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A THEORETICAL STUDY OF THE ELECTRONIC STRUCTURE  
OF TRANSITION-METAL COMPLEXES

by

James Wyman Richardson

A Dissertation Submitted to the  
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DOCTOR OF PHILOSOPHY

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## I. INTRODUCTION

### A. Nature and Purpose of the Problem

Compounds of the transition elements have remained of vital interest to chemists for well over a century. They present a fascinating variety of physical and chemical properties from one extreme to another. Their colors range from the infrared to the ultraviolet. Their chemical reactivities range among all combinations and degrees of thermodynamic stability and kinetic lability. Some compounds are diamagnetic, others paramagnetic and still others ferro- or antiferromagnetic.

Transition elements are characterized by the presence of an incompletely filled shell of d-electrons, whose energies are comparable to the valence shell s- and p-electrons. It is the d-electrons which are responsible for many of the unique properties of the metals and their compounds. At the core of all problems concerning these elements lie three questions: (1) what influence does the environment of the metal atom in a molecule or crystal have upon these d-electrons (2) to what extent do these d-electrons participate in chemical bonding (3) what is the effect of this participation?

Advances in the theoretical consideration of such compounds, with a view toward understanding the variety of physical and chemical properties on the basis of modern valence theory, have been rather sporadic. Progress has not been so great as in, say, the field of diatomic molecules or conjugated carbon compounds;

the major exception has been in the study of magnetic behavior. Of course, the molecular systems subtended by the transition element series are all quite involved, presenting many serious complications of a fundamental nature. On the other hand, the tremendous accumulation of experimental facts about, and comparisons among, compounds of transition elements impels effort in a theoretical direction.

The work to be described in the thesis is such an effort. The main intent has been to try to construct a reasonably quantitative treatment of the electronic structure of transition-metal complexes in such a fashion that the important qualitative aspects of the problem are not lost.

A transition metal complex is considered to be a transition metal atom (or ion) more-or-less symmetrically surrounded by several other atoms (ions) or molecules, each called a ligand group<sup>a</sup>, in such a fashion that the whole assembly can be considered a molecular unit. This molecular unit may be electrically charged or neutral. Isolated from its surroundings, it need not be stable with respect to dissociation into its constituents. In many cases, the definition may be extended to include the solid simple salts of these metals, since the crystal lattices may be described as formed from a large number of molecular units which share ligand groups.

It appears, then, that a useful way in which to begin a theoretical study of electronic structures of these compounds

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<sup>a</sup>This definition is given by Nyholm (1).



is first to consider some simple complex ions in detail, then to extend the arguments in a less rigorous manner to the more complicated situations.

Following this plan, the octahedral ammonia and fluoride complexes of ferric iron have been selected for specific consideration. These complexes are considered to be among the most simple to treat theoretically. The nature of the electronic interactions is considered in detail, and conclusions are drawn which are extended in a general way to more complicated systems.

#### B. Organization of the Thesis

The thesis is divided into seven major chapters. The greater part of the literature survey is given in Chapter II; the remaining portion, which is closely interwoven with the theoretical methods to be used in the present work, is covered in Chapter III. In Chapter IV are given the methods used in obtaining good atomic orbitals for use in the calculations. The application of a rather crude semi-empirical treatment of the complex ions selected is considered and analyzed in Chapter V. The deficiencies of this treatment are corrected in Chapter VI, wherein a quantum mechanical calculation following modern valence theory is applied to the ferric hexafluoride and hexamine complex ions. The results and conclusions from Chapter VI are presented, discussed and briefly summarized in Chapter VII.

## II. REVIEW OF LITERATURE

There have been three general lines of development in the theory of the electronic structure of transition metal complexes; the crystalline field theory of Bethe (2), the hybrid-orbital valence bond theory of Pauling (3) and the molecular orbital theory of Mulliken (4). All three were proposed and, especially the first two, were developed in main outline by 1935. In that year Van Vleck (5) analysed the salient features of each and pointed out the areas of agreement among them. Since that time, physicists have developed the crystalline field theory while chemists have embraced the hybrid orbital valence bond ideas; until very recently the molecular orbital approach has been largely neglected.

Within the past few years, several excellent papers have been published on the subject of transition-metal complexes, which review quite well much of the literature relevant to this work. For such references, therefore, the reader is referred to the following articles: Craig, Maccoll, Nyholm, Orgel and Sutton (6), Nyholm (7), Orgel (8), Taube (9) and Bleaney and Stevens (10).

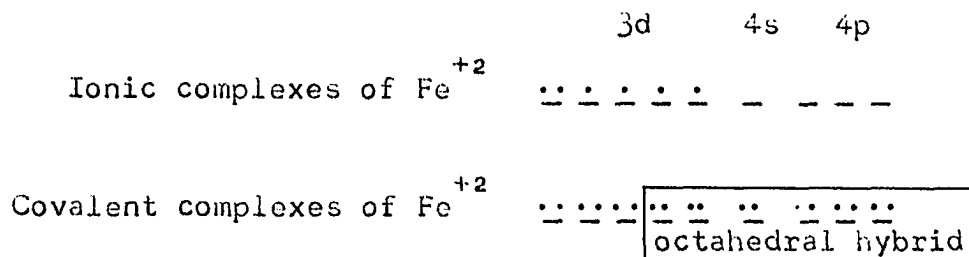
The remainder of this chapter contains an outline of the hybrid-orbital and the crystalline field approaches. The molecular orbital method will be discussed at greater length in a separate chapter. Additional points in all three theories will be considered again in the conclusion to this work.

### A. The Hybrid Orbital Valence Bond Approach

To include the phrase "valence bond" in the description of this approach is somewhat misleading, as no serious attempt has been made to formulate the problem within the framework of the valence bond theory as applied to simpler molecules by such people as Heitler, London, Pauling and Slater. Rather, the approach is derived from the theory of directed valence, which is in turn based upon the concept of hybridization of atomic orbitals into orbitals used for chemical bonding in molecules. The logical extension to a valence bond quantum mechanical calculation has not yet been made.

The major experimental data which have been considered by the theory are the correlations between type of bonding and the measured magnetic properties of the transition metal complexes. For clarity and simplicity, consider the ferrous ion  $\text{Fe}^{+2}$  as a specific example. The electronic configuration exclusive of inner closed shells is  $3d^6$ ; accordingly, the ground state of the gaseous atom is  $^5D_4$ . The observable magnetic moment  $\mu$  associated with the free ion can be computed theoretically (11) from the total angular momentum  $J$  (equal to 4 in this case), which is obtained from the vector sum of the total orbital angular momentum  $L$  and the total spin momentum  $S$ . ( $J = L + S$ ) Excellent agreement is obtained in the case of isolated atoms and also such ions as the rare earths. No similarly good agreement, however, is obtained in the case of

transition metal complexes. Indeed, it appears that the magnetic moment is, very closely, a function only of the spin momentum  $S$  and that the orbital moment is "quenched"; that is, it is observed that  $\mu \sim \sqrt{S(S+1)}$ . Furthermore, a given ion may exhibit different moments in different complexes. These puzzling circumstances were explained by Pauling (3) in the following manner. Diagrammatically indicating the valence shell orbitals by dashes and occupying electrons by dots, two cases are distinguished:

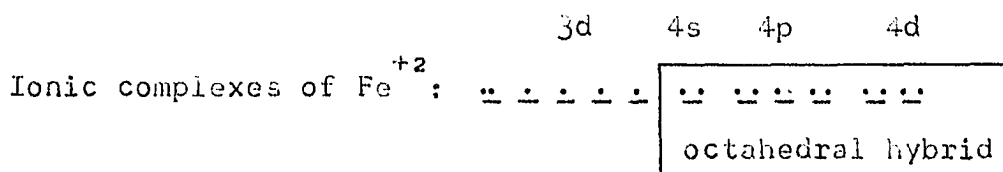


In words, for an ionic linkage the unpaired iron 3d electrons are distributed as in the free ion. But for a covalent complex, two of the 3d orbitals are used up in forming octahedral  $d^2 sp^3$  hybrid orbitals for bonding. The remaining six electrons are forced into the other 3d-orbitals and are necessarily paired. Ionic  $\text{Fe}^{+2}$  complexes, therefore, display a paramagnetism corresponding to four electron spins; and covalent complexes of  $\text{Fe}^{+2}$  are diamagnetic. The quenching of orbital moment will be discussed in the next section.

Similar arguments are easily advanced for other metal ions and other molecular geometries, and are well known. Details

are given in Pauling's "The Nature of the Chemical Bond" (12).

The "Magnetic Criterion for Bond Type", then, is a device for interpreting magnetic properties of transition metal complexes in terms of either of two extreme types of bonding. This rigid "either-or" feature was criticized by Huggins (13), who pointed out that some ionic complexes displayed noticeable covalent characteristics. He suggested that ionic complexes used outer d-orbital octahedral hybrids,  $sp^3d^2$ , for weak covalent bonding. For example,



Of late, this idea has been revived by Taube (9), and it has become quite popular in certain groups. Objections were raised by Pauling (12, footnote p.115), who believed the outer d-orbitals are too highly energetic to allow profitable bonding. Pauling does admit, however, that weak covalent character in ionic complexes may arise from the  $sp^3$  tetrahedral orbitals resonating among the six positions.

The current status of the hybrid orbital approach is that transition metal complexes are in general classified as either "essentially covalent" inner d-orbital hybrid complexes or "essentially ionic" outer d-orbital hybrid complexes. The chief criticism of this state of affairs would seem to be that, in the absence of precise calculations, this approach merely

correlates experimental facts and does not explain these data on any basis of fundamental valence theory. That is to say, one has a mechanism to explain how, but not why, the complexes behave as they do.

An attempt to extend the hybrid orbital approach by inclusion of some quantitative considerations was made by Craig, Maccoll, Nyholm, Orgel, and Sutton (6), in a general survey of compounds in which it is presumed that the chemical bonding involves the use of d-orbitals. Their discussion is based upon the idea of relating the strength of the bond between two atoms of a molecule to the extent to which the bonding orbitals overlap each other. That is, their discussion is drawn from the "Principle of Maximum Overlap" of Maccoll (14) and Mulliken (15). For a given set of atomic orbitals, in a given state of hybridization, the relevant quantity, the so-called "overlap integral" can be obtained theoretically. These overlap integrals may be computed and tabulated for a wide variety of internuclear distances, atomic orbitals and choices of hybridization. In this way, Craig, Maccoll, Nyholm, Orgel and Sutton have set up a basis for comparison among different compounds. Their considerations have established evidence for many of the ways in which d-orbitals may become involved in chemical bonding; they have cited numerous experimental data which correlate with the theoretical conclusions. One specific conclusion of theirs will be mentioned here, for later reference, namely that

it is reasonable to believe, although by no means proven, that the outer-d-orbital hypothesis for ionic complexes is correct.

Admittedly and obviously, there are many additional major factors in chemical bonding which are ignored in this paper. This work does mark an advance from the earlier hybrid orbital discussions in that at least one factor in the bonding is given a semi-quantitative consideration. Nevertheless, this work can in no way be considered as an effort to explain chemical and physical properties from first principles, so to speak.

#### B. The Crystalline Field Theory Approach

In contrast to the highly qualitative approach to examining the electronic structure of the transition metal complexes offered by the hybrid orbital theory, crystalline field theory has become extremely precise and highly involved in mathematical description. All the resources of modern quantum mechanical theory have been utilized in refining what is a very simplified model of the general transition metal complex. In large measure, the stimulation toward this refinement has come from the recent acquisition of new and precise physical measurements on these compounds by microwave spectroscopy.

It is not necessary, nor even relevant, to review here all the recent advances in the application of crystalline field theory to the study of the electronic structure of transition metal complexes. The reasons for this will become

evident after the molecular orbital approach has been discussed. Rather, the general ideas behind crystal field theory will be exposed along with a brief summary of the theoretical uses to which it has been put.

Basically, the problem is to consider what happens to an isolated metal atom when it is placed in the perturbing field of its surroundings in a crystal or molecule. The underlying assumption for almost all later work is that the perturbing field can be represented as arising from various combinations of point charges, point dipoles, and constant electric or magnetic fields, any or all of which interact with the electrons of the metal atom.

#### 1. Outline of the theory of atomic structure

Any understanding of crystalline field theory, however, simplified; must be based upon an understanding of the theory of atomic structure and spectra. No more than a bare outline can be given here, of course; and for a fuller treatment, reference is made to any of the standard advanced quantum mechanics texts and, most particularly, to the classic of Condon and Shortley (16). The discussion which follows will be slanted toward the transition elements, and specifically toward the first transition series, scandium to zinc.

The quantum mechanical problem begins with the consideration of the energy operator for the system. For an N-electron atom referred to the nucleus as fixed, the energy operator -- called



the Hamiltonian operator,  $H$  -- is equal to the sum of the kinetic energy operators,  $T = \frac{1}{2} \nabla^2$ , and the potential energy operators,  $V$ . That is, for an  $N$ -electron atom with nuclear charge  $Z$  (using atomic units<sup>a</sup>)

$$H = - \frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \frac{Z}{r_i} + \sum_{i>j}^N \frac{1}{r_{ij}} .$$

Obviously the Hamiltonian operator is a function of all the coordinates of all the  $N$  electrons, i.e.  $H = H(1,2,3\dots N)$ , where the numbers refer to electronic coordinates. It follows then, that the wave function,  $\Phi$ , associated with  $H$  through the Schroedinger Equation

$$H\Phi = E\Phi ,$$

is also a function of all coordinates of all electrons, i.e.  $\Phi = \Phi(1,2,3\dots N)$ .

For the simplest case of all, the hydrogen atom,  $N = 1$ ; and the exact solution of the Schroedinger Equation may be obtained in a straightforward manner. For  $N \geq 2$ , immediate difficulty is encountered from the presence of the cross terms

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<sup>a</sup> Atomic units will be used frequently throughout this thesis. Important quantities include: Planck's constant equals  $2\pi$ ; unit energy is twice the ionization potential of the hydrogen atom (27.204 electron volts); unit mass is the electronic mass; unit charge is the electronic charge; and unit distance is the Bohr radius, 0.5292 angstrom units. A complete listing is given in Condon and Shortley (16, Appendix).

in the potential energy,  $\frac{1}{r_{ij}}$ , which couple the motions of the electrons. With helium-like atoms the problem is still tractable by taking the wave function to include the variable  $r_{ij}$ . For all other systems, it has been necessary to resort to simplifications. The technique has been to replace the sum of all inter-electronic interactions by a smoothed potential term  $U(r_i)$ ; that is, the  $i$ -th electron is now taken to move in an averaged potential field of the remaining electrons and independently of them, as regards relative motion. The difference between  $U(r_i)$  and the exact expression is considered later in the theory by the methods of perturbation theory. The effect of this substitution is to make  $H$  become the sum of independent one-electron operators,  $h_i$  and, therefore, to make  $\Phi$  become the product of one-electron wave functions,  $\varphi_i$ . It has been shown by Slater (17) and Fock (18) that the solution of the Schroedinger Equation in this approximation is replaced by the solution of the equations

$$h_i \varphi_i = \epsilon_i \varphi_i \quad (i = 1, 2 \dots N) .$$

$\epsilon_i$  is that part of the total energy of the system which may be associated with the  $i$ -th electron, or, more precisely, with that electron which is described by  $\varphi_i$ . The precise forms to be chosen for  $h_i$  will be discussed later in this thesis.

Without going into further detail at this point, we may state that the solution of these equations yields a set of one-electron wave functions, similar in general to the wave

functions obtained from the solution of the hydrogen atom problem. The spin and angular parts of the total wave functions are identical in both cases, and expressible in analytic form. The radial part, however, must be obtained numerically by the Self-Consistent-Field (SCF) method of Hartree and Fock. (For a recent discussion and listing of atoms treated up to 1946, see Hartree (19).) Each function  $\phi_i$  is characterized by a set of four quantum numbers:  $\pm$ ,  $m_{\pm}$ ,  $m_s$ ,  $n$ .<sup>a</sup> The configuration of a particular atomic state is described by giving the number of electrons having specified  $n$  and  $\pm$  values. Again using  $\text{Fe}^{+2}$  as an example, its configuration is indicated by  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ .

In this case, there are only six electrons available to be distributed among the ten allowed  $3d$  one-electron functions. What this means is that there exist several  $\Phi$ 's, or atomic states corresponding to this configuration. The total number, however, is severely restricted by the Pauli Exclusion Principle, i.e. the anti-symmetry requirement upon  $\Phi$ . Each of these states may be described in terms of the total angular momentum of the whole atom. Letting  $\pm_i$  and  $s_i$  equal the orbital angular momentum (quantum number) and spin-angular momentum, respectively, of the  $i$ -th electron, the two vectors  $L$  and  $S$  are defined as the vector sums of  $\pm_i$  and  $s_i$  respectively. Since the

---

<sup>a</sup>To prevent confusion in the typescript between the numerical  $\underline{1}$  and the alphabetical  $\underline{l}$ , the former will be written  $\underline{1}$  and the latter  $\underline{l}$ , where possibility of confusion may exist.

vector sums over closed shells of electrons vanish, attention may be directed solely to the open 3d shell, for further consideration of the problem.

In the approximation of the Hamiltonian operator so far considered, all these various  $\Phi$ 's, or atomic states, have equal energies. This degeneracy, however, is lifted when the perturbation of the neglected specific  $\frac{1}{r_{ij}}$  interactions is included. This perturbation is computed for each state. As a general rule (Hund's rule) it is found that, of all the allowed states, those of the largest  $S$  are lowest in energy; of all those, the one of largest  $L$  is lowest. Even at this point, there remains degeneracy in the total angular momentum,  $J = L + S$ , arising from the possibility of several relative orientations of  $L$  with respect to  $S$ . This last degeneracy is lifted when account is taken of the coupling between the orbital and spin angular momenta (the spin-orbit coupling).

Summarizing; the state of an atom may be described in terms of the total energy, the total spin momentum, the total orbital momentum and the total atomic momentum. These quantities are expressed explicitly in terms of the individual energies and momenta of the one-electron wave functions, taken in antisymmetrized product form, corresponding to the original spherically symmetric atomic problem.

## 2. Introduction of crystalline or molecular field effects

Upon introducing the free ion into a molecule or crystal several things occur. First, the electrons of the ion exchange with the electrons in the rest of the molecule or crystal. This exchange is considered in the valence-theoretical approaches; in crystalline field theory, this effect is considered small and ignored. Second, there is introduced into the Hamiltonian operator for the isolated atom additional kinetic and potential energy terms which transform it into the Hamiltonian operator for the whole system. If attention is directed only to the metal atom and electronic exchange is ignored, then it is sufficient to ignore also the added kinetic energy terms and to consider exclusively the new potential energy effects.

In all cases of immediate physical interest, the environment of the metal atom is, essentially, highly symmetric, it is convenient to discuss ideal symmetries first and to treat small departures later. The symmetries considered are octahedral, tetrahedral and hexagonal. In the atom, it was found that the condition of spherical symmetry was sufficient to determine all but the radial part of the wave functions. In the lower symmetries of the new environment, it is found that the symmetry is still sufficiently high to place important restrictions upon the one-electron wave functions. The problem, first undertaken by Bethe (2), is to itemize those restrictions and to approximate the new wave functions.

