_{e}B(\hat{L}_{z}+g_{e}\hat{S}_{z})| +> = <+|\beta_{e}B(g_{xz}\hat{S}_{x}+g_{yz}\hat{S}_{y}+g_{zz}\hat{S}_{z})| +>$$

and solving for  ${\rm g}^{}_{\rm ZZ}$  we get

$$g_{zz} = g_e - 2 \sum_{n \neq 0} \frac{\langle \psi_0 | \xi(r) \hat{L}_z | \psi_n \rangle \langle \psi_n | \hat{L}_z | \psi_0 \rangle}{E_n - E_0}$$

It can be shown<sup>8</sup> easily that the general expression for the elements of the g tensor is given by

$$g_{ij} = g_{e} - 2 \sum_{n \neq 0} \frac{\langle \psi_{o} | \xi(r) \hat{L}_{i} | \psi_{n} \rangle \langle \psi_{n} | \hat{L}_{j} | \psi_{o}}{E_{n} - E_{o}} \quad [i, j = x, y, z]$$
(6)

From the above general expression for the components of the g tensor it follows that they are determined by the ground state electronic wave function, the excited state wavefunctions of appropriate symmetry, the energy differences between the ground and the various excited states and the spin-orbit coupling constants of the various atoms. The evaluation of g-tensor components will be discussed later.

#### B. Theory of the Hyperfine Interaction (A)

The hyperfine interaction tensor (A) may be written as a sum of the anisotropic part arising from the dipolar interaction between the unpaired electron and the nuclear magnetic moments plus an isotropic part attributed to a Fermi contact interaction. Since the anisotropic part of the hyperfine interaction tensor is traceless, the experimentally measured hyperfine tensor can be factored into the anisotropic and isotropic parts.

For a transition metal complex with the unpaired electron in the d orbital one would expect the isotropic hyperfine coupling constant to be zero since the square of the d orbital wavefunction is zero at the nucleus. But experimentally it is seen that isotropic hyperfine interaction does exist in transition metal complexes. This can be accounted for by invoking either configuration interaction or core polarization<sup>9</sup>.

The hyperfine interaction term in the spin Hamiltonian

is

$$\hat{\mathcal{F}} = \hat{S} \cdot \hat{A} \cdot \hat{I} , \qquad (7)$$

where  $\hat{A}$  is the hyperfine interaction tensor,  $\hat{S}$  the fictitious spin operator and  $\hat{I}$  the nuclear spin operator. In this discussion we consider only the anisotropic part of the A tensor. In the complete Hamiltonian (Chapter II), the interaction of the spin and the orbital angular momenta of the unpaired electron with the magnetically active  $(I \neq 0)$  nucleus is given by

$$\mathcal{F}_{\text{Pert}} = \mathcal{F}_{\text{IL}} + \mathcal{F}_{\text{DD}} \tag{8}$$

$$\mathcal{L}_{IL} = P' \sum_{i} \frac{\hat{L}_{i} \cdot \hat{I}_{i}}{r^{3}}$$

$$\mathcal{H}_{DD} = P' \sum_{i,j} I_i \frac{F_{ij}}{r^3} S_j$$

$$P' = g_e g_n \beta_e \beta_n$$
,

where  $\mathcal{H}_{IL}$  and  $\mathcal{H}_{DD}$  represent the nuclear spin orbit and the electron-nuclear dipolar interactions, respectively. In the expression for  $\mathcal{H}_{DD}$ ,  $F_{ij}$  is a linear combination of normalized real spherical harmonics. Since Equations (7) and (8) represent the same interaction, we have

$$\hat{s} \cdot \hat{A} \cdot \hat{I} = \sum_{i} \hat{s}_{i} A_{ij} \hat{I}_{j} = P' \sum_{i} \left[ \frac{\hat{L}_{i} \hat{I}_{i}}{r^{3}} + \sum_{j} \hat{I}_{i} \frac{F_{ij}}{r^{3}} \hat{s}_{j} \right]$$
(9)

Using the expression for |+> of Equation (4), evaluating the matrix element

.

$$\begin{array}{c|c} <+| & \hat{\Sigma} & \hat{S}_{1}A_{1j}\hat{I}_{j}|+> = P'<+| & \sum_{i} [\frac{\hat{L}_{i} & \hat{I}_{i}}{r^{3}} + \sum_{j} \hat{I}_{i} & \frac{F_{1j}}{r^{3}} \hat{S}_{j}]|+> \\ \end{array}$$
(10)

and solving for  ${\rm A}^{\phantom{\dagger}}_{_{\rm ZZ}}$  , we get

$$A_{zz} = P'[<\psi_{o}|\frac{F_{zz}}{r^{3}}|\psi_{o}> + \sum_{n\neq 0} \{2 - \frac{\langle\psi_{o}|\xi(r)\hat{L}_{z}|\psi_{n}>\langle\psi_{n}|\frac{\hat{L}_{z}}{r^{3}}|\psi_{o}>}{E_{o} - E_{n}}$$

+ 
$$\sum_{\alpha,\beta} i \varepsilon_{\alpha\beta z} \frac{\langle \psi_{o} | \xi(r) L_{\alpha} | \psi_{n} \rangle \langle \psi_{n} | \frac{F_{\beta z}}{r^{3}} | \psi_{o} \rangle}{E_{o} - E_{n}} \}],$$

where  $\epsilon_{\alpha\beta z}$  is the Levi-civita symbol. A rather lengthy computation of matrix elements similar to the one in Equation (10) can be used to evaluate the various elements of the anisotropic part of the A tensor. The general expression for the anisotropic hyperfine interaction tensor  $(A_{\alpha\beta})$  is given by

$$A_{\alpha\beta} = P'[\langle\psi_{0}|\frac{F_{\alpha\beta}}{r^{3}}|\psi_{0}\rangle + \sum_{n\neq 0}^{\Sigma}\{2\frac{\langle\psi_{0}|\xi(r)\hat{L}_{\alpha}|\psi_{n}\rangle\langle\psi_{n}|\frac{\hat{L}_{\beta}}{r^{3}}|\psi_{0}\rangle}{E_{0} - E_{n}}$$
$$+ \sum_{\gamma,\delta}i\varepsilon_{\delta\alpha}\frac{\langle\psi_{0}|\xi(r)\hat{L}_{\gamma}|\psi_{n}\rangle\langle\psi_{n}|\frac{F_{\delta\beta}}{r^{3}}|\psi_{0}\rangle}{E_{0} - E_{n}}\}] \qquad (11)$$

From the general expression for the anisotropic hyperfine coupling constant of Equation (11), it follows that the factors which determine the magnitude of hyperfine interaction (dipolar) are the ground and excited state wavefunctions, the energy difference between the ground and the various excited states of appropriate symmetry, the spin-orbit coupling constants and  $\langle r^{-3} \rangle$  values of the atomic orbital containing the unpaired electron. The expression of Equation (11) had been derived earlier by Keijzers et al.<sup>10</sup> using a different method.

#### C. Evaluation of g and A Tensor Components

The evaluation of the principal components of g and A tensors using the general expressions of Equations (6) and (11) requires the estimation of various types of matrix elements. Some approximations are made in the evaluations of certain types of matrix elements and are given below

(1) 
$$\langle \psi_{0} | \xi(\mathbf{r}) \hat{L}_{\alpha} | \psi_{n} \rangle$$

In the one-particle approximation being used the spinorbit coupling operator  $\xi(\mathbf{r})$  is given by

$$\xi(\mathbf{r}) \simeq \frac{h^2}{2m^2c^2} \langle \frac{1}{r} \frac{dV}{dr} \rangle = \frac{e^2h^2z'}{2m^2c^2} \langle r^{-3} \rangle, \quad V = -\frac{Z'e^2}{r},$$

where Z' is the effective nuclear charge, with this approximation for the spin-orbit operator only one center integrals are retained in evaluating the above matrix element, since the contribution to  $\langle r^{-3} \rangle$  are small and may be neglected in the overlap region.

(11) 
$$\langle \langle \psi_n^K | \frac{L_\beta}{r^3} | \psi_0^K \rangle$$
 and  $\langle \psi_n^K | \frac{F_{\delta \alpha}}{r^3} | \psi_0^K \rangle$ 

Only the matrix elements of the following type are retained

$$<\phi_n^K | \frac{\hat{\mathbf{L}}_{\beta}}{r^3} | \phi_0^K > \text{ and } <\phi_n^K | \frac{F_{\delta \alpha}}{r^3} | \phi_0^K >$$
,

where K refers to the nucleus for which the hyperfine interaction is computed, since r is the distance between the nuclei of interest and the unpaired electron.

The expressions relating the g- and A-tensor components to the electronic excitation energies, atomic spin-orbit coupling constants,  $\langle r^{-3} \rangle$  values and the coefficients of atomic orbitals in the molecular orbitals for systems with  $C_{4v}$  symmetry are given in Chapter V and the relative importance of the various parameters for transition metal oxohalo complexes are discussed there.

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#### CHAPTER IV

# AN INTRODUCTION TO THE SELF-CONSISTENT FIELD $\label{eq:multiple-scattering} \text{Multiple-scattering } \textbf{X} \textbf{\alpha} \text{ Theory}$

The electronic structure and properties of any molecule, in any of its stationary states, can in principle be determined by solving the Schrödinger (time-independent) equation. The exact solution of the Schrödinger equation has only been possible for atoms and molecules with one electron because of the mathematical and computational complexities involved in its solution. So approximate solutions of the Schrödinger equation are generated to obtain information of chemical value from theory.

There are many different procedures based on the variation principle available for solving for approximate solutions of the Schrödinger equation. These schemes for developing approximate solutions can be classified into two categories, the ab initio and the semi-empirical methods. The ab initio method has the well known Hartree-Fock self-consistent field theory as its basis while the semi-empirical methods attempts to mimic the ab initio method. The X- $\alpha$  multiple scattering self-consistent field method fits well into the traditional gap between the

ab initio and the semi-empirical approaches.

The multiple-scattering X $\alpha$  self-consistent field method is a computationally convenient method for developing an approximately quantitative description of the electronic structure of many-electron systems. The two main features of the MS-X $\alpha$ -SCF method are the X $\alpha$  approximation for the exchange contribution to the total potential and the multiple scattering method of solving the modified one-electron equations. Although the two approximations are often used in conjunction, they are logically distinct and each may be used without the other.

A complete discussion of the historical development of the MS-Xa-SCF method can be found in Slater's autobiography<sup>1</sup>. The Xa approximation and its application, with emphasis on atoms and solids are given in detail in Volume IV of "Quantum Theory of Molecules and Solids" by Slater<sup>2</sup>. The complete derivation of the system of equations for the MS-Xa-SCF method has been given in the reviews by Johnson<sup>3</sup> and by Weinberger <u>et al.</u><sup>4</sup>. In addition to these, there are a few reviews dealing with the outline of the method and application to molecules<sup>5-7</sup>.

### A. Hartree-Fock Equations and the $X_{\alpha}$ Approximation<sup>2</sup>

For a system of N electrons moving in the potential field due to nuclei, the Schrödinger equation is

$$\hat{\mathcal{F}}\psi(1,2\ldots N) = E\psi(1,2,\ldots N)$$
(1)

where  $\mathcal{H}$  is the Hamiltonian operator,

$$\hat{\boldsymbol{\mu}} = \sum_{i=1}^{N} f(i) + \sum_{i>j} g(i,j). \qquad (2)$$

Here the first term is the one-electron operator and the second the two-electron operator

$$f(\mathbf{i}) = -\nabla_{\mathbf{i}}^{2} - \sum_{u=1}^{M} \frac{Z_{u}}{r_{u\mathbf{i}}}$$
(3)

$$g(i,j) = \frac{2}{r_{i,j}}$$
, (4)

where the first term in Equation (3) is the kinetic energy operator and the second term represents the electron nuclear attraction. The summation over u in Equation (3) takes into account the electron nuclear interaction involving all the nuclei in the system. The two-electron operator g(i,j) of Equation (4) accounts for the electron-electron repulsion. The above Hamiltonian is in Rydberg units.

The N electron wavefunction  $\psi(1,2,\ldots,N)$  is written as a single determinantal function in terms of N one-electron functions  $\chi_i$ , each of which is a product of a spatial function and a spin function,

$$\psi(1,2,...N) = A\chi_1(1)\chi_2(2)...\chi_N(N)$$
,

where

$$\langle \chi_{i} | \chi_{j} \rangle = \delta_{ij}$$
 (5)

and A is the antisymmetrizer. The orthonormal set of one-electron functions  $\{\chi_i\}_{i=1}^N$  are determined using the variation principle so that

$$E = \langle \psi(1, 2, ..., N) | \mathcal{F} | \psi(1, 2, ..., N) \rangle$$
 (6)

is a minimum. On varying the set of function  $\{\chi_i\}_{i=1}^N$ independently with the orthogonality constraint (Equation 5) we get the Hartree-Fock equation for the spin orbital  $\chi_i$ ,

$$\{ \hat{\mathbf{f}} + \sum_{j=1}^{N} \int_{\chi_{j}^{*}(2)g(1,2)(1-\hat{P}_{12})\chi_{j}(2)d\tau(2)\}\chi_{1}(1) = \varepsilon_{1}\chi_{1}(1)$$

$$(7)$$

where  $\hat{P}_{12}$  is a permutation operator.

The second term in the Hartree-Fock equation (Equation (7)) for  $\chi_1$  can be rewritten as

$$\sum_{j=1}^{N} \int d\tau (2) \chi_{j}^{*}(2) g(1,2) (1-P_{12}) \chi_{j}(2) \chi_{i}(1)$$

$$= \sum_{j=1}^{N} \chi_{i}(1) \int d\tau (2) \chi_{j}^{*}(2) g(1,2) \chi_{j}(2)$$

$$- \sum_{j=1}^{N} \chi_{j}(1) \int d\tau (2) \chi_{j}^{*}(2) g(1,2) \chi_{i}(2) \qquad (8)$$

The spin integration in Equation (8) results in a factor of +1 multiplying the spatial integral for the first term on the R.H.S. of Equation (8), while the second term vanishes unless  $\chi_1$  and  $\chi_j$  have the same spin component. Hence the potential energy contribution (excluding the nuclear attraction) in the Hartree-Fock equation can be written as

$$\hat{\nabla}(1)\chi_{1}(1) = \sum_{j}^{||} \chi_{1}(1)f\chi_{j}^{*}(2)g(1,2)\chi_{j}(2)d\tau(2) + \sum_{j}^{\perp} \chi_{1}(1)f\chi_{j}^{*}(2)g(1,2)\chi_{j}(2)d\tau(2) - \sum_{j}^{||} \chi_{j}(1)\chi_{j}^{*}(2)g(1,2)\chi_{1}(2)d\tau(2)$$
(9)

The terms in Equation (9) can be written in the following forms (Equations (9)-(12)):

$$\sum_{j}^{||} \chi_{1}(1) \int \chi_{j}^{*}(2) g(1,2) \chi_{j}(2) d\tau(2)$$

$$= \chi_{1}(1) \int \rho^{||} (2) g(1,2) dV(2) \qquad (10)$$

where  $\rho^{||}(2) = \sum_{j}^{||} \int d\xi(2)\chi_{j}^{*}(2)\chi_{j}(2)$  is the density of electrons with the same spin as  $\chi_{i}$  at the terminus of a position vector  $\vec{r}_{2}$ . The integration in the expression for  $\rho^{||}(2)$  is the spin integration.

$$\sum_{j}^{\perp} x_{1}(1) \int x_{j}^{*}(2) g(1,2) x_{j}(2) d\tau(2) = x_{1}(1) \int \rho^{\perp}(2) g(1,2) dV(2)$$
(11)

where  $\rho(2) = \sum_{j=1}^{j} \int d\xi(2) \chi_{j}^{*}(2) \chi_{j}(2)$  is the density of electrons with spins opposite to that hosted by  $\chi_{1}$ .

$$-\sum_{j}^{||} x_{j}(1) f x_{j}^{*}(2) g(1,2) x_{i}(2) d\tau(2) = -\sum_{j}^{||} x_{j}(1) \frac{x_{i}(1)}{x_{i}(1)} f x_{j}^{*}(2) g(1,2) x_{i}(2) d\tau(2) = -x_{i}(1) f \sum_{j}^{||} \frac{(x_{j}(1) x_{j}^{*}(2) x_{i}(2))}{x_{i}(1)} g(1,2) d\tau(2) (12)$$

We now define the exchange charge density  $\rho_{1}^{\text{ex}}(1,2)$  as

$$\rho_{i}^{ex}(1,2) = \sum_{j} \frac{\chi_{j}(1)}{\chi_{i}(1)} \int d\xi(2) \chi_{j}^{*}(2) \chi_{i}(2)$$

and using Equations (10)-(12) can write the Hartree-Fock equation determining  $\chi_1$  as

$$\{\hat{\mathbf{f}} + f\rho^{||}(2)g(1,2)dv(2) + f\rho^{||}(2)g(1,2)dv(2) - f\rho^{ex}(1,2)g(1,2)dv(2)\}\chi_{i}(1) = \varepsilon_{i}\chi_{i}(1).$$
(13)

Since

$$f_{\rho}$$
 (2) $dv(2) = N_{||}$  and  $f_{\rho}$  (2) $dv(2) = N_{|}$ 

where  $N_{||} + N_{\perp} = N$ , the total number of electrons. The electron hosted by orbital  $\chi_i$  thus seems to interact with itself via Coulombs law, which is physically unrealistic. This self interaction is cancelled by a part of the exchange charge density. The number of electrons in the exchange charge density is

$$f_{\rho}^{ex}(1,2)dv(2) = \sum_{j}^{||} \frac{x_{j}(1)}{x_{i}(1)} f_{\chi_{j}^{*}(2)\chi_{i}(2)d\tau(2)}$$
$$= \sum_{j}^{||} \frac{x_{j}(1)}{x_{i}(1)} \delta_{ij} = 1 ,$$

or exactly one electron, and as particle 2 tends to 1

$$\lim_{2 \to 1} \rho_{i}^{ex}(1,2) \qquad \sum_{j}^{\nu} \frac{\chi_{j}(1)}{\chi_{i}(1)} < \chi_{j}^{*}(1)\chi_{i}(1)^{>} \text{spin}$$

$$= \sum_{j}^{||} f_{X_{j}}^{*}(1) X_{j}(1) d\xi(1) = \rho (1)$$

the exchange charge density is equal to the density of electrons with the same spin as electron 1.

Hence, in the immediate vicinity of electron 1 the exchange charge density is equal to the density of electrons with the same spin as electron 1. The exchange charge is dense around 1 = 2 and goes to zero rapidly as the electrons are separated.

In this region, therefore,  $\chi_1$  is determined by

$$(\hat{f}(1) + \int \frac{\rho^{\perp}(2)}{r_{12}} dv(2) \chi_{1}(1) = \varepsilon_{1}\chi_{1}(1)$$
  
for 1 close to 2.

Thus the following picture then emerges within the Hartree-Fock model: "Each electron moves in the field of the nucleus, the electrons of the opposite spin, and those of parallel spin outside an 'exchange hole' or 'Fermi hole', which follows around wherever it goes".<sup>8</sup>

The exchange charge density has a different form for each wavefunction. The total exchange charge, however, equals one electronic charge in each case, and its value when point 1 equals point 2 is in each case equal, so that the net size of the Fermi hole must be approximately the same for each wavefunction, even though it may differ in shape and other details. Thus, a great error may not be made if the actual Fermi holes, which are different for each  $\chi_i$ , are replaced by an average value taken to be the same for all  $\chi_i$ 's. This forms the basis of X $\alpha$  self-consistent field calculations.

In the X<sub>a</sub> approximation the different exchange charge density for each orbital of the Hartree-Fock model is replaced by a weighted mean of the exchange charge densities, the weighting factor being the probability that an electron found at the position symbolized by 1 should be found in the ith spin orbital. The density of charge of spin-up electron at position 1, arising from the ith spin orbital, is  $n_i \chi_i^*(1)\chi_i(1)$ , and the total density of spinup electron at this position is  $\sum_{K+} n_K \chi_K^*(1)\chi_K(1)$ . Here it is assumed that  $\chi_i$  is a spin orbital corresponding to spinup electron. Hence the probability that an electron at position 1 with spin-up should be in the ith spin orbital is

$$\frac{n_{i}\chi_{i}^{*}(l)\chi_{i}(l)}{\sum_{K\uparrow}n_{K}\chi_{K}^{*}(l)\chi_{K}(l)}$$

The desired weighted mean of the exchange potential is then

$$[V_{XHF1+}(1)]_{av} = - \frac{\sum \sum n_{i}n_{j}f\chi_{1}^{*}(1)\chi_{1}^{*}(2)g(1,2)\chi_{j}(1)\chi_{1}(2)dv(2)}{\sum K_{1}^{2}n_{K}\chi_{K}^{*}(1)\chi_{K}(1)}$$

where  $n_{i}$ ,  $n_{j}$  and  $n_{K}$  are the occupation numbers of the respective orbitals. A similar expression can be written for the spin-down case. The above expression for the exchange potential can be evaluated exactly for a free electron gas for which the spin orbitals are plane waves. If one carries through the calculation<sup>9</sup>, the result is

$$[V_{XHF1+}(1)]_{av} = -6[\frac{3}{4\pi}\rho+(1)]^{1/3} = V_{XS+}(1)$$

where  $\rho^{\dagger}(l) = \sum_{i \uparrow} n_i \chi_i^{\dagger}(l) \chi_i(l)$ .

In the  $X\boldsymbol{\alpha}$  approximation the exchange potential is rewritten as

$$V_{X\alpha\uparrow}(1) = \alpha V_{XS\uparrow} = -6\alpha \left[\frac{3}{4\pi}\rho\uparrow(1)\right]^{1/3},$$

where  $\alpha$  is an adjustable parameter. In Slater's approximation<sup>10</sup> for the exchange potential, the exchange potential of the Hartree-Fock equation is replaced by its average, and this in turn is replaced by its value for a free electron gas. On the other hand if one replaces the exchange potential in the total energy expression by its statistical equivalent as Gaspar, Kohn and Sham<sup>12</sup> did, and then varies the spin orbital  $\chi_1$  in this statistical expression for total energy, one obtains a one-electron equation for the spin orbital with  $V_{XS+}(1)$  having only two-third of the value obtained by Slater's method. If in the statistical expression for total energy, the exchange potential term is replaced by  $\frac{3}{2}\alpha$  times the Gaspar-Kohn-Sham value, the following expression for the total energy is obtained

$${}^{\leq}E_{X\alpha} {}^{\geq} = \sum_{i} n_{i} f_{\chi_{1}^{*}(1)} f_{\chi_{1}(1)} dv(1)$$

$$+ \frac{1}{2} f_{\rho}(1)_{\rho}(2)g(1,2) dv(1) dv(2)$$

$$- \frac{9}{2} \alpha (\frac{3}{4\pi})^{1/3} f\{[\rho+(1)]^{4/3}+[\rho+(1)]^{4/3}\} dv(1)$$

$$(14)$$

If in this expression for the total energy the spin orbitals are varied to minimize energy, the following one electron equation is obtained

$$[-\nabla_{1}^{2} + \nabla_{c}(1) + \nabla_{X\alpha^{\dagger}}(1)]_{\chi_{i^{\dagger}}(1)} = \varepsilon_{iX\alpha}\chi_{i^{\dagger}}(1)$$
(15)

where

$$V_{c}(1) = -\frac{2z}{r_{1}} + \sum_{j} n_{j} f_{\chi_{j}^{*}(2)\chi_{j}(2)g(1,2)dv(2)}$$
$$V_{\chi_{\alpha}^{*}}(1) = -6\alpha [\frac{3}{4\pi} \rho^{*}(1)]^{1/3}$$

The Equations (14) and (15) are the total energy expression and the equation for the one electron orbitals in the X $\alpha$  approximation, respectively.

## B. Determination of $\alpha$ in the X $\alpha$ Method

In the total energy expression of the Xa model,

$$\langle E_{X\alpha} \rangle = \sum_{i} n_{i} f_{\chi_{1}^{*}(1)} f_{\chi_{1}^{i}(1)} dv(1)$$

$$+ \frac{1}{2} f_{\rho}(1)_{\rho}(2)g(1,2) dv(1) dv(2)$$

$$- \frac{9}{2} \alpha (\frac{3}{4})^{1/3} f_{\rho^{*}(1)} f_{\rho^{*}(1)} + [\rho^{*}(1)]^{4/3} dv(1)$$

The X $\alpha$  exchange term appears with a negative sign and is linear in  $\alpha$ . So  $\alpha$  cannot be determined by minimizing the energy. There are three sets of  $\alpha$  values available for the various atoms. One of the criteria used for determining  $\alpha$  is to choose  $\alpha$  so that  $\langle E_{\chi\alpha} \rangle$  is exactly equal to the configuration averaged Hartree-Fock total energy<sup>12</sup>. The  $\alpha$  values so determined show a smooth variation with atomic number;  $\alpha$  decreases with atomic number, being around 0.78 for the two electron atom, decreasing to a range of 0.72-0.70 for the 3d transition series and remaining almost constant thereafter at 0.69. The  $\alpha$ 's determined in this manner are the most widely used in molecular calculations. The second procedure is to use X $\alpha$  atomic orbitals and Hartree-Fock operators to compute the virial ratio (-V/T) and choose  $\alpha$  to get the best number for the virial ratio<sup>13</sup>. In the third procedure for determining  $\alpha$ , a linear variation of Fermi-hole density is assumed with the appropriate boundary values<sup>14</sup>. The  $\alpha$  values depend on the number of electrons with each spin type as shown in the following equations

$$\alpha_{\uparrow} = \frac{8}{27} \left(\frac{4\pi^2}{3}\right)^{1/3} \frac{\frac{1}{n_{\uparrow}} + \frac{1}{2}}{\left(\frac{1}{n_{\downarrow}} + \frac{1}{3}\right)^{2/3}}$$
(16)

$$\alpha = (n_{\uparrow}\alpha_{\uparrow} + n_{\downarrow}\alpha_{\downarrow})/(n_{\downarrow} + n_{\downarrow}), \qquad (17)$$

where  $n_{\uparrow}$  is the number of electrons with spin up ( $\alpha$  spin),  $n_{\downarrow}$  the number of electrons with spin down ( $\beta$  spin) and  $\alpha_{\uparrow}$  is the  $\alpha$  value for spin up electrons. The expression for  $\alpha_{\downarrow}$  is similar to that of Equation (16). These socalled theoretical  $\alpha$  values reproduce the atomic number dependence of  $\alpha$  values determined by the first procedure in all details. The  $\alpha$  values determined by this procedure also fall in the range 1.0 to 0.6666.