The argument developed by Bethe follows the theory of atomic structure. The basis for further development is the set of one-electron wave functions, derived or assumed to have been derived, for the spherical atom. Again all the states arising from the ground configuration are degenerate. But now, in addition to the perturbations of the specific  $\frac{1}{r_{ij}}$  interactions and the spin-orbit coupling, there must be included the perturbation of the potential terms arising from the new environment. This last perturbation may be less than, greater than or intermediate between, the first two; each such case must be treated separately. In the transition-metal complexes, it appears that spin-orbit coupling effects are least important and that the crystal or molecular potential terms are either greater than or comparable to the specific  $\frac{1}{r_{ij}}$  terms. In either event, the degeneracy of the wave functions within a particular  $n, l$  set may be removed by the nonspherical environment.

The most important result of this fact is that the atomic one-electron wave functions,  $\phi_i$ , may no longer be even approximate eigenfunctions of the total Hamiltonian. Rather, when the perturbation treatment is carried out, it is found instead that the proper one-electron wave functions to be used as the basis for further study are certain linear combinations of the original atomic wave functions, the forms of which are rigorously prescribed by the symmetry of the environment of the metal atom. Both for clarity on this point and for later

reference, the 3d, 4s and 4p functions are listed in Table 1 in the forms they take in the spherically symmetric atom and in a cubic (octahedral or tetrahedral) environment. (This latter form is convenient in that the wave functions are all real; they are usually taken in this form even when symmetry does not require it.)

From an examination of these new wave functions, it is found that they are such that the orbital angular momenta of the electrons they describe are exactly zero. In other words, the cubic field of the molecule or crystal has forced the electrons of the atom into a new set of wave functions, such that their orbital angular momentum is "quenched". On the other hand, when the spin-orbit interaction perturbation is also included, a small amount of orbital moment is reintroduced.

In the cubic field case, the original ten-fold degenerate (including spin degeneracy) set of 3d functions is split into one four-fold and one six-fold degenerate set  $e_g$  and  $f_{2g}$  respectively, in Mulliken's notation.<sup>a,b</sup> Returning to the  $Fe^{+2}$  example, the six electrons in the 3d shell again may be distributed among the ten wave functions; in this instance the

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<sup>a</sup> The  $e_g$  and  $f_{2g}$  parts of the symbols refer to the irreducible representations of the group  $O_h$  to which the two kinds of d functions belong. The group theoretical aspects of this classification will be touched upon in Chapter III; in practice the symbols  $e_g$  and  $f_{2g}$  serve mostly as labels. In the crystal field literature, Bethe's conventions are usually followed. He defined  $d_y \equiv e_g$  and  $d_z \equiv f_{2g}$ .

<sup>b</sup> The space functions  $d_{z^2}$  and  $d_{x^2-y^2}$  are contained in  $e_g$ ;  $d_{xz}$ ,  $d_{xy}$  and  $d_{yz}$  are contained in  $f_{2g}$ .

Table 1. Comparison of 3d, 4s and 4p wave functions for atoms and for cubic molecules and crystals<sup>a</sup>

Type	Free atom case		Cubic case	
	Abbreviation <sup>b</sup>	Analytical form <sup>c</sup>	Abbreviation <sup>d</sup>	Analytical form
3d	3d <sub>0</sub>	$R_{3d}(3\cos^2\theta - 1)$	3d <sub>z<sup>2</sup></sub>	3d <sub>0</sub>
	3d <sub>+1</sub>	$R_{3d} \sin 2\theta e^{+im\phi}$	3d <sub>xz</sub>	$2^{-1/2}(3d_{+1} + 3d_{-1})$
	3d <sub>-1</sub>	$R_{3d} \sin 2\theta e^{-im\phi}$	3d <sub>yz</sub>	$-i2^{-1/2}(3d_{+1} - 3d_{-1})$
	3d <sub>+2</sub>	$R_{3d} \sin^2\theta e^{+2im\phi}$	3d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	$2^{-1/2}(3d_{+2} + 3d_{-2})$
	3d <sub>-2</sub>	$R_{3d} \sin^2\theta e^{-2im\phi}$	3d <sub>xy</sub>	$-i2^{-1/2}(3d_{+2} - 3d_{-2})$
4s	4s	R <sub>4s</sub>	4s	R <sub>4s</sub>
4p	4p <sub>0</sub>	$R_{4p} \cos \theta$	4p <sub>z</sub>	4p <sub>0</sub>
	4p <sub>+1</sub>	$R_{4p} \sin \theta e^{+im\phi}$	4p <sub>x</sub>	$2^{-1/2}(4p_{+1} + 4p_{-1})$
	4p <sub>-1</sub>	$R_{4p} \sin \theta e^{-im\phi}$	4p <sub>y</sub>	$-i2^{-1/2}(4p_{+1} - 4p_{-1})$

<sup>a</sup>Taken from Eyring, Walter and Kimball (20, pp.88,89).

<sup>b</sup>The subscripts indicate the value of  $m_{\pm}$  associated with the particular wave function.

<sup>c</sup> $R_{n\pm}$  indicates the radial part of the atomic wave function, given in either numerical or analytic form.

<sup>d</sup>The subscripts here indicate the result of multiplying the angular parts of the cubic analytic forms by  $r^2$  and transforming from spherical polar to rectangular coordinates. The notation is that of Eyring, Walter and Kimball.



Pauli Principle is less restrictive, and more atomic (in the crystal field sense) states are allowed.

The first quantitative effort at calculating the effects of the crystal field upon the atom was made by Penney and Schlapp (21). They expanded the electric potential of the environment of the atom in a general Taylor's series, the coefficients in which were used as adjustable parameters. Although the series is infinite, when the integrals of perturbation theory are computed, all terms beyond the fourth vanished identically. From these calculations, Penney and Schlapp were able to interpret the magnetic properties of several rare earth and transition-metal hydrated ions. One major quantity they computed in terms of one parameter is the separation between the  $d_{eg}$  and the  $df_{2g}$  orbitals. This separation they arbitrarily set equal to  $10Dq$ ,  $Dq$  being the adjustable parameter. It was established by them that  $d_{eg}$  is higher in energy than  $df_{2g}$ , for octahedral configurations of negative groups about the metal atom, and the reverse for tetrahedral configurations. See Figure 1. Further calculations based on the Penney and Schlapp model were made by Howard (22) for ferrocyanide ion, by Finkelstein and Van Vleck (23) on chrome alum, and by Kotani (24) for all octahedral cyanide complexes. In all cases, agreement with experiment has been remarkably good.

These successes led Hartmann and coworkers (25,26,27) to try to calculate the splitting of the d functions without

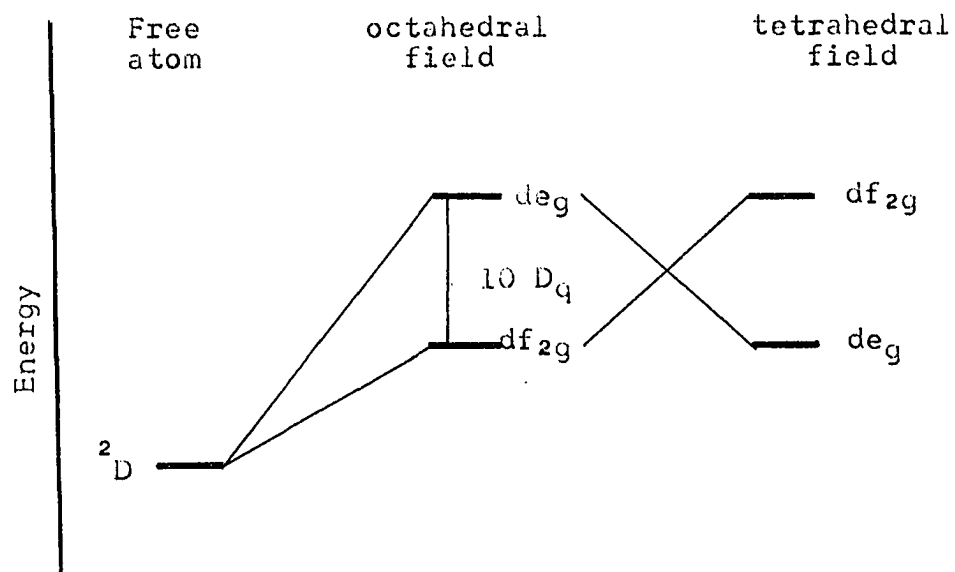


Figure 1. Cubic field splitting of the ground state energy levels of an atom whose configuration is a single d-electron.

including parameters. They selected the complex ions  $V(H_2O)_6^{+3}$  and  $Ti(H_2O)_6^{+3}$ , and chose as a model the metallic ion surrounded octahedrally by six point dipoles whose moment equalled the experimentally determined dipole moment of the water molecule. The results were qualitatively in agreement with earlier work, but the separations between the 3d levels were calculated to be approximately one-half the values observed from spectra.

In a similar attempt, Kleiner (28) tried to compute the separation in  $Cr(H_2O)_6^{+3}$ , except that he chose to use a model of the water molecule more realistic than a point dipole. He assumed electrons in the water molecule not to be point charges, but to move in reasonable atomic-like orbitals, and calculated the resulting 3d energy levels. He found an even smaller splitting than Hartmann; but, more significantly, the  $d_{eg}$  level was obtained not higher, but lower than the  $df_{2g}$  level.

This sort of disquieting result led Orgel (29,30) to conclude that quantitative calculations based upon the crystal field model were futile. He decided, rather, that effort should be concentrated in making use of the value of the arbitrary parameters of the Penney and Schlapp theory to interpret spectra and to draw inferences about the nature of the various ligand groups. The same computational techniques have been used in a much refined manner by Tanabe and Sugano (31) and were published in two papers which actually predate the recent one of Orgel (32). Here the cubic field perturbations of each of the low states of the transition-metal ions are computed as

functions of the parameter  $Dq$ . A value of  $Dq$  is then determined which gives a reasonable interpretation of the spectra of the various transition-metal complexes. The general conclusions from Orgel's work are: (i) that  $10 Dq$  is about 1.2 ev for hydrated divalent ions and about 2.5 ev for hydrated trivalent ions; (ii) the common ligands complexing with a given metal ion produce  $Dq$  values which increase in the general order

$I^- < Br^- < Cl^- < F^- < H_2O < \text{oxalate} < \text{pyridine}$

$< NH_3 < \text{ethylene diamine} < NO_2^- < CN^-$

This ordering deserves some comment. The sequence follows what chemical experience indicates about increasing covalency in bonding, except for the reversal in the halide series. Here the implication is that  $I^-$  is more ionic than  $F^-$ , etc. Orgel offers no explanation for this anomaly.<sup>a</sup>

Orgel has given a graphic illustration of how crystalline field theory explains the occurrence of two possible spin moments for complexes of the same transition-metal ion but with different ligands. (29) In Figure 2 there are indicated the energies for two states of a hypothetical metal ion,  $^3X$  and  $^1Y$ , and the levels into which they might be split by a cubic field, plotted as functions of the parameter  $Dq$ . To the left of the point a, the triplet level is the lower and the complex is

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<sup>a</sup>Williams (34) has very recently discussed this ordering; it will be considered again later in the thesis.

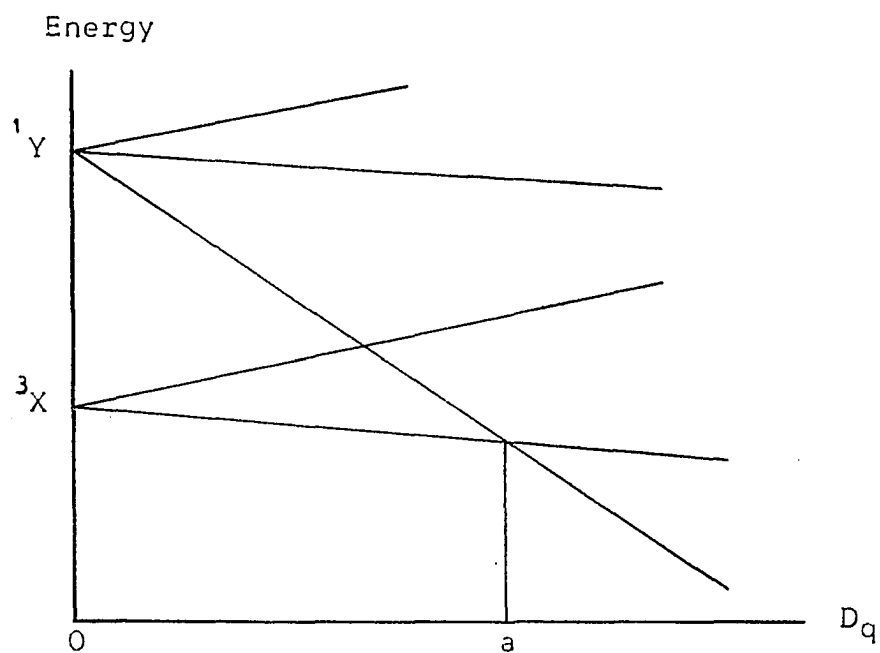


Figure 2. Crystalline field explanation for the existence of two spin moments in different complexes of a hypothetical transition-metal ion.

paramagnetic ("essentially ionic"); to the right, the singlet is the lower, and the complex is diamagnetic ("essentially covalent"). In this regard,  $Dq$  is implied to be a rough measure of the "covalent-ness" of the metal to ligand bonding. From this, Orgel concludes that there is no definite discrete distinction between ionic and covalent bonds, rather, that the transformation from one to the other is continuous. However, there may be a rapid variation in the region of the critical value (point a of Figure 2).

Mention should also be made of the experimental and theoretical work done in J. Bjerrum's group in Denmark (35-40). They have, in essence, extended Hartmann's work to other transition-metal complex ions, but by computing  $Dq$  over ranges of metal-ligand distances and assumed dipole moments for the various ligands. Their success in interpreting spectra on this basis led Ballhausen (36,38) to conclude that crystalline field theory is adequate to account for most of the experimental material, and that the overlap and exchange effects cannot have much importance.

Despite the seeming successes of semi-empirical crystalline field theory in the interpretation of the spectra of transition-metal spectra, doubts were being raised in another quarter, from measurements of properties other than the energy levels. It will be recalled that in the earlier discussion of the crystalline field theory it was found that, although ideal cubic or hexagonal fields removed the orbital angular momentum,

later inclusion of the spin-orbit coupling reintroduced a small amount of orbital moment. An additional amount is allowed if the symmetry of the environment about the metal ion is distorted, as, say, by the Jahn-Teller effect (41).

Departures from "spin-only" moments can be detected and measured by paramagnetic resonance.<sup>a</sup> For many cases it is possible to compute the unquenched orbital contributions from a knowledge of the  $d_{eg} - d_{f_{2g}}$  separation (obtainable from the analyses of optical spectra, as described above) and the constant characteristic of the spin-orbit coupling (obtained from the atomic spectra). From the recent work of the Oxford group<sup>b</sup>, it appeared that significant discrepancies are present.

Concurrently, studies of the hyperfine structure of the paramagnetic resonance spectra of paramagnetic second and third series transition-metal complexes such as  $\text{IrBr}_6^{-2}$  revealed that the unpaired electron is distributed such that it interacts to some extent with the nuclei of the ligands. This fact is in conflict with one of the fundamental assumptions of the whole crystalline field approach; it caused Owen and Stevens (43) to reconsider the molecular orbital theories as they applied to transition-metal complexes. Within the formalism of the molecular orbital theory, Stevens (44) has shown a possible way to resolve the difficulties of interpreting, on

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<sup>a</sup> See the reviews by Bleaney and Stevens (10).

<sup>b</sup> See for example Griffiths, Owen and Ward (42).

an absolute theoretical basis, optical and magnetic data. Since 1953, the ideas of Stevens have been extended by many others to different complexes.

Whereas the work described in this thesis involves quantum mechanical calculations based upon the molecular orbital method, a logical development of the application of molecular orbital theory to transition metal complexes is given in a separate chapter. In the course of the development, interrelations with the crystalline field theory are indicated, and further references to the literature are given.



### III. THE MOLECULAR ORBITAL APPROACH

#### A. General Considerations

The molecular orbital (MO) approach to the study of the electronic structure of transition-metal complexes is being given special attention in a separate chapter for two reasons: (a) The MO method has been selected as the basis for the further research to be reported in this thesis. A thorough analysis of the fundamentals of its application is appropriate, since current chemical thinking is so closely geared to the hybrid orbital approach. (b) Although it is true that, at the present date, most of the general background describing the MO approach to these compounds has been given in the literature,<sup>a</sup> only portions of the whole picture have been treated in any one article. It is considered desirable to give single integrated account at this point of the discussion.

The general philosophy of the MO method has, of course, been discussed at great length by numerous authors (see, for example, Coulson (49)) and need not be gone into here. The important point is that, just as in the theory of atomic structure (outlined in Chapter II), the basic MO theory of molecules treats electrons as moving in the force field of the whole molecule, without regard to particular notions of chemical bonding. Thus there is a formal equivalence between the

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<sup>a</sup> See the following: Van Vleck (5), Van Vleck and Sherman (45), Owen (46,47), Griffith (48), Williams (34) and Orgel (33).

quantum mechanical description of the isolated atom and of the isolated molecule; naturally, the molecule, presenting a many-centered problem, is a more difficult system to treat. In fact, even with present computational equipment, it is not possible to solve the Schroedinger Equation directly for the eigenfunctions and eigenvalues corresponding to any molecular problem of chemical interest, unless extreme modifications are made in the Hamiltonian operator for the system. Thus there arises the immediate necessity for approximations. In the case of both MO theory and valence bond (VB) theory, the usual method is to assume a reasonable form for the wave function and compute energies from them by substitution into the energy equation.

$$E = \frac{\int \bar{\Phi} H \Phi dv}{\int \bar{\Phi} \Phi dv},$$

which is obtained from the Schroedinger Equation.

In MO calculations it is customary to expand the one-electron MO's in terms of the sets of atomic functions or atomic orbitals (AO's) belonging to the individual atoms which comprise the molecule. This approximation of Linear Combinations of Atomic Orbitals for Molecular Orbitals (LCAO MO) is exact, in general, if an infinite set is assumed. However, the expansion is usually limited to the inner shell and valence shell AO's of the constituent atoms. The coefficients in the expansions for the MO's are obtained according to the Variation Principle by minimizing the one-electron orbital energies

( $\mathcal{E}$ ) and solving the resulting secular equations.

Again, as with the atomic problem, it may happen that the inherent symmetry of the molecule may place important restrictions upon the forms of the MO's, which restrictions in the LCAO approximation, amount to specifying exactly certain of the coefficients in the expansions and reducing the complexity of the secular equation.

The translation of symmetry requirements into specifications upon the MO's is given by the methods of group theory. See Eyring, Walter and Kimball (20) for a simplified treatment and for references to more comprehensive works.

#### B. Molecular Orbitals for Octahedral Complexes

Attention will be directed mainly toward the octahedral complexes of the first transition-metal series with ligands which are atoms or ions of first-row elements. It will be assumed that the complexes exhibit full octahedral symmetry; departures from ideality will be considered later. For convenience, the AO's of all complexes will be oriented with respect to the same Cartesian coordinate system. The metal atom is placed at the origin, and the six attached atoms are placed at equal distances along the axes. The ligand atoms are numbered in the following order:  $+x = 1$ ,  $+y = 2$ ,  $+z = 3$ ,  $-x = 4$ ,  $-y = 5$ ,  $-z = 6$ .

In forming the LCAO MO's from the valence shell AO's, it is very desirable to take advantage of the symmetry

restrictions at the start. Accordingly, the orbitals of the metal atom and of the six ligand atoms are collected into certain combinations of symmetrically equivalent AO's, which transform according to the irreducible representations of the group  $O_h$ . That is, each combination, when transformed by some operation of the point group, behaves in a manner specified by the point group character table, which is unique for each group.

These combinations of AO's, for convenience called symmetry orbitals (SO's), may be constructed either by a process of inspection or by group theoretical methods. Functions belonging to the "a" irreducible representations are non-degenerate; to the "e", doubly degenerate; to the "f", triply degenerate.<sup>a</sup> After the functions have been derived, the symbols for the irreducible representations serve merely as

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<sup>a</sup> Just as each individual one-electron MO must possess certain transformation properties within the octahedral point group, so does the total N-electron antisymmetrized wave function  $\Phi$ , which specifies a particular molecular state of a given configuration. These symmetry properties are also obtained either by inspection or by group theoretical methods. To differentiate between symmetries of MO's and of molecular states, the convention of Mulliken (50) will be followed: the irreducible representations of MO's will be given with small letters, e.g.,  $e_g$ ; those of molecular states by capital letters, e.g.,  $E_g$ . Spin multiplicity is indicated by a left superscript, e.g.,  $^3E_g$ . Thus the irreducible representation has a formal equivalence to the orbital angular momentum of an isolated atom. Indeed, in a group theoretical treatment of atomic structure, the two are identical; see, for example, Wigner (51).

labels. Some details about the application of group theory and references are given in Appendix A.

The valence shell SO's for the simple octahedral complex are given in Table 2, in terms of the AO's appropriate for the symmetry of the molecule and given in Table 1.<sup>a</sup>

If the MO's were expressed in pure LCAO form, each MO would then depend upon 33 coefficients arising from the valence shell orbitals alone; the corresponding secular equation would be a 33x33 determinant, with each element, in general, non-zero. Direct solution of such a determinant is impractical. If, on the other hand, the AO's are first redistributed into SO's as above described, and the integrals expressed in terms of them, then large numbers of elements in the secular equation (namely, those which are cross terms between SO's from different symmetry species)<sup>b</sup> become identically zero. After appropriately arranging rows and columns, it becomes obvious that the original 33x33 determinant can be factored into products of determinants of much smaller order. Each factor can be identified with a particular representation or with a particular subspecies of one. (In  $f_{1u}$ , for example,  $4p_x$ ,  $4p_y$  and  $4p_z$  each define a subspecies.) The solutions of each one of these determinants results in corresponding MO  $\phi_i$  of the

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<sup>a</sup>The  $\sigma$ -type SO's were first published by Van Vleck (5). The  $\pi$ -type bonding SO's are given by Stevens (44), among several others.

<sup>b</sup>For an excellent qualitative discussion of the manner in which symmetry considerations are applied to the solution of molecular problems, see Moffitt (52).

Table 2. Valence shell symmetry orbitals for octahedral complexes.<sup>a</sup>

Irre- ducible represent- ation	Metal <u>SO's</u>	<u>Ligand</u>	
		$\sigma$ -type <u>SO's</u>	$\pi$ -type <u>SO's</u>
$a_{1g}$	$\chi_1=4s$	$\sigma_1 = \sqrt{1/6}(\psi_1+\psi_2+\psi_3+\psi_4+\psi_5+\psi_6)$	none
$f_{1u}$	$\chi_2=4p_x$	$\sigma_2 = \sqrt{1/2}(\psi_1-\psi_4)$	$\pi_2=1/2(x_2+x_3+x_5+x_6)$
	$\chi_3=4p_y$	$\sigma_3=\sqrt{1/2}(\psi_2-\psi_5)$	$\pi_3=1/2(y_1+y_3+y_4+y_6)$
	$\chi_4=4p_z$	$\sigma_4 = \sqrt{1/2}(\psi_3-\psi_6)$	$\pi_4=1/2(z_1+z_2+z_4+z_5)$
$e_g$	$\chi_5=d_{z^2}$	$\sigma_5 = \sqrt{1/12}(2\psi_3+2\psi_6-\psi_2-\psi_4-\psi_5)$	none
	$\chi_6=d_{x^2-y^2}$	$\sigma_6 = 1/2(\psi_1+\psi_4-\psi_2-\psi_5)$	
$f_{2g}$	$\chi_7=d_{xy}$	none	$\pi_7=1/2(y_1-y_4+x_2-x_5)$
	$\chi_8=d_{xz}$		$\pi_8=1/2(z_1-z_4+x_3-x_6)$
	$\chi_9=d_{yz}$		$\pi_9=1/2(z_2-z_5+y_3-y_6)$
$f_{1g}$	none	none	$\pi_{10}=1/2(x_2+x_3-x_5-x_6)$
			$\pi_{11}=1/2(y_1+y_3-y_4-y_6)$
			$\pi_{12}=1/2(z_1+z_2-z_4-z_5)$
$f_{2u}$			$\pi_{13}=1/2(y_1+y_4-x_2-x_5)$
			$\pi_{14}=1/2(z_1+z_4-x_3-x_6)$
			$\pi_{15}=1/2(z_2+z_5-y_3-y_6)$

<sup>a</sup>Explanation of terminology: The  $\psi$  functions can be any linear combination (hybrid) of ligand s and p $\sigma$  orbitals. The orbitals in the  $\pi$ -bond column are abbreviated  $x = p_x$ ,  $y = p_y$ ,  $z = p_z$ . All orbitals, both metal and ligand, are oriented with respect to the same coordinate system. The metal atom is placed at the origin; the ligand atoms are placed along the axes and are numbered in the following order:  $+x = 1$ ,  $+y = 2$ ,  $+z = 3$ ,  $-x = 4$ ,  $-y = 5$ ,  $-z = 6$ .

molecule. In general  $\varphi_i$  has the form

$$\varphi_i = a_i \chi_i + b_i \sigma_i + c_i \pi_i ,$$

where the  $\chi_i$ ,  $\sigma_i$ , and  $\pi_i$  are defined in Table 2.

For aid in visualizing the special character of the MO's and their transformation properties, qualitative drawings of the MO's are given in Figure 3. Only one MO of a given symmetry species is indicated, since the others may be obtained by a simple interchange of the coordinate axes. The exception is the  $e_g$  set, to which belong  $d_{z^2}$  and  $d_{x^2-y^2}$ . For this particular choice of representing the d-orbitals, these two degenerate functions do not at all look alike, nor do the SO's of the ligand with which they combine. The MO for  $d_{x^2-y^2}$  is given in Figure 3;  $d_{z^2}$  is given by itself.

From an inspection of Table 2 or Figure 3 it is observed that the  $f_{1g}$  and  $f_{2u}$  MO's are identically equal to the ligand SO's, since there are no metal orbitals with which to combine. These two  $\pi$ -type orbitals, therefore, are non-bonding (N) and are completely specified by the symmetry of the molecule. The analytic forms for the remaining MO's have been given, at various times, by several authors.<sup>a</sup> Upon determining the coefficients by the variational method, one energy level is obtained per coefficient, so to speak. In the remainder of this

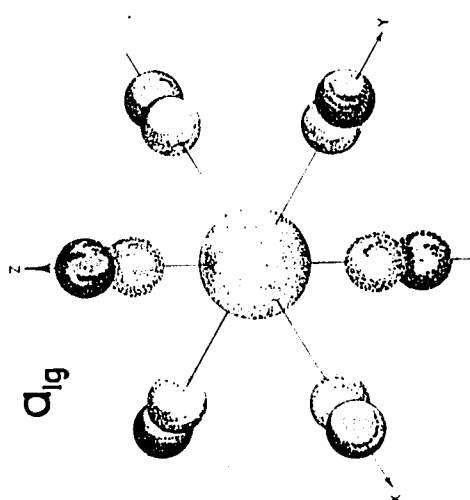
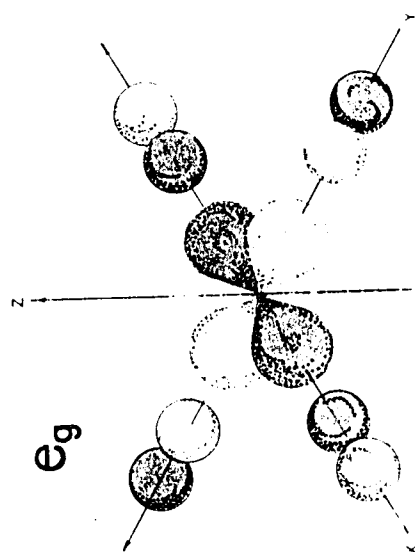
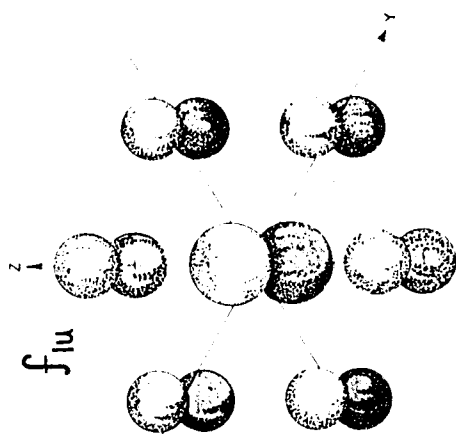
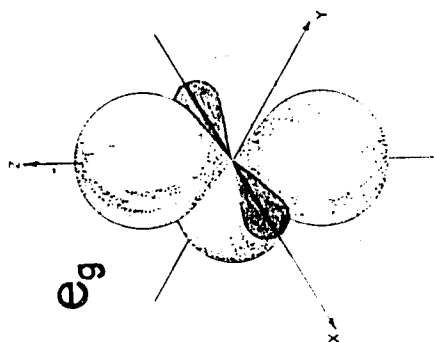
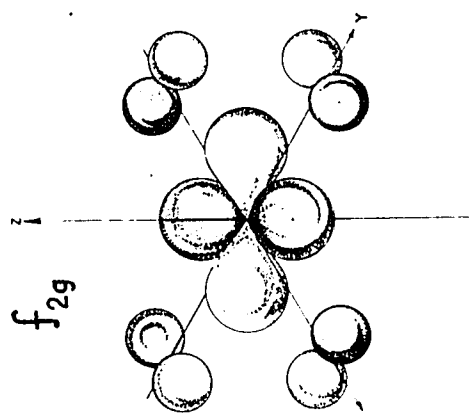
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<sup>a</sup>See references given in footnote, p.27.

Figure 3. Pictorial representation of the molecular orbitals.

In the drawings, shading has been used to differentiate between positive and negative regions of the functions. For the degenerate  $f_{1u}$  and  $f_{2g}$  MO's only one from each degenerate set is pictured. The others are obtained by a simple rotation of the coordinate system. On the other hand, only the  $e_g$  MO derived from the  $3d_{x^2-y^2}$  AO of the metal is shown. The general features of the  $3d_{z^2}$  AO are also indicated, however.





chapter, we shall discuss, in a qualitative fashion, the nature of these energy levels and how they are influenced by changes in the type of ligand and metal atom.

### C. Qualitative Analysis of the Molecular Orbital Energy Levels

#### 1. The $\sigma$ -bond system

First, let us examine a hypothetical complex ion wherein there is no possibility of  $\pi$ -bonding. The MO's reduce to the form  $\phi_i = a_i\chi_i + b_i\sigma_i$ ,  $i = 1, 2, \dots, 6$ ;  $\phi_7$ ,  $\phi_8$  and  $\phi_9$  equal  $d_{xz}$ ,  $d_{yz}$  and  $d_{zx}$ , respectively, and also are nonbonding. Assume that the form of the  $\psi_i$ 's which enter the  $\sigma_i$  is already specified, and that the other hybrid ligand AO orthogonal to (one for each ligand atom) can also be considered as nonbonding. Consider a hypothetical complex in which the bonds are roughly non-polar, i.e. in a bonding MO an electron has equal probability of being either at the metal or at some part of the ligand. Another way of putting this is that, under these circumstances, the metal and ligand are approximately equal in electronegativity. Then it follows that  $a_i \approx b_i$ . The bonding MO's (corresponding to the lower roots of the secular equations) will then be considerably lower in energy than the atomic orbitals of either the metal or the ligand from which the MO was formed. The anti-bonding MO's (corresponding to the higher roots of the secular equations) will be, on the other hand, of considerably higher energy. This case

is illustrated in Figure 4 (a). Consider the effect of causing the ligands to become more electronegative, that is, the energy of the ligand AO's to become more negative with respect to the metal orbitals. It is intuitively obvious, and borne out by calculation, that the bonding electrons shift out more "into" the region of ligands; thus the bonds become more polar. Conversely, anti-bonding electrons will concentrate more on the metal atom. The electronic structure is described by the same sort of functions, but with altered coefficients; here  $b_i \gg a_i$  in the bonding MO's. The energy level scheme for this case is illustrated in Figure 4 (b).

The electrons of the complex are assigned to the derived MO's by the familiar "Aufbau" principle of atomic structure. In a typical complex, all non-bonding MO's, as well as the six bonding MO's (the  $d^2 sp^3$  combination) will be occupied by electron pairs. The remaining electrons (always equal to the number of valence shell electrons originally present in the transition-metal ion) will be distributed as follows: The first three will go unpaired into the triply degenerate  $f_{2g}$  level (Hund's rule of maximum multiplicity on the molecular scale). If there are more electrons to be accommodated, they will either pair up with those already in the  $f_{2g}$  MO's or will go unpaired into the anti-bonding  $2e_g$  MO's, maintaining maximum multiplicity. The choice -- and this is the crux of the whole problem -- depends upon the energy separation between the  $f_{2g}$  and the  $2e_g$  levels in comparison to the energy of inverting

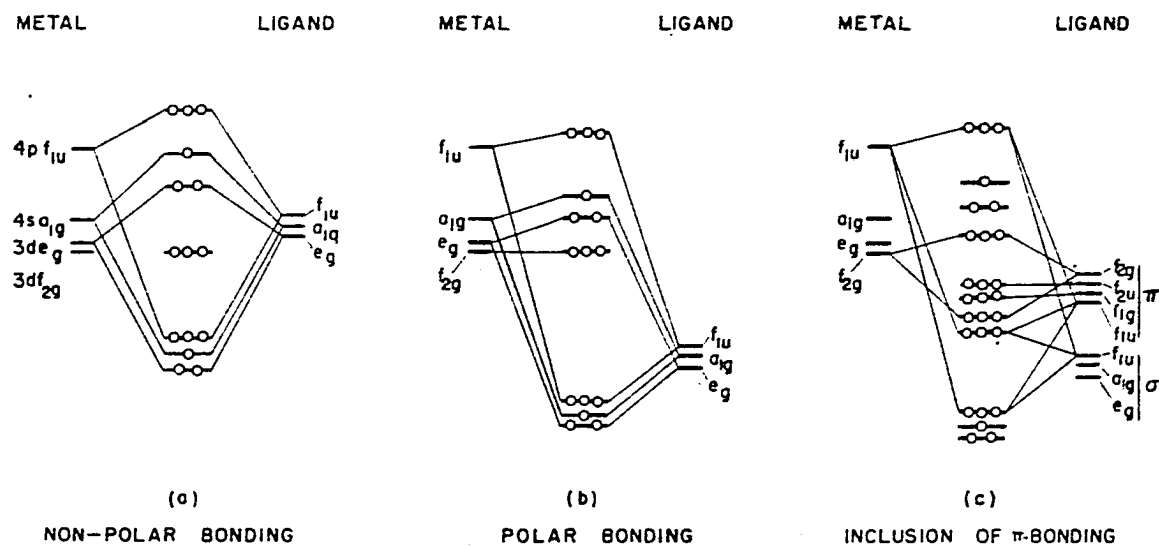


Figure 4. Scheme of molecular orbital energy levels

the spin of an electron in the field of the others. For the transition elements, this latter energy is of the order of 2 to 3 eV (33).

## 2. Inclusion of $\pi$ -bonding

When the possibility of  $\pi$ -bonding is also considered, the system of energy levels becomes somewhat more complicated. From Table 2, it is seen that one new  $f_{1u}$  level will be formed; furthermore, the  $f_{2g}$  level, formerly non-bonding, will interact with  $\pi$ -type orbitals of the ligands, giving rise to two triply degenerate levels, one bonding and the other anti-bonding. The nature of these additional interactions is indicated in Figure 4 (c), for a hypothetical complex ion of intermediate electronegativity. It is seen that the inclusion of  $\pi$ -bonding admits the possibility of additional stabilization of the molecule and, at the same time, tends to decrease the separation between the anti-bonding  $e_g$  and  $f_{2g}$  levels.

Most six-coordinated complexes of the transition-metals are closely octahedral insofar as the  $\sigma$ -bonding system is concerned. That is to say, the metal-ligand bonds lie essentially along the coordinate axes specifying the configuration, regardless of the nature of the ligand  $\sigma$ -orbitals.

On the other hand, the nature of the  $\pi$ -type interactions is various. In the simplest of complexes, such as  $\text{FeF}_6^{-3}$ , the  $\pi$ -interactions are precisely as described in the preceding section; that is, they arise from the lone-pair electrons in

the pure  $p\pi$ -orbitals of the ligands. In another comparatively simple case,  $\text{Fe}(\text{NH}_3)_6^{+3}$  for example, the  $p\pi$ -orbitals of each nitrogen atom are already involved in bonding to the hydrogen atoms. Nevertheless, further interaction with the metal atom must take place in the complex; this hyperconjugation is probably of second-order importance, and the usual tendency is to ignore it.

The most common transition-metal complex of all, the hydrated ion, deserves separate comment. This case combines features of the two already discussed, in that  $\pi$ -type interactions may arise from both lone-pair electron and hyperconjugative effects. Further specification of the bonding is complicated by lack of precise knowledge of the relative orientation of the water molecule with respect to the remainder of the complex ion. Crystal field calculations have implicitly assumed that the point charge-dipole interaction requires the metal atom to be coplanar with the water molecule. If on the other hand, there actually is appreciable "chemical" bonding present, it is not altogether certain whether the water molecule might not be tipped in one direction so as to present a more favorable bonding orbital to the metal. Even in a purely electrostatic model, it is possible that a small deformation from coplanarity might stabilize the system.<sup>a</sup>

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<sup>a</sup> It is relevant to point out that there exists some meagre evidence that the water molecules are tipped, in some cases at least such as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (53). Also, a comparison between known crystal structures of hexammine and iso-electronic

The largest number of six-coordinated complex ions of present chemical interest are much more complicated than any of the types mentioned above. Only a few, such as  $\text{CN}^-$ ,  $\text{CNO}^-$  or  $\text{CNS}^-$ , present full octahedral symmetry. The remainder of this group are the chelate complexes, each of which is a problem unto itself. The  $\pi$ -type interactions may be all combinations of lone-pair electrons, hyperconjugation and existing  $\pi$ -MO systems in the chelating molecules. This last possibility has many ramifications, since it is thought that the metal atom may become a part of an extensive conjugated system throughout the whole complex ion. This interesting subject will not be pursued further in this thesis.