# C. Interpretation of $X_{\alpha}$ Eigenvalues and Slater Transition States<sup>15</sup>

The eigenvalue  $\varepsilon_{iHF}$  of the Hartree-Fock method is a finite difference of energies  $\langle E_{HF} \rangle$  for the two states for which the occupation number  $n_i$  of the ith spin orbital differs by unity. On the other hand, the eigenvalue  $\varepsilon_{iX\alpha}$  of the X $\alpha$  method is given by

$$\epsilon_{iX\alpha} = \frac{\partial}{\partial n_i} < E_{X\alpha} >, \qquad (18)$$

<u>i.e.</u>, a partial derivative instead of a finite difference. The total energy in the  $X\alpha$  method can be written as

$$E_{X\alpha} = \sum_{i=1}^{n} \langle i | i \rangle + \frac{1}{2} \sum_{i=j=1}^{n} n_{j} \langle i | | j \rangle + c\alpha \{ \langle \rho_{+}^{4/3}(1) \rangle + \langle \rho_{+}^{4/3}(1) \rangle \},$$
(19)

where  $n_{\rm K}$  is the occupancy of the spin orbital  $\chi_{\rm K},$  which is a solution of the following one-electron equation

$$\{f_{1} + \sum_{j} \chi_{j}^{*}(2)\chi_{j}(2)g(1,2)dv(2) + \frac{4}{3}c\alpha\rho_{\uparrow}^{1/3}\}\chi_{K\uparrow}(1) = \epsilon_{K}\chi_{K\uparrow}(1),$$
(20)

where  $f_1$  and g(1,2) are the one- and two-electron operators defined earlier and

From Equation (20) the  $X_{\mbox{\scriptsize $\alpha$}}$  eigenvalue can be written as

$$\varepsilon_{K} = \langle K | K \rangle + \sum_{j} n_{j} \langle K | | j \rangle + \frac{4}{3} C \alpha \langle \chi_{K^{\dagger}}(1) \chi_{K^{\dagger}} \rho_{\dagger}^{1/3}(1) \rangle.$$
(21)

The unrelaxed ionization potential  $I_K^{ur}$  for the K<sup>th</sup> orbital can be calculated by setting  $n_K = 1$  for the neutral state and  $n_K = 0$  for the ion in Equation (20) and taking the difference, keeping the  $\chi_i$ 's the same as in the neutral case. Thus

$$I_{K}^{ur} = E^{+} - E^{0} = -\langle K | K \rangle - \sum_{\substack{j \neq K}} n_{j} \langle K | | j \rangle - \frac{1}{2} \langle K | | K \rangle + C_{\alpha} \langle \rho_{K^{+}}^{4/3}(1) - \rho_{+}^{4/3}(1) \rangle, \qquad (22)$$

where

$$\rho_{K\uparrow} = \rho_{\uparrow}(1) - n_{K}\chi_{K}^{*}(1)\chi_{K}(1)$$

The last term on the R.H.S. of Equation (22) can be rewritten as

$$C\alpha < \rho_{\uparrow}^{4/3}(1)[(1 - \frac{\chi_{K}^{*}(1)\chi_{K}(1)}{\rho_{\uparrow}(1)})^{4/3} - 1] > .$$

Binomial expansion and neglect of all higher powers of  $\chi_{K}^{*}(1)\chi_{K}(1)/\rho_{\uparrow}(1)$ , which are expected to be small, enables us to write this term as

$$-\frac{4}{3} C_{\alpha} < \chi_{K}^{*}(1) \chi_{K}(1) \rho_{\uparrow}^{1/3}(1) > .$$

Thus,

$$I_{K}^{ur} = -\langle K | K \rangle - \sum_{\substack{j \neq K}} n_{j} \langle K | | j \rangle - \frac{1}{2} \langle K | | K \rangle - \frac{4}{3} C \alpha \langle \chi_{K}^{*}(1) \chi_{K}(1) \rho_{\dagger}^{1/3}(1) \rangle$$
(23)

and from Equations (21) and (23), we get

$$I_{K}^{ur} = - \varepsilon_{K} + \frac{1}{2} < K | | K > .$$
 (24)

In the Hartree-Fock theory, the unrelaxed ionization potential (Koopmans' approximation) is given by

$$I_{K}^{ur} = -\varepsilon_{K}^{HF} = E_{HF}^{+}(K) - E^{\circ} , \qquad (25)$$

where  $E_{\rm HF}^+(k)$  is the Hartree-Fock energy of the system with

the electron in the  $K^{th}$  orbital removed and  $E^{O}$  that of the neutral system.

Equations (24) and (25) show that the X $\alpha$  eigenvalue does not have the same physical significance as in the Hartree-Fock theory. In the X $\alpha$  method, the eigenvalue differs from the ionization potential by the self-interaction term  $\frac{1}{2}$ <K||K>. It is easy to trace the origin of this discrepancy. In the Hartree-Fock theory, the selfinteraction term is exactly cancelled by part of the exchange term; but in the X $\alpha$  method, because of the exchange approximation, no such cancellation occurs and this unphysical term appears in the expression for  $I_{\rm K}$ .

In the Slater transition-state method of calculating ionization potential the eigenvalue  $\varepsilon_{\rm K}$  of the orbital of interest is calculated for a state midway between the neutral and ionized states, namely when half an electron is removed from the K<sup>th</sup> orbital. The unrelaxed eigenvalue  $\varepsilon_{\rm K}$  for the transition state  $n_{\rm K} = \frac{1}{2}$  can be written as

$$\epsilon_{K}(n_{K}=\frac{1}{2})=\langle K | K \rangle + \sum_{\substack{j \neq K}} n_{j} \langle j | | K \rangle + \frac{1}{2} \langle K | K \rangle + \frac{4}{3} C \alpha \langle \chi_{K}^{*}(1) \chi_{K}(1) \rho_{\uparrow}^{1/3}(1) \rangle$$
(26)

after expanding the exchange term and neglecting all highe powers of  $\chi_{K}^{*}(1)\chi_{K}(1)/2\rho_{\uparrow}(1)$ . On comparing with Equations (23) and (24) we get

$$I_{K}^{ur} = -\varepsilon_{K}(n_{K} = \frac{1}{2}) = -\varepsilon_{K} + \frac{1}{2} \langle K | | K \rangle$$

However, in actual transition-state calculations, the SCF eigenvalue equations are solved for the occupancy  $n_{\rm K} = \frac{1}{2}$ , which therefore involves some relaxation (complete relaxation is not included since the whole electron is not removed). These eigenvalues, which we denote by  $\epsilon_{\rm K}^{\rm tr}$ , are then identified with the negative of the relaxed ionization potential,  $I_{\rm K}^{\rm rel}$ , <u>i.e.</u>,

$$I_K^{rel} = - \varepsilon_K^{tr}$$

There is empirical justification for this assumption from the reported<sup>16</sup> agreement between  $\varepsilon_{K}^{tr}$  values and  $\Delta E(=(E^{+}(K) - E^{O})$  where the E's are the total energies) values. Then the relaxation contribution to the ionization potential is given by

$$\Delta E_{K}^{rel} = I_{K}^{ur} - I_{K}^{rel} = - \varepsilon_{K} + \frac{1}{2} \langle K | | K \rangle + \varepsilon_{K}^{tr}$$

It has been shown that the main effect of the transition-state procedure is to correct for the self energy of the electron in the X $\alpha$  approximation and that the transition state eigenvalues do not include any correlation effects<sup>15</sup> as had been suggested earlier<sup>17</sup>. Recently it has again been shown that the X $\alpha$  approximation does not include any correlation effects<sup>18</sup>.

### D. Multiple Scattering SCF Method<sup>3,4</sup>

The multiple scattering SCF method is based on the geometrical partitioning of a molecule or a cluster into three fundamental types of regions, namely, atomic, interatomic and extramolecular. The one-electron Schrödinger equation is numerically integrated within each region in the partial-wave representation for sphericallyaveraged potential in the atomic and extramolecular region and volume-averaged potential in the interatomic region. The wavefunctions and their first derivatives are joined continuously throughout the various regions of the cluster via multiple-scattering theory. This procedure leads to a rapidly convergent set of equations which are numerically solved for the molecular orbital energies and wavefunctions. This entire numerical procedure is repeated, using the wavefunctions obtained at each iteration to generate a charge density and new potential, until self-consistency is attained.

The three fundamental types of regions into which a molecule is partitioned are:

(i) Atomic: The region within nonoverlapping spheres centered on the constituent atoms (spheres can be made to overlap too).

(ii) Interatomic: The region between the 'inner' atomic spheres and an 'outer' sphere surrounding the

entire molecule.

(iii) Extramolecular: The region exterior to the outer sphere.

The one-electron Schrödinger equation (in Rydberg units)

$$[-\nabla^2 + V(r)]\psi(r) = E\psi(r)$$

is solved in each of the different regions for the appropriate local potential V(r)

$$V(\mathbf{r}) = V_{c}(\mathbf{r}) + V_{X\alpha}(\mathbf{r}).$$

The local potential includes the Xa approximation to the exchange potential in addition to the Coulomb potential.

$$V_{c}(1) = -\frac{2Z}{r_{1}} + \sum_{j} n_{j} f_{\chi_{j}^{*}(2)\chi_{j}(2)g(1,2)dv(2)} g(1,2) = \frac{2}{r_{12}}$$
$$V_{X\alpha}(1) = -6\alpha [\frac{3}{4\pi}\rho(1)]^{1/3}.$$

#### (1) <u>Muffin-tin Approximation</u>:

In the muffin-tin approximation the local potential field of V(r) of a molecule or a cluster is replaced by a set of individual, non-overlapping spherically symmetric potentials  $V^{i}(r_{i})$  around each atomic site  $R_{i}$ ,



Figure 1. Partition of space for a triatomic molecule.
where  $R_i$  refers the atomic site to the origin of the cluster (Figure 1). A spherically-averaged potential is used in the region outside the outer sphere while a volume-averaged or a constant potential is used in the inter-atomic region.

Thus, within the 'muffin-tin' approximation, the potential field is replaced by a model potential of the following form

 $V^{1}(|\mathbf{r}-\mathbf{R}_{1}|); \quad |\mathbf{r}-\mathbf{R}_{1}|=\mathbf{r}_{1} \leq \mathbf{b}_{1} \quad \mathbf{i} = 1, \dots \mathbf{N}$  $V(\mathbf{r}) = V^{0}(|\mathbf{r}-\mathbf{R}_{0}|); \quad |\mathbf{r}-\mathbf{R}_{0}|=\mathbf{r}_{0} > \mathbf{b}_{0}$  $\overline{V} \qquad ; \quad \text{otherwise.}$ 

The potential energy at an arbitrary point  $\vec{r}$  of the molecule can be expanded as a superposition

$$V(\vec{r}) = \sum_{j} V^{j}(|\vec{r} - \vec{R}_{j}|)$$

of free-atom or free ion SCF-X<sub> $\alpha$ </sub> potentials centered at positions R<sub>j</sub>. The potential energy is represented inside each atomic region I by expanding the superposition in a series of spherical harmonics.

$$V_{I}(\vec{r}) = \sum_{L} V_{L}(\vec{r}) Y_{L}(\vec{r}) \qquad L = (l,m)$$

The muffin-tin approximation consists of using only the first term L = (0,0) (spherically symmetric) in the spherical harmonic expansion of the superposed potential. In the muffin-tin approximation the potential in a particular atomic region includes not only the contribution of the atom located there, but also the sphericallyaveraged contribution of all the other atomic potentials to that region.

### 2. Secular Equations

Consider a molecule with the geometry as shown in Figure 1. The outer sphere will be denoted with an index i = 0, and atomic spheres with i > 0.

The wavefunction  $\psi(\mathbf{r})$  in regions of spherically-symmetric potential (interior to the ith (i > 0) sphere and exterior to the outer sphere) can be written as

 $\psi(\mathbf{r}) = \sum_{L} C_{L}^{i} R_{L}^{i}(\mathbf{r}_{i}; E) Y_{L}(\mathbf{r}_{i}); \quad L = (\ell, m) \quad (27).$   $0 \leq \mathbf{r}_{i} \leq b_{i} \quad \text{for all } i > 0$   $b_{o} \leq \mathbf{r}_{o} \leq \infty \quad \text{for } i = 0,$ 

where the quantities  $C_{L}^{i}$  are coefficients to be determined,  $Y_{L}(r_{i})$  are real spherical harmonics and  $R_{L}^{i}(r_{i};E)$  solutions of the radial Schrodinger equation in region i, corresponding to the trial eigenvalue E and angular momentum 1:

$$\{-\frac{1}{r_{1}^{2}}\frac{d}{dr_{1}}r_{1}^{2}\frac{d}{dr_{1}}+\frac{\ell(\ell+1)}{r_{1}^{2}}+V^{1}(r_{1})-E\}R^{1}(r_{1},E)=0$$
(28)

For all regular scattering potentials  $V^{i}(r_{i}) \underline{i.e.}$ ,

$$\lim_{r_{1} \to 0} [r_{1}^{2} v^{1}(r_{1})] = 0$$

Two independent solutions of Equation (28) exist which behave at the origin i as  $r_1^{\ell}$  and  $r_1^{-\ell-1}$ , respectively.

Two boundary conditions are necessary to make a solution of Equation (28) unique. The first is a condition of regularity for  $R_{\ell}^{i}(r_{i}, E)$ , and is sufficient to identify one of the two solutions mentioned up to a multiplicative constant, <u>i.e.</u>,

$$R_{\ell}^{i}(r_{i}, E) \rightarrow \text{const. } r_{i}^{\ell}; i > 0$$
$$r_{i}^{\neq 0}$$

which characterizes the asymptotic behavior of  $R_{l}^{1}(r_{1},E)$ .

In the intersphere region (<u>i.e.</u>, region of constant potential) the Schrodinger equation takes the following form

$$\{-\nabla^2 + K^2\}\psi(\mathbf{r}) = 0, \quad K^2 = (\overline{V} - E).$$
 (29)

The solution of Equation (29) around any scatterer i > 0 can be divided into an incident wave  $\psi_{inc}^{i}(r)$  and a scattered wave  $\psi_{SC}^{i}(r)$ ,

$$\psi(\mathbf{r}) = \psi_{inc}^{i}(\mathbf{r}) + \psi_{SC}^{i}(\mathbf{r}); \quad i > 0$$
 (30)

$$\psi_{inc}^{i}(\mathbf{r}) = \begin{bmatrix} \sum_{L}^{L} B_{L}^{i} i_{\ell} (Kr_{i}) Y_{L}(r_{i}); & E < \overline{V}; & i > 0 \\ \\ \sum_{L}^{L} B_{L}^{i} j_{\ell} (Kr_{i}) Y_{L}(r_{i}); & E > \overline{V}; & i > 0 \quad (31) \end{bmatrix}$$

$$\psi_{SC}^{i}(\mathbf{r}) = \sum_{L}^{\Sigma} A_{L}^{i} K_{\ell}^{(1)}(Kr_{i}) Y_{L}(r_{i}); \quad E < \overline{V}; \quad i > 0$$

$$\sum_{L}^{\Sigma} A_{L}^{i} \mu_{\ell}(Kr_{i}) Y_{L}(r_{i}); \quad E > \overline{V}; \quad i > 0$$
(32)

$$j_{\ell}(X)$$
 - spherical Bessel function  
 $\mu_{\ell}(X)$  - spherical Neumann function  
 $i_{\ell}(X) = i^{\ell}j_{\ell}(X)$  - Modified spherical Bessel function  
 $K_{\ell}^{(1)}(X) = -i^{-\ell}h_{\ell}^{(1)}(iX)$  - Modified Henkel function of  
the first kind.

For any scatterer i > 0 the incident wave  $\psi_{inc}^{i}(r)$  is regular when expanded about the center of the scatterer, while the corresponding scattered wave  $\psi_{SC}^{i}(r)$  is irregular at the center of the scatterer when analytically continued. The second boundary condition is to match continuously the wavefunction and its first derivative interior to a sphere i > 0, at the sphere boundary  $b_i$  with the corresponding quantities derived from the field [Equation (30)] around this sphere. In order to satisfy this condition, it is necessary and sufficient to equate the amplitudes and the logarithmic derivatives taken at the sphere boundary  $r_1 = b_1$ ,

ie 
$$A_{L}^{i} = t_{\ell}^{i}(E)B_{L}^{i}$$

$$-\frac{[i_{\ell}(Kb_{1}), R_{\ell}^{1}(b_{1}, E)]}{[K_{\ell}^{(1)}(Kb_{1}), R_{\ell}^{1}(b_{1}, E)]}; \quad E < \overline{V}$$

$$t_{\ell}^{1}(E) = (34)$$

$$-\frac{[j_{\ell}(Kb_{1}), R_{\ell}^{1}(b_{1}, E)]}{[\mu_{\ell}(Kb_{1}), R_{\ell}^{1}(b_{1}, E)]}; \quad E > \overline{V}$$

where the square bracket in (34) symbolizes the following Wronskian form

$$[f(x),g(x)] = f(x) \frac{dg}{dx} (x) - g(x) \frac{df}{dx} (x) ;$$

 $t_l^i(E)$  is frequently called the 'scattering factor'.

We can express the amplitudes  $A_L^i$  of the scattered waves  $\psi_{SC}^i(r)$  in terms of the coefficients  $C_L^i$  of Equation

(27) by matching the wavefunctions at the sphere boundaries. For example, for E <  $\overline{V}$  we obtain

$$C_{L}^{i}R_{\ell}^{i}(b_{i}, E) = B_{L}^{i}i_{\ell}(Kb_{i}) + A_{L}^{i}K^{(1)}(Kb_{i})$$

$$= \{t_{\ell}^{i}(E)^{-1}i_{\ell}(Kb_{i}) + K^{(1)}(Kb_{i})\}A_{L}^{i}$$

$$A_{L}^{i} = \frac{[i_{\ell}(Kb_{i}), R_{\ell}^{i}(b_{i}, E)]}{[i_{\ell}(Kb_{i}), K_{\ell}^{(1)}(Kb_{i})]}C_{L}^{i}$$
(35)

$$[i_{\ell}(Kb_{i}), K_{\ell}^{(1)}(Kb_{i})] = (-1)^{\ell+1}/Kb_{i}^{2}$$
$$[j_{\ell}(Kb_{i}), \mu_{\ell}(Kb_{i})] = 1/Kb_{i}^{2}$$

$$A_{L}^{i} = Kb^{2}C_{L}^{i} \qquad (-1)^{\ell+1}[i_{\ell}(Kb_{i}), R_{\ell}^{i}(b_{i}, E)]; \quad E < \overline{V} \qquad (36)$$
$$[j_{\ell}(Kb_{i}), R_{\ell}^{i}(b_{i}, E)]; \quad E > \overline{V}$$

For the region exterior to the outer-sphere region

$$\psi(\mathbf{r}) = \sum_{\mathrm{L}} C_{\mathrm{L}}^{\mathrm{o}} R_{\ell}^{\mathrm{o}}(\mathbf{r}_{\mathrm{o}}, \mathrm{E}) Y_{\mathrm{L}}(\mathbf{r}_{\mathrm{o}})$$
(37)

and the regularity of the solution is required for large  $\ensuremath{\mathbf{r}}$ 

ie 
$$\lim_{r_0 \to \infty} R_{\ell}^0(r_0, E) = 0.$$

Hence, we have a different situation from that in the i > 0 case for solution of Equation (29) in the inter-sphere region

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$$\psi(\mathbf{r}) = \psi_{\text{inc}}^{\circ}(\mathbf{r}) + \psi_{\text{SC}}^{\circ}(\mathbf{r}) , \qquad (38)$$

namely, the incident wave  $\psi_{inc}^{o}(r)$  is irregular at the origin of the outer sphere and the scattered wave  $\psi_{SC}^{o}(r)$  regular;

$$\psi_{\text{inc}}^{\circ}(\mathbf{r}) = \sum_{L}^{\Sigma} B_{L}^{\circ} \chi_{\ell}^{(1)}(Kr_{\circ}) Y_{L}(r_{\circ}); \quad E < \overline{V}$$

$$\sum_{L}^{\Sigma} B_{L}^{\circ} \mu_{\ell}^{\circ}(Kr_{\circ}) Y_{L}(r_{\circ}); \quad E > \overline{V}$$
(39)

$$\Psi_{SC}^{o}(\mathbf{r}) = \sum_{L}^{\Sigma} A_{L}^{o} \mathbf{i}_{\ell} (Kr_{o}) Y_{L}(r_{o}); \quad E < \overline{V}$$

$$\sum_{L} A_{L}^{o} \mathbf{j}_{\ell} (Kr_{o}) Y_{L}(r_{o}); \quad E > \overline{V}$$

$$(40)$$

By analogy to the i > 0 case, we can express the amplitudes  $A_{\rm L}^{\rm O}$  of the scattered wave in terms of  $B_{\rm L}^{\rm O}$  or  $C_{\rm L}^{\rm O}$ ,

$$A_{L}^{O} = t_{\ell}^{O}(E)B_{L}^{O}$$

$$- \frac{[K_{\ell}^{(1)}(Kb_{O}), R_{\ell}^{O}(b_{O}, E)]}{[i_{\ell}(Kb_{O}), R_{\ell}^{O}(b_{O}, E)]}; \quad E < \overline{V}$$

$$t_{\ell}^{O}(E) = (41)$$

$$-\frac{[\mu_{\ell}(Kb_{o}), R^{o}_{\ell}(b_{o}, E)]}{[j_{\ell}(Kb_{o}), R^{o}_{\ell}(b_{o}, E)]}; \quad E > \overline{V}$$

.

$$A_{L}^{O} = Kb_{O}^{2}C_{L}^{O} \qquad (-1)^{\ell+1}[R_{\ell}^{O}(b_{O}, E), K_{\ell}^{(1)}(Kb_{O})]; \quad E < \overline{V}$$

$$[R_{\ell}^{O}(b_{O}, E), \mu_{\ell}(Kb_{O}]; \quad E > \overline{V} .$$
(42)

Method of constructing a unique wavefunction  $\psi(\textbf{r})$  for the whole cluster.

1. The incident wave corresponding to any site i > 0 equals the superposition of the scattered waves from all other scatterers, including the one from the outer sphere:

$$\sum_{L} A_{L}^{i} t_{\ell}^{i} (E)^{-1} i_{\ell} (Kr_{i}) Y_{L}(r_{i}) = \sum_{J} (1 - \delta_{iJ}) \sum_{L'} A_{L}^{J}, K_{\ell'}^{(1)} (Kr_{J}) Y_{L}, (r_{J})$$

$$+ \sum_{L'} A_{L}^{0}, i_{\ell}, (Kr_{0}) Y_{L}, (r_{0}); \quad E < \overline{V}$$

$$\sum_{L} A_{L}^{i} t_{\ell}^{i} (E)^{-1} j_{\ell} (Kr_{i}) Y_{L}(r_{i}) = \sum_{J} (1 - \delta_{iJ}) \sum_{L'} A_{L}^{J}, \mu_{\ell'} (Kr_{J}) Y_{L}, (r_{J})$$

$$+ \sum_{L'} A_{L}^{0}, j_{\ell}, (Kr_{0}) Y_{L}, (r_{0}); \quad E > \overline{V} .$$

$$(44)$$

2. The incident wave for i = 0 has to match the sum of the scattered waves from all scattering regions i > 0.

$$\sum_{L} A_{L}^{\circ} t_{\ell}^{\circ} (E)^{-1} K_{\ell}^{(1)} (Kr_{\circ}) Y_{L}(r_{\circ})$$

$$= \sum_{j,L} A_{L}^{j}, K_{\ell}^{(1)} (Kr_{j}) Y_{L}, (r_{j}); \quad E < \overline{V}$$
(45)

$$\sum_{L} \sum_{L} \sum_{\ell} \sum_{\ell} \sum_{\ell} \sum_{\ell} \sum_{\ell} \sum_{\ell} \sum_{j,L} \sum_{\ell} \sum_{j,L} \sum_{\ell} \sum_{\ell}$$

In order to treat only the center i in Equations (43) and (44) we expand all scattered waves, j > 0,  $j \neq i$ , as incident waves at the site i by means of the following scattered-wave expansion theorems, and according to the follow-ing coordinate relations<sup>3</sup>,

$$K_{\ell}^{(1)}(K|r_{2}-r_{1}|)Y_{L}(r_{2}-r_{1}) = 4\pi \sum_{L'} (-1)^{\ell+\ell'} \sum_{L''} I_{L''}(L;L') \times K_{\ell''}^{(1)}(Kr_{1})Y_{L''}(r_{1})i_{\ell'}(Kr_{2})Y_{L'}(r_{2}) = r_{1}>r_{2}$$

$$K_{\ell}^{(1)}(K|r_{2}-r_{1}|)Y_{L}(r_{2}-r_{1}) = 4\pi \sum_{L'} (-1)^{\ell+\ell'} \sum_{L''} I_{L''}(L;L') \times I_{\ell''}(Kr_{1})Y_{L''}(r_{1})K_{\ell'}^{(1)}(Kr_{2})Y_{L'}(r_{2}) = r_{1} < r_{2}$$

$$i_{\ell}(K|r_{2}-r_{1}|)Y_{L}(r_{2}-r_{1}) = 4\pi\sum_{L'}(-1)^{\ell+\ell'}\sum_{L''}I_{L''}(L;L')$$
$$i_{\ell''}(Kr_{1})Y_{L''}(r_{1})i_{\ell'}(Kr_{2})Y_{L'}(r_{2})$$

$$\mu_{\ell}(K|r_{2}-r_{1}|)Y_{L}(r_{2}-r_{1}) = 4\pi\sum_{L'}i^{\ell'-\ell}\sum_{L''}i^{-\ell''}I_{L''}(L;L')$$

$$\mu_{\ell''}(Kr_{1})Y_{L''}(r_{1})j_{\ell}(Kr_{2})Y_{L'}(r_{2}) = r_{1}>r_{2}$$

$$\mu_{\ell}(K|r_{2}-r_{1}|)Y_{L}(r_{2}-r_{1}) = 4\pi\sum_{L}i^{\ell'-\ell}\sum_{L''}i^{-\ell''}I_{L''}(L;L')$$
$$j_{\ell''}(Kr_{1})Y_{L''}(r_{1}) \mu_{\ell}(Kr_{2})Y_{L}(r_{2}) r_{1}$$

$$j_{\ell}(K|r_{2}-r_{1}|)Y_{L}(r_{2}-r_{1}) = 4\pi\sum_{L}i^{\ell}i^{\ell}\sum_{L}i^{-\ell}I_{L}(L;L')$$
$$j_{\ell}(Kr_{1})Y_{L}(r_{1})j_{\ell}(Kr_{2})Y_{L}(r_{2})$$

where 
$$I_{L''}(L;L') = \int_{0}^{2\pi} d\phi \int_{0}^{\pi} \sin\theta d\theta Y_{L''}(\theta,\phi) Y_{L}(\theta,\phi) Y_{L}(\theta,\phi) Y_{L}(\theta,\phi)$$
  
 $r_{j} = r - R_{j} = r_{i} + R_{i} - R_{j} = r_{i} - R_{ij}$   
 $R_{ij} = R_{j} - R_{i}$ 

The constants  ${\rm I}_{{\rm L}^{\,\prime\prime}}({\rm L}\,;{\rm L}\,')$  are called 'Gaunt' numbers and can

be expressed in terms of Clebsch-Gordan coefficients.