#### D. Further Specification of the Molecular Electronic System

##### 1. Formation of molecular electronic states

So far in this chapter, there has not been mentioned any reference to the quantum mechanical techniques of solving the molecular problem presented by the transition-metal complexes within the framework of MO theory, beyond the specification of

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(Footnote a, p.39 continued). hexaaquo complexes reveals that the former seem largely to be highly symmetric, whereas the latter are deformed to much lower crystal symmetries. In such a comparably symmetrical state as the coplanar arrangement, the water complexes probably would not be so different in crystal structure. However, this is not a strong argument. Some structural work in this regard would be quite beneficial to further theoretical considerations of the hydrated ions.

the general forms of the MO's themselves. The actual computational considerations will be left to succeeding chapters. What will be treated here is the manner of attack, in comparison to that used in the theory of atomic structure.

Actually, the atomic and the molecular problems proceed along very similar lines. The Hamiltonian operators are identical, except for the inclusion of nuclear repulsion terms and attraction terms between the electrons and the additional nuclei. The N-electron operator is recast into a sum of one-electron operators, in an analogous fashion; thus the one-electron MO's of Section B of this chapter become appropriate. There is thus a one-to-one correspondence between the AO's of the metal atom and the MO's of the molecule.

The one-electron Schroedinger Equations are solved for the MO's (using the Variation Principle where necessary) and for their energies. These energies are the energies indicated schematically in Figure 4.

The electrons of the complex ion are next assigned to the derived MO's; this assignment defines the molecular electronic configuration. Using a paramagnetic complex of  $\text{Fe}^{+2}$  as an example, and neglecting the inner shells of both the metal and the ligands, the electronic configuration is indicated by<sup>a</sup>

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<sup>a</sup> The MO's of the same symmetry are numbered in order of increasing energy, this particular ordering being taken from Figure 4 (c). Unless it is specifically noted to the contrary, numbering will begin with the bonding orbitals under consideration.



$1e_g)^4 1a_{1g})^2 1f_{1u})^6 2f_{1u})^6 1f_{2g})^6 1f_{1g})^6 1f_{2u})^6 2f_{2g})^4 2e_g)^2$ : Now both the  $2f_{2g}$  and the  $2e_g$  MO's are incompletely filled; therefore, there exist several ways in which to assign electrons among those ten (including spin) electronic wave functions, limited only by the Pauli Principle. The total degeneracy of the  $2f_{2g})^4 2e_g)^2$  set is equal to that of the  $3d^6$  set, except that it is divided up differently. The symmetries and spin degeneracies of the allowed distributions of  $n$  ( $n = 1$  to  $9$ ) electrons among all possible combinations of the  $2f_{2g}$  and  $2e_g$  MO's have been summarized by Jørgensen (39).<sup>a</sup> The whole listing will not be given here; however, the total electronic symmetry and spin degeneracy for the ground states of the transition elements in octahedral symmetry are given in Table 3. There are two relevant comments at this point.

## 2. The Jahn-Teller effect

First, there are relatively few totally symmetric( $A_{1g}$ ) ground states among the group listed in Table 3. The others are "orbitally degenerate." A general theorem by Jahn and Teller (41) states that such an orbitally degenerate system will spontaneously distort to a symmetry sufficiently lower to remove the orbital degeneracy. On this basis it is expected that all complexes of transition elements which are listed as orbitally degenerate in Table 3 will have lower than octahedral symmetry, i.e., tetragonal, trigonal or orthorhombic. The

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<sup>a</sup> See footnote a, p.30.

nature of this distortion has been discussed by Van Vleck (54). There seems to be no conflict with this conclusion, wherever good experimental measurements have been made.

### 3. Configuration interaction

Second, in addition to the molecular states arising from the lowest configuration, there are generally many additional states arising from configurations only slightly higher in energy. If it should happen that there arise two or more states of the same multiplicity among these lower-lying configurations, the lowest energy state of the molecule must be described as a combination of all the states of that particular symmetry and multiplicity. If there is any interaction between configurations in this manner, then it should be observed that it is no longer proper to say that there necessarily is an integral number of electrons in the  $2e_g$  level, for example, or in the  $2f_{2g}$ . This configuration interaction is not peculiar to MO theory, but arises in an identical fashion in the theory of atomic structure, as well as in the most refined crystalline field calculations (31). Configuration interaction is an appreciable complication in the precise evaluation of molecular properties from purely theoretical considerations; furthermore, it appears to be quite necessary in many cases.<sup>a</sup> One important exception, however, is the  $\text{Fe}^{+3}$  ion, which has

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<sup>a</sup> For a general discussion of the importance of configuration interaction, see Slater (55).

Table 3. Ground state electronic configurations and symmetries of octahedral transition-metal complexes.

No. of d-electrons	Configuration	Ions	Total electronic symmetry	
			Max. spin ("ionic" complex)	Min. spin ("covalent" complex)
1	$f) e)^0$	Sc <sup>+2</sup> Ti <sup>+3</sup>	$^2 F_{2g}$	same
2	$f) e)^0$	Ti <sup>+2</sup> V <sup>+3</sup>	$^3 F_{1g}$	same
3	$f) e)^0$	V <sup>+2</sup> Cr <sup>+3</sup>	$^4 A_{1g}$	same
4	$f) e)^1$	Cr <sup>+2</sup> Mn <sup>+3</sup>	$^5 E_g$	
5	$f) e)^2$	Mn <sup>+2</sup> Fe <sup>+3</sup>	$^6 A_{1g}$	
	$f) e)^0$			$^2 F_{1g}$
6	$f) e)^2$	Fe <sup>+2</sup> Co <sup>+3</sup>	$^5 F_{2g}$	
	$f) e)^0$			$^1 A_{1g}$
7	$f) e)^2$	Co <sup>+2</sup> Ni <sup>+3</sup>	$^5 F_{2g}$	
	$f) e)^1$			$^2 E_g$
8	$f) e)^2$	Ni <sup>+2</sup>	$^3 A_{1g}$	
9	$f) e)^3$	Cu <sup>+2</sup>	$^2 E_g$	

in the larger spin state, a totally symmetric ground state,  ${}^6A_{1g}$ . There probably are no other states within at least 5 eV available for configuration interaction.

#### E. Comparison with the Other Methods

The qualitative MO description of the electronic structure of transition-metal complexes is not much better than either the hybrid orbital or the crystalline field with regard to understanding the chemical and physical properties from first principles, as the phrase was used previously. In the quantitative aspect, the deficiencies of the crystalline field assumptions render it of little value toward furthering chemical understanding, whereas neither the VB nor the MO approaches have heretofore been considered at all quantitatively. On the other hand, the crystalline field theory is quite powerful in the rather detailed analyses of spectral and magnetic properties, while within the valence bond formulation it is quite difficult to discuss excited states even in a qualitative manner.

In the remainder of this chapter it will be indicated how the MO approach combines the advantage of both the other theories.

##### 1. Comparison with the hybrid orbital approach

Allowing for the possibility of partial covalent character in the "ionic" complexes, either through 4s, 4p or 4d

hybridization or through "3-electron" bonding by two of the d-orbitals (8), both MO theory and VB theory conclude that there should be no discontinuous change in the degree of covalency in the bonding on passing from "essentially covalent" to "essentially ionic" complexes. This fact has been pointed out by Orgel (29) and others on several occasions. It must be admitted that, in the absence of quantitative considerations, neither approach offers an explanation of why one certain complex ion will be "covalent" and another "ionic", as judged on the basis of magnetic data. On the other hand, the experience of others considering different (simpler) systems has been that the MO method offers more advantages when a quantitative aspect is taken.<sup>a</sup> Thus there is within the MO method a (probably) better way to place the theory upon a more firm basis.

There is one particular problem, encountered in the hybrid orbital picture and discussed at great length by Craig (56) and Craig, Maccoll, Nyholm, Orgel and Sutton (6). This problem concerns the "compatibility" of the 3d-, 4s-, and 4p-orbitals which form the octahedral, tetrahedral or other hybrids of transition-metal chemistry. The arguments presented in the two papers quoted proceed along somewhat arbitrary, though probably reasonable, lines. It is important to observe that similar problems do not occur in the MO description.

There is no a priori requirement that the relative polarities

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<sup>a</sup>For a general discussion of this point, see Slater (55), for example.

of the  $e_g$ ,  $a_{1g}$  and  $f_{1u}$  MO's should be equal, as is assumed implicitly in the simple orbital treatment. Indeed anticipating later results, the relative polarities may be greatly different. Thus, the spacial characteristics of the metal valence-shell orbitals are not of fundamental concern to the philosophy of the MO approach.

There is, of course, no immediate prospect that purely theoretical methods will interpret and correlate all data on transition-metal complexes. From the standpoint of understanding chemical behavior it is important that the theory of chemical bonding have not only quantitative but also descriptive advantages. The usual VB resonance ideas are obviously quite useful and certainly are not to be disparaged. Whether one adopts that viewpoint or the energy level LCAO scheme of the MO approach is in many ways a matter of personal preference. After some terminology and conventions are learned, the MO method is no more difficult to apply and is often quite rewarding.

## 2. Comparison with the crystalline field approach

A comparison of Figures 1 and 4 reveals one important feature in common between the crystalline field and MO treatments. Although the MO energy level diagram is complicated by the presence of numerous other bonding and anti-bonding systems, the portion of it concerned with the electrons in the  $2e_g$  and  $2f_{2g}$  MO's can be identified with the octahedral

splitting of an atomic state constructed from one d-electron. This observation causes one to suspect that even in more complicated cases of several d-electrons, the correspondence is equally close.

Such is indeed found to be true. In crystalline field theory, the one-electron 3d AO's form the basis for constructing the atomic state functions and then the functions appropriate to the reduced symmetry of the crystal or molecular perturbation. In MO theory the one-electron MO's already appropriate for the crystal or molecular symmetry, are used to construct the molecular state functions. There is a one-to-one correspondence between the results of both methods. This correspondence is a direct result of the symmetry of the system; and the differences arise only from the choices of basis functions (MO's versus AO's).

In the light of the quantitative discrepancies encountered in the application of crystalline field theory, it was reasonable to seek an explanation in the MO method, particularly when taken in LCAO approximation. This step was made by Stevens (44) and extended by Owen (46). When the MO's are substituted for AO's throughout the calculations of crystalline field theory, the expressions derived are naturally more numerous and more complicated. But if certain fairly reasonable approximations are made, there are obtained results very similar to those previously obtained. In the present instance, however, many of the calculated quantities, to be compared

with experimental measurements, are dependent upon the coefficients in the  $2e_g$  and  $2f_{2g}$  MO's.

As a consequence of the work of Stevens and Owen, crystal-line field theory has been modified, in essence, by the introduction of two parameters in addition to the original parameter  $Dq$ . Put in the opposite way, the precise analysis of optical and paramagnetic resonance spectra has been found to require consideration not only of the splitting of the 3d-orbitals of the metal ion but also of their delocalization throughout the complex ion.

This interpretation of the available data indicates that the delocalization (i.e., chemical bonding) is not inconsiderable, even in the so-called ionic complexes. For example (47), in the hydrated ions of the first transition series, the  $2e_g$  electrons are roughly 20 per cent delocalized from dipositive metal ions and 40 per cent from tripositive ions. Furthermore, there is additional evidence that in hydrated ions even  $\pi$ -type interactions are not negligible.

### 3. Conclusions

From all recent considerations of the theory of the electronic structure of transition-metal complexes, the conclusion seems inescapable that in all types of complexes covalent bonding is of importance, both in the chemical understanding of the compounds and in the physical interpretation of magnetic and spectral properties. It has been emphasised in



in this chapter that MO theory presents a reasonable method to compromise the two previous viewpoints.

The qualitative aspects of the MO application have been discussed to a large extent in the last year by Orgel, Owen and Williams, and in all cases considered satisfying conclusions were reached. Undoubtedly, these qualitative arguments will be carried much further in the future, and probably with considerable profit. What seems to be missing in the present stage is a precise formulation of the molecular problem within the MO theory. Certainly there is no present hope of treating these complex ions rigorously on a complete theoretical basis; approximations must be used. The advantages of a more precise formulation are two-fold. (a) The nature of many of the interactions present in these molecular systems (on the basis of modern quantum chemical theory) may be revealed, and the relative importance of various factors may be assessed. (b) Quantitative calculations, including necessary approximations, may not produce results in good agreement with experiment. Nevertheless, quantitative evaluation of particular types of interaction are quite useful in more qualitative discussions.

The work reported in the remainder of this thesis is directed toward both these goals.

## IV. SELECTION OF ATOMIC ORBITALS

In the considerations described in the remainder of this thesis, the usual LCAO approximation of MO's is assumed as the most satisfactory available compromise between the exact representation of the best one-electron MO's and the interpretation of the resulting functions in terms of chemical valence theory. Thus it is of immediate importance to specify the nature of the AO's which are to be used in the approximation. Unfortunately, despite much discussion of the subject, no definite conclusions have been reached. It is generally assumed that the Hartree-Fock SCF AO's afford the best choice; however, the presentation makes them useless, in their numerical form, for the analytic evaluation of the energy integral.

One alternative is afforded by the Slater orbitals (57), which are analytic functions resembling the exact solutions of the hydrogen atom problem, but which are specified by parameters that depend upon the nuclear charge ( $Z$ ), the screening by other electrons in the atom ( $s$ ) and the effective principle quantum number ( $n$ ). The rules for obtaining these parameters and functions are given in Slater's original article (57). Another alternative is to transform the results of numerical SCF calculations into analytic form by curve-fitting methods. If this is done systematically, then interpolation becomes possible. General considerations on this subject have been

investigated by Slater (57), Hartree (58), Ridley (59) and Lowdin (60). Both alternatives are used in this thesis; the first for the ligand orbitals, the second for the metal orbitals.

A third alternative might be mentioned. This is to assume hydrogen-like functions for the AO's, but containing parameters which are varied so as to minimize the energy of the atom. This idea was introduced by Zener (61), and extended by Morse, Young and Haurwitz (62), Duncanson and Coulson (63), and Roothaan (64). These orbitals seem not to be frequently used, as yet.

#### A. Ligand Atomic Orbitals

Although good SCF AO's are available for most atoms of the second period, the convenient and usual practice will be followed here, to use Slater orbitals for such atoms. Proof of the validity of this particular approximation is, of course, obtainable by actual computation and comparison with experiment. There is some evidence that in semi-empirical theory, such as Mulliken's Magic Formula (65), the SCF orbitals are superior. The influence of the choice of AO's used in this work will be discussed in Chapter VII.

The analytic forms of the 1s, 2s, 2p, 3s, 3p and 3d Slater orbitals are given in Table 4. Each AO is seen to depend upon one parameter  $\zeta$ , called the orbital exponent by Roothaan (65).  $\zeta$  is related to the two parameters systematised by Slater through the equation

$$\zeta = \frac{Z - s}{n}$$

Table 4. Slater orbitals

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1s	=	$\sqrt{\zeta^3/\pi} e^{-\zeta r}$
2s	=	$\sqrt{\zeta^5/3\pi} r e^{-\zeta r}$
2p <sub>x</sub>	=	$\sqrt{\zeta^5/\pi} r e^{-\zeta r} (\sin\theta \cos\phi)$
2p <sub>y</sub>	=	$\sqrt{\zeta^5/\pi} r e^{-\zeta r} (\sin\theta \sin\phi)$
2p <sub>z</sub>	=	$\sqrt{\zeta^5/\pi} r e^{-\zeta r} (\cos\theta)$
3s	=	$\sqrt{2\zeta^7/45\pi} r^2 e^{-\zeta r}$
3p <sub>x</sub>	=	$\sqrt{2\zeta^7/15\pi} r^2 e^{-\zeta r} (\sin\theta \cos\phi)$
3p <sub>y</sub>	=	$\sqrt{2\zeta^7/15\pi} r^2 e^{-\zeta r} (\sin\theta \sin\phi)$
3p <sub>z</sub>	=	$\sqrt{2\zeta^7/15\pi} r^2 e^{-\zeta r} (\cos\theta)$
3d <sub>z<sup>2</sup></sub>	=	$\sqrt{\zeta^7/18\pi} r^2 e^{-\zeta r} (3\cos^2\theta - 1)$
3d <sub>x<sup>2</sup></sub>	=	$\sqrt{2\zeta^7/3\pi} r^2 e^{-\zeta r} (\cos\theta \sin\theta \cos\phi)$
3d <sub>yz</sub>	=	$\sqrt{2\zeta^7/3\pi} r^2 e^{-\zeta r} (\cos\theta \sin\theta \sin\phi)$
3d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	=	$\sqrt{2\zeta^7/3\pi} r^2 e^{-\zeta r} (\sin^2\theta \cos 2\phi)$
3d <sub>xy</sub>	=	$\sqrt{2\zeta^7/3\pi} r^2 e^{-\zeta r} (\sin^2\theta \sin 2\phi)$

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For the 2s and 2p valence shell AO's of the atoms or ions considered in this thesis, the following  $S$ -values are obtained from Slater's rules:  $S_O = 1.625$ ,  $S_N = 1.95$

$$S_O = 2.275, S_F = 2.425$$

The 1s, 2s, 3s and the 2p, 3p sets of functions are not properly orthogonal as AO's must be. It has been shown, however, that when the total electronic wave function is taken in antisymmetrized form, it is not necessary to use orthogonal AO's. (See Slater (55)). On the other hand, if a simplified problem is considered, wherein inner shell electrons are neglected, it is thought better first to orthogonalize the AO's on each atom. But as a consequence of this simplification, caution must be exercised when interpreting the results of such a calculation. This problem will be treated at various points in the remainder of the thesis. See, further, Mulliken (66).

#### B. Transition-Metal Orbitals

There is some doubt about the applicability of Slater's rules as concerns the transition elements--a problem which has been discussed by Craig (56). One particular questionable feature is that, according to Slater's rules, the 3d electron AO's are not influenced by the ionization of 4s and 4p electrons from the metal. This would appear unreasonable, if the 3d orbitals play a role equal to the 4s and 4p in chemical bonding. Because of such uncertainties, it seemed desirable to

examine the Hartree SCF functions available in this region and to apply curve fitting techniques to them.