We can similarly express the scattered wave for i = 0 in Equations (43) and (44) as an incident wave at the center i. We can rewrite Equations (43) and (44) in terms of the incident waves for a chosen site i, for  $E < \overline{V}$  as

$$\sum_{L}^{A_{L}^{i}} t_{\ell}^{i}(E)^{-1} i_{\ell}(Kr_{i})Y_{L}(r_{i}) = \sum_{J}^{\Sigma} A_{L}^{J}G_{LL}^{JJ}, i_{\ell}(Kr_{i})Y_{L}(r_{i})$$

$$+ \sum_{L,L}^{\Sigma} A_{L}^{0}\Delta_{LL}^{10}, i_{\ell}(Kr_{i})Y_{L}(r_{i}); \quad E < \overline{V}$$
(47)

$$\sum_{L}^{\Sigma A_{LL}} t_{\ell}^{\circ}(E)^{-1} K_{\ell}^{(1)}(Kr_{\circ}) Y_{L}(r_{\circ}) = \sum_{j L, L}^{\Sigma} A_{L}^{j} \Delta_{LL}^{\circ j}, K_{\ell}^{(1)}(Kr_{\circ}) Y_{L}(r_{\circ});$$

$$E < \overline{V}$$
(48)

where

$$G_{LL}^{jj} = (1 - \delta_{ij})^{\ell + \ell'} \sum_{L''} I_{L''} (L;L') \kappa_{\ell''}^{(1)} (K|\bar{R}_{ij}|) Y_{L''}(\bar{R}_{ij}); \quad E < \bar{V}$$

$$i^{\ell - \ell'} \sum_{L''} i^{-\ell''} I_{L''} (L;L')_{\mu_{\ell''}} (K|\bar{R}_{ij}|) Y_{L''}(\bar{R}_{ij}); \quad E > \bar{V}$$

$$\Delta_{LL}^{io}, = 4_{\pi}$$

$$(-1)^{\ell+\ell'} \sum_{L''} I_{L''}(L;L') i_{\ell''}(K|\vec{R}_{io}|) Y_{L''}(\vec{R}_{io}); E < \nabla$$

$$i^{\ell-\ell'} \sum_{L''} i^{-\ell''} I_{L''}(L;L') j_{\ell''}(K|\vec{R}_{io}|) Y_{L''}(\vec{R}_{io}); E > \nabla$$

$$\vec{R}_{io} = \vec{R}_{o} - \vec{R}_{i}$$

and similar equations for  $E > \overline{V}$  can be written. Equating likewise coefficients in Equations (47) and (48) we obtain the following set of equations for  $E < \overline{V}$ , as well as for  $E > \overline{V}$ 

$$A_{L}^{i} t_{\ell}^{i}(E)^{-1} = \sum_{j,L'} A_{L}^{j}, G_{LL}^{jj}, + \sum_{L'} A_{L}^{\circ}, \Delta_{LL}^{i\circ},$$
$$A_{L}^{\circ} t_{\ell}^{\circ}(E)^{-1} = \sum_{j,L'} A_{L}^{j}, \Delta_{LL}^{\circj}, , \qquad (49)$$

which can be writen in a more compact form as

$$\sum_{L',j} \sum \{t_{\ell}^{j}(E)^{-1} \delta_{ij} \delta_{LL}, - G_{LL}^{jj}, \} A_{L}^{j} - \Delta_{LL}^{i0}, A_{L}^{0}, = 0$$

$$\sum_{L'} \{ \sum \Delta_{LL}^{\circ j}, A_{L}^{j}, \} - t_{\ell}^{\circ}(E)^{-1} A_{L}^{\circ}, \delta_{LL}, = 0 .$$
 (50)

This set of linear equations (50) determines the amplitudes of  $A_L^1$  and  $A_L^0$  of the scattered waves and hence also the amplitudes of the incident waves and the coefficients  $C_L^1$  in Equation (27). The homogeneous system of equations (Equation (50)) has a non-trivial solution if, and only if, the determinant vanishes. Since all the terms of Equation (50) are energy dependent, it is necessary to evaluate explicitly this determinant as a function of the energy E and to find the zero locations of this function. Thus, molecular orbital energies correspond to those parameters E for which non-trivial solutions of Equation (50) exists.

The determinant for a given parameter E, and consequently the location of zero, depends on the number of L terms to be included in the summation in Equation (50). It turns out that this summation is very rapidly convergent and the set  $\ell = 0,1,2$  is most likely to be sufficient for many applications to polyatomic molecules including those involving transition metals.

### 3. The Self-consistent Potential Field<sup>19</sup>

For each root  $\varepsilon_{\rm K}$  of the secular determinant (Equation (50)) we get the expansion coefficients for the solution of one-electron Schrödinger equation in the three different types of regions. The corresponding charge density  $\rho^{\rm 1}(r_{\rm 1},\varepsilon_{\rm K})$  in scattering region i being

$$\rho^{i}(\mathbf{r}_{i}, \epsilon_{K}) = \sum_{L} C_{L}^{i} R_{\ell}^{i} (\vec{r}_{i}, \epsilon_{K}) Y_{L} (\vec{r}_{i}) C_{L}^{i*} R_{\ell}^{*} (\vec{r}_{i}, \epsilon_{K}) Y_{L}^{*} (\mathbf{r}_{i}); i \geq 0,$$

$$(51)$$

where the spherically-averaged charge density  $\sigma^{i}(r_{i},\epsilon_{K})$  is given by

$$\sigma^{1}(\mathbf{r}_{1}, \boldsymbol{\varepsilon}_{K}) = 4\pi\rho^{1}(\mathbf{r}_{1}, \boldsymbol{\varepsilon}_{K})\mathbf{r}^{2}, \quad 1 \geq 0.$$
 (52)

The expansion coefficients  $C_{L}^{i}$  are still unnormalized, as are the charge densities in Equations (51) and (52).

The wavefunction corresponding to the energy  $\boldsymbol{\epsilon}_K$  be denoted by  $\psi(\textbf{r},\boldsymbol{\epsilon}_K)$  and must be normalized as follows

$$\frac{1}{N(\varepsilon_{K})} = \int \psi^{*}(\mathbf{r}, \varepsilon_{K}) \psi(\mathbf{r}, \varepsilon_{K}) dv$$

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$$= \sum_{i>00} \int_{0}^{1} \sigma^{i}(r_{i}, \varepsilon_{K}) dr_{i} + \int_{0}^{\infty} \sigma^{0}(r_{o}, \varepsilon_{K}) dr_{o} + \int_{0}^{1} \psi^{*}(r, \varepsilon_{K}) \psi(r, \varepsilon_{K}) dv_{in}$$

$$\lim_{k \to 0} \int_{0}^{1} \sigma^{0}(r_{o}, \varepsilon_{K}) dr_{o} + \int_{0}^{1} \psi^{*}(r, \varepsilon_{K}) \psi(r, \varepsilon_{K}) dv_{in}$$
(53)

where  $N(\epsilon_K)$  is the normalization constant for this orbital. The last integral defines the fraction of charge in the interstitial region.

The normalized total charge density in a scattering region  $i \ge 0$  is given by a sum over all occupied states

$$\sigma^{1}(\mathbf{r}_{1}) = \sum_{K} n_{K} / N(\varepsilon_{K}) \sigma^{1}(\mathbf{r}_{1}, \varepsilon_{K}) , \qquad (54)$$

with  $n_{K}$  being the occupation number of the orbital K. The total charge within a sphere i > 0 is defined as

$$Q_{i} = \int_{0}^{b_{i}} \sigma^{i}(r_{i}) dr_{i}$$
(55)

and exterior to the outer sphere as

$$Q_{o} = \int_{b_{o}}^{\infty} \sigma^{o}(\mathbf{r}_{o}) d\mathbf{r}_{o}$$
(56)

Using these quantities, we can distribute uniformly the remainder  $Q_{in}$  of the total molecular charge

$$Q_{in} = \sum_{i>0} (Z_i - Q_i) - Q_0$$
(57)

throughout the volume of the interatomic region,  $\Omega_{in}$ ,

$$\Omega_{in} = \frac{4\pi}{3} \{ b_0^3 - \sum_{i>0} b_1^3 \}$$
(58)  
$$\rho_c = \frac{Q_{in}}{\Omega_{in}}$$
(59)

In Equation (57),  $Z_i$  is the atomic number for a site i > 0.

From the quantities  $\sigma^{i}(r_{i}), \rho_{c}$  and  $Q_{i}$ , we can derive a new Coulomb potential  $V_{c}^{i}(r_{i})$  as in Equation (61) for a scattering region i > 0 by solving Poisson's equation interior sphere i > 0 (first three terms of Equation (61)) and adding the various Coulomb contributions arising from a hypothetical system of 'effective' point-charge  $\overline{Q}_{i}$ ,

$$\overline{Q}_{i} = Q_{i} + \frac{4\pi}{3} \rho_{e} b_{i}^{3}$$
(60)

located at sites i > 0, in a uniformly negative background  $\rho_c$  together with the corresponding arrangement for the outer sphere.

$$V_{c}^{i}(r_{i}) = 2\{ -\frac{Z_{i}}{r_{i}} + \frac{1}{r_{i}} \int_{0}^{r_{i}} \sigma^{i}(r_{i}) dr_{i} + \int_{r_{i}}^{b_{i}} \sigma^{i}(r_{i}) dlnr_{i}$$

+ 
$$2\pi\rho_{c}b_{0}^{2} - \frac{2\pi}{3}\rho_{c}|R_{i}|^{2} - \sum_{\substack{j\neq i \ j\neq i}} \frac{\overline{Q}_{j}}{|R_{ij}|} - 2\pi\rho_{c}b_{i}^{2} + \int_{0}^{\infty} \sigma^{0}(r_{0}')dlnr_{0}'$$
. (61)

Similarly, the Coulomb potential exterior to the outer sphere is given as

$$V_{c}^{o}(r_{o}) = 2\{-\frac{Q_{o}}{r_{o}} + \frac{1}{r_{o}}\int_{b_{o}}^{r_{o}} \sigma^{o}(r_{o}')dr_{o}' + \int_{r_{o}}^{\infty} \sigma^{o}(r_{o}')d\ln r_{o}' . (62)$$

In order to obtain the Coulomb part  $V_c$  of the constant potential  $\overline{V}$  in the interatomic region, we have to average the various Coulomb contributions from our system of effective point charges and the outer sphere charge, respectively, over the volume  $\Omega_{in}$ . Thus, we obtain

$$\overline{V}_{c} = 4\pi\rho_{c}b_{o}^{2} + 2\int_{b_{o}}^{\infty}\sigma^{o}(r_{o})d\ln r_{o} - \frac{1}{\Omega_{in}}\left\{\frac{16\pi^{2}}{3}\rho_{c}\left[\frac{b_{o}^{5}}{5} - \sum_{i>0}(\frac{b_{i}^{5}}{5}\right]\right\}$$

+ 
$$|R_{i}^{2}|b_{i}^{3}\rangle$$
] +  $\sum_{i>0} \overline{Q}_{i}[4\pi b_{0}^{2} - 4\pi b_{i}^{2} - \frac{4\pi}{3}|R_{i}|^{2} - \frac{8\pi}{3}\sum_{\substack{j>0\\j\neq i}} \frac{b_{j}^{3}}{R_{ij}}]$ .

The exchange part of the potential in any type of region will be a function of the charge density only:

$$V_{X\alpha}^{i}(r_{i}) = -6\alpha_{i} [\frac{3}{8\pi} \rho^{i}(r_{i})]^{1/3}; \quad i \ge 0$$
  
$$\overline{V}_{X\alpha} = -6\overline{\alpha} [\frac{3}{8\pi} \rho_{c}]^{1/3} . \qquad (64)$$

In Equation (64) the constants  $\alpha_1$  and  $\overline{\alpha}$  are the exchange parameters for the scattering regions i and the interatomic region, respectively. The new molecular potential field of 'muffin-tin' form is then given by

$$V^{i}(r_{i}) = V^{i}_{c}(r_{i}) + V^{i}_{X_{\alpha}}(r_{i}); \quad i \ge 0$$

$$\nabla = \overline{V}_{c} + \overline{V}_{X\alpha}$$

### 4. Overlapping-Sphere Model

The principal source of error in the SCF-X<sub> $\alpha$ </sub>-MS method is the assumption of non-overlapping atomic spheres, the muffin-tin approximation. This problem can be circumvented, to high order of approximation, through the straightforward use of overlapping atomic spheres. It has been shown that the use of overlapping spheres with the muffintin approximation for the potential, can be formally justified through the analytic continuation of the multiple scattered wave expansions.<sup>20</sup>.

The secular equations of the scattered wave technique contain two fundamental types of matrix elements, the ondiagonal atomic "scattering elements" and the off-diagonal

"structure elements". The former quantities depend solely on the partial wave solutions of the radial Schrodinger equation for each individual spherical potential, regardless of its range, and therefore are independent of whether or not a neighboring spherical potential overlaps. On the other hand, the structure elements depends only on the molecular geometry, and their mathematical form is derived on the basis of certain standard multipole-type expansion theorems in the angular momentum representations<sup>3</sup>. Similar expansions theorems are also used in the solution of Poisson's equation of classical electrostatics, which is an integral part of the SCF iterative procedure. It has been shown<sup>20</sup> that these theorems are valid over regions of space that can be spanned by both overlapping and non-overlapping spheres. The only restrictions are that each atomic sphere does not overlap a neighboring atom beyond its nucleus and that the outer sphere does not overlap the peripheral atoms beyond their respective nuclei.

The essential idea behind the overlapping sphere model is to distribute the charge in the intersphere region among the various atoms. The nonempirical scheme for choosing overlapping sphere radii now being used is based on the virial theorem<sup>21</sup>. In this procedure the sphere radius is assigned the value of the radius of the sphere around each atom in the initial molecular charge distribution

which encloses the atomic number of electrons. These sphere radii are then varied, with the relative sizes fixed, to get the best value of the virial ratio at self consistency.

# 5. Evaluation of One-electron Properties<sup>22</sup>

The calculation of expectation values over the MS-Xa-SCF wavefunctions can in principle be done using the orbital representations

$$\phi(\mathbf{\dot{r}}) = \sum_{\ell,m} C^{\alpha}_{\ell,m} P^{\alpha}_{\ell}(\mathbf{r}) Y^{m}_{\ell}(\mathbf{\hat{r}}) \quad (\text{Sphere } \alpha)$$
(65)

$$\phi(\vec{r}) = \sum_{\alpha \ l,m} \sum_{\alpha \ l,m} A^{\alpha}_{l,m} J_{l}(r_{\alpha}) \Upsilon^{m}_{l}(\vec{r}_{\alpha}) \quad (\text{Intersphere}) \quad (66)$$

where  $C_{\ell,m}^{\alpha}$  are the expansion coefficients determined by the matching conditions at the sphere boundary, the  $P_{\ell}^{\alpha}(\mathbf{r})$  are the appropriately normalized solutions of the radial Schrödinger equation and  $Y_{\ell}^{m}(\hat{\mathbf{r}})$  are real spherical harmonics. The wavefunction for the intersphere region is a multicenter representation where the sum over  $\alpha$  corresponds to the sum over all the atoms,  $A_{\ell m}^{\alpha}$  are the expansion coefficients and  $J_{\ell}(\mathbf{r}_{\alpha})$  are spherical Bessel functions. The major problem with a direct numerical integration is the complicated shape of the intersphere region and the fact that the charge density can vary widely within it.

The integrals involving one-electron operators are

simple to calculate inside each atomic spheres; the angular integrals over spherical harmonics can be evaluated analytically and the one-dimensional radial integrals can be calculated numerically. In order to avoid the difficulties arising from the integration over the intersphere region. Case and Karplus<sup>22</sup> had proposed a method to divide the intersphere charge among the various atoms by extending the range of the radial variables beyond the atomic sphere radii b\_; that is, the intersphere charge is approximated by a sum of expressions of the form of Equation (65) with the assumption that the overlap between atomic charge distributions can be neglected. Procedure for partitioning the intersphere charge: The intersphere charge is partitioned in proportion to the average charge density at the surface of each atomic sphere multiplied by the part of that surface bordering the intersphere region. The average charge density of the molecular orbital  $\phi(r)$  at the surface of the atomic sphere  $\alpha$  of radius  $\textbf{b}_{\alpha}$  is

 $\sum_{\ell,m} \{ C^{\alpha}_{\ell,m} P^{\alpha}_{\ell}(b_{\alpha}) \}^{2} .$ 

Since the wavefunction is continuous across the sphere boundary, the additional charge in the sphere due to its expansion by an infinitisimal amount is proportional to average density. This quantity has to be multiplied by the surface area of the sphere bordering the intersphere

region. For tangent spheres the area is  $4\pi b_{\alpha}^2$  and the fractional seduction in surface area caused by each overlapping sphere g is

where  $R_{\alpha\beta}$  is the distance between atoms  $\alpha$  and  $\beta$ . If the total intersphere charge is divided among the atoms in this way, the extra charge  $\Delta q_{\ell}^{\alpha}$  for each partial wave can be obtained from

$$\Delta q_{\ell}^{\alpha} = N^{-1} q_{int}^{4} \pi b_{\alpha}^{2} \{1 - \sum_{\alpha \neq \beta} f_{\alpha\beta} \} \sum_{m} \{C_{\ell,m}^{\alpha} P_{\ell}^{\alpha}(b_{\alpha})\}^{2},$$

where the normalization constant N is given by

$$N = \sum_{\alpha \ \ell, m} \sum_{\alpha \ \ell, m} 4\pi b_{\alpha}^{2} \{1 - \sum_{\beta \neq \alpha} f_{\alpha\beta} \} \{C_{\ell m}^{\alpha} P_{\ell}^{\alpha}(b_{\alpha})\}^{2}$$

and  $q_{int}$  is the total intersphere charge. The parameter  $q_{int}$  is calculated by muffin-tin procedures, and its appearance in the expression for  $\Delta q_{l}^{\alpha}$  insures that the normalization of the molecular orbital is consistent with this approximation.

The functional form of the radial function beyond the sphere boundary is determined by extending the radial function inside an atomic sphere by using the leading term of the multicenter expansion in the intersphere region, i.e.,

$$P_{l}^{\alpha}(r) = B J_{l}(r), \quad \text{for } r > b_{\alpha}$$

where

$$J_{\ell}(\mathbf{r}) = J_{\ell}(K\mathbf{r}) \quad \text{for } E > V_{\text{int}}$$
$$= K_{\ell}^{(1)}(K\mathbf{r}) \quad \text{for } E < V_{\text{int}},$$

with  $hK = |2m(E - V_{int})|$ . Here  $V_{int}$  is the value of the constant intersphere potential. The constant B is chosen to make the expansion continuous at  $r = b_{\alpha}$ ; the first derivative is in general discontinuous. It is possible to assume a more flexible functional form and match both the function and its derivative at the sphere boundary. Many properties appear to be rather insensitive to the choice of the functional form.

In order to include the amount of extra atomic charge  $\Delta q_{\ell}^{\alpha}$  the sphere radius is increased to  $b_{\alpha}^{\ell}$  for each value of  $\ell$ . The function  $P_{\ell}^{\alpha}$  as determined above between  $b_{\alpha}$  and  $b_{\alpha}^{\ell}$  are used as the standard muffin-tin orbitals and the functions are assumed to vanish beyond the radius  $b_{\alpha}^{\ell}$ .

The calculation of one-electron properties with the

orbitals defined above is equivalent to the conventional LCAO calculation with the neglect of differential overlap. This procedure has been used by Cook and Karplus<sup>23</sup> to calculate the one-electron properties of LiH. The charge-partitioning procedure was found to introduce errors on the order of those in the X $\alpha$  wavefunction itself and to improve in accuracy with parameter variations that improve the X $\alpha$  wavefunctions.

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#### CHAPTER V

## ELECTRONIC STRUCTURE AND ESR PARAMETERS OF [CrOC1<sub>4</sub>]<sup>1-</sup>

### A. Introduction

The electronic structures of the transition metal oxohalo complexes of the type  $[MOX_n]^{m-}$ , where M = V, Nb, Cr, Mo, W and X = F, Cl, Br, I (n = 4 or 5), have been extensively studied experimentally 1-10 for more than a decade. The basis for the interpretation of the experimental data has been the well-known discussion of the electronic structure of VO<sup>2+</sup> complexes of Ballhausen and Gray<sup>11</sup> based on extended Hückel calculations. These have been followed by similar calculations on the oxopentaquovanadium (IV) ion<sup>12</sup> and on the oxotetrachloro- and oxopentachlorovanadium (IV) ions<sup>13,14</sup>. Recently some ab initio molecular orbital studies have been described for  $CrO^{3+}$  complexes<sup>15,16</sup>. Since there are still many ambiguities in the interpretation of experimental results, we have undertaken a fairly detailed study of the electronic structure of this class of compounds in the hope of providing an understanding of the bonding and consequently a sound basis for the

interpretation of experimental observations.

There are at least two approaches to the study of the bonding characteristics of transition metal complexes when detailed ESR data are available. One may assume an atomic expansion basis for the molecular orbitals and determine the linear expansion coefficients (the MO vector) so as to reproduce the available ESR data,  $^{4-8,17}$ or conversely one constructs as accurate a function as possible for the system under consideration and then calculates the ESR parameters from this function 18-22. Of the two, this latter approach is clearly preferred as it has fewer biases and it is the approach we take in this study. In particular, we use the results of SCF-MS  $X\alpha^{23,25}$  calculations on  $[CrOCl_{\mu}]^{-1}$  to interpret experimental ESR data. We compare our SCF-MS-Xa results with those we have obtained using the EHT<sup>26</sup> as well as with earlier theoretical studies.

### B. Methods

In this section we describe the SCF-MS-X $\alpha$  method and the various modified extended Hückel methods used in the present study.

### (i) The SCF-MS-Xa Method

The SCF-MS-Xa method is a technique used to approximate the solutions to the Hartree-Fock equations for a many electron system. Its underlying assumptions and procedures, along with the results for many systems, are available in the literature  $^{23-27}$ . The two characteristic approximations of the method are the use of the Xa approximation for the exchange potential and the muffin-tin approximation for the potential. In this latter approximation, the most severe of the two, the molecule is partitioned into three fundamental types of regions: atomic, interatomic and extramolecular (this is the region outside a sphere which encloses the "entire" molecule). The potential in the atomic and extramolecular region are spherically averaged while a constant potential is used in the interatomic region. The one electron equations are solved numerically in each of the three regions and the resulting wavefunctions and their first derivatives are joined continuously throughout the various regions.

The use of the  $X_{\alpha}$  approximation for the exchange potential makes the interpretation of one-electron eigenvalues different from that of the Hartree-Fock eigenvalues. The correspondence between the SCF-MS-X $\alpha$  eigenvalues and the Hartree-Fock eigenvalues has been established<sup>28,29</sup>. In the SCF-MS-X $\alpha$  calculation the molecular orbitals are characterized by the charge associated with

each atomic sphere, and with the region outside the outersphere, in terms of the percentage of s,p,d, etc. character and the charge in the intersphere region. The total charge associated with each atom in a molecule is taken to be the sum of the charge inside the atomic sphere around the atom and a fraction of the intersphere charge. The latter was obtained by the intersphere charge partitioning scheme of Case and Karplus<sup>31</sup> in which the intersphere charge is partitioned among the basis functions centered on the various atoms in proportion to the average charge density at the surface of each atomic sphere multiplied by the area of that surface bordering the intersphere region. Thus the fractional s,p,d, etc. character of the contribution of each atom to the molecular orbital can be calculated.

### (ii) The Extended Hückel Method

In the extended Hückel method the molecular orbitals  $(\Psi_i)$  are expanded as linear combinations of atomic orbitals  $(\phi_j)$  and are assumed to be eigenfunctions of an effective one-electron Hamiltonian,  $\hat{H}_{eff}$ . On minimizing the total energy with respect to the molecular orbital coefficients, the following secular equation is obtained

$$Ψ_i = Σ C_{ij}Φ_j$$
[H<sub>ij</sub> - ES<sub>ij</sub>] = 0 ,

where H<sub>ij</sub> and S<sub>ij</sub> are elements of the Hamiltonian and overlap matrices, respectively,

$$H_{ij} = \langle \phi_i | H_{eff} | \phi_j \rangle$$

$$S_{ij} = \langle \phi_i | \phi_j \rangle$$
 .

The secular equation is solved to obtain the orbital energies and the molecular orbitals.

There are many schemes available for approximating the diagonal and off-diagonal Hamiltonian matrix elements and we have explored the following three.

1. In the first, the diagonal matrix elements H<sub>ii</sub> are set equal to the negative of the valence shell ionization energies (VSIE), which are presumed to be functions of the charges q on the atoms,

$$H_{11} = VSIE(q)$$

$$H_{11} = -(Aq^2 + Bq + C).$$

The values of A, B and C which characterize the valence orbitals and configurations are taken from Reference 30. The off-diagonal elements are approximated by the Wolfsberg-Helmholz relation<sup>32</sup>,

Geometry l	Sphere Rad11 (au)	Geometry 2	Sphere Rad11 (au)	ø
r(Cr-0) - 1.519Å	R <sub>Cr</sub> = 2.1550	r(Cr-O) = 1.60Å	R <sub>Cr</sub> = 2.2180	$0.71352 = \alpha_{\rm Cr}$
r(cr-cl) = 2.240Å	R <sub>0</sub> = 1.7767	r(Cr-Cl) = 2.25Å	R <sub>O</sub> = 1.8478	0.74447 = α <sub>0</sub>
<0-Cr-Cl = 104.5°	R <sub>Cl</sub> = 2.6990	<0-Cr-Cl = 95.8°	R <sub>Cl</sub> = 2,7126	0.72325 = α <sub>Cl</sub>
	R <sub>out</sub> = 6.8632		R <sub>out</sub> = 6.9594	$0.72517 = \alpha_{out} = \alpha_{inter}$

Table 1. Geometry, sphere radii and  $\boldsymbol{\alpha}$  values.

$$H_{ij} = \frac{1}{2} K S_{ij} [H_{ii} + H_{jj}]$$

where K is an empirical constant.

2. In our second method we have used the same parameterization scheme for diagonal elements while a weighted H<sub>ij</sub> formula was used for the off-diagonal elements<sup>33</sup>.

3. In the third method, a term representing the interaction of the electron in an orbital i with the electrostatic field arising from the non-zero net charges on the other atoms in the molecule is added to the diagonal elements  $H_{ii}$  and the corresponding changes are made in the way the off-diagonal elements  $H_{ij}$  are evaluated for molecules with non-zero net charge. The details of this Madelung correction have been discussed by Hay <u>et al.<sup>34</sup></u>.

### C. Technical Details

The calculation has been done for two different geometries in  $C_{4v}$  symmetry. The atomic arrangements for both the geometries are given in Table 1. Geometry 1 is based on the crystallographic data for  $[AsPh_4][CrOCl_4]^{35}$  while geometry 2 is the one used in the previous ab initio studies<sup>16</sup>. In both cases the chromium atom is above the basal plane passing through the chlorine atoms.

In the SCF-MS-X $\alpha$  calculations the atomic  $\alpha$  parameters (Table 1) were those of Schwartz<sup>36</sup> and a weighted average of the atomic  $\alpha$  values was used in the interatomic and extramolecular region. The sphere radii were taken to be 90% of the atomic number radii, in accord with the suggestion of Norman<sup>37</sup>, and are given in Table 1. Although the sphere radii were not varied to obtain a correct virial ratio, fairly good results were obtained for -V/T: 1.99992 for geometry 1 and 1.99981 for geometry 2. The outer sphere with origin at the center of nuclear charge of the molecule was chosen to touch the chlorine spheres and serve as a Watson sphere<sup>38</sup> with +1 charge in order to simulate the stabilizing effect of the environment on the ion.

The partial wave expansions were truncated at l = 4for the outer sphere, l = 2 for chromium and l = 1 for oxygen and chlorine. The core energy levels, <u>i.e.</u>, ls, 2s, 2p on chromium, ls on oxygen and ls, 2s, 2p on chlorine, were calculated in each iteration using only the surrounding atomic potentials. The calculations were carried out self-consistently with the convergence criterion that the maximum relative change in potential between two consecutive iterations was lower than  $10^{-4}$ .

The extended Hückel calculations were carried out with the Slater type double-zeta functions for the chromium 3d orbital<sup>39</sup> and single exponent functions for 4s, 4p on

functions
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Table

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A + 0 m						Radial Fu	nction
ALOII	Orbital	А	В	U	۲	Coefflcient	Exponent
Сr	3d	1.829	9.265	4.35	9.3	0.5060	4.95
		1.21	11.90	7.18		0.6750	1.80
		1.21	12.02	8.39			
	ЧS	0.998	7.135	6.59	5.8	1.0	1.425
		0.998	8.288	7.85			
		0.998	7.494	9.28			
	4p	0.899	5.894	3.52	4.3	1.0	0.950
		0.899	6.552	4.69			
		0.899	6.552	4.72			
0	2s	0.0	15.2	33.0	15.2	1.0	2.275
	2p	0.0	15.2	16.4	15.2	1.0	2.275
c1	3s	0.0	10.66	25.93	10.7	1.0	2.033
		0.0	10.66	13.82	10.7	1.0	2.033

				Atomic	Character	٩٩			
	Energy		Chromium		Оху	gen	Chlo	rine	
ОМ	(Ry)	3đ	μs	μp	2s	2p	3s	3p	
4 p	-0.3176	54.00					5.16	38.20	
7e _	-0.3749	63.09				17.97		10.05	
2b <sub>2</sub>	-0.4966	82.18						15.45	
la <sub>2</sub>	-0.5419							98.96	
6e -	-0.5782	2.41		1.26		2.04		92.36	
3b <sub>1</sub>	-0.5895							98.05	
5e	-0.6100					4.52		93.76	
7a <sub>1</sub>	-0.6553			1.65				95.59	
4e	-0.6794	3.36		4.17		3.50		86.72	
$lb_{2}$	-0.7208	18.47						80.73	
6a <sub>1</sub>	-0.7285	2.96	9.34			1.54		82.45	
2b1	-0.7370	42.09						56.06	
3e -	-0.8471	29.91				64.46		4.71	
5a <sub>1</sub>	-1.0468	26.53	2.22	3.43	4.81	62.29			
1b1	-1.4681	2.04					97.50		
2e	-1.4815			1.03			98.07		
4a <sub>1</sub>	-1.5133		1.54				96.66		
3a <sub>1</sub>	-1.9628	11.05	3.78	7.54	74.66				

One electron elgenfunctions and elgenvalues. Table 3.
chromium, 2s,2p on oxygen and 3s, 3p on chlorine. We had used the normal Hückel constant, K = 1.75. The parameters used in the extended Huckel calculations are given in Table 2.

# D. Electronic Structure of [CrOC14]<sup>1-</sup>

The SCF-MS-Xa calculation of the ground electronic state of  $[CrOCl_{\mu}]^{1-}$  predicts the ground state to be  ${}^{2}B_{2}$ in agreement with the earlier ab initio study<sup>16</sup>. The unpaired electron is in the 2b, orbital which is primarily a  $3d_{vv}$  orbital on chromium (Table 3). The fractional charges given in Table 3 for geometry 1 are based on the charge partitioning scheme of Case and Karplus<sup>31</sup>. The highest energy occupied orbitals (4e-la2) are primarily chlorine 3p in character and are essentially non-bonding. The orbitals 1b, and 2b, which follow this non-bonding set account for the bonding between chromium and the chlorine atoms. The next two low-lying orbitals contribute to the bonding between chromium and oxygen and involve two significantly strong bonds: a  $\sigma(5a_1)$  and a  $\pi(3e)$  bond. There are substantial differences between the SCF-MS-X $\alpha$  and the ab initio descriptions of the Cr-O bonding. In order to understand the Cr-O bonding changes in detail we have carried out SCF-MS-X $_{\alpha}$  calculations on CrO and CrO<sup>3+ 40</sup> and have tabulated the fractional atomic character of the orbitals describing the  $\sigma$  and  $\pi$  bonds between chromium

	σ(Cr Atomic Cha	r-0) aracter %	π(Cr-O) Atomic Character %		
	$3d_{z^2}^{Cr}$	2p <sup>0</sup> <sub>z</sub>	3d <sup>Cr</sup> xz,yz	2p <sup>0</sup> <sub>x</sub> ,y	
CrO	22.84	63.54	15.84	76.80	
Cr0 <sup>3+</sup>	30.52	57.46	39.48	58.61	
<sup>a</sup> [CrOCl <sub>4</sub> ] <sup>1-</sup>	26.53	62.29	29.91	64.46	
<sup>b</sup> [crocl <sub>4</sub> ] <sup>1-</sup>	26.96	63.10	26.70	62.82	
c[croci <sub>4</sub> ] <sup>1-</sup>	50.00	35.00	16.00	76.00	

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Table 4. Chromium-oxygen bonding in some oxochromium compounds.

<sup>a</sup>Geometry 1.

<sup>b</sup>Geometry 2.

<sup>c</sup>Ab initio result from Reference 16.

Molecule	Chromium	Oxygen	Chlorine
CrO	0.361	-0.361	
Cr0 <sup>3+</sup>	2.379	0.621	
a[CrOC14]1-	0.957	-0.156	<del>-</del> 0.450
<sup>b</sup> [crocl <sub>4</sub> ] <sup>1-</sup>	0.974	-0.229	-0.436

Table 5. Charge distribution in some oxochromium compounds.\*

<sup>a</sup>Geometry 1.

<sup>b</sup>Geometry 2.

\* The outer sphere charge distributed between Cr and O is in the ratio of atomic numbers in CrO and CrO3+.

÷	and the second	
Geometry	E(2b <sub>2</sub> → 7e)	E(2b <sub>2</sub> + 4b <sub>1</sub> )
Method	KK	KK
	SCF-MS-Xa	
Geometry 1	13.83	19.97
Geometry 2	8.45	20.30
	Extended Hückel	
Geometry 1		
Method 1	9.42	30.82
2	9.59	34.32
3	11.96	38.72
Geometry 2		
Method 1	4.52	31.27
2	4.69	34.94
3	5.97	39.44

Table 6.	Electronic	transition	energies	from	EHT	and
	SCF-MS-Xa c	alculations	5.			

and oxygen in Table 4, along with those of  $[CrOCl_4]^{1-}$ . From the results of Table 4 we conclude that both the  $\sigma$ and  $\pi$  Cr-O bonding in  $[CrOCl_4]^{1-}$  is weaker, compared to that of  $CrO^{3+}$ , than would be anticipated.

The charge distributions in CrO,  $CrO^{3+}$  and  $[CrOCl_4]^{1-}$ obtained from the SCF-MS-Xa calculations are tabulated in Table 5. The extended Hückel charge distribution is critically dependent on the way the calculation is done. For example, the charges on chromium for geometry 1 are +0.364, +0.206 and +1.222 for methods 1, 2 and 3, respectively.

The relative energies of the empty d-orbitals follow the sequence  $d_{xz,yz} < d_{x^2-v^2} < d_{z^2}$  in SCF-MS-X<sub>a</sub> calculations in agreement with the order generally 1-10 used as the basis of interpretation of electronic spectra of  $CrO^{3+}$  complexes, but not with the order found in the ab initio studies<sup>16</sup>. The extended Hückel calculation predicts that the empty d-orbitals lie in the order  $d_{xz,yz} < d_{z^2} < d_{x^2-y^2}$ . The SCF-MS-X $\alpha$  results for the d-d transition energies calculated by the transition-state procedure<sup>23-25</sup>, along with those obtained from EHT calculations are given in Table 6. According to the SCF-MS-Xa results, the first absorption maximum at 13.1 KK in the electronic spectrum should be assigned to the transition  $(2b_2 + 7e)$ , which can be considered a d-d transition  $3d_{xy} \rightarrow 3d_{xz,yz}$ , the  $2b_2$  and 7e orbitals being predominantly 3d in character (Table 3). This

assignment is in agreement with the generally accepted interpretation of the electronic spectra of this class of compounds and with the recent ab initio studies. The same transition energy calculated for geometry 2 predicts an absorption at 8.45 KK in fairly good agreement with the corresponding CI result<sup>16</sup> of 9.9 KK, but lower in energy than the experimental result. Our conclusion from this observation is that the  $3d_{xy} + 3d_{xz,yz}$  transition energy is critically dependent on the angle between the chromium-oxygen and chromium-chlorine bonds and on the chromium-oxygen distance. The next lowest energy d-d transition  $2b_2 + 4b_1$  calculated by the SCF-MS-X $\alpha$  method predicts an absorption at 19.9 KK in good agreement with the experiment (18.1 KK). This assignment of the second absorption band, though in agreement with the generally used<sup>1-10</sup> interpretation, doesn't agree with the polarized single-crystal spectra and CI studies of Garner et al.<sup>16</sup>. The extended Hückel results for the d-d transition energies continue to show a strong dependence on the method of calculation (Table 6).

### E. Theory of g and Hyperfine Interaction Tensors

The theory of g and hyperfine interaction tensors of transition metal complexes is generally based on the perturbation method introduced by Abragam and Pryce<sup>41</sup> for the crystal field model and later modified to include

covalency effects<sup>17</sup>. This general topic has been the subject of many reviews<sup>42</sup> and the perturbation method has been applied to the specific case of transition metal oxohalide complexes of  $C_{4v}$  symmetry by DeArmond <u>et al.</u><sup>4</sup>. In this section we give an outline of our treatment of g and hyperfine interaction (A) tensors indicating the differences from earlier versions.

The following general expressions for the components of the g and A tensors have been obtained from the standard second order perturbation theory treatment of  $g^{43}$  and  $A^{22}$  tensors,

$$g_{\alpha\beta} = g_e - 2 \sum_{n \neq 0} \frac{\langle \psi_0 | \xi(r) \hat{L}_{\alpha} | \psi_n \rangle \langle \psi_n | \hat{L}_{\beta} | \psi_0 \rangle}{E_n - E_0}$$
(1)

$$A_{\alpha\beta} = P'[\langle\psi_{0}|\frac{F_{\alpha\beta}}{r^{3}}|\psi_{0}\rangle + \sum_{n\neq 0} \{\frac{2\langle\psi_{0}|\xi(r)\hat{L}_{\alpha}|\psi_{n}\rangle\langle\psi_{n}|\frac{\hat{L}_{\beta}}{r^{3}}|\psi_{0}\rangle}{E_{0} - E_{n}}$$

+ 
$$\sum_{\gamma,\delta} i \varepsilon_{\gamma\delta\alpha} \frac{\langle \psi_0 | \xi(r) \hat{L}_{\gamma} | \psi_n \rangle \langle \psi_n | \frac{F_{\delta\beta}}{r^3} | \psi_0 \rangle}{E_0 - E_n} \} + \kappa$$
 (2)

$$H_{DD} = P' \sum_{\alpha,\beta} I_{\alpha} \frac{F_{\alpha\beta}}{r^3} S_{\beta} , \qquad (3)$$

where  $\psi_0$  is the orbital containing the unpaired electron, the summation over n is over all excited states,  $\hat{L}_{\alpha}$  is the  $\alpha$ -th component of orbital angular momentum and  $\xi(\mathbf{r})$  is the one-electron spin-orbit coupling operator. In the expression for  $A_{\alpha\beta}$ ,  $F_{\alpha\beta}$  and  $F_{\delta\beta}$ , are linear combinations of normalized real spherical harmonics arising from the electron nuclear dipolar Hamiltonian  $(\hat{H}_{DD})$ , as in Equation (3). P' is a constant equal to  $g_e g_n \beta_e \beta_n$ , where  $g_e$  is the free electron g value,  $g_N$  the g value for the nucleus,  $\beta_e$  and  $\beta_n$  are the electron and nuclear Bohr magneton, respectively, and  $\varepsilon_{\gamma\delta\alpha}$  is the Levi-Civita symbol. The term  $\kappa$  in Equation (2) takes into account the Fermi contact interaction.

The unpaired electron in the system under consideration here is in an orbital of  $b_2$  symmetry  $(C_{4y})$ . So the computation of g and A tensor components requires the evaluation of matrix elements between orbitals of  $b_2$ symmetry and orbitals of  $b_1$  and e symmetry. The molecular orbitals required to compute g- and A-tensor components are:

$$\psi_{b_{1}} = \varepsilon_{1} \phi_{d_{x^{2}-y^{2}}}^{M} - \varepsilon_{2} \phi_{b_{1}(s)} + \varepsilon_{3} \phi_{b_{1}(x,y)} - \varepsilon_{4} \phi_{b_{1}(z)}$$

$$\psi_{b_{1}} = \varepsilon_{1}^{i} \phi_{d_{x^{2}-y^{2}}}^{M} + \varepsilon_{2}^{i} \phi_{b_{1}(s)} - \varepsilon_{3}^{i} \phi_{b_{1}(x,y)} - \varepsilon_{4}^{i} \phi_{b_{1}(z)}$$

$$\phi_{b_{2}(x,y)} = p_{y}^{1} - p_{x}^{2} - p_{y}^{3} + p_{x}^{4}$$

$$\begin{split} \phi_{e(s)}^{1,3} &= (s^{1}-s^{3}); \quad \phi_{e(x)}^{1,3} &= (p_{x}^{1}+p_{x}^{3}); \quad \phi_{e(y)}^{1} = (p_{y}^{1}+p_{y}^{3}) \\ &\qquad \phi_{e(x)}^{1,3} &= (p_{z}^{1}+p_{x}^{3}) \\ \phi_{b_{1}}(s) &= (s^{1}-s^{2}+s^{3}-s^{4}) \\ \phi_{b_{1}}(x,y) &= (p_{x}^{1}+p_{y}^{2}-p_{x}^{3}-p_{y}^{4}) \\ \phi_{b_{1}}(z) &= (p_{z}^{1}-p_{z}^{2}+p_{z}^{3}-p_{z}^{4}) \\ \psi_{b_{2}} &= \beta_{1}\phi_{dxy}^{M} - \beta_{2}\phi_{b_{2}}(x,y) \\ \psi_{e1} &= \alpha_{1}\phi_{4}^{M}p_{x} - \alpha_{2}\phi_{4}^{M}p_{y} + \alpha_{3}\phi_{dxz}^{M} - \alpha_{4}\phi_{dyz}^{M} - \alpha_{5}\phi_{2}^{0}p_{x} \\ &+ \alpha_{6}\phi_{2}^{0}p_{y} + \alpha_{7}\phi_{e(s)}^{1,3} - \alpha_{8}\phi_{e(x)}^{1,3} + \alpha_{9}\phi_{e(y)}^{1,3} \\ &- \alpha_{10}\phi_{e(z)}^{1,3} + \alpha_{11}\phi_{e(s)}^{2,4} - \alpha_{12}\phi_{e(x)}^{2,4} + \alpha_{13}\phi_{e(y)}^{2,4} \\ &- \alpha_{14}\phi_{e(z)}^{2,4} \\ \psi_{e2} &= \alpha_{1}\phi_{4}^{M}p_{x} + \alpha_{2}\phi_{4}^{M}p_{y} + \alpha_{3}^{1}\phi_{dxz}^{M} + \alpha_{4}^{1}\phi_{3yz}^{M} - \alpha_{5}^{1}\phi_{2}^{0}p_{x} \\ &- \alpha_{6}\phi_{2}^{0}p_{y} + \alpha_{7}\phi_{e(s)}^{1,3} - \alpha_{8}\phi_{e(x)}^{1,3} - \alpha_{9}\phi_{e(y)}^{1,3} - \alpha_{10}\phi_{e(z)}^{1,3} \\ \end{pmatrix}$$

 $- \alpha_{11}\phi_{e(s)}^{2,4} - \alpha_{12}\phi_{e(x)}^{2,4} - \alpha_{13}\phi_{e(y)}^{2,4} + \alpha_{14}\phi_{e(z)}^{2,4},$ 





where the  $\phi^{M}$  and  $\phi^{0}$  are orbitals centered on the metal and oxygen atoms, respectively, while the remaining  $\phi$ 's are the symmetry adapted linear combination of chlorine orbitals for the coordinate system shown in Figure 1. The  $\phi_{e}^{2,4}$  in  $\psi_{e1}$  and  $\psi_{e2}$  have the same form as the  $\phi_{e}^{1,3}$  given above. The molecular orbitals  $\psi_{e1}$  and  $\psi_{e2}$  are the lowestlying degenerate empty orbitals of e symmetry, the orbital  $\psi_{b1}$  is the next-lowest-energy empty orbital and  $\psi_{b}$ , is a doubly-occupied orbital of  $b_{1}$  symmetry.

On evaluating the required matrix elements retaining only single center contributions, while evaluating matrix elements involving the spin orbit coupling operator, we get the following expressions for the principal components of the g and A tensors

 $\Delta_{||} = g_e - g_{zz}$ 

$$\Delta_{||}(b_{1}) = \frac{2(2\beta_{1}\epsilon_{1}\lambda_{M}-4\beta_{2}\epsilon_{3}\lambda_{L})}{\Delta E(b_{2}+b_{1})}[2\beta_{1}\epsilon_{1}-2\beta_{1}\epsilon_{2}S(b_{1}(s);d_{x^{2}-y^{2}}) + 2\beta_{1}\epsilon_{3}S(b_{1}(x,y);d_{x^{2}-y^{2}}) - 2\beta_{1}\epsilon_{4}S(b_{1}(z);d_{x^{2}-y^{2}}) + 2\beta_{2}\epsilon_{1}S(b_{2}(x,y);d_{xy}) - \beta_{2}\epsilon_{2}S(b_{1}(s);b_{1}(x,y)) + 2\beta_{2}\epsilon_{2}C(b_{1}(s);b_{1}(x,y)) - \beta_{2}\epsilon_{2}S(b_{1}(s);b_{1}(x,y)) + 2\beta_{2}\epsilon_{2}C(b_{1}(s);b_{1}(x,y)) + 2$$

$$\Delta_{||(b_{1}')} = \frac{-2(2\beta_{1}\epsilon_{1}'\lambda_{M}+4\beta_{2}\epsilon_{3}'\lambda_{L})}{\Delta E(b_{1}'+b_{2})} [2\beta_{1}\epsilon_{1}'+2\beta_{1}\epsilon_{2}'S(b_{1}(s);d_{x}^{2}-y^{2}) - 2\beta_{1}\epsilon_{3}'S(b_{1}(x,y);d_{x}^{2}-y^{2}) - 2\beta_{1}\epsilon_{4}'S(b_{1}(z);d_{x}^{2}-y^{2}) + 2\beta_{2}\epsilon_{1}'S(b_{2}(x,y);d_{x}y) + \beta_{2}\epsilon_{2}'S(b_{1}(s);b_{1}(x,y)) + 4\beta_{2}\epsilon_{2}'Q + \beta_{2}\epsilon_{3}'S(b_{1}(x,y);b_{1}(x,y)],$$
(5)

$$\Delta_{\perp}(el) = \frac{2(\alpha_{3}\beta_{1}\lambda_{M}+2\alpha_{10}\beta_{2}\lambda_{L})}{\Delta E(b_{2}+e)} [\alpha_{3}\beta_{1} - \alpha_{5}\beta_{1}S(2p_{x}^{o}; d_{xz}) + \alpha_{7}\beta_{1}S(e^{1,3}(s); d_{xz}) - \alpha_{8}\beta_{1}S(e^{1,3}(x); d_{xz}) + \alpha_{10}\beta_{1}S(e^{2,4}(z); d_{xz}) - \alpha_{12}\beta_{1}S(e^{2,4}(x); d_{xz}) - \alpha_{1}\beta_{2}S(4p_{x}; e^{1,3}(z)) + \alpha_{3}\beta_{2}S(d_{xz}; e^{1,3}(z)) + \alpha_{5}\beta_{2}S(2p_{x}^{o}; e^{1,3}(z)) + \alpha_{10}\beta_{2}S(e^{1,3}(z); e^{1,3}(z))],$$
(6)

$$A_{zz}^{M}(b_{1}) = -P[\frac{4}{7}\beta_{1}^{2} + \frac{2(2\beta_{1}\epsilon_{1}\lambda_{M}^{-4}\beta_{2}\epsilon_{3}\lambda_{M})\beta_{1}\epsilon_{1}}{\Delta E(b_{2} + b_{1})} + \frac{3}{7\Delta E(b_{2} + e)} \\ \{(\alpha_{3}\beta_{1}\lambda_{M}^{+2}\alpha_{10}\beta_{2}\lambda_{L})\beta_{1}\alpha_{3} + (\alpha_{3}^{*}\beta_{1}\lambda_{M}^{+2}\alpha_{10}^{*}\beta_{2}\lambda_{L})\beta_{1}\alpha_{3}^{*} \\ + (\alpha_{4}\beta_{1}\lambda_{M}^{+2}\alpha_{14}\beta_{2}\lambda_{L})\beta_{1}\alpha_{4} + (\alpha_{4}^{*}\beta_{1}\lambda_{M}^{+2}\alpha_{14}^{*}\beta_{2}\lambda_{L})\alpha_{4}^{*}\beta_{1}\} + \kappa\}$$

$$(7)$$

$$A_{XX}^{M} = A_{YY}^{M} = -P[-\frac{2}{7}\beta_{1}^{2} + \frac{2}{\Delta E(b_{2} + e)} \{(\beta_{1}\alpha_{3}\lambda_{M} + 2\beta_{2}\alpha_{10}\lambda_{L})\alpha_{3}\beta_{1} + (\beta_{1}\alpha_{3}\lambda_{M} + 2\beta_{2}\alpha_{10}\lambda_{L})\beta_{1}\alpha_{3}^{*}\} - \frac{3}{7\Delta E(b_{2} + e)} \{(\alpha_{4}\beta_{1}\lambda_{M} + 2\alpha_{14}\beta_{2}\lambda_{L})\beta_{1}\alpha_{4} + (\alpha_{4}^{*}\beta_{1}\lambda_{M} + 2\alpha_{14}^{*}\beta_{2}\lambda_{L})\beta_{1}\alpha_{4}^{*}\} + (\alpha_{4}^{*}\beta_{1}\lambda_{M} + 2\alpha_{14}^{*}\beta_{2}\lambda_{L})\beta_{1}\alpha_{4}^{*}\} + \kappa]$$
(8)

where  $\lambda_{M}$  and  $\lambda_{L}$  are the single-electron spin-orbit coupling constants for the metal d and halogen p orbitals, respectively. The S terms which appear in the expressions for  $g_{||}$  and  $g_{\perp}$  are the group overlap integrals. In the equation for  $A_{ZZ}^{M}$ , only the contributions from the unoccupied orbital of  $b_{1}$  symmetry are included. P and Q in the above equations are defined as

$$P = g_e g_N \beta_e \beta_N < r^{-3} >_{3d}^{M}$$

$$Q = R < ns \left| \frac{\partial}{\partial K} \right| np_{K} > (K = x, y \text{ or } z),$$

where R is the distance between the metal and halogen atoms and ns, np are Slater type atomic orbitals.

The major difference in the expressions for  $g_{||}$ ,  $g_{\perp}$ ,  $A_{\parallel}^{M}$  and  $A_{\perp}^{M}$  between our treatment and that of DeArmond, et al. 4 arises from the fact that the molecular orbitals we have used in deriving the equations take into account all possible contributions from various atoms. The inclusion of halogen contributions in orbitals of e symmetry makes  $g_{\parallel}$  dependent on the ligand spin-orbit coupling constant  $\boldsymbol{\lambda}_{L}.$  In deriving these equations we have retained all the overlap integrals. The contribution from any low lying occupied  $b_1$  orbital to  $g_{||}$  can be calculated using expressions very similar to that for  $\Delta_{||}(b_1)$ . The expression for  $\Delta_{|}(e2)$  which is not given in the above set of equations, is very similar to that for  $\Delta_{|}(el)$ . The same set of equations can be used to compute the g and A tensor components for hexacoordinated transition metal oxohalo complexes by adding a term involving the overlap between the metal atom and the axial halogen atom to the expression for  $g_{|}$ .

# F. Evaluation of g and A Tensor Components

In the SCF-MS-Xa method the population analysis is done by expanding the nonatomic part of the wavefunction about the atoms and thus the calculation corresponds to a zero-overlap model. Hence we have used the following expressions, obtained by neglecting the terms involving overlap integrals, to compute g and A tensor components

$$\Delta_{\parallel} = g_e - g_{zz}; \quad \Delta_{\perp} = g_e - g_{xx}$$

$$\Delta_{||}(b_{1}) = \frac{2(\beta_{1}\epsilon_{1}\lambda_{M}-4\beta_{2}\epsilon_{3}\lambda_{L})(2\beta_{1}\epsilon_{1}-4\beta_{2}\epsilon_{3})}{\Delta E(b_{2} + b_{1})}$$
(9)

$$\Delta_{\parallel}(b_{1}') = - \frac{2(2\beta_{1}\varepsilon_{1}'\lambda_{M}+4\beta_{2}\varepsilon_{3}'\lambda_{L})(2\beta_{1}\varepsilon_{1}'+4\beta_{2}\varepsilon_{3}')}{\Delta E(b_{1}'+b_{2})}$$
(10)

$$\Delta_{\perp}(e) = \frac{2(\alpha_{3}\beta_{1}\lambda_{M}+2\alpha_{10}\beta_{2}\lambda_{L})(\alpha_{3}\beta_{1}+2\alpha_{10}\beta_{2})}{\Delta_{E}(b_{2}+e)}$$
(11)

$$A_{||}(b_1) = -P[\frac{4}{7}\beta_1^2 + \frac{2(2\beta_1\epsilon_1\lambda_M - 4\beta_2\epsilon_3\lambda_L)\beta_1\epsilon_1}{\Delta E(b_2 + b_1)}$$

+ 
$$\frac{6}{7} \frac{(\alpha_3 \beta_1 \lambda_M + 2\alpha_{10} \beta_2 \lambda_4)}{\Delta E(b_2 \neq e)}$$
 +  $\kappa$ ] (12)

$$A_{\perp} = -P[-\frac{2}{7}\beta_{1}^{2} + \frac{11}{7} \frac{(\alpha_{3}\beta_{1}\lambda_{M} + 2\alpha_{10}\lambda_{2}\lambda_{L})}{\Delta E(b_{2} \neq e)} \alpha_{3}\beta_{1} + \kappa] . \quad (13)$$

where  $A_{||}(b_1)$  includes only the contribution from the empty  $b_1$  orbital. The contribution from other orbitals of  $b_1$  symmetry to  $A_{||}$  can be included by adding terms similar to the second term in the expression for  $A_{||}$ .

To take into account the charge in the outer sphere region we have distributed the outer sphere charges associated with the molecular orbitals needed for computing g and A tensor components among the ligand atoms in the ratios of their atomic numbers. The additional charge was further partitioned into s and p portions for each atom in the ratio of net s and p populations. In the SCF-MS-Xa model the square of the molecular orbital coefficients in Equations (9)-(13) has been identified with the fractional charge associated with the corresponding partial wave<sup>27</sup>.

The computation of  $g_{||}, g_{\perp}, A_{||}$  and  $A_{\perp}$  requires the magnitudes for  $\lambda_{\rm M}$ ,  $\lambda_{\rm L}$ ,  $< r^{-3} > 3^{\rm d}$  and the electronic excitation energies, in addition to the molecular orbital coefficients. There is no obviously "correct" value of the spin orbit coupling constant of the metal or the chlorine to use in evaluating the ESR parameters. In most analyses of EPR data the spin-orbit coupling constants are assigned values based on assumed values of the charges on the atoms, or on some other empirical procedure<sup>44</sup>. This method of assigning values for  $\lambda_{\rm M}$  doesn't make any significant difference in results if the variation of  $\lambda_{\rm M}$  with charge on

		<r<sup>-3&gt;<sup>3d</sup> (au)</r<sup>		Spin orbit constant ()	coupling ( <sup>3d</sup> ) cm <sup>-1</sup>
Config- uration	Charge	Xα	Hartree Fock	Χα	Expt.
3d <sup>5</sup> 4s <sup>1</sup>	0	2.910		246.80	185
3a <sup>5</sup>	l	3.011	2.974	255.21	190
3a <sup>4</sup>	2	3.530	3.453	301.75	230
3a <sup>3</sup>	3	4.063	3.961	351.03	275
3d <sup>2</sup>	4	4.609	4.482	402.85	325
3d <sup>l</sup>	5.	5.170	4.993	457.58	380

Table 7. Chromium spin orbit coupling constants and  $\langle r^{-3} \rangle^{3d}$  values.

the metal is not drastic, as in the case of copper where  $\lambda_{Cu}$  varies only from 817 cm<sup>-1</sup> for Cu(3d<sup>9</sup>4s<sup>2</sup>) to 828 cm<sup>-1</sup> for Cu<sup>2+</sup>(3d<sup>9</sup>). On the other hand, for metals like chromium for which the spin-orbit coupling constant varies from 185 cm<sup>-1</sup> for Cr(3d<sup>5</sup>4s<sup>1</sup>) to 380 cm<sup>-1</sup> for Cr<sup>5+</sup>(3d<sup>1</sup>)<sup>45</sup> such assignments are difficult to make since  $g_{||}$  and  $g_{\perp}$  are critically dependent on the choice of the value for  $\lambda_{M}$ . This makes it difficult to interpret the observed trends in measured ESR parameters.