### 1. Available SCF atomic orbitals

Actually, the numerical wave functions available for the transition-metal series are not very impressive. Not many atoms have been treated, and of these, the approximation of neglecting the antisymmetry requirement upon the wave function has usually been made. At the time the work described in this section was completed, such numerical wave functions for the following atoms of the first long period had been published:  $\text{Ti}^{+2}$  (68),  $\text{Cr}^0$  (69,70),  $\text{Cr}^{+2}$  (69),  $\text{Fe}^0$  (71),  $\text{Cu}^{+1}$  (72),  $\text{Zn}^0$ ,  $\text{Ga}^{+2}$ ,  $\text{Ga}^{+3}$ ,  $\text{Ge}^0$ ,  $\text{Ge}^{+2}$ ,  $\text{As}^0$ ,  $\text{As}^{+1}$ ,  $\text{As}^{+2}$  and  $\text{As}^{+3}$  (73). Also,  $\text{Cu}^{+1}$  including the antisymmetry requirement (74), was published.

Recently, there have been reported complete Hartree-Fock calculations for the wave functions of  $\text{Mn}^{+2}$  (75), for three configurations of  $\text{Fe}^0$  ( $d^6 s^2$ ,  $d^7 s$ , and  $d^8$ ) by Stern (76), and also for  $\text{Fe}^0$  ( $d^6 s^2$ ) a highly refined calculation by Wood (77), in which the electrons of one spin were considered separate from the electrons of the opposite spin. Although these last two treatments might seem to furnish excellent AO's for use in the problems described below, they still do not include any information about the nature of the wave functions relevant to the ionized states probably encountered in the transition-metal complex ions.

Thus it is necessary to develop a systematic scheme of representing these numerical functions, so as to allow interpolation for desired electronic configurations and states of ionization. This general problem has been attacked by Hartree and Lowdin. For use here, however, a less ambitious program was undertaken and aimed at obtaining needed wave functions directly.

## 2. Systematic curve fitting methods for 3d atomic orbitals

It has been observed that the 3d functions obtained from the Hartree method vary with distance from the nucleus in a manner quite similar to that of the Slater functions. This suggests that a sum of "Slater-like" 3d functions might represent the numerical AO's rather well, the coefficients and orbital exponents being varied so as to give a good fit to the curve. In fact, Slater found (57) that a sum of three such functions was quite satisfactory. In this work, a two-function fit has been sought. For consistency, only the SCF AO's not including the antisymmetry requirement were systematized.

The analytic function chosen to represent the radial part of the 3d Hartree function thus has the form

$$R_{3d}(r) \sim r^2 \left\{ \alpha_1 e^{-\beta_1 r} + \alpha_2 e^{-\beta_2 r} \right\},$$

with  $\alpha_1$ ,  $\alpha_2$ ,  $\beta_1$  and  $\beta_2$  to be determined in some systematic fashion. The method used will now be described.

The parameter  $\beta_1$  was fixed so that the first term should dominate in the region of the maximum in the Hartree radial function. This was accomplished by setting

$$\beta_1 = \frac{2}{r_{\max}}$$

where  $r_{\max}$  is the radius of the maximum of the radial function. Figure 5 shows the results, giving  $\beta_1$  as a function of the atomic number  $Z$ . Two useful properties are observed. First, there is a strong, though not perfect, linear variation of  $\beta_1$  with  $Z$ . Second, except for Cr, it appears that the value of  $\beta_1$  is largely independent of the degree of ionization.

Next, values for  $\beta_2$  were determined. The tabulated numerical values were divided by  $r^2$ ; this operation converts the radial functions into functions of exponential type only. These transformed functions were then divided by  $e^{-\beta_1 r}$ . The logarithm of this result was plotted against  $r$ . Assuming the analytic form given above is reasonably correct, the numerical function graphed should be represented by

$$\log \{ \alpha_1 + \alpha_2 e^{(\beta_1 - \beta_2)r} \}.$$

Since by the choice of  $\beta_1$  it results that  $\beta_2 < \beta_1$ , for large values of  $r$  this last obtained function should very nearly equal

$$\log \alpha_2 + (\beta_1 - \beta_2)r.$$



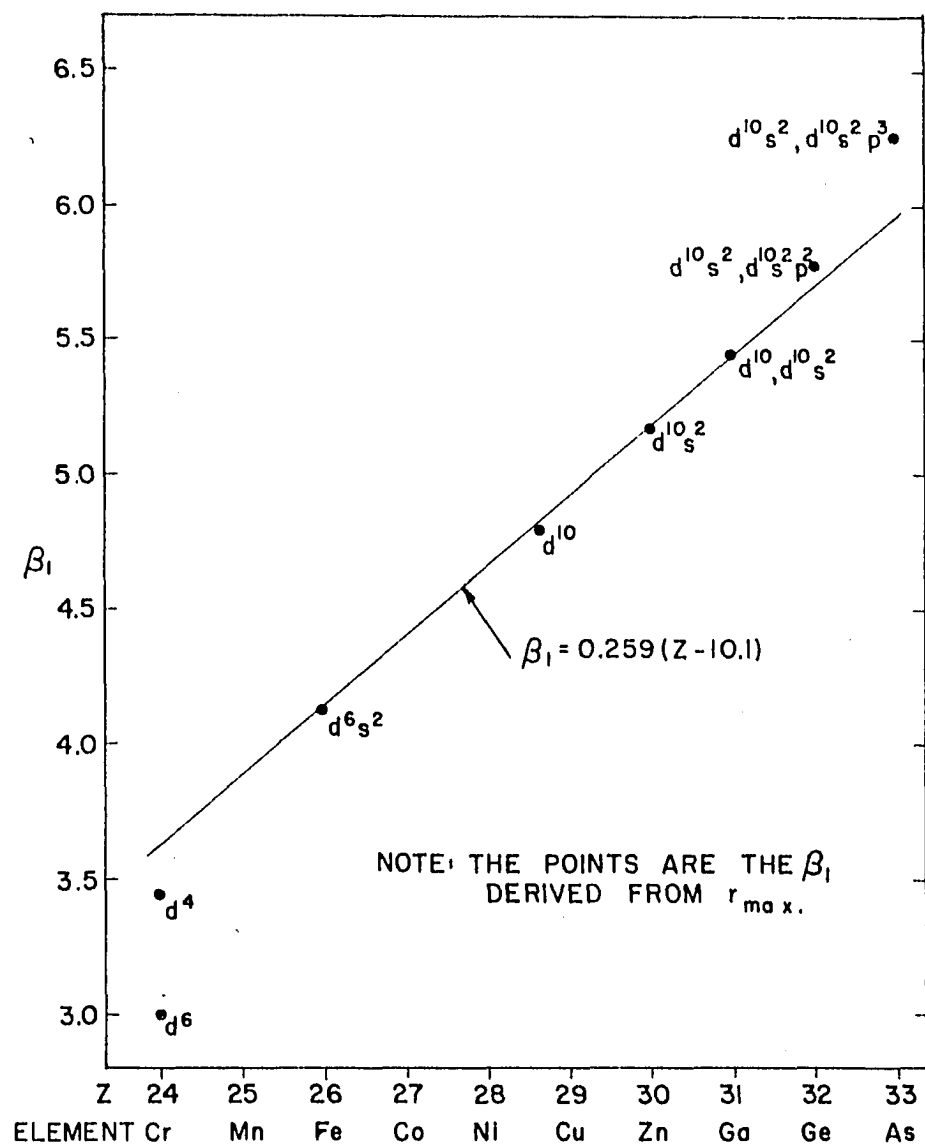


Figure 5. Variation of  $\beta_2$  with Z

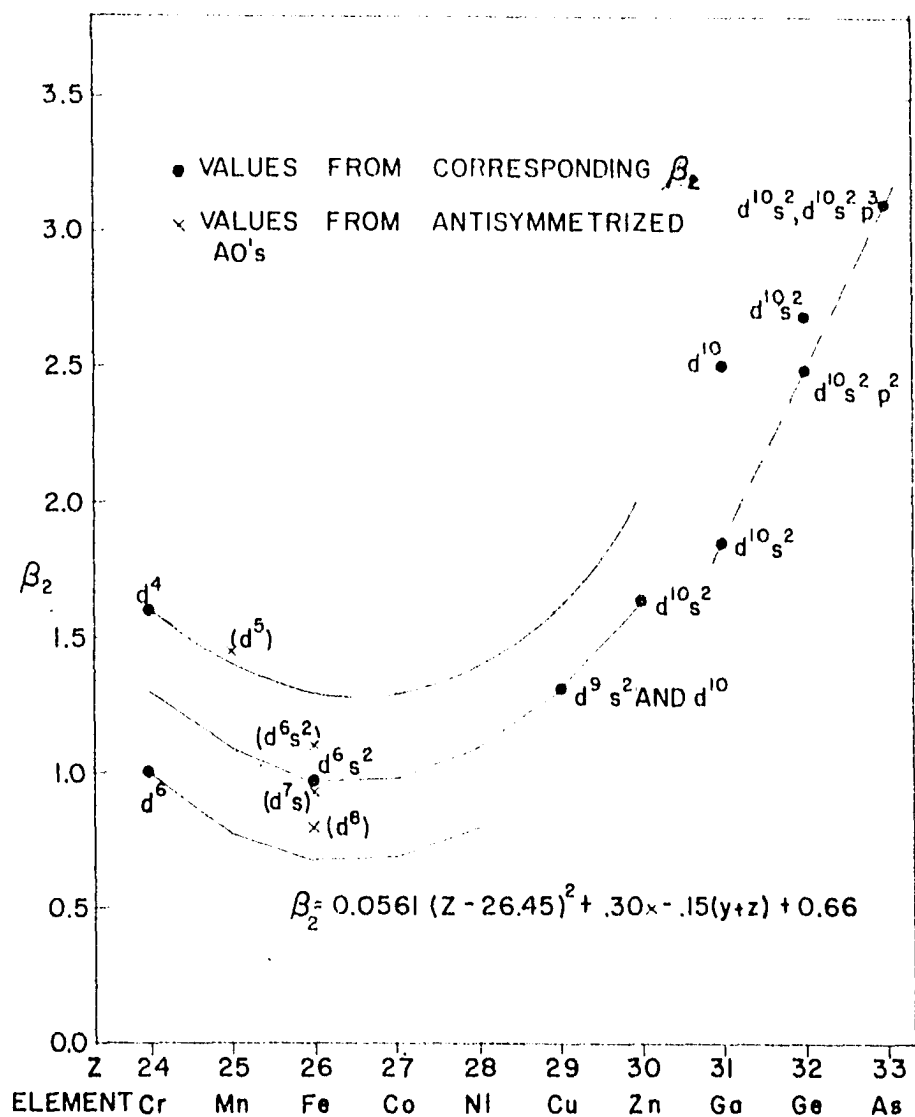
That is, for large  $r$  the curve approaches a straight line of limiting slope  $(\beta_1 - \beta_2)$ . Thereby  $\beta_2$  is determined graphically in terms of  $\beta_1$ .

This procedure was carried out for two different cases: (1) using a  $\beta_1$  as obtained from  $r_{\max}$  and (2) using a  $\beta_1$  obtained from a straight-line fit to the exact value (see Figure 5). For each of the eleven atoms considered, both choices of  $\beta_1$  resulted in essentially the same value of  $\beta_2$ . In other words,  $\beta_2$  is characteristic of the outer portion of the wave function more-or-less independently of the inner portion; and apparently it is this quantity which changes most as the degree of ionization changes. The derived values of  $\beta_2$  are plotted in Figure 6.

Values of  $\alpha_1$  and  $\alpha_2$  were then found by fitting the analytic functions to the tabulated SCF AO's at several points, using the derived values of  $\beta_1$  and  $\beta_2$ . In attempting to systematize the values of the  $\alpha$ 's so determined, it was discovered that  $\log \alpha_1$  varies quite linearly with  $Z$  and is reasonably independent of degree of ionization. If this functional dependence is assumed, then finally  $\alpha_2$  must be fixed by the normalization requirement for the total wave function.

Given the values of  $\beta_2$ , the following formulas for finding  $\alpha_1$  and  $\beta_1$  were established:

$$\begin{aligned}\beta_1 &= 0.259(Z - 10.1) \\ \log_{10} \alpha_1 &= 0.1112(Z - 13) \quad .\end{aligned}$$

Figure 6. Variation of  $\beta_2$  with Z

The parameter  $\beta_2$  was much more difficult to systematize. It was immediately apparent that the value of  $\beta_2$  is greatly influenced by the presence of 4s electrons. The formula finally devised is not claimed to be unique, but it is consistent with all the data available at the time. For the metal atom or ion  $M^{+(x-y)}$  with electronic configuration  $3d)^{Z-18-x} 4s)^y 4p)^z$  the formula was established:

$$\beta_2 = 0.0561(Z - 26.45)^2 + 0.30x - 0.15(y + z) + 0.66 \quad .$$

These three formulas are presumed to hold in the region between Ti and Zn. The quadratic behavior of  $\beta_2$  with a minimum between Fe and Co is taken to imply that deviation from pure hydrogen-like 3d functions is a maximum in this region.

### 3. 4s and 4p functions for iron

Knowledge of the 4s and 4p functions for the transition metals is even less satisfactory than of the 3d functions. Even though Manning and Goldberg (71) obtained the 4s function for the iron atom, there is no reliable method for assessing the variation of this function with degree of ionization. No iron 4p functions are available, and the nearest one for comparison is the  $Ga^0$  4p orbital. It is apparent, therefore, that the nature of the 4s and 4p orbitals must remain rather speculative throughout the calculations.

The technique of curve-fitting for the iron 4s function was as follows: a polynomial in  $r$  was constructed such that

it had roots at the zeros of the radial function (neglecting, however, the innermost zero). The tabulated radial function was then divided by this polynomial, resulting in a new tabulated function roughly exponential in character. The 4s radial function is then expressed by

$$R_{4s}(r) \sim (r - r_1)(r - r_2)e^{-\gamma r}.$$

To approximate roughly the 4p orbital, a similar sort of curve fitting was done for the 4s and 4p orbitals of  $\text{Ga}^0$ . The iron 4p was then constructed in the same proportion to the iron 4s as the gallium 4p bore to the 4s. These radial functions resulted:

$$R_{4s}(r) = (1.938r^2 - 2.752r + 0.703)e^{-0.964r}$$

$$R_{4p}(r) = (1.320r^2 - 2.080r + 0.477)e^{-1.20r}$$

Converting to sums of normalized Slater-like functions these become

$$R_{4s}(r) = (1.640)3s(0.964) - (0.819)2s(0.964) + (0.117)1s(0.964)$$

$$R_{4p}(r) = (1.654)3p(1.20) - (1.142)2p(1.20) + (0.1814)1p(1.20)$$

where  $n\ell(\xi)$  signifies a normalized Slater-like AO whose orbital exponent is  $\xi$ .

It is to be noted that, in the procedure for obtaining  $R_{4s}$  and  $R_{4p}$ , one power of  $r$  in the polynomial factor was omitted in each case. The result is that the sum of analytic functions extends only to the  $3s$  and the  $3p$  AO's, a very desirable feature from the standpoint of simplifying further calculations. A byproduct, however, is the introduction of a  $1p$  function, which has only analytical significance and causes no complications.

It is surely evident already that Hartree SCF calculations are needed for configurations involving  $4p$  orbitals as well as for different degrees of ionization.

#### 4. Results and comments

For purposes of further calculation it is convenient to have the numerical AO's expressed in terms of normalized functions. This further specification modifies the  $\alpha$  coefficients in the  $3d$  AO's so that now

$$R_{3d}(r) = \alpha'_1 3d(\xi_1) + \alpha'_2 3d(\xi_2) \quad .$$

The final derived parameters are given in Table 5, along with the corresponding values of the orbital exponent deduced from Slater's rules.

(a) Goodness of fit. In attempting a curve fitting procedure such as described above, one must compromise between being accurate and being systematic in reproducing the AO's. It is not easy to determine when the most favorable situation is

Table 5. Final parameters for the analytic function.

$$R_{3d}(r) = r^2 \{ \alpha_1 e^{-\beta_1 r} + \alpha_2 e^{-\beta_2 r} \} = \alpha'_1 3d(\beta_1) + \alpha'_2 3d(\beta_2)$$

	Z	Config.	$\alpha_1$	$\beta_1$	$\alpha_2$	$\beta_2$	$\alpha'_1$	$\alpha'_2$	$\rho$
Cr <sup>+2</sup>	24	d <sup>4</sup>	21.10	3.600	1.223	1.597	0.565	0.563	1.649
Cr <sup>0</sup>	24	d <sup>6</sup>	21.10	3.600	.288	.996	0.565	0.548	1.417
Mn <sup>+2</sup>	25	d <sup>5</sup>	27.26	3.859	1.038	1.378	0.570	0.539	1.866
Cu <sup>+</sup>	29	d <sup>10</sup>	75.86	4.895	0.643	1.325	0.693	0.569	2.500
Ga <sup>+3</sup>	31	d <sup>10</sup>	126.5	5.413	3.552	2.721	0.813	0.254	3.167
Ga <sup>+</sup>	31	d <sup>10</sup> s <sup>2</sup>	126.5	5.413	2.595	2.421	0.813	0.279	3.167
As <sup>0</sup>	33	d <sup>10</sup> s <sup>2</sup> p <sup>3</sup>	211.1	5.931	0.781	3.817	0.985	0.0002	3.500
As <sup>+3</sup>	33	d <sup>10</sup> s <sup>2</sup>	211.1	5.931	0.781	3.817	0.985	0.0002	3.500
Cr <sup>0</sup>	24	d <sup>4</sup> s <sup>2</sup>	21.10	3.600	0.652	1.297	0.565	0.224	1.649
Mn <sup>0</sup>	25	d <sup>5</sup> s <sup>2</sup>	27.26	3.859	0.375	1.078	0.570	0.684	1.866
Fe <sup>0</sup>	26	d <sup>6</sup> s <sup>2</sup>	35.90	4.138	0.273	0.990	0.591	0.671	2.083
Co <sup>0</sup>	27	d <sup>7</sup> s <sup>2</sup>	45.47	4.377	0.274	0.981	0.615	0.695	2.300
Ni <sup>0</sup>	28	d <sup>8</sup> s <sup>2</sup>	53.73	4.636	0.376	1.095	0.649	0.649	2.517
Cu <sup>0</sup>	29	d <sup>9</sup> s <sup>2</sup>	75.86	4.895	0.444	1.175	0.693	0.599	2.500
Zn <sup>0</sup>	30	d <sup>10</sup> s <sup>2</sup>	97.97	5.154	1.153	1.667	0.748	0.457	2.951
Fe <sup>+1</sup>	26	d <sup>6</sup> s	35.90	4.138	0.424	1.121	0.591	0.674	2.083
Fe <sup>+2</sup>	26	d <sup>6</sup>	35.90	4.138	0.626	1.271	0.591	0.641	2.083
Fe <sup>+3</sup>	26	d <sup>5</sup>	35.90	4.138	1.193	1.571	0.591	0.582	2.200

reached. In other words, there is no precise measure of how much accuracy must be sacrificed in order to achieve a means of interpolating for unknown wave function. Ridley (59) and Lowdin (60) have tried an entirely different and much more involved approach which presumably should yield better interpolated functions, but there is little information on which to base judgment.