The value of  $\langle r^{-3} \rangle_M^{3d}$  required to calculate A tensor components is generally taken from the  $\langle r^{-3} \rangle_M^{3d}$  values calculated using the atomic Hartree-Fock wavefunctions.

The spin-orbit coupling constant  $\lambda_{Cr}$  for the various oxidation states of chromium were computed using the Xawavefunction and the single particle approximation for  $\lambda_{Cr}^{3d}$ , <u>i.e.</u>,

$$\lambda_{\rm Cr}^{\rm 3d} \approx \frac{e^2 \hbar^2}{2m^2 c^2} < \frac{1}{r} \frac{dV}{dr} >_{\rm 3d} = \frac{e^2 \hbar^2}{2m^2 c^2} z' < r^{-3} >_{\rm 3d_1}$$

where z' is the effective nuclear charge; the values are given in Table 7. Even though this simple approximation doesn't correctly take into account the exchange effects<sup>46</sup>, the relative values and the variations are comparable to the experimental numbers<sup>45</sup>. The  $\lambda_{Cr}^{3d}$  and  $\langle r^{-3} \rangle_{Cr}^{3d}$  required to calculate the ESR parameters were calculated for the formal valence configuration of Cr in  $[\operatorname{CrOCl}_{4}]^{1-}$  of  $3s^{1.964} 3p^{5.786} 3d^{4.453} 4s^{0.334} 4p^{0.505}$ . By this procedure we obtained  $\lambda_{Cr}^{3d} = 289.36 \text{ cm}^{-1}$  and  $\langle r^{-3} \rangle_{Cr}^{3d} = 3.390$  au for the valence configuration of chromium  $3s^{1.964} 3p^{5.786} 3d^{4.453} 4s^{0.334} 4p^{0.505}$  for geometry 1 of  $[\operatorname{CrOCl}_{4}]^{1-}$  and  $\lambda_{Cr}^{3d} = 288.51 \text{ cm}^{-1}$  and  $\langle r^{-3} \rangle_{Cr}^{3d} =$ 3.382 au for the valence configuration of chromium  $3s^{1.975} 3p^{5.861} 3d^{4.359} 4s^{0.338} 4p^{0.490}$  for geometry 2 of  $[\operatorname{CrOCl}_{4}]^{1-}$ . We had used for the ligand spin orbit coupling constant  $(\lambda_{L})$  a value of 667.05 cm<sup>-1</sup> obtained from an Xa calculation on the chlorine atom.

We consider first the calculation of  $g_{||}$ , which is determined by mixing of  ${}^{2}B_{1}$  excited states into the  ${}^{2}B_{2}$ ground state (Equation (9)). Using the electronic excitation energy for the transition  $2b_2 \rightarrow 4b_1$  (Table 6), and computed spin-orbit coupling constants we obtained a value of 1.9793 for  $g_{||}$  which is not in agreement with the experimental value  $g_{||} = 2.006$ . The fact that the experimental  $g_{||}$  is greater than the free-electron g value indicates that the contributions from low\_lying  ${}^{2}B_{T}$  states arising from the promotion of an electron from a doubly occupied b<sub>1</sub> orbital to the singly-occupied 2b<sub>2</sub> orbital should be important. We had calculated (Equation (10)) the contribution to  $g_{||}$  from two such states, namely the one arising from the excitation  $3b_1 \rightarrow 2b_2$  with the excitation energy of 15,350 cm<sup>-1</sup> and the one from  $2b_1 \rightarrow 2b_2$ with the excitation energy  $28,530 \text{ cm}^{-1}$ . On adding the

contributions from all the three states we get a value of 2.040 for  $g_{||}$ , which is greater than the free electron g value and in fairly good agreement with the experimental value. If  $g_{||}$  is computed including only the contribution from the chromium from all the three states the value is 1.980. This indicates the importance of including the ligand contribution in evaluating g tensor components.

The magnitude of  $g_{\perp}$  is determined primarily by the contribution from the low-lying empty orbital of e symmetry<sup>16</sup>. The value obtained for  $g_{\perp}$  using the excitation energy of 13,830 cm<sup>-1</sup> for the transition  $2b_2 + 7e$  and the calculated spin-orbit coupling constants is 1.978, in excellent agreement with the experimental value of 1.979.

In the spin-restricted molecular orbital approximation in which we had done all the calculations, the Fermi contact interaction parameter  $\kappa$  vanishes. So  $\kappa$  was determined using the following equation

$$A_{0} = -\kappa P - (g_{e} - g)P$$
,

where  $A_0$  is the isotropic hyperfine coupling constant,  $g_e$  is the free-electron g value and g the experimental average g value for the complex. The values of  $g_{||}$ ,  $g_{\perp}$ ,  $A_{||}^{Cr}$  and  $A_{\perp}^{Cr}$  calculated using SCF-MS-X $_{\alpha}$  wavefunctions and computed spin-orbit coupling constants, along with the results of ab initio studies<sup>16</sup> and available

				Cr Hyper. (;	fine Intera x10 <sup>4</sup> cm <sup>-1</sup> )	ction <sup>d</sup>
			ഫ	A	Р	Aiso
Geometry l SCF-MS-Xα	2.040 (1.980)	1.978 (1.980)	1.999 (1.980)	33.66	10.25	
Geometry 2 SCF-MS-Xα	2.041 (1.980)	1.959 (1.965)	1.986 (1.970)			
Ab Initio SCF <sup>c</sup>	1.992 (2.007)	1.968 (1.977)	1.976 (1.987)			
Experiment	2.006	1.979	1.988			18.1
<sup>a</sup> The contributions <sup>b</sup> The results obtai <sup>c</sup> The results of Re	from <sup>2b</sup> 1, 3b ned neglectin ference [16],	l, and <sup>4</sup> b <sub>l</sub> o g the ligand after scalin	rbitals inclu contributior g the calculs	lded. Is are given ted transi	n in parenth tion energie	leses. es are
given in parenthe	ses.					

ESR parameters of [CrOC14]1-.a,b

Table 8.

 $d_{\kappa} = 0.52h$  was estimated from experimental data.

Method		Charge on chromium <sup>a</sup>	Spin-orbit coupling constant (cm <sup>-1</sup> )	<r-3,3d (au)</r-3,3d 
			Geometry l	
Method	1	0.364	177.20	2.877
	2	0.206	170.77	2.808
	3	1.222	212.13	3.249
			Geometry 2	
Method	1	0.366	177.28	2.878
	2	0.212	171.01	2.811
	3	1.196	211.07	3.238

Table 9. Estimated chromium spin-orbit coupling constants  $(\lambda^{3d})$  and  $\langle r^{-3} \rangle^{3d}$ .

<sup>a</sup>From extended Hückel calculations.



Figure 2. Plot of spin orbit coupling constant  $(\lambda_{Cr}^{3d})$  versus charge on chromium  $(Q_{Cr})$ .



Figure 3. Plot of spin orbit coupling constant  $(\lambda_{Cr}^{3d})$ versus  $\langle r^{-3} \rangle_{Cr}^{3d}$ .

experimental results, are given in Table 8.

In the extended Hückel model for calculating g and A tensor components one has no choice but to guess the  $\lambda_{Cr}^{3d}$  and  $\langle r^{-3} \rangle_{Cr}^{3d}$  values based on the formal charge on chromium obtained from the molecular orbital calculation. The  $\lambda_{Cr}^{3d}$  values were therefore obtained from a plot (Figure 2) of  $\lambda_{Cr}^{3d}$  for the various oxidation states versus the corresponding charges on chromium, assuming a linear relationship of  $\lambda_{Cr}^{3d}$  with the charge on chromium (Table 8). The  $\langle r^{-3} \rangle_{Cr}^{3d}$  values were obtained from a plot  $\lambda_{Cr}^{3d}$  versus  $< r^{-3} >_{Cr}^{3d}$  Hartree-Fock values<sup>47</sup> for the various oxidation states of chromium (Figure 3) again assuming a linear dependence of  $\lambda_{Cr}^{3d}$  on  $\langle r^{-3} \rangle_{Cr}^{3d}$ . Using this procedure for a charge of +0.364 on chromium in  $[CrOCl_{\mu}]^{1-}$ , we obtain from Figure 2,  $\lambda_{Cr}^{3d} = 177.20 \text{ cm}^{-1}$ ; the value of  $< r^{-3} >_{Cr}^{3d}$  corresponding to this value of  $\lambda_{Cr}^{3d}$  from Figure 3 is 2.877 The spin-orbit coupling constant obtained by this au. method turns out to be lower than the value for the neutral chromium  $(3d^{5}4s^{1})$  atom. We had used the set of numbers for  $\lambda_{Cr}^{3d}$  given in Table 9 for our calculations as there doesn't seem to be any other systematic way to assign the values for  $\lambda_{Cr}^{3d}$ . For the chlorine spin orbit coupling constant we used a value of 587  $\text{cm}^{-1}$ .<sup>48</sup> The results for the g- and A-tensor components (Equations (4-8)), using the extended Hückel wavefunctions obtained by the three different methods we have described earlier, are given in

					Cr Hyperfir constants <sup>b</sup>	ne coupling (x10 <sup>4</sup> cm <sup>-1</sup> )
Method	1	g	g⊥		A	L <sup>A</sup>
				Geometry l		
Method	1	2.091	1.971		26.11	10.11
	2	2.088	1.977		27.07	9.44
	3	2.057	1.985		32.34	10.28
				Geometry 2		
Method	1	2.084	1.931		26.88	11.20
	2	2.072	1.934		27.12	10.51
	3	2.055	1.936		32.36	11.52

Table 10. Extended Hückel results for g and A tensor components<sup>a</sup>.

<sup>a</sup>The contributions from two occupied orbitals of b<sub>l</sub> symmetry also included.

 ${}^{b}\kappa$  = 0.524 was estimated from experimental data.

Table 10.

From the results in Table 8 it is clear that  $g_{\perp}$  calculated for geometry 2 of  $[CrOCl_4]^{1-}$  is lower than the experimental number. This dependence of the  $g_{\perp}$  value on geometry can be explained based on the fact that the  $2b_2 \neq 7e$  transition energy required to calculate  $g_{\perp}$  is critically dependent on geometry.

The  $g_{||}$  values calculated from the extended Hückel methods 1 and 2 are greater than the free-electron g value even when only the contribution from the low-lying empty orbital of  $b_1$  symmetry is included. This problem can be taken care of by using  $\lambda_{Cr}^{3d}$  values greater than 204.0 cm<sup>-1</sup>, which corresponds to a charge of greater than +1.0 On chromium. This type of dependence of computed g-tensor components on spin-orbit coupling constant makes the calculation of ESR parameters involving empirically determined values for spin-orbit coupling constants unreliable.

We have shown the importance of including the contributions to g tensor components from occupied orbitals. It becomes practically impossible, without making too many assumptions, to determine the molecular orbital coefficients from the expressions for g and A tensor com-Ponents if the contributions from occupied orbitals are included. Thus, even in the case of molecules with fairly high symmetry, the first approach to study the bonding

c haracteristics of transition metal complexes in which one estimates MO coefficients from ESR data appears to be too difficult.

## G. Conclusions

We conclude from this study that reasonably good estimates of the g tensor components can be obtained from SCF-MS-Xa wavefunctions and the required spin orbit coupling constants calculated for the appropriate valence Configuration of the atom on which the unpaired electron is centered using atomic Xa wavefunctions. Another con-Clusion that we have reached is that the ligand contribution to g tensor shift is important in addition to the Contributions to g tensor components from occupied orbitals. We think the difficulties involved in calculating g tensor components using extended Hückel wavefunctions and empirical values for spin orbit coupling constants have been clearly demonstrated. REFERENCES

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#### CHAPTER VI

# AN SCF-MS-X STUDY OF d<sup>1</sup> TRANSITION METAL OXOHALO COMPLEXES

#### A. Introduction

The elements at the beginning of the transition metal Series have a remarkable ability to form oxycations with the general formula MO<sup>n+</sup>. Most of these oxycations, even though not stable, form a wide variety of complexes, the most extensively studied being those of vanadium, niobium, chromium, molybdenum and tungsten. The electronic structures of the halogen complexes of these oxycations have been the subject of detailed experimental studies for the last several years<sup>1-14</sup>, especially since the pioneering ⇐★ tended Hückel molecular orbital studies on VO<sup>2+</sup> complexes ◦ f Ballhausen and Gray.<sup>15</sup> Their work has been followed by few similar ones 16, 17 and, more recently, by studies a employing ab initio methods<sup>11,12</sup>. In spite of this activity, there are still many ambiguities in the interpretation of experimental spectroscopic results. We have therefore undertaken a fairly detailed study of the electronic structure of the transition metal oxohalo complexes

of the type  $[MOX_n]^{m-}$ , where M = V, Nb, Cr, Mo, W and X = F, Cl, Br (n = 4 and 5), in the hope of understanding the basic features of bonding and therefore providing a sound basis for interpreting the experimental results for this class of compounds.

The relatively small number of ab initio studies of the electronic structure of systems as large as the one under investigation here is primarily because of the enormous computational effort required for such studies. We have chosen to carry out our studies in the Xa approxi $mation^{18-20}$ , which was developed from the beginning with the transition metal systems in mind and has been used numerous times with considerable success<sup>19-21</sup>. The goals Of this study are four-fold: first, to understand the Similarities and differences in bonding characteristics  $\circ \mathbf{f}$  the penta- and hexacoordinated d<sup>1</sup> oxycation complexes: Second, to explain the observed trends in g and metal-hyperfine interaction tensor components, and thus to resolve the existing ambiguities in the interpretation of electron Spin resonance parameters; third, to use computed d-d transition energies to perhaps resolve the ambiguities in the assignment of bands in the electronic spectra; and fourth, to test the capability of SCF-MS-Xa method to reproduce the observed trends accurately.

#### B. Methods

In this section a brief description of the SCF-MS-Xa method and the computational details are given.

# (i) The SCF-MS-Xa Method

The SCF-MS-Xa method is a technique used to approximate the solutions to the Hartree Fock equations for many electron systems. Its underlying assumptions, procedures and results for many systems are available in the literature 18-20. The two characteristic approximations of the method are the use of the Xa approximation for the exchange potential and the muffin-tin approximation for the potential. In this latter approximation, the most severe of the two, the molecule is partitioned into three fundamental types of regions; atomic, interatomic and extramolecular, the latter is the region outside a sphere which encloses the "entire" molecule. The potential in the atomic and extramolecular region is spherically averaged while a constant potential is used in the interatomic region. The oneelectron equations are solved numerically in each of these regions and the resulting wavefunctions and their first derivatives are joined continuously throughout the various regions.

The use of the Xa approximation for the exchange potential makes the interpretation of one-electron eigenvalues different from those of the Hartree-Fock

[MOX <sub>n</sub> ] <sup>m-</sup>	м-о (Å)	M-X <sub>eq</sub> (Å)	M-X <sub>ax</sub> (Å)	<0-M-X <sub>eq</sub> (°)
[VOF,] <sup>2-</sup>	1.63	1.97		98.5°
[voci,] <sup>2-</sup>	1.63	2.42		98.5
$\left[ \text{VOF}_{5} \right]^{3-}$	1.63	1.97	2.16	90
[voc1 <sub>5</sub> ] <sup>3-</sup>	1.63	2.42	2.67	90
[CrOF <sub>4</sub> ] <sup>1-</sup>	1.519	1.79		104.5
$[\operatorname{Crocl}_{h}]^{1-}$	1.519	2.240		104.5
$[CrOF_{5}]^{2-}$	1.519	1.79	2.01	90
[croc1 <sub>5</sub> ] <sup>2-</sup>	1.519	2.24	2.389	90
[MoOF,] <sup>1-</sup>	1.610	1.88		105.2
[MoOC1,] <sup>1-</sup>	1.610	2.333		105.2
[MoOBr,] <sup>1-</sup>	1.610	2.47		105.2
$\left[M_{0}OF_{F}\right]^{2}$	1.610	1.88	2.08	90
[MoOC1 <sub>5</sub> ] <sup>2-</sup>	1.610	2.333	2.600	90
[wor,] <sup>1-</sup>	1.63	1.90		106
[woci,] <sup>1-</sup>	1.63	2.35		106
$[WOBr_4]^{1-}$	1.63	2.49		106
[NbOF <sub>4</sub> ] <sup>2-</sup>	1.68	1.84		99
[NbOF <sub>5</sub> ] <sup>3-</sup>	1.68	1.84	2.06	90

Table 1. Geometrical data<sup>a</sup> for  $[MOX_n]^{m-}$  complexes.

<sup>a</sup>Some of these values are experimental and others have been estimated; see text.
eigenvalues. The correspondence between the SCF-MS-Xa eigenvalues and the Hartree-Fock eigenvalues has been established<sup>22,23</sup>. In the SCF-MS-X $\alpha$  calculation the molecular orbitals are characterized by the charge associated with each atomic sphere, and the region outside the outersphere, in terms of the percentage of s, p, d, etc. character and the charge in the intersphere region. The total charge associated with each atom in a molecule is taken to be the sum of the charge inside the atomic sphere around the atom and a fraction of the intersphere charge. The latter has been obtained by the scheme of Case and Karplus<sup>24</sup> in which the intersphere charge is partitioned among the basis functions centered on the various atoms in proportion to the average charge density at the surface of each atomic sphere, multiplied by the area of that surface bordering the intersphere region. Thus the percentage s, p, d, etc. character of the contribution of each atom to the molecular orbital can be calculated.

## (ii) Computational Details

We have carried out SCF-MS-X $\alpha$  calculations with overlapping spheres for the transition metal oxohalo complexes of the type  $[MOX_n]^{m-}$  in  $C_{4v}$  symmetry for geometrical data given in Table 1. Despite the fact that this class of compounds has been the subject of detailed studies, there are very few compounds for which crystallographic

	R <sub>Metal</sub>	R <sub>Oxygen</sub>	R (eq) Halogen	R (ax) Halogen	aln <sup>=a</sup> out	Virial Ratio (-V/T)	
[VOF <sub>1</sub> ] <sup>2-</sup>	2.3153	1.8749	2.0677		0.73489	2.00054	
[voci <sub>4</sub> ] <sup>2-</sup>	2.3865	1.8733	2.8319		0.72551	2.00022	
[vor <sub>c</sub> ] <sup>3-</sup>	2.3036	1.8725	2.0639	2.1920	0.73523	2.00005	
[voci <sub>5</sub> ] <sup>3-</sup>	2.3774	1.8698	2.8251	3.0084	0.72518	2.00000	
[Nb0F <sub>1</sub> , ] <sup>2-</sup>	2.2936	1.8222	1.8862		0.73293	1.99935	
[Nb0F5] <sup>3-</sup>	2.2799	1.8197	1.8842	2.0480	0.73356	1.99911	
[croF <sub>1</sub> ] <sup>]-</sup>	2.0687	1.7780	1.9496		0,73455	2.00005	
[crociu] <sup>1-</sup>	2.1550	1.7767	2,6990		0.72517	1,99992	
[croF <sub>c</sub> ] <sup>2-</sup>	2.0577	1.7733	1.9453	2.1176	0.73494	1.99945	
[croci <sub>5</sub> ] <sup>2-</sup>	2.1407	1.7702	2.6925	2.7994	0.72489	1.99964	
[MoOF <sub>4</sub> ] <sup>]-</sup>	2.2793	1.7594	1.9157		0.73286	1.99980	
[MoOCI <sub>4</sub> ]	2.3713	1.7586	2.6669		0.72348	1.99989	
[MoOBr <sub>4</sub> ] <sup>1-</sup>	2.3855	1.7582	2.9090		0,71202	1.99995	
[MoOF <sub>E</sub> ] <sup>2-</sup>	2.2668	1.7571	1.9134	2.0648	0.73349	1.99955	
[MoOC1 <sub>5</sub> ] <sup>2-</sup>	2.3622	1.7548	2.6652	2.8839	0.72345	1.99975	
[WOF <sub>1</sub> ]	2.3612	1.7490	1.8984		0.74507	2.00007	
$[\text{wocl}_{4}]^{1-}$	2.4604	1.7483	2.6414		0.73644	2.00012	
$[\text{WOBr}_{4}]^{1-}$	2.4777	1.7481	2.8807		0.73299	2.00009	

Sphere radii (R)<sup>a</sup>,  $\alpha$  values and virial ratios for  $[MOX_n]^{m-}$  complexes. Table 2.

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	Atomic a Values	
$\alpha_{\rm V} = 0.71556$	$\alpha_0 = 0.74447$	$\alpha_0^{t} = 0.75181$
$\alpha_{\rm Nb} = 0.70357$	$\alpha_{\rm F} = 0.73732$	$\alpha_{\rm F}^{\rm t} = 0.74764$
$\alpha_{\rm Cr} = 0.71352$	$\alpha_{\rm Cl} = 0.72325$	$\alpha_{C1}^{t} = 0.73471$
α <sub>MO</sub> = 0.70341	$\alpha_{\rm Br} = 0.70606$	$\alpha_{Br}^{t} = 0.72953$
α <sup>t</sup> = 0.72803 <sup>b</sup>		

<sup>a</sup>The sphere radii are in au.

 $^{b}\text{The}$  theoretical  $\alpha$  values ( $\alpha^{t}$ ) are from Reference 28.

data are available. The atomic arrangements for  $[VOCl_4]^{2-}$ ,<sup>25</sup>  $[CrOCl_4]^{1-}$ ,<sup>14</sup> and  $[MoOCl_4]^{1-14}$  were obtained from the crystallographic data, while for  $[NbOF_5]^{3-}$  the geometry of  $[NbOF_5]^{2-26}$  was used. Since the available geometrical data show that the metal atom is above the plane formed by the halogen atoms in the case of pentacoordinated complexes our calculations on pentacoordinated species em= ployed a similar distorted square pyramidal geometry. For all hexacoordinated complexes the calculations were done with the metal in the plane formed by the equatorial halogen atoms, based on the structure of  $[NbOF_5]^{2-}$ .<sup>26</sup> The geometrical data for complexes for which no structural data are available were estimated based on the structure of related systems.

The values for the atomic  $\alpha$  parameter (Table 2) for all complexes, with the exception of tungsten complexes, were taken from Schwartz<sup>27</sup>. For all atoms in the tungsten complexes we had used the theoretical  $\alpha$  values of Gopinathan <u>et al</u>.<sup>28</sup>, since the Schwartz  $\alpha$  value is not available for tungsten. In the intersphere and the outersphere regions weighted averages of the atomic  $\alpha$  values were used. The sphere radii were taken to be 90% of the atomic number radii, following the suggestion of Norman<sup>29</sup>, and are given in Table 2. Although the sphere radii were not varied to obtain the correct values of the virial ratios, fairly good results were obtained for the virial ratios (Table 2). The outer sphere, with origin at the center of nuclear charge of the molecule, was chosen to touch the halogen sphere and serve as a Watson sphere<sup>30</sup> with a positive charge equal in magnitude to that of the anion, in order to simulate the stabilizing effect of the environment on the ion. In order to get a converged solution for  $[NbOF_4]^{2-}$ and  $[NbOF_5]^{3-}$ , the charge on the Watson sphere had to be increased to +3 and +4, respectively.

The partial wave expansions were truncated at l = 4for the outer sphere, l = 2 for the metals except tungsten and l = 1 for oxygen and the halogens. The core energy levels, for example 1s, 2s, 2p on chlorine, were calculated in each iteration using only the surrounding potentials. In the case of tungsten complexes the completely filled tungsten 4f orbitals were not treated as core orbitals because they had an energy higher than the 5s orbitals. All the calculations were carried out self consistently, with the convergence criterion that the maximum relative change in potential between two consecutive iterations was lower than  $10^{-4}$ .

#### C. Electronic Structures

The SCF-MS-X $\alpha$  calculations of the ground electronic states of all the penta- and hexacoordinated complexes predict the ground state to be  ${}^{2}B_{2}$  in agreement with the earlier molecular orbital studies  ${}^{11,12,15-17}$  and the available spectroscopic data. In these complexes, where

Atomic Character %	Vanadium Oxygen Fluorine	3d 4s 4p 2s 2p 2s 2p	91.49 8.22	6.40 49.66 42.89	20.17	1.68 95.95	98.93	1.74 96.21	5.46 3.31 89.35	16.21 26.74 56.09	8.98	11.30 1 <sup>4</sup> .33 71.13	21.66 76.20	28.26 3.42 1.38 53.07 12.21	7.35 2.79 5.78 83.07	1.56 97.97	1.92 96.25	
	Vanadium	3d 4s	91.49	6.40						16.21	8.98	11.30	21.66	28.26	7.35 2.79		1.92	81/ L
	Ялерси	(Ry)	-0.2286	-0.5345	-0.5551	-0.5714	-0.5812	-0.6148	-0.6245	-0.6501	-0.6610	-0.6627	-0.6795	-0.7345	-1.6554	-1.9265	-1.9328	
		MO	2b,	6e -	la <sub>2</sub>	5e -	3b,	7a <sub>1</sub>	4e	3e	$1b_{2}$	6a <sub>1</sub>	2b,	5a,	4a <sub>1</sub>	2e_	lb,	+ (

Table 3. Molecular orbitals of  $[VOF_{l_l}]^{2-}$ .

				Atomic	Character	<b>F</b> 2			
	Fnerøv		Vanadlum		Oxy	gen	Chloi	rine	
ОМ	(Ry)	3đ	Чs	μp	2s	2p	3s	3p	
2b <sub>2</sub>	-0.3060	91.88						7.76	
la <sub>2</sub>	-0.4600							98.95	
6e -	-0.4810	1.07		1.45				95.35	
3b <sub>1</sub>	-0.4935							98.67	
5e -	-0.4973					9.4l		89.12	
7a,	-0.5314			1.15				96.98	
4e -	-0.5484	2.54		3.77				91.54	
$1b_2$	-0.57277	8.88						90.12	
2b_	-0.57285	28.33						69.64	
6a,	-0.5963	3.33	9.29					83.12	
3e -	-0.6597	21.39		1.65		69.16		7.62	
5a,	-0.8321	23.84	3.08	4.47	3.12	65.11			
1b,	-1.3552	1.38					98.25		
Ze _	-1.3608						98.61		
4a,	-1.3788		1.12				97.57		
3aı	-1.7654	9.42	3.73	7.57	TT.77	2.15			

Table 4. Molecular orbitals of  $[VOC1_4]^{2-}$ .

[vor <sub>5</sub> ] <sup>3-</sup> .
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Table

					Atom	ılc Chara	cter %			
	Energy	Vana	dium		0 <b>x</b> )	rgen	Fluorf	ne(Eq)	Fluorin	e(ax)
ОМ	(Ry)	3đ	ЦS	μp	2s	2p	2s	2p	2s	2p
2b <sub>2</sub>	-0.1649	91.76						7.93		
7e <sup>c</sup>	-0.4502 -0.4502	7.5		<i>су</i> с		51.90 8 63		39.63 0.24		75,75
yal 6e	-0.4701					1.39		9.28		88.00
la,	-0.5051							99.42		
5e'	-0.5210			1.75				94.88		
3b1	-0.5318			50 C				99.37 72.00		7 00
ual Lel	-0.5714			1.45				88.36		5.09
lb,	-0.6089	8.74		•				90.43		
3e <sup>c</sup>	<b>-</b> 0.6117	13.09		1.4		25.86		56.24		2.6
7a <sub>1</sub>	-0.6137		11.09			13.41		68.32 77 32		4.20
2D 7D	$\frac{1}{2}$	71.34		o c	ר ר	11 66				2 R7
oal ral	-0.0091	29.23			1.2 1.7	41.00		<b>14.14</b>		10.5
la Lal	-1.8027			0.44	03.41				98.17	
2e1	-1.8723			1.6			98.24			
lb,	-1.8802	2.0					97.86			
3al	-1.8925		1.5				97.29			

					Ator	nic Chara	acter %				
	Fnerøv	Vana	adium		0x1	ygen	Chlor:	ine(Eq)	Chlorf	lne(ax)	
MO	$(Ry)^{J}$	3đ	ЧS	4p	2s	2p	3s	3p	3s	3p	
2b,	-0.2742	92.06						7.48			
7e <sup>c</sup>	-0.4102	N						15.48		82.11	
9a,	-0.4118			2.36		1.92		12.11		78.99	
lar	-0.4374							98.83			
6e ć	-0.4476	1.90		1.19		7.08		87.0			
5e	-0.4708	ı				9.36		82.28		6.21	
Зb,	-0.4716							98.86			
8a,	-0.5088			1.35				85.37		10.18	
4e <sup>1</sup>	-0.5200	1.92		3.17				85.95		6.81	
2b,	-0.5466	27.54						70.07			
$1b_{1}^{+}$	-0.5478	8.67						90.19			
7a'	-0.5720	3.90	8.69					80,92		2.16	
3et	-0.6368	19.34		2.02		61.61		16,20			
6a,	-0.7866	24.35	3.12	4.18	2.76	64.35					
5a,	-1.2609								98.32		
lb¦	-1.3287	1.38					98,22				
2et	-1.3332						98.59				
Ча,	-1.3505		1.04				96,81				
$3a_1$	-1.7179	8.59	3.06	7.16	78.19	1.83					

Table 6. Molecular orbitals of [VOC15]<sup>3-</sup>.

the metal atoms have a formal d<sup>1</sup> configuration, the unpaired electron is in an orbital of b<sub>2</sub> symmetry which is primarily a metal d<sub>xy</sub> orbital. The occupied molecular orbitals and orbital energies for  $[VOF_4]^{2-}$ ,  $[VOC1_4]^{2-}$ ,  $[VOF_5]^{3-}$  and  $[VOC1_5]^{3-}$ , which are representative examples of this class of molecules, are given in Tables 3, 4, 5 and 6, respectively; the fractional charges were obtained by the charge partitioning scheme of Case and Karplus<sup>24</sup>. The molecular orbitals of the remaining complexes are given in Appendix 1.

The molecular orbitals of the pentacoordinated complexes (Tables 3 and 4) can be divided into four groups. The first set of orbitals are the three lowest-lying virual orbitals, plus the orbital of  $b_2$  symmetry containing the unpaired electron, each with a substantial metal d contribution. The occupied orbitals which follow this set are essentially non-bonding in nature and are halogen p type orbitals. These are followed by an orbital of  $b_1$ symmetry which accounts for the bonding between the metal and the halogen atoms. The next two lower-energy orbitals contribute to the metal oxygen bonding a  $\sigma$  and a pair of  $\pi$  bonds. The orbitals still lower in energy are the nonbonding oxygen 2s, halogen s type orbitals and the lowlying metal s and p type orbitals.

The hexacoordinated complexes (Tables 5 and 6) have four more occupied molecular orbitals in addition to those



igure 1. Percentage d contribution to M=0  $\sigma$  and  $\pi$  bonds in MO<sup>n+</sup> and [MOX<sub>m</sub>]<sup>n-</sup> where M = V, Cr, Mo, X = F, Cl and m = 4 and 5.

described for the pentacoordinated complexes. Of these three, two of e symmetry and one of  $a_1$  symmetry are higher in energy than the equatorial-halogen p orbitals. The orbital of  $a_1$  symmetry corresponds to a rather weak  $\sigma$  bond between the metal and the axial halogen atom and involves the lowest unoccupied metal p type orbital and the halogen p-type orbital. An interesting feature of this metalaxial halogen bonding is that it does not involve any contribution from metal d orbitals.

There are some common features of the bonding in the penta- and hexacoordinated complexes. The metal-oxygen bonding involves both  $\sigma$  and  $\pi$  type bonding and is significantly stronger than the metal equatorial halogen bonding and the metal-axial halogen bonding in hexacoordinated complexes. In order to understand the metal-oxygen bonding in these complexes we have carried out SCF-MS-X $\alpha$  calculations on the corresponding metal oxycations.  $^{\rm 31}$  As expected, in the oxycations there is multiple bonding between the metal and oxygen, a  $\sigma$  and a pair of  $\pi$  bonds, but there are differences compared to the corresponding complexes. The variation in the metal d orbital contribution to the metal-oxygen bonding orbitals in vanadium, chromium and molybdenum complexes and the corresponding oxycations are illustrated in Figure 1. The metal d orbital contribution to both the  $\sigma$  and  $\pi$  bonding orbitals follows the sequence Cr>Mo>W and in the case of both

Metal	Oxygen	Halogen(Eq)	Halogen(Ax)
1.814	+0.186		
1.056	-0.480	-0.644	
0.807	-0.331	-0.619	
1.059	-0.543	-0.688	-0.766
0.830	-0.358	-0.673	-0.780
2.176	-0.176		
1.522	-0.847	-0.669	
2.380	0.620		
1.319	-0.235	-0.521	
0.957	-0.156	-0.450	
1.316	-0.317	-0.578	-0.688
0.994	-0.182	-0.537	-0.661
2.673	0.327		
1.639	-0.419	-0.556	
1.222	-0.198	-0.506	
1.096	-0.813	-0.478	
1.660	-0.489	-0.616	-0.708
1.245	-0.240	-0.567	-0.735
2.676	0.323		
1.364	-0.377	-0.498	
0.989	-0.153	-0.459	
0.881	-0.132	-0.447	
	Metal 1.814 1.056 0.807 1.059 0.830 2.176 1.522 2.380 1.319 0.957 1.316 0.994 2.673 1.639 1.222 1.096 1.660 1.245 2.676 1.364 0.989 0.881	MetalOxygen1.814+0.1861.056-0.4800.807-0.3311.059-0.5430.830-0.3582.176-0.1761.522-0.8472.3800.6201.319-0.2350.957-0.1561.316-0.3170.994-0.1822.6730.3271.639-0.4191.222-0.1981.096-0.8131.660-0.4891.245-0.2402.6760.3231.364-0.3770.989-0.1530.881-0.132	MetalOxygenHalogen(Eq) $1.814$ $+0.186$ $1.056$ $-0.480$ $-0.644$ $0.807$ $-0.331$ $-0.619$ $1.059$ $-0.543$ $-0.688$ $0.830$ $-0.358$ $-0.673$ $2.176$ $-0.176$ $-0.669$ $1.522$ $-0.847$ $-0.669$ $2.380$ $0.620$ $-0.521$ $0.957$ $-0.156$ $-0.450$ $1.316$ $-0.317$ $-0.578$ $0.994$ $-0.182$ $-0.537$ $2.673$ $0.327$ $-0.556$ $1.222$ $-0.198$ $-0.506$ $1.096$ $-0.813$ $-0.478$ $1.660$ $-0.489$ $-0.616$ $1.245$ $-0.240$ $-0.567$ $2.676$ $0.323$ $-0.498$ $0.989$ $-0.153$ $-0.447$

Table 7. Charge distribution in  $[MOX_n]^{m-}$  complexes.

			:					
Complex	(n-1)f	ns	du	nd	s(1+n)	d( 1+1)	nf	
vo <sup>2+</sup>		1.979	5.849	2.880	9110	0.251		
[voF <sub>4</sub> ] <sup>2-</sup>		1.975	5.810	3.241	0.325	0.593		
[voc14] <sup>2-</sup>		1.973	5.818	3.531	0.342	0.529		
[vof5] <sup>3-</sup>		1.975	5.823	3.195	0.321	0.627		
[voci <sub>5</sub> ] <sup>3-</sup>		1.975	5.826	3.488	0.326	0.554		
Nbo <sup>2+</sup>		1.967	5.750	2.584	0.061	0.205		
[nddf4] <sup>2-</sup>		1.930	5.050	3.086	0.289	1.124		
[NbOF <sub>5</sub> ] <sup>3-</sup>		1.928	5.052	3.022	0.291	1.199		
cr0 <sup>3+</sup>		1.974	5.856	3.406	0.094	0.195		
[croF <sub>4</sub> ] <sup>1-</sup>		1.965	5.783	4.027	0.319	0.587		
[croc1 <sub>4</sub> ] <sup>1-</sup>		1.964	5.786	4.453	0.334	0.505		
[croF5] <sup>2-</sup>		1.964	5.782	3.995	0.320	0,623		
[croci <sub>5</sub> ] <sup>2-</sup>		1.965	5.794	4.375	0.317	0.555		

Electron distribution in the metal orbitals of  $\left[\text{MOX}_n\right]^m\text{-}$  complexes. Table 8.

Complex	(n-1)f	ns	du	nđ	s( I+n)	d( 1+u)	Ju
Mo0 <sup>3+</sup>		1.959	5.731	3.162	0.086	0.231	
[MoOF4] <sup>]-</sup>		1.943	5.522	3.850	0.329	0.717	
[MoOC14]		1.938	5.572	4.326	0.340	0.602	
[MoOBr <sub>4</sub> ] <sup>1-</sup>		1.935	5.559	484.4	0.343	0.585	
[MoOF5] <sup>2-</sup>		1.942	5.525	3.781	0.314	0.778	
[MoOC15] <sup>2-</sup>		1.938	5.575	4.250	0.337	0.655	
w03+	11.922	1.955	5.655	3.017	0.093	0.286	2.249
[wor <sub>4</sub> ] <sup>1-</sup>	13.827	1.933	5.388	3.713	0.332	0.902	0.540
[wocı <sub>4</sub> ] <sup>1-</sup>	13.701	1.933	5.388	4.210	0.353	0.842	0.583
[WOBr <sub>4</sub> ] <sup>1-</sup>	13.663	1.928	5.353	4.383	0.359	0.838	0.596

Table 8. Continued.

vanadium and niobium complexes the metal contributions are lower than those in molybdenum complexes. In the fluoro complexes the metal-oxygen  $\sigma$  bonding orbitals have a larger contribution from the metal d orbitals than they have in the corresponding chloro and bromo complexes. On the other hand, the extent of metal-oxygen  $\pi$  bonding is sensitive to the nature of the ligand atoms. The molecular orbital which represents the  $\pi$  bonding between metal and oxygen in the fluoro complexes has a significant contribution from a fluorine p type orbital (3e orbitals of Table 3 and 4). The metal participation in the metaloxygen  $\pi$  bonding in the fluoro chloro and bromo complexes is lower than in the corresponding metal oxycation. The metal-halogen bonding, though weaker than the metal-oxygen bonding, increases in strength in the sequence F<Cl<Br, as would be anticipated based on the electronegativity of the ligands.

A few general trends in the nature of bonding in this class of molecules can be obtained from the charge distribution (Table 7) and the electron distribution on the metal atoms (Table 8). In the fluoro complexes the metal atoms have larger positive charge compared to the corresponding chloro and bromo complexes, reflecting the greater ionic character of the fluoro complexes. The charge on the metal varies by a very small amount on going from a pentacoordinated complex to the corresponding hexacoordinated complex,

Complex	E(d <sub>xy</sub> →d <sub>xz,yz</sub> )	$E(d_{xy} + d_{x^2-y^2})$	Ref. <sup>b</sup>
[VOF <sub>4</sub> ] <sup>2-</sup>	7350	15470	
[voc14]2-	9220 (11750)	12950 (13500)	32
[VOF <sub>5</sub> ] <sup>3-</sup>	6150 (13660)	15580 (18200) 34	
[voci <sub>5</sub> ] <sup>3-</sup>	8230 (15500)	13060 (16400)	33
[CrOF,] <sup>1-</sup>	11960	23480	
$[croci_{\mu}]^{1-}$	13830 (13100)	19980 (18100) <sup>c</sup>	12
$[CrOF_{5}]^{2-}$	7350 (8350)	24800 (22330) <sup>C</sup>	10,11
[croci <sub>5</sub> ] <sup>2-</sup>	12320 (12380)	20740 (18530)	10
[MoOF <sub>4</sub> ] <sup>1-</sup>	15360	32040	
$[MOOCI_{\mu}]^{1-}$	17450 (14300)	25240 (22600) <sup>C</sup>	14
$[MoOBr_{\mu}]^{1-}$	17560 (14810)	24140 (22730)	35
$[M_0OF_5]^{2-}$	8890 (12700)	34460 (21600)	35
[MoOC1 <sub>5</sub> ] <sup>2-</sup>	12290 (13700)	26670 (22400)	35 <b>,</b> 11
[wof <sub>u</sub> ] <sup>1-</sup>	15800	32590	
[woci <sub>µ</sub> ] <sup>1-</sup>	17890	26120	
[WOBr <sub>4</sub> ] <sup>1-</sup>	18000	24580	

Table 9. Electronic transition (d-d) energies<sup>a</sup> (cm<sup>-1</sup>) in [MOX<sub>n</sub>]<sup>m-</sup> complexes.

<sup>a</sup>The numbers in parentheses are the experimental d-d transition energies.

<sup>b</sup>The references given are for the experimental number.

<sup>c</sup>These absorption bands were not assigned to the  $d_{xy} \rightarrow d_{x^2-y^2}$  transition in the experimental work.

indicating a rather weak metal-axial halogen bonding. The low occupation numbers of the low-lying unoccupied metal s and p type orbitals indicate that these metal orbitals don't have a significant role in the bonding of these complexes.

#### D. Electronic Excitation Energies

The three lowest-lying virtual orbitals of both the penta- and hexacoordinated complexes have a large metal d character and the relative energies of these metal d orbitals follow the sequence  $d_{xz,yz} < d_{x^2-y^2} < d_{z^2}$ , in agreement with the order generally used<sup>1-10,15-17</sup> as the basis for interpretation of the electronic spectra of this class of compounds. The SCF-MS-Xa results for the d-d transition energies calculated by the transition-state procedure<sup>18-20</sup> are given in Table 9, along with available experimental results.

The lowest energy absorption maximum in the electronic spectra of this class of molecule is assigned according to the experimental, as well as the molecular orbital studies, to the excitation of the unpaired electron in the molecular orbital of  $b_2$  symmetry to the lowest-energy unoccupied orbital of e symmetry, which has a large metal d orbital contribution. Our calculated excitation energies for this transition (Table 9) are in fairly good agreement with



Figure 2. Plot of electronic transition (d-d) energies for  $[MOX_5]^{n-}$  where M = V, Cr, Mo and X = F, Cl.



Figure 3. Plot of electronic transition energies for  $[MOX_{4}]^{n-}$  where M = V, Cr, Mo, W and X = F, Cl.



Figure 4. Plot of electronic transition energies for  $[MOX_4]^{n-}$  where M = Mo, W and X = F, Cl, Br.

experiment for a large number of molecules. As we had shown<sup>41</sup>, the lowest energy excitation energy is dependent on the angle between the metal-oxygen and metal-halogen bond and on the metal-oxygen distance. It is therefore not really surprising to note that for some complexes the computed  $d_{xy} + d_{xz,yz}$  transition energy doesn't agree with the experimentally observed value as well as for other complexes, since the geometries of quite a few of these complexes were guessed based on the available data for similar complexes. The lowest d-d transition energies follow the sequence X = F<Cl<Br for  $[MOX_{4}]^{n-}$ , and  $[MOX_{4}]^{n-} >$  $[MOX_{5}]^{(n+1)-}$  for any halogen (Figures 2, 3, and 4).

The variations in the second d-d transition  $d_{xy} + d_{x^2-y^2}$  are essentially the same as those for the  $d_{xy} + d_{xz,yz}$  transition energy. Recently, the two lowest-energy bands in the electronic spectra of  $[CrOCl_4]^{1-}$ ,  $[CrOF_5]^{2-}$  and  $[MoOCl_4]^{1-}$  had been assigned differently from the generally used identification of the first and the second-lowest energy absorption bands to the  $d_{xy} + d_{xz,yz}$  and  $d_{xy} + d_{x^2-y^2}$  transitions based on single-crystal polarized spectra and ab initio studies<sup>11-14</sup>. The first absorption band in  $[CrOCl_4]^{1-}$  was assigned to the usual  $d_{xy} + d_{xz,yz}$  transition while the second band was assigned to  $Cr-O(\pi) + Cr-O(\sigma^*)^{12}$ . According to the SCF-MS-X<sub>a</sub> results the transition  $Cr-O(\pi) + Cr-O(\sigma^*)$  corresponds to an energy greater than 80,000 cm<sup>-1</sup>, while the computed d-d transition energies are in good agreement with the two lowest energy

bands in the electronic spectra of  $[CrOCl_4]^{1-.41}$  For  $[CrOF_5]^{2-}$  our computed d-d transition energies are in agreement with the electronic spectral assignments of Ziebarth et al.<sup>10</sup> In the case of  $[MoOCl_4]^{1-}$ , the SCF-MS-X $\alpha$  value for the transition energy  $Mo-O(\pi) + Mo-O(\sigma^*)$  assigned by Garner et al.<sup>14</sup> to the band at 22,600 cm<sup>-1</sup> is greater than 70,000 cm<sup>-1</sup>, while the computed d-d transition energies seem to be in fair agreement with the two lowest-energy absorption bands in the electronic spectra (Table 9).

# E. Evaluation of g and Hyperfine Interaction Tensor Components

The principal components of the g and the hyperfine interaction (A) tensors which characterize the electron spin resonance spectra of transition metal complexes have been used widely to study the nature of bonding in these complexes and the changes in bonding within a class of compounds. The two approaches generally used in utilizing the measured ESR spectral parameters to investigate the bonding are: (1) the coefficients of the atomic orbitals in the molecular orbital containing the unpaired electron and in a few lowlying virtual orbitals, are determined using the experimental values of the g and A tensor components; 3-5,8,9,36 (11) secondly, one computes the principal components of the g and hyperfine interaction tensors using the molecular orbitals obtained by one of the (usually semi-empirical) molecular

orbital methods and compares them with the experimental values. When the two sets agree the orbitals used in the computation are assumed to give a good description of the bonding in the compound under investigation<sup>37-40</sup>. Even for molecules with as high a symmetry as the penta- and hexacoordinated transition metal oxohalo complexes, the first approach requires more experimental data than one has, while the second method is critically dependent on the molecular orbitals used. Note however, as we have shown earlier<sup>41</sup>, that the latter is clearly the most objective approach and so is the one used in this study. Both the procedures depend heavily on the choice of values for parameters such as the spin-orbit coupling constants and  $< r^{-3} >$  values.

There are some interesting similarities and differences in the experimental values of the principal components of the g and A tensors of the penta- and hexacoordinated transition metal oxohalo complexes of vanadium, chromium, molybdenum and tungsten. For all vanadyl complexes the value of  $g_{||}$  is less than that of  $g_{\perp}$ , while  $g_{||}$  is greater than  $g_{\perp}$  for the chloro- and bromo-complexes of chromium and molybdenum. In addition some of the chromium and molybdenum complexes have a  $g_{||}$  greater than the freeelectron g value of 2.0023. It has been suggested by Kon <u>et al.</u><sup>2</sup> that for chromium complexes the contribution from the low-lying occupied orbital of  $b_1$  symmetry should

be included in evaluating  $g_{||}$ , while Manoharan <u>et al</u>.<sup>4</sup> included the ligand contribution to  $g_{||}$  to account for the above-mentioned difference in the principal components of the g tensor for this class of compounds. We have investigated the relative merits of both suggestions using g and A tensor components calculated from the SCF-MS-Xa wavefunctions.

The following equations which have been discussed earlier<sup>41</sup>, were used in the computation of  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}^{M}$  and  $A_{\perp}^{M}$ :

 $\Delta_{\parallel} = g_e - g_{zz}; \quad \Delta_{\perp} = g_e - g_{xx}$ 

$$\Delta_{||}(b_1) = \frac{2(2\beta_1\epsilon_1\lambda_M^{-4}\beta_2\epsilon_3\lambda_L)(2\beta_1\epsilon_1^{-4}\beta_2\epsilon_3)}{\Delta E(b_2 + b_1)}$$
(1)

$$\Delta_{\parallel}(b_{1}') = \frac{-2(2\beta_{1}\epsilon_{1}'\lambda_{M}+4\lambda_{2}\epsilon_{3}'\lambda_{L})(2\beta_{1}\epsilon_{1}'+4\beta_{2}\epsilon_{3}')}{\Delta E(b_{1}'+b_{2})}$$
(2)

$$\Delta_{\perp}(e) = \frac{2(\alpha_{3}\beta_{1}\lambda_{M}+2\alpha_{10}\beta_{2}\lambda_{L})(\alpha_{3}\beta_{1}+2\alpha_{10}\beta_{2})}{\Delta E(b_{2} \neq e)}$$
(3)

$$A_{zz}^{M}(b_{1}) = -P[\frac{4}{7}\beta_{1}^{2} + \frac{2(2\beta_{1}\varepsilon_{1}\lambda_{M}-4\beta_{2}\varepsilon_{3}\lambda_{L})}{\Delta E(b_{2} \neq b_{1})}\beta_{1}\varepsilon_{1} + \frac{6}{7}\frac{(\alpha_{3}\beta_{1}\lambda_{M}+2\alpha_{1}0\beta_{2}\lambda_{L})}{\Delta E(b_{2} \neq e)}\alpha_{3}\beta_{1} + \kappa]$$
(4)

$$A_{xx}^{M} = A_{yy}^{M} = -P[-\frac{2}{7}\beta_{1}^{2} + \frac{11}{7} \frac{(\alpha_{3}\beta_{1}\lambda_{M}+2\alpha_{10}\beta_{2}\lambda_{L})}{\Delta E(b_{2} + e)} \alpha_{3}\beta_{1} + \kappa],$$

$$P = g_{e}g_{N}\beta_{e}\beta_{N} \langle r^{-3} \rangle_{M}^{nd},$$
(5)

where  $\beta_1$  and  $\beta_2$  are the coefficients of the metal d and halogen  $p_{x,y}$ -type orbitals in the molecular orbital ( $b_2$ ) containing the unpaired electron,  $\varepsilon_1$  and  $\varepsilon_3$  the corresponding coefficients for the low-lying unoccupied orbital of  $b_1$  symmetry and  $\alpha_3$  and  $\alpha_{10}$  are the metal  $d_{xz,yz}$  and halogen  $P_z$  orbital coefficients of the low-lying unoccupied orbital of e symmetry;  $\varepsilon_1^i$  and  $\varepsilon_3^i$  are the coefficients of the metal d and halogen  $p_{x,y}$  orbitals of the occupied orbital of  $b_1$ symmetry;  $\lambda_M$  and  $\lambda_L$  are the one-electron spin-orbit coupling constants for the metal d and halogen p orbitals, respectively,  $\kappa$  takes into account the Fermi contact interaction, and the appropriate excitation energies are denoted by  $\Delta E$ .

The contribution from any occupied orbital of  $b_1$ symmetry to  $g_{||}$  can be calculated using expressions very similar to that for  $\Delta_{||}(b_1)$ . In the equation for  $A_{zz}^M(b_1)$ only the contribution from the unoccupied orbital of  $b_1$ symmetry is included. The contributions from the occupied orbital of  $b_1$  symmetry to  $A_{zz}$  can be included by adding terms similar to the second term in the expression for  $A_{zz}^M(b_1)$ .

In order to take into account the charge in the outer

sphere region, we have distributed the outer sphere charge associated with the molecular orbitals needed for computing g and A tensor components among the ligand atoms in the ratio of atomic number. The additional charge was further partitioned into s and p fractions for each atom in the ratio of the net s and p populations. In the SCF-MS-Xa model the squares of the molecular orbital coefficients in Equations (1-5) have been identified with the fractional charges associated with the corresponding partial waves.

The computation of  $g_{||}$ ,  $g_{|}$ ,  $A_{||}$  and  $A_{|}$  requires knowledge of the magnitude of  $\lambda_{M}, \lambda_{T}, \langle r^{-3} \rangle_{M}$  and of the electronic excitation energies, in addition to the molecular orbital coefficients. The required electronic excitation energies were calculated by the transition-state procedure 18-20. The magnitude of computed ESR parameters depends critically on the values assigned for  $\boldsymbol{\lambda}_{M}\text{,}$   $\boldsymbol{\lambda}_{L}$  and  $\langle r^{-3} \rangle_{M}$ . The spin orbit coupling constants ( $\lambda_{M}$ ) and values of  $\langle r^{-3} \rangle_{M}$  for the metal d orbital are sensitive function of the valence electron configuration of the metal<sup>41</sup>. This makes the choice of values for these parameters, from those available for the various oxidation states and configurations, very difficult in any systematic manner. The spin orbit coupling constants  $\lambda_M$  were computed for the formal valence configurations of the metals (Table 8), using the atomic  $X\alpha$  wavefunction for the appropriate configuration and the single-particle approximation for  $\lambda_{M}$ , <u>i.e.</u>,

Complex	$\lambda_{\rm M}^{\rm nd}$ (cm <sup>-1</sup> )	$< r^{-3} >_{M}^{nd}$ (au)	$P_{M}^{nd}$ (x10 <sup>4</sup> cm <sup>-1</sup> )
[VOF <sub>4</sub> ] <sup>2-</sup>	220	2.762	129.43
[voci <sub>4</sub> ] <sup>2-</sup>	209	2.625	123.00
[VOF <sub>5</sub> ] <sup>3-</sup>	221	2.774	129.99
[voci <sub>5</sub> ] <sup>3-</sup>	210	2.639	123.66
[CrOF <sub>4</sub> ] <sup>1-</sup>	308	3.594	-36.13
[CrOCi <sub>4</sub> ] <sup>1-</sup>	289	3.382	-34.00
[CrOF <sub>5</sub> ] <sup>2-</sup>	309	3.609	-36.28
[croc1 <sub>5</sub> ] <sup>2-</sup>	292	3.414	-34.32
[MoOF <sub>11</sub> ] <sup>1-</sup>	895	4.851	-56.24
[MoOCI <sub>4</sub> ] <sup>1-</sup>	835	4.532	-52.55
$[MoOBr_{ll}]^{1-}$	820	4.453	-51.63
$[MOOF_5]^2$ -	902	4.890	-56.70
[MoOC1 <sub>5</sub> ] <sup>2-</sup>	842	4.572	-53.00
[WOF,]] <sup>1-</sup>	3254	8.919	
[woci,] <sup>1-</sup>	3170	8.694	
	3158	8.650	

Table 10. Computed values of  $\lambda_M^{nd}$ ,  $\langle r^{-3} \rangle_M^{nd}$  and  $P_M^{nd}$ .

$$\lambda_{\rm M} = \frac{e^2 \hbar^2}{2m^2 c^2} < \frac{1}{r} \frac{dV}{dr} > = \frac{e^2 \hbar^2}{2m^2 c^2} Z^1 < r^{-3},$$

where z' is the effective nuclear charge; these are given in Table 10. The ligand spin orbit coupling constants  $\lambda_L^{np}$  were calculated for the neutral atoms in a similar manner (Table 10). The  $\langle r^{-3} \rangle_M$  values used in computing the A tensor components were also calculated for the formal valence configurations of the metals in the complexes (Table 10). Note that for tungsten valence electron configurations given in Table 8, since we couldn't locate the 5f orbital which is very high in energy, the  $\lambda_W^{5d}$  were computed for two configurations where the 5f population was added to the 6s and 6p orbitals, respectively. The  $\lambda_W^{5d}$  computed for these configurations differ only by about 30 cm<sup>-1</sup> and we used the higher  $\lambda_W^{5d}$  value in evaluating the ESR parameters for the tungsten complexes.