Thus, it will merely be stated that there has been derived here a systematic means of producing 3d AO's for any particular electronic configuration of the transition elements of the first long period. These systematic AO's in general reproduce the known Hartree SCF AO's within about ten per cent (on the average). Unfortunately, the process of systematization selected causes the maximum of the fitted function no longer to coincide with that of the Hartree curve. (Although the first term of the analytic function is a maximum at  $r_{\max}$ , the second term is still increasing at that point.) The result is that the analytic fitted function is somewhat less than the Hartree curve near the maximum, but becomes somewhat greater for larger  $r$ .

(b) Effect of introducing the antisymmetry requirement.

It is also important to consider what might be the effect upon the AO's when the antisymmetry requirement is included in the derivation of the SCF AO's. This question has been investigated rather carefully by Hartree and Hartree (74) in the case of  $\text{Cu}^+$ . The observation is that the radial function becomes



drawn in slightly more toward the nucleus. Thus this effect might be expected to increase the discrepancy between the analytic fitted functions and the better SCF AO's.

Since all this work was completed, there have appeared reports of the work by Wood (77) and Stern (76). Stern's calculations were recently curve fit by the same techniques. It was observed that the maxima were shifted inward as in  $\text{Cu}^+$ , so that the previous choice of  $\beta_1$  did not give a good fit to his results in the region of the maximum. On the other hand, the values of  $\beta_2$  derived from his results differed only by a small constant amount from those predicted from the interpolation formula. Similar conclusions were obtained from the recent  $\text{Mn}^{+2}$  calculations of Hartree (75). These later results are encouraging for two reasons. First, they give some assurance for the validity of the quadratic behavior found for  $\beta_2$ . Second, they imply that if a good SCF calculation is done for one particular configuration of a given transition-metal atom, then it may be possible to make a reasonably good estimate for a different configuration or for a neighboring atom.

Within the antisymmetry requirement there is no need for the electrons of one spin to occupy orbitals identical to those occupied by the equivalent electrons of opposite spin, for the case of atoms with incompletely filled shells (that is, with unpaired electrons). In the usual SCF treatment of such atoms, this additional identity property is assumed;

Wood, however, has not made this simplification in his reported calculations. The advantages of this sort of treatment will be indicated in Chapter VI.

(c) Comparison with Slater orbitals. It is even more difficult to compare the analytic fits to the Slater functions in any significant way. It is observed from Table 5 that the orbital exponents for the Slater orbitals lie between the  $\beta_1$  and  $\beta_2$  values. Thus it would appear that the Hartree AO's tend to be somewhat more diffuse than the Slater orbitals despite the fact that their maxima lie within the maxima of the Slater orbitals.<sup>a</sup> There was revealed the expected weakness of the Slater functions in not allowing for the influence of the 4s and 4p electrons upon the 3d. It was found that the screening of one 3d electron by a 4s electron is about half the screening of one 3d electron by another, so far as the outer parts of the wave function is concerned.

On the other hand, it is interesting that roughly half the electron density in the 3d shell appears to be distributed independent of degree of ionization, as revealed by the essential constancy of  $\beta_1$  for a given atom.

As a general conclusion it might be expected that quantities such as coulomb effects relating to the 3d metal orbitals

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<sup>a</sup> These conclusions support those of Craig, et al., (6) with regard to the comparative diffuseness of the 3d and 4s electrons. It has already been pointed out, however, that this is of no essential concern in the MO approach.

will be rather insensitive to changes of the electron configuration of a particular atom, but that other quantities such as the overlapping of the 3d orbital with neighboring atoms in a molecule may be more sensitive to those changes.

## V. THE WOLFSBERG AND HELMHOLZ APPROACH TO THE ELECTRONIC STRUCTURE OF TRANSITION-METAL COMPLEXES

Heretofore there has not been mentioned two discussions of a quantitative nature which have been published concerning transition-metal compounds. Both are based upon the considerations of Mulliken's Magic Formula (65). Since this is based in turn upon theoretical studies of simple first-row diatomic molecules, its extension to transition-metal complex ions is very probably strained.

One study is the direct application of the Magic Formula to the alkyl derivatives of the transition metals by Jaffe (78). The other, which departs in detail from the Magic Formula, is contained in the paper on  $\text{MnO}_4^-$ ,  $\text{CrO}_4^{2-}$  and  $\text{ClO}_4^-$  by Wolfsberg and Helmholtz (79) and the paper on  $\text{CrO}_3\text{F}^-$  and  $\text{CrO}_2\text{Cl}_2$  by Helmholtz, Brennan and Wolfsberg (80). In these two papers the MO method is formally applied to these (nearly) tetrahedral ions, although the terms in the energy integral are all approximated in a manner strongly reminiscent of the Magic Formula.

The Wolfsberg and Helmholtz approximations are quite crude indeed; it cannot be said that they afford any quantitative evaluation of the nature of the electronic interactions in transition-metal compounds. Nevertheless, these approximations incorporate many of the general concepts of chemical bonding, such as overlap of bonding orbitals and electronegativity. Thus the results are of qualitative interest.

Since the work of Wolfsberg and Helmholz offers the only published effort approaching a quantitative nature involving compounds of the transition metals, it is relevant to apply this method to complex ions of the type considered in this thesis for two reasons; first, to display the qualitative aspects of the MO theory applied to the complexes, and second, to allow comparisons to be made with the much more detailed treatment presented later. Although Wolfsberg and Helmholz discussed only tetrahedral molecules, their method would seem applicable to octahedral complexes, as well, if there exists any rational basis for their approximations.

#### A. Application of the Method

##### 1. Summary of the method

The molecular orbital problem involves the solution of secular equations, which have the form

$$\det |H(i,j) - G(i,j)E| = 0 ,$$

where

$$H(i,j) \equiv \int u_i H u_j dv \qquad G(i,j) \equiv \int u_i u_j dv$$

and  $u_i$  and  $u_j$  are SO's which form the MO's. The  $G(i,j)$  are called group overlap integrals; for  $i = j$ ,  $G(i,j) = 1$  (if the SO's are properly normalized) and for  $i \neq j$ ,  $G(i,j)$  may be reduced to a linear combination of overlap integrals involving only AO's. For example, in the  $A_{1g}$  MO  $G(i,j) = G(4s, \sigma_1)$  reduces in the following manner

$$\begin{aligned}
 G(i,j) &= \int (4s)(\sigma_1) dv = \frac{1}{\sqrt{6}} \int (4s)(\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6) dv \\
 &= \sqrt{6} \int (4s)(\psi_1) dv = \sqrt{6} S(4s, \psi_1) .
 \end{aligned}$$

The other  $G(i,j)$  reduce in a similar fashion. The values of the overlap integrals encountered in the present problems may be obtained from tables or calculated from formulas, both of which have been published. For some details and references, see Appendix C.

The  $H(i,i)$  terms correspond roughly to the coulomb energy of an electron on the  $i^{\text{th}}$  atom or linear combination of atoms. Thus  $H(4s, 4s)$  is approximated by the ionization potential (IP) of the 4s electron from the metal atom, and  $H(\sigma_1, \sigma_1)$  by the IP of an electron from a  $\sigma$  orbital of the ligand. These IP's are adjusted in a rough manner so as to correspond to the IP's of atoms (or ions) of a charge equal to that assigned to the atom in the molecule.

The  $H(i,j)$  terms are obtained from the formula

$$H(i,j) = (1/2)G(i,j)F^X \{H(i,i) + H(j,j)\} .$$

$F^X$  is an empirical constant determined so as to give results in good agreement with experiment in one molecule and then applied to the other molecules. For  $\sigma$ -type bonding,  $F^X = F^\sigma = 1.67$ ; for  $\pi$ -type  $F^X = F^\pi = 2.00$ .

To apply the method, then, it is necessary to have overlap integrals and IP's for the AO's involved in bonding.

The IP's may be obtained from an examination of atomic spectra, as compiled, for example, by Moore (81) or from molecular ionization potentials. Once metal-ligand distances have been established, overlap integrals may be computed for the various ligands to be investigated. Those problems will be considered in that order.

## 2. Ionization potentials

From an examination of spectral data given by Moore for iron, the following valence-state IP's were determined:

	$\text{Fe}^0$	$\text{Fe}^{+1}$	$\text{Fe}^{+2}$
3d	-8.1 ev	-15.9 ev	-30.6 ev
4s	-7.8	-14.8	-28.4
4p	-5.2	-12.4	-25.4

These values were graphed and a smooth curve drawn through so as to allow interpolation for IP's for fractional charge on the iron atom. See Figure 7.

For the fluoride and ammonia ligands, these IP's were obtained:

$$2p(\text{F}^-) = -3.63 \text{ ev}$$

$$2p(\text{F}^0) = -20.9 \quad \text{See Skinner and Pritchard (82)}$$

$$\text{lone pair}(\text{NH}_3) = -11.2 \text{ ev} \quad \text{See (83)}$$

Rough calculations were also made for the cyanide complex.

For the lone pair on the carbon atom

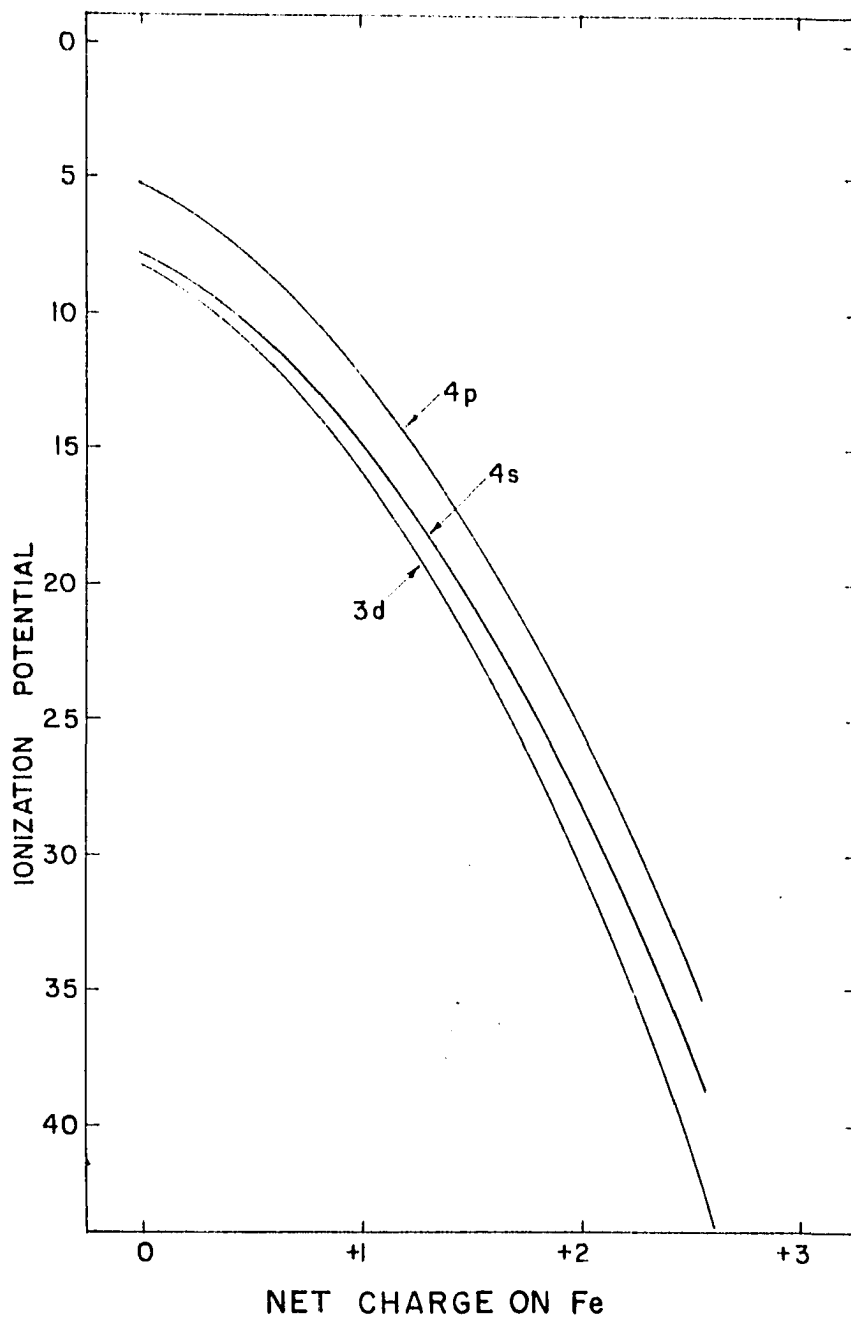


Figure 7. Valence-state ionization potentials for iron



$IP(CN^-) = 3.6 \text{ ev}$       See Pritchard (84)

$IP(CN^0) = 14.0$       See (83)

Inspection of the energy levels of the CO molecule calculated by Sahni (85) indicates that the bonding  $\pi$ -MO of CN may lie about 1 ev below the non-bonding lone pair, and that there is an anti-bonding MO approximately 7 ev above the lone pair.

Linear interpolation was used to obtain IP's for fractional charges on the ligands.

### 3. Metal-ligand distances

There seems to be a distressing lack of information about precise distances within many transition-metal complex ions in crystals. Of the two complexes of main interest,  $Fe(NH_3)^{+3}$  and  $FeF_6^{+3}$ , no crystal structure work at all has been reported for the first and only an inaccurate study for the second; see Wyckoff (86). Thus one is forced to improvise distances from other information. The selections made are necessarily arbitrary.

Pauling's covalent radii were used for the ammonia complex. Since the complex is ionic according to the hybrid-orbital picture, it might seem more fair to use ionic radii. But, then, the ionic radius of a neutral ammonia molecule is a doubtful quantity. Using the sum of the ionic  $Fe^{+3}$  and van der Waals  $N^0$  radii gives an Fe--N distance of 2.1 Å; partial positive charge on the ammonia might possibly be ex-

pected to increase this value. On the other hand, if the covalent radii were used, a distance of about  $1.93 \text{ \AA}$  results. But here one may question the relevance to  $\text{Fe}(\text{NH}_3)_6^{+3}$  of the iron radius in pyrite and of half the N--N distance in hydrazine. Off-hand, it might seem that the difference may be of lesser importance as it is in the Wolfsberg and Helmholz treatment. But in the more refined theory, the ultimate choice is critical. At any rate, since one of the contentions advanced in this thesis is that covalent bonding is of significance in these complexes, it seemed consistent at the time the choice was made to assume the covalent radius sum.

The Fe--F distance used is based upon a somewhat better estimate. Although the  $\text{FeF}_6^{-3}$  structure has not been examined closely, Stout and Reed (87) have found the Fe--F distance in  $\text{FeF}_2$  to be about  $2.07 \text{ \AA}$ . Under similar circumstances, one might expect the  $\text{Fe}^{+3}$ --F distance to be shorter. But in an independent octahedral complex ion, F--F repulsions are likely to keep the metal-ligand distance longer. Thus the  $2.07 \text{ \AA}$  distance seems quite reasonable for  $\text{FeF}_6^{-3}$ .

For the  $\text{Fe}(\text{CN})_6^{-3}$  ion, the Fe--C distance ( $=1.85 \text{ \AA}$ ) was taken from the study of  $\text{Fe}(\text{CN}.\text{CH}_3)_4(\text{CN})_2$ . See Wells (88, p.544).

It should be borne in mind that there is no guarantee that any crystal distances are relevant to a study of isolated complex ions, since the electric fields of other ions in the crystal may stabilize the complex at different bond distances.

Conversely, it is also true that to yield information of chemical interest it is necessary to treat the complexes in their experimentally encountered environments; this point will be touched upon later.

#### 4. Ligand orbitals

Before proceeding to the calculation of overlap integrals, it is necessary to consider the nature of the bonding AO's which the ligands present to the metal.

In the fluoride complex, it was assumed that only the 2p orbital was involved. Certainly it is to be expected that the ion will be polarized to some extent by the admixture of some 2s character to the  $\psi$ 's; there does not exist any convenient way to assess properly the amount or influence of this polarization. Hence, it was neglected in the calculations, although in one trial MO it was included in a very rough manner.

The nature of the lone pair electrons on the ammonia molecule has been a subject for speculation for many years. Mulliken (89), in considering the spectra of the molecule, decided that the lone pair orbital is an essentially pure 2p AO on the nitrogen. See also Mulliken (90). His type of argument has been criticized by Ellison (91) in an analysis of the electronic structure of the water molecule, where somewhat the same problem arises. Recent interpretations of the dipole moment from absolute intensity measurements in the infra red spectrum of the molecule by Horning and McKean (92) and McKean and Schatz (93) indicate that the lone pair electrons are in

a more-nearly tetrahedral hybrid AO on the nitrogen. However, the interpretations of these data proceed along rather arbitrary lines. For the qualitative purpose of the Wolfsberg and Helmholz approach, a pure tetrahedral orbital was specified for the lone pair electrons. Further consideration of this point is given in the following chapters.

As an estimate of the electron distribution to be expected in the  $\text{CN}^-$  ion, the results of Sahni's (85) calculations upon the iso-electronic CO molecule were used. For the lone pair  $\sigma$ -electrons on the carbon and the  $\pi$ -electrons, these wave functions were taken:

$$= (0.690)2s_{\text{C}}(1.625) + (0.720)2p\sigma_{\text{C}}(1.625)$$

$$= (0.4162)2p\pi_{\text{C}}(1.625) + (0.8145)2p\pi_{\text{O}}(2.275)$$

## 5. Overlap integrals

The following information was used in the calculation of overlap integrals: (a) the iron 3d, 4s and 4p AO's derived in Chapter IV, (b) Slater orbitals for N, C, O and  $\text{F}^-$ , (c) the metal-ligand distances of paragraph 3, and (d) the ligand orbitals discussed in paragraph 4. Values of the group overlap integrals needed are related to the overlap integrals by

$$\begin{aligned} a_{1g} \quad G &= \sqrt{6}S(4s, \psi) \\ e_g \quad G &= (4/3)\sqrt{3}S(3d_{z^2}\sigma, \psi) \\ f_{2g} \quad G &= 2S(3d\pi, \xi) \end{aligned}$$

$$f_{1u\sigma} \quad G = \sqrt{2}S(4p\sigma, \psi)$$

$$f_{1u\pi} \quad G = 2S(4p\pi, \xi)$$

Values were obtained by interpolation into tables given in the literature. For 3d overlaps, four different configurations of iron were assumed. Since there was available only one 4s and 4p set of AO's, there was obtained only one set of overlap integrals. Calculated values are given in Table 6 and graphed in Figure 8.