The values of  $g_{||}$ , which are determined by mixing of  ${}^{2}B_{1}$  excited states into the  ${}^{2}B_{2}$  ground state (Equation (1)), have been calculated using the computed  $\lambda_{M}$  values (Table 10) and electronic excitation energies (Table 9). We first consider the evaluation of  $g_{||}$  for the vanadium complexes. In this case, since the  ${}^{2}B_{1}$  states arising from the promotion of an electron from the occupied molecular orbitals of  $b_{1}$  symmetry to the orbital containing the unpaired electron had very large electronic excitation energies and

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Table 11.

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Complexes	calc.	Exp.	Calc.	Exp.	Ref.	
[VOF4] <sup>2-</sup>	1.938 (1.924)	1.932	1.955 (1.956)	1.973	43	
[vocı <sub>4</sub> ] <sup>2-</sup>	1.948 (1.920)	1.948	1.968 (1.970)	1.979	32	
[VOF <sub>5</sub> ] <sup>3-</sup>	1.937 (1.923)	1.937	1.944 (1.948)	1.977	4	
[voci <sub>5</sub> ] <sup>3-</sup>	1.947 (1.919)	1.945	1,962 (1.965)	1.985	ſ	
[croF <sub>4</sub> ] <sup>1-</sup>	1.959	1.959	1.967	1.968	4	
[croc1 <sub>4</sub> ] <sup>1-</sup>	2.040	2.006	1.980	1.979	42	
		1.959		1.969	• • 4	
[crof <sub>5</sub> ] <sup>2-</sup>	1.963	1.961	1.943	1.975	10	
[croci <sub>5</sub> ] <sup>2-</sup>	2.043	2.008	1.966	1.977	2	
[MoOF4] <sup>]-</sup>	1.898	1.895	1.927	1.925	43	
[MoOCl4]	1.994	1.965	1.946	1.947	43	
[MoOBr <sub>4</sub> ] <sup>1-</sup>	2.141		1.947			
[MoOF5] <sup>2-</sup>	1.903	1.874	1.869	1.911	4	

	B		້		
Complexes	Calc.	Exp.	Calc.	Exp.	Ref.
[Mooc15] <sup>2-</sup>	1.980	1.963	1.917	1.940	4
[woF <sub>4</sub> ] <sup>1-</sup>	1.624	1.599	1.741	1.672	8
[woc1 <sub>4</sub> ] <sup>1-</sup>	1.622	1.79	1.801	1,75	8
[wobr <sub>4</sub> ] <sup>1-</sup>	1.695	1.796	1.810	1.903	8

<sup>a</sup>The numbers in parentheses were calculated without including the ligand contribution.

Table 11. Continued.

thus make only negligible contribution to  $g_{||}$ , only the contribution from the lowest unoccupied orbital of  $b_1$  symmetry was included. For  $[VOCl_4]^{2-} g_{||}$  calculated including the ligand contribution is 1.948, which is in very good agreement with the experimental value of 1.9480. If the ligand contribution is neglected, however,  $g_{||}$  has a value of 1.9201 indicating the importance of the ligand contribution in calculating  $g_{||}$  (see Table 11). The  $g_{||}$  values for the fluoro complexes of chromium (Table 11) and molybdenum (Table 11) were calculated by including only contributions from the lowest-lying unoccupied orbital of  $b_1$  symmetry, just as in the case of the vanadium complexes.

For the evaluation of  $g_{||}$  for  $[CrOCl_5]^{2-}$ ,  $[MoOCl_4]^{1-}$ ,  $[MoOCl_5]^{2-}$  and  $[MoOBr_4]^{1-}$ , it was found necessary to include the contributions from the occupied orbitals of  $b_1$  symmetry, as shown earlier for  $[CrOCl_4]^{1-41}$  in order to account for the fact that for these complexes  $g_{||}$  has a value greater than  $g_1$ . For all the chloro complexes of chromium and molybdenum, as well as for  $[MoOBr_4]^{1-}$ , there are two  $^2B_1$  states which arise from the occupied orbitals of  $b_1$ symmetry having electronic excitation energies comparable to the  $^2B_1$  state from the lowest-energy unoccupied orbital of  $b_1$  symmetry. Thus, for example, for  $[MoOCl_4]^{1-}$ the computed  $g_{||}$  is 1.9963, including the contributions from all the three  $^2B_1$  states, while the corresponding value including only the contribution from  $^2B_1$  state

arising from the lowest unoccupied orbital is 1.9112. This latter value is smaller than the computed  $g_{\parallel}$  value of 1.9462. For  $[MoOCl_4]^{1-}$ , though the computed  $g_{||}$  value of 1.9963 is not in very good agreement with the experimental value of 1.965, the experimental observation that  $g_{||}$ >  $g_{\parallel}$  is predicted correctly. If  $g_{\parallel}$  for  $[MoOCl_4]^{1-}$  is computed neglecting the ligand contribution but including all the three  ${}^{2}B_{1}$  states, the value is 1.9261 which is again lower than  $g_{\parallel}$ . This indicates the importance of including the ligand contributions as well as the contributions from both the  ${}^{2}B_{1}$  states arising from the occupied orbitals of  $b_1$  symmetry. The values of  $g_{||}$  for all the chloro and bromo complexes of chromium and molybdenum given in Table 11 were computed including the contributions from all the three  ${}^{2}B_{1}$  states mentioned above. The magnitude of g<sub>1</sub>, which is primarily determined by the low-lying unoccupied orbital of e symmetry<sup>12</sup> was computed for all the complexes (Table 11).

For all the tungsten complexes, only the contributions to  $g_{||}$  from the  ${}^{2}B_{1}$  state arising from the lowest-lying unoccupied  $b_{1}$  orbital was included, since the other  ${}^{2}B_{1}$ states were found to be rather high in energy. We note however, that for the tungsten complexes relativistic effects, which were not included in the present study, may be important in determining the relative energies of various excited states. The computed principal components

		•	ł					
	A    (x	10 <sup>4</sup> )cm <sup>-1</sup>	OIX) TY	4).cm <sup>-1</sup>	A <sub>o</sub> (x10 <sup>4</sup> )c			
Complexes	Calc.	Exp.	Calc.	Exp.	Exp.	¥	Ref. <sup>b</sup>	
[VOF <sub>4</sub> ] <sup>2-</sup>	-174.37	-182.00	-70.33	-66.70	-105.13	0.769	43	
[voci <sub>4</sub> ] <sup>2-</sup>	-163.87	-168.80	-64.85	-62.80	- 98.00	0.763	32	
[vor <sub>c</sub> ] <sup>3-</sup>	-173.13	-178.50	-68.95	-64.05	-102.20	0.748	ħ	
[voci <sub>5</sub> ] <sup>3-</sup>	-167.20	-173.00	-67.64	-63.80	-100.20	0.779	£	
[croF <sub>1</sub> ] <sup>1-</sup>	38.93		12.19		21.45	0.555	4	
[crocl <sub>n</sub> ] <sup>1-</sup>	33.61		10.26		18.10	0.518	14	
[crof <sub>c</sub> ] <sup>2-</sup>	40.71		14.55		23.09	0.597	4	
[croci <sub>5</sub> ] <sup>2-</sup>	33.46		10.75		18.20	0.515	5	
[MoOF <sub>1</sub> ]	81.18	85.38	38.36			0.868 <sup>a</sup>		
$[MOOCI_n]^1-$	72.70	75.85	35.56	34.42	48.23	0.868	43	
[MoOBr <sub>u</sub> ] <sup>1-</sup>	67.35		35.24			0.868 <sup>a</sup>		
[MoOF <sub>g</sub> ] <sup>2-</sup>	88.68	92.93	47.41	45.13	61.06	0.974	4	
[MoOCI <sub>5</sub> ] <sup>2-</sup>	70.50	74.7	34.74	32.60	46.63	0.818	4	
<sup>а</sup> The к value	is that f	or [MoOCl <sub>4</sub> ]	1					
<sup>b</sup> The referenc	es are fo	r the exper	imental da	ta.				

Computed values of  $A_{||}$  and  $A_{|}$  for  $[MOX_n]^{m-}$ . . Table 12.

of the g tensor of  $[WOX_4]^{1-}$  (X = F, Cl, Br) are compared with the corresponding values for the hexacoordinated species since there are no experimental results available for the pentacoordinated complexes. For  $[WOF_4]^{1-}$  and  $[WOBr_4]^{1-}$  the computed  $g_{||}$  value is less than  $g_1$ , as observed experimentally for  $[WOF_5]^{2-}$  and  $[WOBr_5]^{2-}$ .<sup>8</sup> For  $[WOCl_4]^{1-}$  the computed  $g_{||}$  is less than  $g_1$  and for  $[WOCl_5]^{2-}g_{||}$  is found experimentally to be greater than  $g_{|}$ .

The Fermi contact interaction parameter  $\kappa$  in the expressions for the principal components of the A tensor, vanishes in the spin-restricted molecular orbital approximation in which we had carried out all the calculations.  $\kappa$  was determined using the following equation:

$$A_{o} = -\kappa P - (g_{a} - g) P,$$

where  $A_0$  is the isotropic hyperfine coupling constant,  $g_e$ is the free-electron g value and g the experimental average g value for the complex. The values of P, which was defined earlier, and of the experimental isotropic hyperfine coupling constant used in evaluating  $\kappa$  are given in Table 10. The computed values of the principal components of the A tensors for vanadium, chromium and molybdenum complexes are given in Table 12. For the chloro complexes of chromium and molybdenum, as well as for  $[MoOBr_{\mu}]^{1-}$ , the contributions from all the three  ${}^{2}B_{1}$  states to  $A_{||}$  were included. All the computed  $A_{||}$  values are smaller than the experimental values, while the  $A_{\perp}$  values are larger than the corresponding experimental values. Even then the experimental trends are reproduced fairly well (Table 12).

The computed principal components of the g tensor reproduce the experimental trends very well, even though the numerical values for some complexes are not as good as for others. For  $[CrOF_5]^{2-}$  and  $[MoOF_5]^{2-}$  the calculated relative values of  $g_{||}$  and  $g_{\perp}$  are the reverse of the experimental values. This could be due to the inaccuracies in the geometrical data used in the calculation, since the magnitude of  $g_{\perp}$  has been shown<sup>41</sup> to depend on the angle between the metal-oxygen and metal-halogen bonds.

## F. Conclusion

We conclude from this study that there are many similarities in the electronic structure and properties of the halide complexes of the d<sup>1</sup> oxycations of vanadium, niobium, chromium, molybdenum and tungsten. The one major difference between the vanadium oxohalide complexes and those of chromium and molybdenum is that for both the fluoro and chloro complexes of vanadium, the  ${}^{2}B_{1}$  excited states arising from the occupied orbitals of b<sub>1</sub> symmetry are much higher in energy than those of the corresponding
chromium and molybdenum complexes. This accounts for the observation that for all vanadyl complexes  ${\tt g}_{|\,|}$  values are lower than  $g_{\parallel}$ . We have also shown that it is again the rather high energy of the  ${}^{2}B_{1}$  excited states arising from occupied  $b_1$  orbitals of fluoro complexes of chromium and molybdenum that makes the significant differences in the ESR spectra of these complexes compared to the corresponding chloro and bromo complexes. The importance of including the ligand contributions in computing the g tensor components has been clearly demonstrated. We agree with the conclusions of Garner et al.11-14 that it is not possible to assume that the two lowest-energy absorption bands in the electronic spectra are d-d transitions for all the oxohalo complexes of vanadium, chromium and molybdenum. In spite of the numerous limitations of the SCF-MS- $X_{\alpha}$  method, the trends in the principal components of the g and A tensors of this class of complexes have been calculated to a surprisingly high degree of accuracy. The SCF-MS-Xa model thus appears to be a useful theoretical model for systems as large as those studied here, which are not readily amenable to ab initio studies.

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 $R_0 = 1.8741 \text{ au}$ , for  $VO^{2+}$ ,  $R_{Nb} = 2.2936 \text{ au}$ ,  $R_0 = 1.8222 \text{ au}$  for NbO<sup>2+</sup>,  $R_{Cr} = 2.119 \text{ au}$ ,  $R_0 = 1.7776 \text{ au}$  for  $CrO^{3+}$ ,  $R_{Mo} = 2.3253 \text{ au}$ ,  $R_0 = 1.7590 \text{ au}$  for  $MoO^{3+}$  and  $R_W = 2.4108 \text{ au}$  and  $R_0 = 1.7486 \text{ au}$  for  $WO^{3+}$ .

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#### CHAPTER VII

EPR STUDIES OF 
$$[VOF_4]^2$$
,  $[MoOF_4]^1$   
and  $[MoOCl_4]^1$ 

The transition metal oxohalo complexes of the type  $[MOX_5]^{n-}$ , where M = V, Nb, Cr, Mo, W and X = F, Cl, Br and I, have been the subject of detailed EPR studies.<sup>1-20</sup> The g, metal hyperfine, and ligand hyperfine tensors have been used to investigate the nature of bonding in these compounds. On the other hand very little work has been done on the corresponding pentacoordinated oxohalo complexes<sup>21,22</sup>. Since EPR spectroscopy provides a very sensitive probe for the detection and measurement of the effects of small changes in bonding, we have undertaken a fairly detailed study of the single-crystal EPR spectra of  $[VOF_4]^{2-}$ ,  $[MoOF_4]^{1-}$  and  $[MoOCl_4]^{1-}$  in the hope of getting a better understanding of the differences in the bonding between the penta- and hexacoordinated transition metal oxohalo complexes.

The pentacoordinated transition metal complexes form a class of compounds of considerable interest with the structures possessing a diversity of forms between the two limiting symmetries of trigonal bipyramidal (D<sub>3h</sub>

symmetry) and square pyramidal  $(C_{4v} \text{ symmetry})$ .<sup>22-24</sup> The energy barrier between these two structures is predicted<sup>25</sup> to be small for species with five equivalent ligands, and examples are observed to occur in both symmetry classes.<sup>26,27</sup> On the other hand, complexes having an axial ligand different from the other four tend to form square pyramidal complexes.<sup>24</sup> The pentacoordinated oxohalo complexes under investigation here fall in the latter category.

ESR studies of  $VO^{2+}$  and  $Cr^{3+}$  in  $(NH_4)_2SbCl_5^{21}$  and  $Fe^{3+}$  in  $(NH_4)_2SbF_5^{28}$  have been found to provide pentacoordinated species  $[VOCl_4]^{2-}$ ,  $[MoOF_4]^{1-}$  and  $[FeF_5]^{2-}$ , respectively, while for  $Cr^{3+}$  in  $K_2SbF_5$  the species which predominates<sup>29</sup> is trigonally distorted  $[CrF_6]^{3-}$ . ESR spectra of  $[MoOCl_4]^{1-}$  have been studied in solution<sup>31</sup> as well as in a diluted single crystal of  $[AsPh_{\mu}][NbOCl_{\mu}]$ .<sup>32</sup> We have carried out the ESR studies of the fluoro complexes of  $VO^{2+}$  and  $MoO^{3+}$  in ammonium pentafluoroantimonate(III) and the chloro complex of  $Mo0^{3+}$  in ammonium pentachloroantimonate(III). The ligand hyperfine interactions have been observed for the fluoro complexes at room temperature and for the chloro complex at low temperature. We have used the results from our earlier SCF-MS-X $\alpha$  studies on this class of compounds  $3^2$  to interpret the observed g and metal hyperfine interaction tensors.

### A. Experimental

Ammonium pentafluoroantimonate(III) was made by evaporating a solution of 3 moles of  $NH_{\mu}F$  and 1 mole of  $SbF_{2}$ in distilled water. Ammonium pentachloroantimonate(III) was made by evaporation of a solution containing SbCl, and  $\mathrm{NH}_{4}\mathrm{Cl}$  in the molar ratio 3:4 in dilute hydrochloric acid.<sup>30</sup> The single crystals of  $(NH_4)_2SbF_5$  containing about 1% by weight of VO<sup>2+</sup> were obtained by slow evaporation of a solution of  $(NH_4)_2SbF_5$  and  $NH_4F$  in the molar ratio of 1:1 with about 1-2% by weight of  $VOSO_4 \cdot 7H_2O$ . The single crystals of  $(NH_4)_2SbF_5$  containing  $[MOOF_4]^{1-}$ were made by dissolving  $(NH_4)_2SbF_5$  and  $NH_4F$  in water in mole proportion of 1:1, adding a solution of ammonium molybdate in hydrofluoric acid reduced with metalic tin and allowing the solution to evaporate slowly. The single crystals of  $(NH_4)_2SbCl_5$  containing  $[MoOCl_4]^{1-}$  were made by dissolving SbCl3 and  $NH_{4}Cl$  in dilute hydrochloric acid in the molar ratio of 3:4, adding a solution of ammonium molybdate in hydrochloric acid reduced with mettalic tin and allowing the solution to evaporate slowly.

EPR spectra were recorded for the single crystals using a Varian E-4 X-band spectrometer. The powder measurements were made using powdered samples of the single crystals.



Figure 1. Crystal structure of  $(NH_4)_2SbF_5$  with internuclear distances given in Angstrom units.

#### B. Results

# 1. Tetrafluoro Complexes of Oxovanadium(IV) and Oxomolybdenum(V)

The diamagnetic host lattice used in single-crystal studies of fluoro complexes has ammonium pentafluoroantimonate. This forms orthorhombic crystals with each antimony ion at the center of a distorted octahedron in which five of the vertices are fluoride ions and the sixth is the sterically-active lone pair associated with trivalent antimony.<sup>31</sup> The details of the structure are shown in Figure 1, where it may be noted that the axial-fluoride-Sb-lone pair direction is parallel to the b-axis of the crystal (Sb-F<sub>ax</sub> = 1.916 Å) with the antimony ion displaced 0.382 Å from the center of the rectangle formed by the four axial fluorines (Sb-F = 2.075 Å) towards the lone pair. Two classes of antimony sites related by a center of inversion, and magnetically equivalent, are defined in this way (Figure 1).

The vanadyl  $(VO^{2+})$  and molybdenyl  $(MoO^{3+})$  ions can replace either Sb<sup>3+</sup> or  $[Sb-F]^{2+}$  of the  $[SbF_5]^{2-}$  ions in  $(NH_4)_2SbF_5$  to form either the hexa- or the pentacoordinated complex, or a mixture of both. The ESR study of the single crystals of both the systems,  $VO^{2+}$  in  $(NH_4)_2SbF_5$  and  $MoO^{3+}$ in  $(NH_4)_2SbF_5$ , shows intense resonances associated with only one site of a magnetic species. The angular variation of the ESR spectra for each system was studied by



Figure 2. Coordinate system for the analysis of g and A tensors of pentacoordinated transition metal oxohalo complexes.

recording the spectra at room temperature for every 10° rotation about the crystal a, b and c axes. For both the systems, the rotation study about the crystal b-axis shows spectra which are independent of the rotation angle. This shows that  $VO^{2+}$  and  $MoO^{3+}$  replace either  $Sb^{3+}$  or  $[Sb-F_{ax}]^{2+}$  of the  $[SbF_5]^{2-}$  ion and that the metal-oxygen bond is either along the b-axis or directed on the surface of a cone making a fixed angle to the b-axis. Since the EPR spectra are independent of the angle in the ac plane one can further conclude that both the systems are axially symmetric.

(1) <u>Tetrafluoro oxovanadate(IV) Ion</u> - The Zeeman and metal hyperfine interaction tensors are considered to originate at the metal nuclei and a coordinate system is chosen with the z-axis along the metal-oxygen bond and the x and y axes in the equatorial plane formed by the four halide ligands (Figure 2). The origin for each halogen hyperfine interaction tensor is the halogen atom and the coordinate system has the z axis parallel to the metaloxygen bond, the x-axis along the metal-halogen bond and the y axis chosen to form a right-handed coordinate system (Figure 2).

The electronic Zeeman and metal hyperfine tensors obey the relationships













$$g = (g_z^2 \cos^2\theta + g_x^2 \sin^2\theta \cos^2\phi + g_y^2 \sin^2\theta \sin^2\phi)^{1/2}$$
(1)

and

$$gA^{M} = (A_{z}^{2}g_{z}^{2}\cos^{2}\theta + A_{x}^{2}g_{x}^{2}\sin^{2}\theta\cos^{2}\phi + A_{y}^{2}g_{y}^{2}\sin^{2}\theta\sin^{2}\phi)^{1/2},$$
(2)

where the angle  $\theta$  and  $\phi$  relate the external magnetic field vector  $B_{c}$  to the z and x axes, respectively (Figure 2). The ESR spectrum for  $\theta = 0^{\circ}$  corresponds to  $g_z$  and  $A_z$ while that for  $\theta = 90^{\circ}$  and  $\phi = 0^{\circ}$  corresponds to  $g_r$ and  $A_x$  and that for  $\theta = 90^{\circ}$  and  $\phi = 90^{\circ}$  corresponds to g, and  $A_y$ . In the case of VO<sup>2+</sup> in (NH<sub>4</sub>)<sub>2</sub>SbF<sub>5</sub>, it was found that  $g_x = g_y$  and  $A_x = A_y$ , since the spectra are angle independent for rotations about the b axis, as would be expected for an axially symmetric system. The angular variation of g and  $A^V$  for rotations about the crystal a and c axes are given in Figures 3, 4, 5 and 6, respectively. In the plot of g versus the rotation angle for rotations about the crystal a and c axes (Figures 3 and 5) there are two maxima separated by about 30°. The values of  $G_{||}$ ,  $G_{|}$ ,  $A_{||}$  and  $A_{|}$  were determined from the measured magnetic field values for the various  ${\rm m}_{\rm T}$  transitions by a least-squares fitting procedure using the following equations, which are correct to second order:

$$B_{0} = B(m_{I}) + A_{||}^{m}I + A_{I}^{2} \frac{[I(I+1) - m_{I}^{2}]}{2B(m_{I})} (\theta = 0^{\circ})$$

Rotation Axis	g	g⊥	A	A⊥
a	1.9318	1.9718	-199.61	-74.36
b		1.9728		<del>-</del> 72.95
С	1.9325	1.9742	-198.41	-73.11

Table 1. Single-crystal ESR parameters of  $[VOF_4]^{2-}$ .

$$B_{o} = B(m_{I}) + A_{I}m_{I} + (A_{I}^{2} + A_{I}^{2}) \frac{[I(I+1) - m_{I}^{2}]}{4B(m_{I})} (\theta = 90^{\circ})$$
$$B_{o} = hv/g\beta$$

The values of  $g_{||}, g_{\perp}, A_{||}$  and  $A_{\perp}$  determined in this way from angular variation studies in ab and bc planes are given in Table 1, along with the values of  $g_{\perp}$  and  $A_{\perp}$ determined from b-axis rotation studies. The spin-Hamiltonian parameters determined from different planes agree within experimental error.

We have observed the fluorine hyperfine interaction at room temperature. When the applied magnetic field is along the crystal b axis each of the vanadium hyperfine lines is split into five lines with a separation of 10 G and intensity ratios of approximately 1:4:6:4:1. The fluorine hyperfine interaction was not observed at any other orientation of the crystal with respect to the applied magnetic field at room temperature. We have assigned the observed ESR spectra to the species  $[VOF_4]^{2-}$ based on the observed fluorine hyperfine interaction and the fact that one would have observed ten fluorine hyperfine lines had the species been  $[VOF_5]^{3-.16}$ 

The EPR spectra at low temperatures were too complex to analyze, as we could not follow the angular variations of the many different sets of vanadium hyperfine lines that appear at low temperatures.







Figure 8. Simulated ESR spectrum of polycrystalline sample of  $[VOF_4]^{2-}$  in  $(NH_4)_2SbF_5$ .







The analysis of the ESR spectra of the powder sample (Figure 7) gave spin Hamiltonian parameter values close to those obtained from the single crystal studies. The powder spectrum was simulated using the spin Hamiltonian parameter values obtained from single crystal studies (Figure 8).

(ii) <u>Tetrafluoro oxymolybdate(IV) Ion</u> - The molybdenyl  $(MoO^{3+})$  ion in single crystals of  $(NH_4)_2SbF_5$  is a system very similar to that of  $VO^{2+}$  in  $(NH_4)_2SbF_5$ . For the axially symmetric  $MoO^{3+}$  in  $(NH_4)_2SbF_5$  system, the coordinate axes of Figure 2 were used in the analysis. ESR spectra were recorded for every 10° rotation in the crystal bc, ac and ab planes. Even though fairly well resolved spectra were obtained at room temperature, the molybdenum hyperfine lines were observed only at certain orientations of the crystal with respect to the applied magnetic field because of the large fluorine hyperfine interaction.

The variation of g with angle in the crystal bc and ab planes is given in Figures 9 and 10. In the bc plane g remains a constant from  $\theta = 80^{\circ}$  to  $\theta = 100^{\circ}$ . So  $g_{||}$ and  $g_{\perp}$  were determined by fitting the experimental  $g^2$ values to the equation

 $g^2 = \alpha + \beta \cos 2\theta + \gamma \sin 2\theta$ 





Rotation Axis	<sup>g</sup>	₽⊥	A <sup>d</sup>	A⊥
a	1.8948	1.9253	95.5	
b		1.9256		
с	1.8945	1.9254	95.5	

Table 2. Single-crystal ESR parameters of  $[MoOF_4]^{1-}$ .

<sup>d</sup>Hyperfine coupling constants are in gauss.

where  $\theta$  is the angle the applied magnetic field makes with the crystal b axis. Using the  $\alpha,\ \beta$  and  $\gamma$  values determined by the least-squares procedure, g<sup>2</sup> values were computed for all angles and were found to have the minimum at  $\theta = 0^{\circ}$  and the maximum at  $\theta = 90^{\circ}$  corresponding to  $g_{\parallel}$ and  $g_{|}$ , respectively. The same procedure was carried out for data in the ab plane and the minimum and maximum in  $g^2$  were found to occur again at  $\theta = 0^\circ$  and  $\theta = 90^\circ$ . The  $g_{||}$  and  $g_{|}$  values so obtained from rotation studies in the two different planes agree within experimental error and are given in Table 2. The g value for rotation . about the crystal b axis was found to be invariant to the rotation angle and is equal to the  $g_{\parallel}$  value determined from the bc and ab planes (Table 2). For  $\theta = 0^{\circ}$  the molybdenum hyperfine interaction could be measured in both the ab and bc planes and was found to be 95.5°. This value was assigned to A ||. The A value could not be measured from the single-crystal studies as very intense fluorine hyperfine lines mask the relatively weak molybdenum hyperfine lines.

For  $\theta = 0^{\circ}$  and  $\phi = 0^{\circ}$ , no fluorine hyperfine interaction was observed (Figure 11) thus indicating that  $A_z$  (<sup>19</sup>F) was smaller than the linewidth of the spectrum. For  $\theta = 90^{\circ}$  and  $\phi = 0^{\circ}$  or 90° the fluorine hyperfine structure on the molybdenum I = 0 line consists of a nine line pattern (Figure 12). For the case  $A_x$  (<sup>19</sup>F)  $\neq A_y$ (<sup>19</sup>F)  $\neq 0$  one expects nine fluorine hyperfine lines with



Figure 13. ESR spectrum of polycrystalline sample of  $[MoOF_4]^{1-}$  in  $(NH_4)_2SbF_5$  at 77° K.

•



Crystal structure of  $(NH_{4})_{2}Sb^{Cl}_{5}$  with internuclear distance given in Angstrom. Figure 14.

relative intensity ratios 1:2:1:2:4:2:1:2:1, which is approximately what was observed (Figure 12). From these data  $A_x$  (<sup>19</sup>F) and  $A_y$  (<sup>19</sup>F) were assigned the values -15 G and 55 G, respectively.

The ESR spectrum of the powder sample (Figure 13) is not well enough resolved to do a complete analysis. The spectrum could not be analyzed by simulation as the simulation program available does not properly take into account the ligand hyperfine interaction.

## 2. Tetrachlorooxomolybdate(V) Ion

Ammonium pentachloroantimonate forms monoclinic crystals with the b axis coinciding with the needle axis. Each antimony is at the center of an approximately octahedral configuration of ligands in which five vertices are occupied by chloride ions and one vertex is occupied by the lone pair of electrons associated with antimony in a 3+ oxidation state. Antimony ions, surrounded by four chlorine ligands  $(Sb-Cl_1 = 2.62 \text{ Å } 1 = 1-4)$ , lie in sheets with the fifth chloride  $(Sb-Cl_5 = 2.36 \text{ Å})$  either above or below the sheet as shown in Figure 14. Antimony sites are equivalent, with the b axis parallel to the longer side of the rectangle formed by four chloride ligands and the Sb-Cl<sub>5</sub> axis parallel to an axis 40° from a in the ac plane. If no distortion occurs upon substitution of paramagnetic ions into antimony sites,
















Table 3. Single crystal ESR parameters of $[MoOCl_4]^{1-}$	Table	3.	Single	crystal	ESR	parameters	of	[MoOC14]1.	
--	-------	----	--------	---------	-----	------------	----	------------	--

g <sub>xx</sub> = 1.9461	
	$A_{  } = 83.19G$
gyy = 1.9474	$A_1 = 37.75G$
g <sub>zz</sub> = 1.9650	1

the sites should be indistinguishable by ESR, as was observed experimentally.

ESR spectra were recorded every 10° for rotation of the single crystal about the a, b and c\* axes. The spectra in all the crystal planes indicated the presence of only one magnetic site. ESR spectra at all the crystal orientations with respect to the applied magnetic field consisted of a central intense line corresponding to the molybdenum I = 0 nucleus and three relatively weak hyperfine lines on either side of the central line arising from Mo<sup>95,97</sup> (I = 5/2). The measured g<sup>2</sup> values in each plane were leastsquares fitted to the equation

 $g^2 = \alpha + \beta \cos 2\theta + \gamma \sin 2\theta$ 

and the maximum and minimum  $g^2$  values were determined. The  $g^2$  tensor was diagonalized using Schonland's method to obtain the principal components of the g tensor (Table 3). The  $g_{xx}$  and  $g_{yy}$  values determined by Schonland's method are 1.9461 and 1.9474, respectively. Since the differences between  $g_{xx}$  and  $g_{yy}$  are small, MoO<sup>3+</sup> in  $(NH_4)_2SbCl_5$  is to a first approximation, an axially symmetric system. The angular variation of g and A in the crystal bc\*, ac\* and ab planes is given in Figures 15, 16, 17, 18, 19 and 20. The g value in the ac plane has a maximum at 40° from the a axis corresponding to  $g_{||}$  indicating

that the Mo-O axis is oriented along Sb-Cl<sub>5</sub> axis. The A || and A values were determined by fitting the measured  $g^2A^2$  values from the ac\* plane to the equation

$$g^2 A^2 = \alpha + \beta \cos 2\theta + \gamma \sin 2\theta$$

and are given in Table 3.

The ligand hyperfine interaction even though observed at low temperature could not be analyzed, as all the lines were not well resolved. According to Boorman <u>et al</u>.<sup>32</sup> the  $g_{av}$  values of  $[MoOCl_4]^{1-}$ ,  $[MoOCl_4(H_2O)]^{1-}$  and  $[MoOCl_5]^{2-}$ are 1.951, 1.947 and 1.940, respectively. Our measured  $g_{av}$ value of 1.9528 indicates that the magnetic species is  $[MoOCl_4]^{1-}$  in the present case.

## C. Discussion

The interpretation of the ESR spin Hamiltonian parameters of transition metal oxohalo complexes of the type  $[MOX_n]^{m-}$ , where M = V, Nb, Cr, Mo, W and X = F, Cl, Br, I (n = 4 or 5) is generally based on the discussion of the electronic structure of vanadyl complexes by Ballhausen and Gray<sup>33</sup>, and similar studies on chromyl and molybdenyl complexes by Gray <u>et al</u>.<sup>34,35</sup>, all based on extended Hückel calculations. For deriving expressions relating the spin-Hamiltonian parameters to the molecular orbitals of the system, it was generally assumed that the complexes have  $C_{4v}$  symmetry and that the unpaired electrons are in orbitals of  $b_2$  symmetry. The molecular orbitals necessary for the discussion are then written as

 $|B_{2}\rangle = \beta_{2}|d_{xy}\rangle - \beta_{2}|\Phi_{b_{2}}\rangle$  $|B_{1}\rangle = \beta_{1}|d_{x^{2}-y^{2}}\rangle + \beta_{1}'|\Phi_{b_{1}}\rangle$  $|E\rangle = \varepsilon|d_{xz}, d_{yz}\rangle - \varepsilon'|\Phi_{ex}, \Phi_{ey},$ 

where the ligand orbitals  $\Phi$  are group orbitals of appropriate symmetry. These molecular orbitals are used to derive expressions for  $g_{||}$ ,  $g_{\perp}$ ,  $A_{||}$  and  $A_{\perp}$  using the standard second-order perturbation theory treatment of Abragam and Pryce<sup>39</sup>. For the transition metal oxohalo complexes, DeArmond <u>et al</u>.<sup>6</sup> have derived the required expressions. The expressions for  $g_{||}$ ,  $g_{\perp}$ ,  $A_{||}$  and  $A_{\perp}$  are functions of metal and ligand spin-orbit coupling constants and  $\langle r^{-3} \rangle$  values, in addition to the molecular orbital coefficients. It is customary in using these expressions to solve for the molecular orbital coefficients and  $\langle r^{-3} \rangle$  values of spin-Hamiltonian parameters and assumed values for spin-orbit coupling constants and  $\langle r^{-3} \rangle$  values. The molecular orbital coefficients so obtained depend critically on the choice of values for

	[MoOF4] <sup>]-</sup>	[MoOC14] <sup>]</sup>	[ MoC	)F <sub>5</sub> ] <sup>2-</sup>	[ M00	c1 <sub>5</sub> ] <sup>2-</sup>
	SCF-MS-Xa	SCF-MS-Xa	Expt. <sup>a</sup>	SCF-MS-Xa	Expt. <sup>a</sup>	SCF-MS-Xa
ß <sub>2</sub>	0.9217	0.9055	0.956	4710.0	0.905	0.8902
β <sub>1</sub>	0.8075	0.7629	0.891	0.7856	0.754	0.7574
ω	0.8489	0.8268	0.960	0.8712	0.901	0.8488
						فتراد فبالمتعادين بالمتناز بنيتها المستجم وأباد كركول والمستار بترك

Molecular orbital coefficients for molybdenyl complexes. Table 4.

<sup>a</sup>From Reference 16.

	[VOF4] <sup>2-</sup>	Γνος	,14] <sup>2-</sup>	[vc	) <sub>F5</sub> ] <sup>3–</sup>	[ voc	بر <sub>5</sub> ] <sup>3–</sup>	
	SCF-MS-Xa	Expt. <sup>a</sup>	SCF-MS-Xa	Expt. <sup>b</sup>	SCF-MS-Xa	Expt. <sup>c</sup>	SCF-MS-Xα	
β <sub>2</sub>	0.9565	0.98	0.9585	0.957	0.9579	<1.0	0.9595	
β <sub>1</sub>	0.8702	0.995	0.8340	<1.0	0.8724	<1.0	0.8371	
ы	0.8967	1.007	0.8832	<1.0	0.9050	0.992	0.8895	
e								

Molecular orbital coefficients for vanadyl complexes. Table 5.

<sup>a</sup>From Reference 21.

<sup>b</sup>From Reference 15.

<sup>c</sup>From Reference 6.

spin-orbit coupling constants and  $\langle r^{-3} \rangle$  values. In addition to this it was found necessary to include contributions from occupied orbitals of b<sub>1</sub> symmetry to account for the observed g tensor components of chloro and bromo complexes of chromium and molybdenum (Chapter VI). It becomes practically impossible, without making too many assumptions, to solve for the molecular orbital coefficients from the expressions for g- and A-tensor components if the contributions from occupied orbitals are included.

The derivation of the expressions for spin Hamiltonian parameters and the methods used in the computations, are discussed in Chapters V and VI. The molecular orbital coefficients  $\beta_2$ ,  $\beta_1$  and  $\epsilon$  computed from experimental g- and A tensor components of vanadyl and molybdenyl complexes are given along with those obtained from SCF-MS-Xa calculations for comparison in Tables 4 and 5. The molecular orbital coefficients estimated from experimental data are larger than the values obtained from the SCF-MS-X $\alpha$ method. The coefficient of the metal  $d_{yy}$  orbital  $\beta_2$ in the molecular orbital containing the unpaired electron is larger for the hexacoordinated vanadium complexes than for the pentacoordinated vanadium complexes and the reverse order is observed for molybdenum complexes (Tables 4 and 5). Another interesting observation is that  $\beta_1$ is larger for vanadium complexes than for molybdenum complexes.

Complex	g	<sup>g</sup> ⊥	$A^{a}_{  }$	Aå⊥	Ref.
[VO(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	1.9331	1.9813	182.8	72.0	33
[VOF <sub>4</sub> ] <sup>2-</sup>	1.932	1.973	182.0	66.7	This work
[voc1 <sub>4</sub> ] <sup>2-</sup>	1.9478	1.9793	168.8	62.8	21
[vof <sub>5</sub> ] <sup>3-</sup>	1.937	1.977	178.5	64.05	15
[voc1 <sub>5</sub> ] <sup>3-</sup>	1.9450	1.9847	173.0	63.8	6

Table 6. Spin Hamiltonian parameters for vanadyl complexes.

<sup>a</sup>Hyperfine coupling constants are given in  $10^{-4}$  cm<sup>-1</sup>.

	g	<sup>g</sup> ⊥	A	A⊥	Ref.
[MoOF <sub>4</sub> ] <sup>1-</sup>	1.895	1.925	85.38		This work
[MoOC14] <sup>1-</sup>	1.9650	1.9468	75.85	34.42	This work
[MoOF <sub>5</sub> ] <sup>2-</sup>	1.874	1.911	92.93	45.13	16
[MoOC1 <sub>5</sub> ] <sup>2-</sup>	1.9632	1.940	74.7	32.6	16

Table 7. Spin Hamiltonian parameters for molybdenyl complexes.

For all vanadium oxohalo complexes  $g_{\parallel \parallel}$  is less than  $g_{\parallel}$  while  $g_{\parallel}$  is greater than  $g_{\parallel}$  for the chloro complexes of molybdenum. There have been two proposals to account for this observation. Kon and Sharpless were of the opinion that  $g_{||}$  was greater than  $g_{|}$  because for chloro complexes there is more than one  ${}^{2}B_{1}$  state which makes contribution to  $g_{\parallel \parallel}$  while Manoharan and Rogers proposed that it was the large chlorine spin-orbit coupling constant that caused this reversal of the relative magnitudes of  $\textbf{g}_{|\,|}$ and  $g_{\parallel}$ . From our SCF-MS-X $\alpha$  studies we conclude that the chloro complexes of molybdenum have more than one  ${}^{2}B_{1}$ state that contributes to the  $g_{||}$  value, while for vanadium complexes only one  ${}^{2}B_{1}$  state arising from a low-lying virtual orbital of b, symmetry was observed. It was found necessary to take into account the ligand contributions to the g-tensor components to explain the observed trends. A detailed discussion of these factors is given in Chapter VI.

There is only a very slight difference between the spin-Hamiltonian parameters of penta- and hexacoordinated vanadium complexes. The A-tensor components of the tetrafluorooxovanadium complex are larger than those of the pentafluorooxovanadium complex while for the chloro complexes the reverse is observed (Tables 6 and 7). For molybdenum complexes the g-tensor components are larger for the penta- than for the hexacoordinated complexes.

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APPENDIX A

				Atom	ic Charac	ter %			
	Ялерои		Chromlum		0xy	gen	Fluo	rine	
MO	(Ry)	3đ	4s	4p	2 <b>s</b>	2p	2s	2p	
2b2	-0.4549	84.73						14.84	
ع اھم	-0.6776							99.19	
_ 6e	-0.6935	0.71		1.22		27.88		69.10	
5e	-0.7133	2.65		0.75		4.99		89.88	
3b <sub>1</sub>	-0.7155	0.22						98.66	
Ta,	-0.7746			2.75		3.21		92.46	
4e -	-0.7783			5.72		12.43		80.01	
faر	-0.8286		10.65		0.26	10.42		75.78	
$1b_{2}$	-0.8539	16.34						82.65	
3e -	-0.8627	28.80				29.21		41.04	
2b <sub>1</sub>	-0.8945	31.36					0.57	66.46	
5a,	-0.9774	32.47	0.50	2.46	2.55	51.54		9.09	
4a,	-1.8684	8.60	2.65	5.40	81.89	1.21			
2e _	-2.0828	0,40	1.87				91.19		
lb <sub>1</sub>	-2.0893	2.79					96.70		
3a <sub>1</sub>	-2.1166	0.73	2.00	0.25			96.41		

Table 1. Molecular orbitals of [CrOF4]<sup>1-</sup>.

$\begin{bmatrix} -0.0301 & 20.03 \\ 1 & -1.0174 & 26.62 & 2.21 & 3.26 & 4.22 & 61.34 & 0.50 & 0.57 & 0.97 \\ 1 & -1.3635 & 0.66 & 0.11 & 0.24 & 0.17 & 0.31 & 1.48 & 96.43 \end{bmatrix}$	The Chlorine (axial) 3p 3s 3p 3p 3p 3s 3p 19.52 22.29 19.52 98.60 91.25 98.65 98.65 98.65 98.65 98.75 9.39 72.83 9.39 72.93 9.39 72.15 9.39 72.93 9.39 72.15 9.39 72.15 9.39 72.15 9.39 72.15 9.39 72.15 9.39 72.15 9.39 72.15 9.39 72.15 9.39 72.15 9.39 72.15 9.39 72.15 9.15 9.15 72.15 9.15 9.15 72.15 72.15 7	cchlor cchlor 3s 3s 1.29 0.59 0.59 97.15 97.15 97.15	ifc Chara rgen 2p 3.03 9.10 0.41 1.68 61.53 61.53 61.34 0.31	Atom 0xy 2s 4.22 0.17	4p 3.35 1.53 3.37 3.37 3.37 3.37 3.37 3.37 3.37 3	mium 4s 8.75 0.11 1.34	Chroi 3d 79.79 1.52 2.40 2.40 2.40 2.40 2.15 4.46 42.15 26.62 26.62 26.03 26.62 2.23 1.16	Energy (Ry) (Ry) (Ry) (Ry) (Ry) (Ry) (Ry) (Ry	
2b <sup>2</sup> -1.4389 2.23 97.15	1.36	97.99 94.86	0 よ の	76 00	1.09 7 03	1.34 3 71	ן. 1.16 מע מר	-1.4452 -1.4751 -1.0321	al al al
	78.31 2.15 55.33 5.33	1.29 0.59	1.68		c c	8.75	40.13 4.46 42.15	-0.7155 -0.7155	LD2 201 201
$\begin{bmatrix} b_2 & -0.6898 & 20.73 \\ a_1 & -0.7017 & 4.46 \\ 2b_1 & -0.7155 & 42.15 \\ 2b_1 & -0.7155 & 42.$	80.53 8.75 79.87 0.52 14.12 81.42 9.39		9.10 0.41		2.02 3.37		0.91 2.84	-0.5764 -0.6225 -0.6389	tel tel
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	90.00 91.25 08 65		2.03		1.53		2.40	-0.5404	e b b b b c
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	19.52 22.29 75.12 15.69 72.83		3.03		3.35		79.79 1.52	-0.4672 -0.4935 -0.5022	b al
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3p 3s 3p	38	2p	2s 2	4p	4s	3d	Energy (Ry)	Q
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	[otvo] ontro[d] out	teter %	ilc Chara	Atom					

Table 2. Molecular orbital of  $[CrOCl_5]^{2-}$ .

					Aton	ıic Chara	cter \$			
	Fnerøv	Chro	mium		Оху	rgen	Flue	orine	Fluorin	e (axial)
МО	(Ry)	3d	4s	4p	2s	2p	2s	2p	2s	2p
2b <sub>2</sub>	-0.3964	83.73		( (		L C		15.92		
ya <sub>l</sub> 7el	-0.5623	0.55		3.20		ر٥.ر		C0./		87.37
e e - O r	-0.6041	4.53				35.04		56.94		2.4
Je 2 Je 2	-0.6512			1.84		2.46				1,03
281 801	-0.7086	0.45		1.75				89.12 89.12		7.03
4e 7a <sub>l</sub>	-0.7200		10.58	4.79 0.62		12.10		89.37 72.54		3.22
1b2 3e2	-0.7961 -0.8236	17.68 23.67		0.94		37.27		81.79 36.07		1.57
cal 6al	-0.8539 -0.9319	31.90 33.12	0.47	1.91	2.51	49.22		9.37		2.34
5al	-1.8067	7.74	2.13	5.48	79.02	1.00		• •	4.18	
4al 2el	-1.9043 -2.0209	1.03		2.01	3.03		77.79		93.30	
lb,	-2.0383	3.13					96,63			
$3a_1$	-2.0583	0.83	2.19				96.20			

Table 3. Molecular orbitals of [CrOF<sub>5</sub>]<sup>2-</sup>.

				Atom	lc Charac	ter 🖌			
	Пиерец	Mo	lybdenum		Oxy	gen	Fluo	rine	
МО	(Ry)	hd.	5s	Бр	2 <b>s</b>	2p	2s	2p	
2b2	-0.3113	84.98						14.51	
6e	-0.6783	1.60		3.35		45.46		48.26	
la <sub>2</sub>	-0.6956							99.17	
5е -	-0.7193	2.13		1.32		3.89		90.81	
3b <sub>1</sub>	-0.7262							98.72	
4e	-0.7527			3.37		4.70		90.30	
7a <sub>1</sub>	-0.7581	1.02	2.35	3.07		13.39		78.60	
6a <sub>1</sub>	-0.7902		9.69			10.45		76.77	
$1b_2$	-0.8564	14.97						83,99	
3e -	-0.8616	25.13				22.46		51.07	
2b,	-0.9180	26.15						71.21	
5a,	-0.9558	30.86		1.85	2.51	43.62		19.39	
4a,	-1.7868	10.45	2.42	7.72	78.56				
2e 2	-2.0713			3.46			95.28		
lb <sub>1</sub>	-2.1090	3.66					95.73		
3a <sub>1</sub>	-2.1101		1.97				95.89		

Table 4. Molecular orbitals of  $[MoOF_4]^1$ .

				Atom	lc Charac	ter <b>%</b>			
	Япеиац		Molybdenum		Oxy	gen	Chlo	rine	
ОМ	(Ry)	μđ	5s	Бр	2s	2p	3s	3p	
2b2	-0.4364	82.00						17.38	
la,	-0.5658							98.95	
6e -	-0.5925	1.45		1.64	2.43			92.47	
3b,	-0.6046							98.37	
5e t	-0.6226				3,87			94.48	
7a,	-0.6572			1.82	1.04			95.73	
Че	-0.6716	1.48		4.35	6.85			85.27	
faر	-0.7161	1.30	10.16		2.54			82.56	
1b <sub>2</sub>	-0.7312	18.84						80.35	
2b,	-0.7745	35.55						61.90	
3e 1	-0.8688	31.08				61.28		6.95	
5a,	-1.0650	28.53	1.55	2.94	5.32	59.84		1.37	
2e	-1.4873		1.15				97.76		
lb,	-1.4893	2.99					96.47		
4a,	-1.5154		1.63				96.49		
3a <sub>1</sub>	-1.9330	13.93	3.30	10.60	70.35	1.79			

Table 5. Molecular orbitals of  $[MoOCl_{4}]^{1-}$ .

	4.	d	.59	.76	.06	.06	.64	,98	.20	. 55	,16	.90	.88					
	romine	7	19	98	92	98	95	95	86	82	78	57	m					
	В	Чs								1.05					97.09	98.14	96.88	
ter %	'gen	2p					2.65		5.00				64.89	60.52				2.07
ilc Charac	0 <b>x</b>	2s			2.02					1.87				5.81				68.74
Atom		5р			1.53			1.65	3.98					3.07				11.28
	olybdenum	5s								10.17				1.73			1.35	3.48
	Æ	4d	47.97		2.17				2.59	1.75	21.05	39.77	30.44	27.66	2.45			14.41
	F.nerøv	(Ry)	-0.4351	-0.5090	-0.5399	-0.5521	-0.5740	-0.6089	-0.6268	-0.6712	-0.6826	-0.7205	-0.8633	-1.0717	-1.4138	-1.4166	-1.4426	-1.9445
		OM	2b2	laj	6e -	3b <sub>1</sub>	5e -	7a,	4e	6a <sub>1</sub>	$1b_{2}$	2b,	3e -	5a,	1b,	2e	4a <sub>1</sub>	3a <sub>1</sub>

Table 6. Molecular orbitals of  $[MoOBr_{4}]^{1-}$ .

	ne (axial)	2p		78.06 90.00		1.54	<b>N</b>	1.55	1.44	6.86		2.96	-	4.5					
	Fluor1	2 <b>s</b>													3.34	94.09			
	orine	2p	15.44	3.69 8.14	49.35	99.52 90.26	99.50	93.35	94.32	61.23	83.43	44.93	71.31	20.85					
acter %	Fluc	2 <b>s</b>											1.03	0.52		00 90		95.84 95.49	
nic Chara	ygen	2p		10.98 0.57	44.91	2.77	•	0.85	1.37	17.60		28.87		38.93					
Ator	0x1	2s								0.29				2.59	76.37	2.84			
	m	Бр		4.46		4.08	•	3.41	1.86	0.55				1.08	7.89	99 C	3.00		
	lolybdenu	5s								11.08					2.13		÷.	1.64	
	2	٩d	84.17	0.20	4.78					0.65	16.02	22.40	26.70	30.36	9.22	1.82		1.97 4.14	
	Fnerøv	(Ry)	-0.5881	-0.8895 -0.9212	-0.9407	-0.9873 -0.9895	-1.0179	-1.0419	<b>-1.</b> 0444	-1.0740	-1.1400	-1.1482	-1.2210	-1.2599	-2.0643	-2.2626	-2.3400	-2.3987 -2.4004	
		МО	2b,	9al 7al	e c	la2 Ge2	3b,	ter	Ja,	la¦	لەر 1	3e'	۲b٦		Ja Ja	La da da	e e	3aı lb'	-

Table 7. Molecular orbitals of [MoOF5]<sup>2-</sup>.

[MoOC15] <sup>2-</sup>	
of	
orbitals	
Molecular	
 ®	
Table	

					Aton	nic Chará	acter %			
	Energy	2.	<b>Molybdenu</b>	m	0 <b>x</b> 3	/gen	Chlo	rine	Chlorine	(axial)
MO	(Ry)	4d	5s	5p	2s	2p	3 s	3p	3 <b>s</b>	3p
2b2	-0.4148	79,25						שר טכ		
ga,	-0.4999	0.41		2.96		2.54		96'9		84 05
7et	-0.4946			I				11,42		86.77
2a,	-0.5482							99.23		•
6e <sup>+</sup>	-0.5585	0.61	2.09			1.56		93,81		
3b <sub>1</sub>	-0.5861							99.26		
5et	-0.5906					9.74		85.33		4.13
8a,	-0.6220			1.45		0.42		90.72		5.97
4e <sup>-</sup>	-0.6316	1.24		3.65				88.73		
7a,	-0.6957	1.92	10.30	1		3.47		79.96		וכיו
1b <sup>5</sup>	-0.7038	21.94						77.52		1
2b1	-0.7653	36.22						61.37		
3e <sup>+</sup>	-0.8628	28.52				62.45		7.51		
6a,	-1.0562	27.79	1.50	2.87		58.34		1.75		
5a1	-1.3470	0.57	l			0.56		\ - 	97.70	
lbi	-1.4661	3.46					96.13			
4a1	-1.4848	1.50	1.50				95.95			
2et	-1.4539			1.28			98.32			
3a,	-1.9254	13.84	3.22	10.38	70.50	1.71				
4				)	•	•				

				Atom:	1c Charact	ter %		
	Ниелеи		Niobium		0x yį	gen	Fluo	rine
ОМ	(Ry)	þţ	53	5р	2s	2p	2s	2p
2b <sub>2</sub>	-0.3245	87.48						11.37
6e_	-0.8652	5.63		1.71		75.97		15.17
7a <sub>1</sub>	-0.9222	12.79	6.78	2.91		59.35		15.07
5e	-0.9641	1.38		5.43				89.44
lap	-0.9838							98.95
3b,	-1.0192							98.69
4e <sup>-</sup>	-1.0354			1.61		0.62		96.28
6a,	-1.0519		1.82	1.37				94 <b>.</b> 71
3e -	-1.0956	11.48				7.55		79.56
۶a	-1.1342	16.24	2.08			9.70		68.54
$1b_2$	-1.1407	10.55						88.10
_ 2b_	-1.1851	20.04	0.16					76.95
4a,	-1.8812	6.66	1.79	7.73	83.10			
2e -	-2.3017	0.25		12.17			85.59	
3a <sub>1</sub>	-2.3901	1.39	2.51	0.97			94.50	
lb <sub>1</sub>	-2.4037	4.39					94.87	

Table 9. Molecular orbitals of  $[NbOF_4]^{1-}$ .

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0F4]1-
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of
orbitals
Molecular
10.
Table

				At	comic Cha	racter %			
	Ниеиси		Tung	sten		0 <b>x</b> y	gen	Fluo	rine
ОМ	Liter 6.7 (Ry)	4f	Ъđ	6s	бр	2s	2p	2s	2p
3b <sub>2</sub>	-0.2580		85.24						14.03
7e	-0.6647	2.19	2.44		3.98		52.51		37.59
laj	-0.6909								100.0
4b,	-0.7261	1.26							98.06
6e -	-0.7344	2.91	1.00		0.62		2.88		91.24
5е	-0.7427	0.39			0.33		1.20		93.95
8a,	-0.7460	0.30	0.99	1.30	3.42		12.35		80.1
7a,	-0.8076	2.12		9.45			10.12		76.12
2b2	-0.8460		14.27						84,40
4e -	-0.8495	0.63	23.62		0.52		19.00		55.00
3b,	-0.9151	0.46	24.39					0.95	72.42
6a <sub>1</sub>	-0.9420	1.31	27.56		1.6	3.64	47.65		16.69
5a,	-1.7935	3.03	11.67	2.6	8.17	72.53	1.69		
2b1	-2.1093	0.46	3.91					94.98	
3e	-2.0706	0.67	0.73		3.52			94.55	
μa,	-2.1065	0.36	0.80	2.34	0.47			95.50	

h

			Ĕ	A Sector	tomic Cha	racter %			50 2
ИО	Energy (Ry)	μſ	5d 5d	suen 6s	бр	2s 2	gen 2p	3s	3p 3p
3b <sub>2</sub>	-0.4130		81.99						17.32
۱aر La	-0.5641								100.0
7e _	-0.5951	1.14	1.00		1.37		3.08		91.66
4 p 1	-0.6027	0.58							98.41
je t	-0.6249	1.31			0.60		2.60		94.67
3a,	-0.6512				2.12		1.24		95.39
Je -	-0.6658	0.20	1.15		5.10				83.00
2b2	-0.7262		18.90						80.22
7a,	-0.7266	0.80	2.57	10.28			1.75	1.09	81.79
3b,	-0.7774		34.14					1.14	62.99
te t	-0.8639	2.28	30.45		0.33		58.76		7.83
5a,	-1.0793	2.7	22.32	1.34	2.34			8.4	61.77
3e	-1.4873	0.3	0.64		1.24			97.27	
2b,	-1.4904		3.35					95.90	
5a,	-1.5141		06.0	1.87	0.24			96.17	
la l	4I00.2-	5.17	14.99	3.67	11.16	59.80	5.17		

Table 11. Molecular Orbitals of  $[WOCl_4]^{1-}$ .

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