### B. Solution of the Secular Equations

Considering only valence shell AO's on the iron and the  $\psi$  and  $\xi$  AO's on the ligands, there are three 2x2 determinantal secular equations to solve for the  $\text{Fe}(\text{NH}_3)_6^{+3}$  complex, and two 2x2 and one 3x3 equations for the  $\text{Fe}(\text{CN})_6^{-3}$  and  $\text{FeF}_6^{-3}$  complexes. The solution of these equations was perfectly straightforward. A sort of self-consistent approach was adopted, along the lines suggested in part by Wolfsberg and Helmholtz. At the conclusion of one cycle of calculations, the charged distribution resulting from the derived MO's was calculated and used as a basis for estimating new values of the  $H(i,i)$  quantities.<sup>a</sup> This process was repeated until the

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<sup>a</sup> In the MO  $\phi = a\chi + b\sigma$ , the charge distribution of the electron so described is given by  $\phi^2 = a^2\chi^2 + 2ab\chi\sigma + b^2\sigma^2$ . Integrating both sides of the equation over all space gives  $1 = a^2 + 2abG(\chi, \sigma) + b^2$ ; that is, the fraction  $a^2$  of the electron is "on" the metal,  $b^2$  "on" the ligand and  $2abG$  in the overlap region. It is usual practice (see Mulliken (94)) to compute formal charges by dividing the overlap charge between the two

Table 6. Overlap integrals

<u>MO</u>	<u>Configu- ration</u>	<u>Group overlap integrals</u>		
		<u>Fe(NH<sub>3</sub>)<sub>6</sub></u>	<u>FeF<sub>6</sub></u>	<u>Fe(CN)<sub>6</sub></u>
A <sub>1g</sub>	Fe <sup>0 6 2</sup> d s	0.604	0.242	0.802
f <sub>1u</sub> <sup>σ</sup>	Fe <sup>0 6 2</sup> d s	.441	.297	.526
f <sub>1u</sub> <sup>π</sup>		--	.122	.188
e <sub>g</sub>	Fe <sup>0 6 2</sup> d s	.520	.162	.560
	Fe <sup>+1 6</sup> d s	.546	.196	.600
	Fe <sup>+2 6</sup> d	.533	.217	.594
	Fe <sup>+3 5</sup> d	.456	.215	.511
f <sub>2g</sub>	Fe <sup>0 6 2</sup> d s	--	.231	.460
	Fe <sup>+1 6</sup> d s	--	.205	.448
	Fe <sup>+2 6</sup> d	--	.181	.392
	Fe <sup>+3 5</sup> d	--	.125	.278

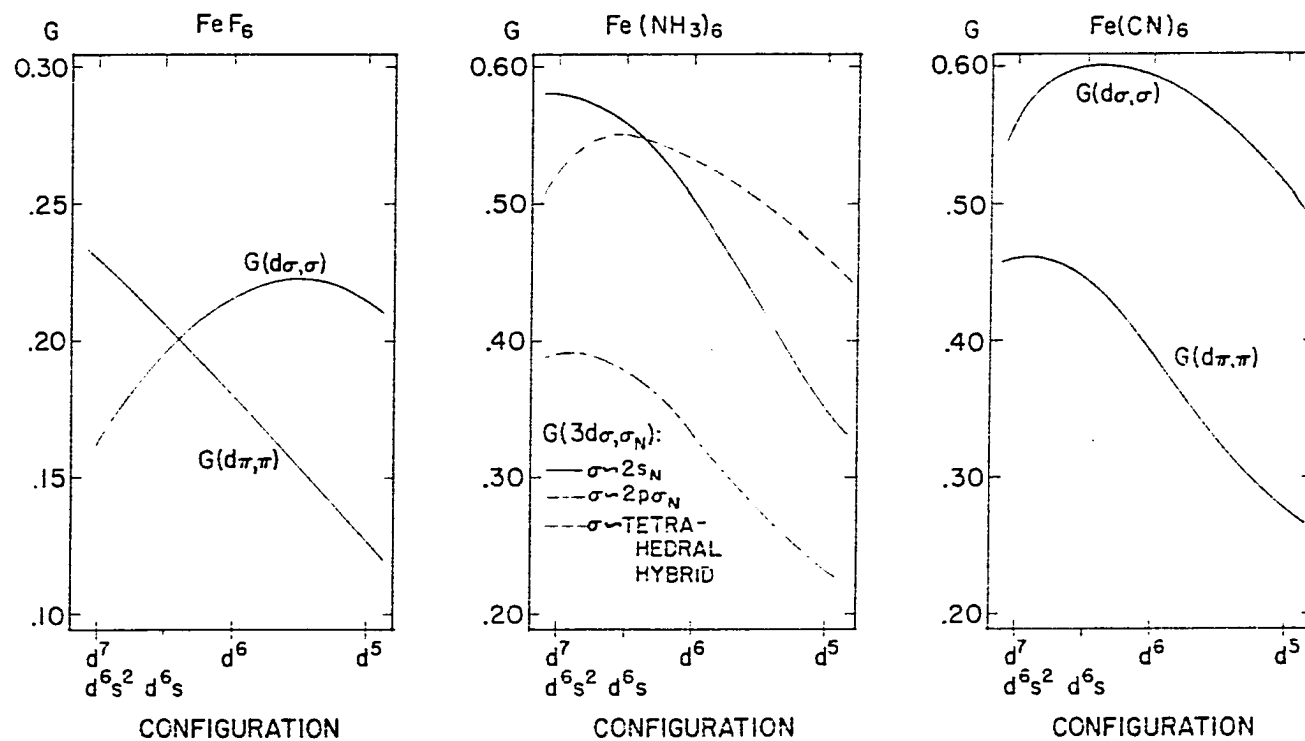


Figure 8. Variation of group overlap integrals with electronic configuration of Fe

derived charge distribution was in reasonable agreement with that assumed.

### 1. Ammonia complexes with iron

In the Wolfsberg and Helmholz approximation it is immaterial so far as the method is concerned whether  $\text{Fe}^{+2}$  or  $\text{Fe}^{+3}$  complexes are considered; or for that matter, whether the complexes are octahedral or tetrahedral, so long as the proper secular equations are set up and the correct group overlap integrals are used. Accordingly, all four combinations were investigated; details relevant to the tetrahedral molecules are given by Wolfsberg and Helmholz (79) and by Zaslow (95).

Since the final net charges assigned to the iron were quite small, the overlap integrals were kept constant for all four cases. The group overlap integrals used are:

<u>Fe(NH<sub>3</sub>)<sub>6</sub></u>			<u>Fe(NH<sub>3</sub>)<sub>4</sub></u>		
<u>MO</u>	<u>Integral</u>	<u>Value</u>	<u>MO</u>	<u>Integral</u>	<u>Value</u>
a <sub>1g</sub>	(4s, $\sigma_1$ )	0.604	a <sub>1</sub>	(4s, $\sigma_1$ )	0.444
f <sub>1u</sub>	(4p, $\sigma_2$ )	0.441	f <sub>1</sub>	(4p, $\sigma_2$ )	0.360
e <sub>g</sub>	(3d, $\sigma_5$ )	0.520	f <sub>1</sub>	(3d, $\sigma_2$ )	0.300

The values of  $H(i,i)$  selected for the final cycles are:

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(Footnote p. 78 continued). SO's of the MO. Thus the charge on the metal was computed from the values of  $a^2 + abG$  for each MO.



<u>i</u>	<u>Fe(NH<sub>3</sub>)<sub>6</sub><sup>+2</sup></u>	<u>Fe(NH<sub>3</sub>)<sub>6</sub><sup>+3</sup></u>	<u>Fe(NH<sub>3</sub>)<sub>4</sub><sup>+2</sup></u>	<u>Fe(NH<sub>3</sub>)<sub>4</sub><sup>+3</sup></u>
4s	-8.06 ev	-9.97	-9.30	-10.38
3d	-7.46	-8.77	-8.10	- 9.18
4p	-6.06	-7.37	-6.70	- 7.78
σ	-11.2	-11.2	-11.2	-11.2

The bonding energy levels derived seemed reasonable; however, the anti-bonding levels all turned out exceedingly high. In particular, the separation between the  $f_{2g}$  and the  $2e_g$  levels was impossibly large to allow the complex ion to have five unpaired electrons, as experimentally revealed. Analysis of the discrepancy is revealed only after the detailed treatment reported in the next chapter. At the time, explanation was sought within the framework of the approach being used.

No such problems were encountered by Wolfsberg and Helmholz; but in the considerations which led to Mulliken's Magic Formula, similar disparities were noted in treating  $\text{He}_2^+$ . Here, just as in the  $e_g$  MO system, there are both bonding and anti-bonding electrons contributing to the net electronic energy. It appeared to Mulliken that the repulsive character of the anti-bonding level was over-emphasized by the nature of the approximations. To temper these repulsions, he introduced an empirical parameter  $\mu$ , and found that it was a function defined by

$$\mu = (1 - G)(2\nu + \frac{1}{1+G})$$

The new parameter  $\nu$  was found to be nearly constant for a wide range of simple molecules and was set equal to 0.7. It was assumed to hold for the complex ions, as well. Analogous to its use in the Magic Formula, the  $\mu$ -factor was applied in the present work in the following fashion:

For the  $2e_g$  MO  $\varphi = a\chi - b\sigma$ ,

$$\mathcal{E} = \int \varphi H \varphi dv = a^2 H(\chi, \chi) + b^2 H(\sigma, \sigma) - 2\mu ab H(\chi, \sigma) .$$

The molecular energy levels for the iron ammines, derived under these assumptions are indicated in Figure 9.

## 2. Fluoride complexes with iron

Both the octahedral ferrous and ferric complexes were considered. Exactly the same techniques were applied here as in the ammonia cases, even to the inclusion of the  $\mu$ -factor in the  $2f_{2g}$  and  $2e_g$  energy levels. Following Wolfsberg and Helmholtz, the ligand  $\sigma$  AO's were lowered 1 ev below the  $\pi$  AO's. The results are indicated in Figure 10. Notice that  $2f_{2g}$  lies higher than  $2e_g$ , an order which is independent of the  $\mu$ -factor.

## 3. Cyanide complexes with iron

By the time the cyanide complexes were considered, inadequacies in the Wolfsberg and Helmholtz approximation had become apparent; however, one cycle was carried out. One might treat the  $CN^-$  ion like a halogen ion, and consider only the interaction of the  $\sigma$  and  $\pi$  electrons of the ion with the

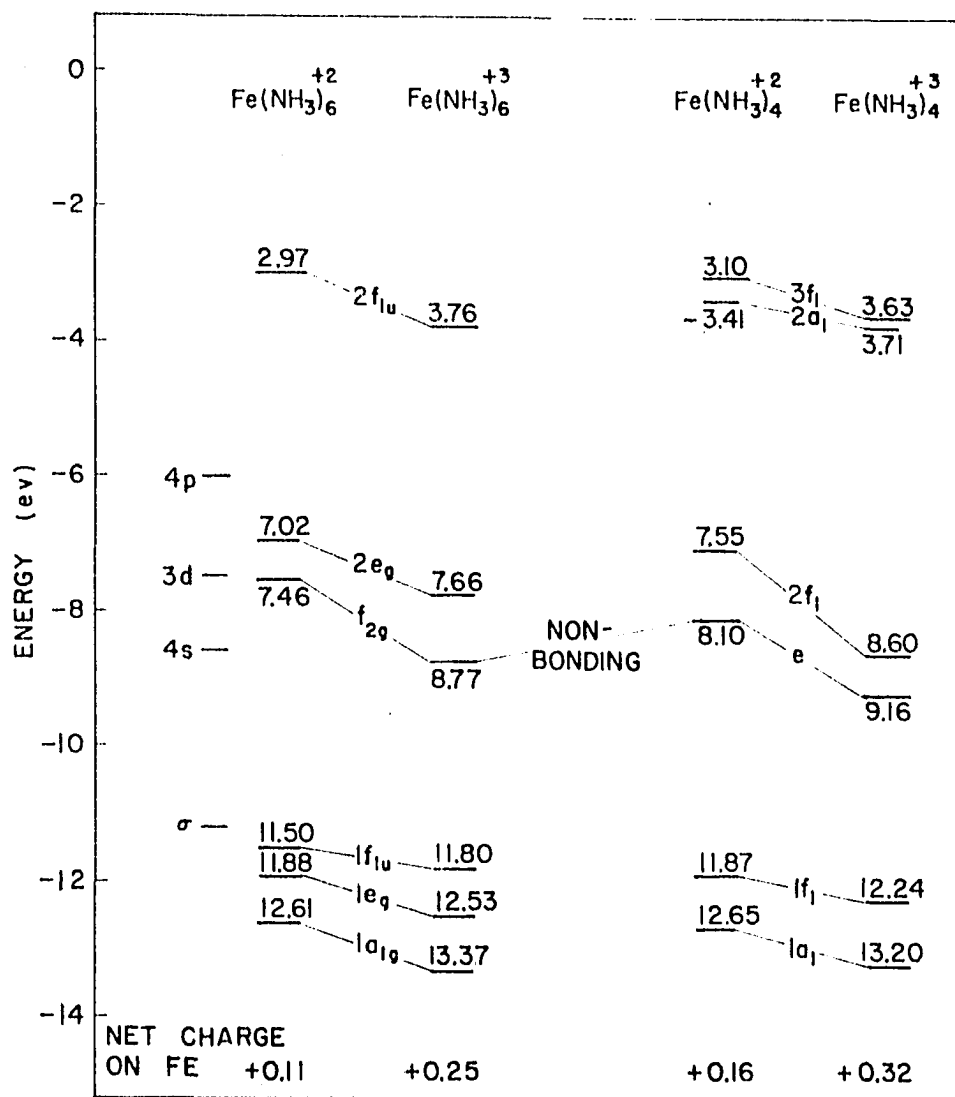


Figure 9. Energy levels calculated for iron-ammonia complexes by the Wolfsberg and Helmholz approach

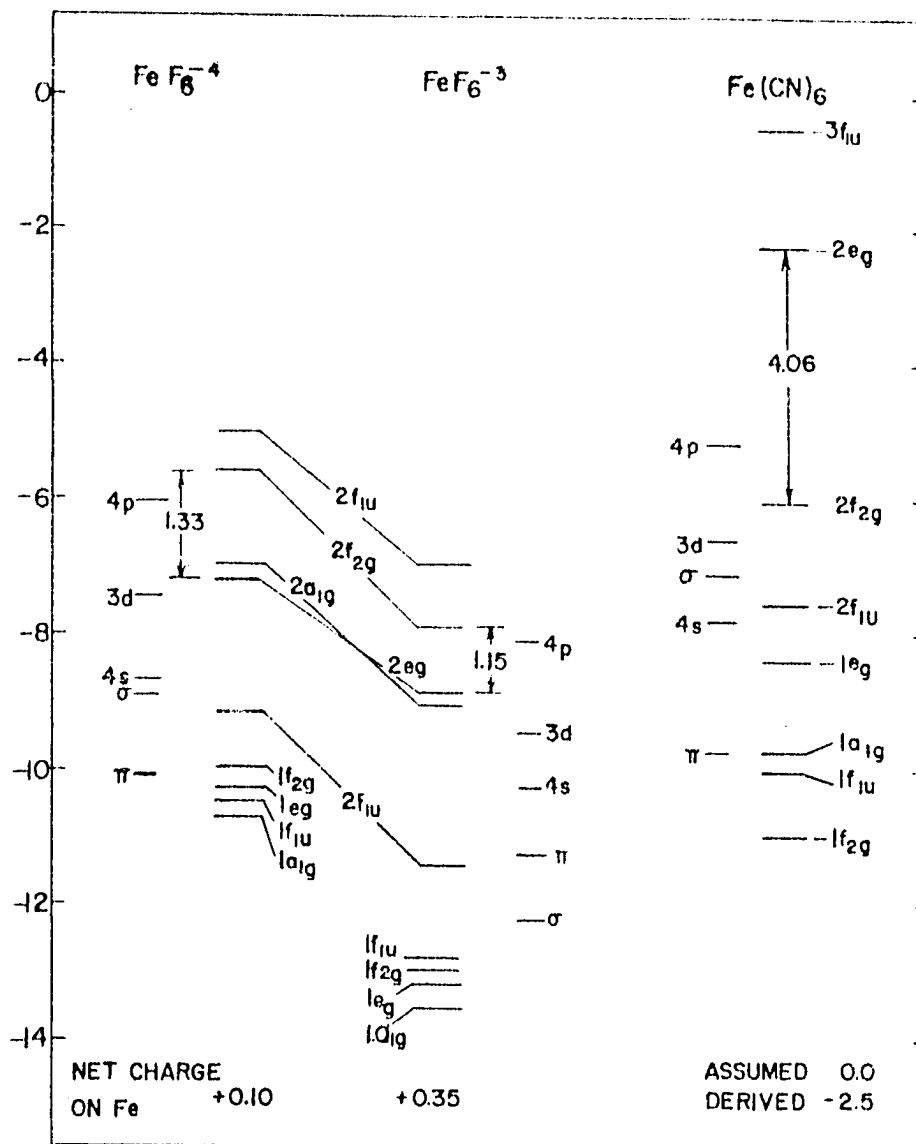
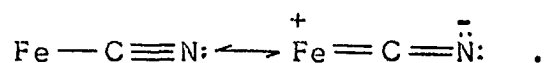


Figure 10. Energy levels calculated for  $\text{FeF}_6^{4-}$ ,  $\text{FeF}_6^{3-}$  and  $\text{Fe}(\text{CN})_6$  by the Wolfsberg and Helmholz approach

metal. More properly, the secular equation should be expanded to include the independent interactions of the C and the N with the metal and with each other. There are two equivalent ways of doing this: (a) form the MO's of the complex from the metal AO's combined with carbon SO's and nitrogen SO's; (b) form the MO's of the complex from the metal AO's combined with SO's formed from the bonding and anti-bonding MO's of the  $\text{CN}^-$  ion. Formally the difference is merely in arranging terms; but the second has advantages in approximating the integrals as well as in interpreting the nature of the interaction.

If one wishes to describe the interaction as between cyanide and iron, and not as among iron, carbon and nitrogen, then it is convenient to choose functions of the cyanide as a whole to combine with the metal. In valence bond resonance theory, this added feature of the interaction in cyanide is indicated by the resonance relationships



The effect in both the MO and the VB descriptions is to remove charge from the iron.

As an illustration of the manner in which this additional interaction operated in the  $\text{Fe}(\text{CN})_6$  system, the  $f_{2g}$  MO levels were derived, both including and excluding interaction with the anti-bonding  $\text{CN}^-$   $\pi$  MO's. Rough calculations indicate that upon including the anti-bonding  $\text{CN}$  MO, the  $2f_{2g}$  level is

lowered in energy by about 2 ev and an extra  $1/5$  electron per  $f_{2g}$  MO is shifted from the metal to the ligand. These figures are magnified five- or six-fold when it is noted that all the odd electrons of the complexes are housed in these MO's (since it is experimentally known that the electrons are as paired up as possible).

Similar considerations apply also to the  $\sigma$ -MO systems, except that there the anti-bonding  $\sigma$ -MO's are concentrated farther from the metal, on the nitrogen. Hence, overlap with them will be appreciably smaller and the importance of interaction with the anti-bonding state will be less in the  $e_g$  than in the  $f_{2g}$  MO's.

### C. Comments on the Results

The usefulness of the Wolfsberg and Helmholz method, as applied here to transition-metal complexes, lies in giving a quantitative flavor to the qualitative MO considerations advanced earlier. What it offers, really, is a means of assessing the extent of interaction between metal and ligand in a MO correlation diagram. The  $H(i,i)$  terms are seen to be obtained in a fashion strongly related to Mulliken's (96) suggestion for setting up a scale of absolute electronegativities; while the overlap integral effect upon bond strengths is incorporated into the  $H(i,j)$  terms. Thus this approach would seem to go a step beyond the ideas of Craig et al. (6). How much beyond, however, is questionable.

In systems where there are no local concentrations of excess charge, such as in neutral diatomic molecules or perhaps even in  $\text{MnO}_4^-$ , the approximations derived may have some justification in theory. In systems such as many transition-metal complexes, it is expected that local charge excesses will occur. Then the coulomb effects of those excesses must become important. In particular, for the fluoride complex, the partial negative charge on the fluorides must raise the  $2e_g$  level with respect to the  $2f_{2g}$  level,<sup>a</sup> probably even to reverse the order determined.

Such coulomb effects must be of extreme importance in the discussion of transition-metal complexes in general. Since, however, there is no opportunity in the Wolfsberg and Helmholz approximations for introducing coulomb effects from local charge concentrations, this method was abandoned. Although it is not fair to imply that no useful conclusions can be drawn from the treatment, none will be indicated here.

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<sup>a</sup>In crystalline field theory, this electrostatic interaction provides the entire source of splitting of the 3d orbitals.

VI. LCAO MO SELF-CONSISTENT FIELD TREATMENT  
OF  $\text{Fe}(\text{NH}_3)_6^{+3}$  AND  $\text{FeF}_6^{-3}$

A. Introduction

There is a major step from a simple MO treatment of the electronic structure of molecules to any sort of rigorous quantum mechanical calculation of the properties of those systems. It is well known that the simple molecules and conjugated hydrocarbons have been treated with varying degrees of preciseness; this particular subject is adequately reviewed elsewhere and will not be considered here. The logical extension of the numerical Hartree-Fock SCF method developed for atoms breaks down in application to molecular systems, since molecules are not spherically symmetric and the calculations become exceedingly difficult and complex on that account.

Within the framework of the LCAO MO theory, however, there remains a possibility for introducing self-consistency. This step was completed by Roothaan (97), and the LCAO MO SCF theory is presently considered to be the best purely theoretical approximation method for computing molecular properties. Details of the SCF theory are given by Roothaan (97); practical aspects of the application to actual computations are given by Mulligan (98) in his treatment of  $\text{CO}_2$ . References to published treatments of other molecular problems have recently been given by Scherr (99). Thus these subjects will be



considered here only in the context of the application of the method to  $\text{Fe}(\text{NH}_3)_6^{+3}$  and  $\text{FeF}_6^{-3}$ .

Roothaan's SCF procedure itself is comparatively simple to execute. The major obstacle to the full exploitation of the method comes in the necessity for accurately computing the large numbers of complicated integrals which occur even in the simple diatomic molecules. It is presently believed that once the most efficient methods for the integral calculations have been derived and programmed for high-speed electronic computers, purely theoretical treatments of the larger molecules will become tractable.

In the absence of exact calculation of all molecular integrals, there have been a large number of LCAO MO SCF treatments containing one or more simplifications. These simplifications include (a) neglect of inner shell electrons, (b) neglect or approximate calculation of certain integrals and (c) empirical evaluation of other integrals, or groups of integrals, by experimental measurements, such as atomic spectra. The greater the complexity of the electronic system, the greater the need for simplifications.

Use of such simplifications has been classed as semi-empirical theory by Mulliken. One semi-empirical LCAO MO SCF scheme has been investigated extensively by Pariser and Parr (100,101,102) for analysis of the  $\pi$ -electron systems of conjugated hydrocarbon molecules. Extensions to hetero- systems have been advanced by them (103) and by Kon (104).

Particularly relevant to the present discussion is the calculation of some electronic levels of  $\text{SF}_6$  by Duncan (105). Actually his calculations are purely theoretical except for the neglect of inner-shell-valence shell interactions, and for other approximations regarding the calculation of integrals. A detailed qualitative discussion of this whole general problem has been given by Mulliken (94).

The line of attack followed in this chapter is to examine the LCAO MO SCF energy expression in all its detail for the particular electronic systems under consideration. Approximations of the type indicated above are then introduced, eliminating certain kinds of integrals and allowing the estimation of large groups of terms by means of ionization potentials. The development of the final energy terms appearing in the secular equations of the MO problem follows roughly the discussion of Mulliken.

During the course of the development, the basis for the Wolfsberg and Helmholtz approximation becomes apparent as well as the reasons for its deficiencies. But more important, it is believed that a reliable theoretical framework for discussing the electronic structure of transition-metal complexes is established. In particular, the influence upon the bonding MO's of the unpaired anti-bonding electrons (heretofore completely neglected in all previous discussions of these complexes) will be investigated.

During the theoretical development, it is necessary to introduce a number of symbols; for convenience, they are collected and identified in the Glossary.

## B. The Fock Operator

### 1. Definition of the molecular spin orbitals

For reasons that will become apparent below, it is necessary to begin this part of the study of transition-metal complexes by further specifying the MO's to be used for the calculations. Each of the MO's previously derived and discussed is, it will be recalled, merely the space part of the complete one-electron wave function,  $\lambda$ , (by Roothaan (97) called the Molecular Spin Orbitals (MSO's)) which describe the spin as well as the space distribution of a particular electron. If it is assumed that the orbital motion of an electron is separable from the spin, then the MSO's are factorable into a space part (the MO  $\varphi$ ) and a spin part ( $\eta$ ):

$$\lambda = \varphi \eta$$

The spin function  $\eta$  has only the two eigenvalues:  $m_s = + 1/2$  and  $m_s = - 1/2$ . If  $\varphi$  and  $\eta$  are normalized then  $\lambda$  is also.

It is really the  $\lambda$ 's which are of fundamental importance in the theory of molecular electronic structure. But, since the spin function can frequently be considered immediately and thereafter explicitly neglected (with certain restrictions), the usual theoretical development proceeds in terms of the  $\varphi$ 's.

In the formal discussion which follows, it is necessary to adopt conventions regarding the ordering of the  $\lambda$ 's and the  $\varphi$ 's.  $\lambda$ 's will be identified as  $\lambda_k$  ( $k \geq 1$ ). The scheme of ordering is given in Table 7. Notice that each MO and each SO may be numbered according to the MSO to which it belongs; this convention is adopted. Thus there will be two MSO's and two MO's associated with every MO species; it will be found that, in general, these two associated MO's are not necessarily identical. The further convention is adopted that the  $\lambda$ 's with  $k$  odd will describe electrons with  $m_s = +1/2$  and those with  $k$  even will describe electrons with  $m_s = -1/2$ .

## 2. Form of the Fock operator

(a) General development. The general development of the energy operator appropriate to the SCF approach to molecular theory has been given in rigorous and rather detailed form by Roothaan (97). It will be necessary, however, for purposes of the present treatment, to generalize his discussion slightly. Departures from the general scheme are minor and quite obvious, so that only the necessary outline will be given here.

In the discussion which follows, electronic coordinates will be specified by  $\mu$  and  $\nu$ ; MSO's and MO's will be identified by subscripts  $i$ ,  $j$  and  $k$ .  $d\tau(\mu)$  will be the volume element in the four-dimensional (real plus spin) space of the  $\mu^{\text{th}}$  electron.  $dv(\mu)$  will be the volume element in real space.

For the general molecular problem, the usual  $N$ -electron Hamiltonian operator is written:

$$H = \frac{1}{2} \sum_{\mu} \nabla_{\mu}^2 - \sum_{a,\mu} \frac{z_a}{r_{a\mu}} + \sum_{\mu\nu} \frac{1}{r_{\mu\nu}} = \sum_{\mu} H^c(\mu) + \sum_{\mu\nu} \frac{1}{r_{\mu\nu}}, \quad (1)$$

where  $z_a$  is the charge on the  $a^{\text{th}}$  nucleus and  $r_{a\mu}$  is the distance of the  $\mu^{\text{th}}$  electron from the  $a^{\text{th}}$  nucleus. The summations here are over all  $N$  electrons and all nuclei of the system.

The total electronic energy,  $E$ , of the system is obtained from

$$E = \iint \dots \bar{\Lambda} H \Lambda d\tau(\mu) d\tau(\nu) \dots, \quad (2)$$

in which  $\Lambda$  is the antisymmetrized product of all occupied MSO's  $\lambda_i$ .

For any closed shell<sup>a</sup> structure and also for certain other electronic states,  $\Lambda$  is expressible as a single determinant (Slater determinant). For these cases it is found by direct expansion of Equation 2 that

$$E = \sum_i H_i + \sum_{i,j} (J_{ij} - K_{ij}) \quad (3)$$

where the summations are over all  $N$  MSO's.

Formally, Equation 3 is identical to

$$E = \sum_i \left\{ H_i + \sum_j (J_{ij} - K_{ij}) \right\} = \sum_i E_i \quad (4)$$

---

<sup>a</sup>Roothaan (97, p.71) defines an electron shell "as a set of MSO's, in which (1) every MO occurs twice, namely, once with either spin, and (2) if there is degeneracy on account of the molecular symmetry, the MO's in the shell form a complete degenerate set. Accordingly, a closed-shell structure refers to an antisymmetrized product which is made up of complete electron shells."

Table 7. Ordering of the molecular spin orbitals.

$$\lambda_k = \varphi_k \eta_k = (a_k \chi_n + b_k \sigma_n + c_k \pi_n) \eta_k$$

The n's refer to the numberings given in Table 2.

B = bonding, N = non-bonding, A = anti-bonding.

Just one of the MSO's of a symmetry class are given. The spin function has been omitted.

For complex ions in which  $\pi$ -type interactions are not considered:

- a) there are no  $\pi$  SO's present in the forms of  $\varphi_k$ .
- b) the MSO's for  $20 \leq k \leq 43$  are not present.
- c)  $f_{2g}$  B becomes  $f_{2g}$  N.

Note a: These MSO's include the remaining valence shell orbitals not specifically incorporated into the secular equations. They are formed from the hybrid AO's orthogonal to the  $\psi$  functions and will be considered non-binding. See Table 2.

Note b: These MSO's include all orbitals not otherwise accounted for.

Table 7. Ordering of the molecular spin orbitals.

$$\lambda_k = \varphi_k \eta_k = (a_k \chi_n + b_k \sigma_n + c_k \pi_n) \eta_k$$

k	n	type	Representative form
1-2	1	$a_{1g}$ B	$a(4s) + b(\sigma_1)$
3-8	2,3,4	$f_{1u}$ B	$a(4p_x) + b(\sigma_2) + c(\pi_2)$
9-12	5,6	$e_g$ B	$a(d_{z^2}) + b(\sigma_5)$
13-18	7,8,9	$f_{2g}$ B	$a(d_{xy}) + c(\pi_7)$
19-24	10,11,12	$f_{2u}$ N	$\pi_{10}$
25-30	13,14,15	$f_{1g}$ N	$\pi_{13}$
31-36	2,3,4	$f_{1u}$ B	$a(4p_x) + b(\sigma_2) + c(\pi_2)$
37-42	7,8,9	$f_{2g}$ A	$a(d_{xy}) + c(\pi_7)$
43-46	5,6	$e_g$ A	$a(d_{z^2}) + b(\sigma_5)$
47-48	1	$a_{1g}$ A	$a(4s) + b(\sigma_1)$
49-54	2,3,4	$f_{1u}$ A	$a(4p_x) + b(\sigma_2) + c(\pi_2)$
55-56		N	see note a, p. 95
67			see note b, p. 95

In Equations 3 and 4<sup>b</sup>

$$H_i = \int \bar{\lambda}_i(\mu) H^c \lambda_i(\mu) d\tau(\mu) = \int \bar{\varphi}_i(\mu) H^c \varphi_i(\mu) dv(\mu) \quad (5)$$

$$\begin{aligned} J_{ij} &= \bar{J}_{ij} = J_{ji} = \bar{J}_{ji} \\ &= \int \bar{\lambda}_i(\mu) \lambda_i(\mu) \frac{1}{r_{\mu\nu}} \bar{\lambda}_j(\nu) \lambda_j(\nu) d\tau(\mu) d\tau(\nu) \\ &\equiv [\bar{\varphi}_i \varphi_i | \bar{\varphi}_j \varphi_j] = \int \bar{\varphi}_i(\mu) \varphi_i(\mu) \frac{1}{r_{\mu\nu}} \bar{\varphi}_j(\nu) \varphi_j(\nu) dv(\mu) dv(\nu) \end{aligned} \quad (6a)$$

$$\begin{aligned} K_{ij} &= \bar{K}_{ij} = K_{ji} = \bar{K}_{ji} = \int \bar{\lambda}_i(\mu) \lambda_j(\mu) \frac{1}{r_{\mu\nu}} \bar{\lambda}_j(\nu) \lambda_i(\nu) d\tau(\mu) d\tau(\nu) \\ &= \int \bar{\varphi}_i(\mu) \varphi_j(\mu) \frac{1}{r_{\mu\nu}} \bar{\varphi}_j(\nu) \varphi_i(\nu) dv(\mu) dv(\nu) \left. \begin{array}{l} \text{for spin } i \\ \text{for spin } j \end{array} \right\} \quad (6b) \\ &\equiv [\bar{\varphi}_i \varphi_j | \bar{\varphi}_j \varphi_i] \\ &= 0 \quad \text{for spin } i \neq \text{spin } j. \end{aligned}$$

In Equations 5, 6a and 6b, use is made of the orthogonality properties of the spin functions  $\eta$ , which are contained in Equation 7:

$$\begin{aligned} \int \bar{\lambda}_i \lambda_j d\tau &= \int \bar{\lambda}_i \bar{\eta}_i \lambda_j \eta_j d\tau = \int \bar{\varphi}_i \varphi_j dv \quad \text{spin } i = \text{spin } j \\ &= 0 \quad \text{spin } i \neq \text{spin } j \end{aligned} \quad (7)$$

Equation 4 suggests that the total energy  $E$  can be expressed as a sum of one-electron energies  $E_i$ , which are

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<sup>b</sup> The definition of the general electrostatic interaction integrals,  $[\bar{\varphi}_j \varphi_j | \bar{\varphi}_i \varphi_i]$  and  $[\bar{\varphi}_i \varphi_i | \bar{\varphi}_j \varphi_j]$ , is in accordance with the proposals of Ruedenberg, Roothaan and Jaunzemis (106). Only a slight departure from their conventions will be made here: a point charge at center  $c$ , say, will be indicated by a delta function,  $\delta_c$ . The physical interpretation of  $[\bar{\varphi}_j \varphi_j | \bar{\varphi}_i \varphi_i]$ , for example, is "the magnitude of the electrostatic interaction between charge distributions  $(\bar{\varphi}_j \varphi_j)$  and  $(\bar{\varphi}_i \varphi_i)$ ."



derived from integration of one-electron energy operators operating upon one-electron wave functions: that is,

$$E_i = \int \bar{\lambda}_i(\mu) F(\mu) \lambda_i(\mu) d\tau(\mu) \quad (8)$$

Such is indeed the case; the formal development parallels that given, e.g., by Roothaan (97) and will not be repeated here.  $F(\mu)$  will be called the Fock operator and is defined by

$$F(\mu) = H^c(\mu) + \sum_j \left\{ [\bar{\lambda}_j(\nu) \lambda_j(\nu)] - [\bar{\lambda}_j(\nu) \cdot | \lambda_j(\nu)] \right\} . \quad (9)$$

The coulomb operators  $[\bar{\lambda}_j \lambda_j]$  and the exchange operators  $[\bar{\lambda}_j \cdot | \lambda_j]$  are defined by their operational effect upon some MSO  $\lambda_i$  by<sup>a</sup>

$$\begin{aligned} \{[\bar{\lambda}_j(\nu) \lambda_j(\nu)]\} \lambda_i(\mu) &= \left\{ \int \bar{\lambda}_j(\nu) \lambda_j(\nu) \frac{1}{r_{\mu\nu}} d\tau(\nu) \right\} \lambda_i(\mu) \\ \text{or } \{[\lambda_j \lambda_j]\} \lambda_i &\equiv [\bar{\lambda}_j \lambda_j] \lambda_i ; \end{aligned} \quad (10a)$$

$$\begin{aligned} \text{and } \{[\bar{\lambda}_j(\nu) \cdot | \lambda_j(\nu)]\} &= \left\{ \int \bar{\lambda}_j(\nu) \lambda_j(\nu) \frac{1}{r_{\mu\nu}} d\tau(\nu) \right\} \lambda_j(\mu) \\ \text{or } \{[\lambda_j \cdot | \lambda_j]\} \lambda_i &= [\bar{\lambda}_i \lambda_j | \lambda_j] \text{ if spin } i = \text{spin } j \quad (10b) \\ &= 0 \text{ if spin } i \neq j . \end{aligned}$$

When Equations 10a and 10b are substituted into Equations 9, and Equation 9 into Equation 8, there results

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<sup>a</sup>

This form for the exchange and coulomb operators is here introduced for the first time. It supplements nicely the conventions of Ruedenberg, Roothaan and Jaunzemis (106), and is convenient for later use.

$$E_i = H_i + \sum_j (J_{ij} - K_{ij}) \quad (11)$$

which, when summed over  $i$ , verifies Equation 4. This justifies the choice of the Fock operator.

(b) Specialization for half-filled shells. The discussion presented above applies only to those antisymmetrized product wave functions which can be written in the form of a single (Slater) determinant. The closed shell structures are such cases, as are also the half-filled shell structures, if the spin degeneracy is not considered. In effect, this restriction means that the equation developed may be applied only to molecular states which are orbitally non-degenerate within the symmetry of the molecule. For degenerate cases, it is necessary to include additional exchange terms. It has been seen that the ferric complexes with five unpaired spins have the ground state  ${}^6A_{1g}$ ; this is one of the reasons why ferric complexes were selected for detailed treatment in this thesis.

The nature of the relation of the determinantal method to the Hartree-Fock scheme has been discussed by e.g., Slater (55), Lowdin (107, 108) and Roothaan (97). Recently a new method for generalizing the Hartree-Fock scheme for degenerate systems has been presented by Lowdin (109). It is worth pointing out, however, that if the Jahn-Teller effect is sufficiently pronounced, then orbital degeneracy problems will not occur in cases of experimental interest, at least for the transition-metal complexes and other non-linear molecules.

For closed shell states there are, by definition, as many electrons with plus spins as there are with minus spin. Thus it obtains, making recognition of Equation 10b, that

$$E_i = H_i + 2 \sum J_{ij} - \sum K_{ij} \quad (\text{sum here over } \underline{MO} \text{ species}). \quad (12)$$

If on the other hand, there is present in the total electronic system one or more half-filled shells, there will be more  $K_{ij}$  terms corresponding to one than to the other. Accordingly it is advantageous to introduce a further convention in specifying  $E_i$  which includes the requirements of Equations 10a and 10b:

$$E_i = H_i + \sum_j J_{ij} - \sum_j^s K_{ij} \quad (13)$$

where the superscript  $s$  indicates that the summation is to proceed over  $j$  even only or over  $j$  odd only, that is, according to whether the  $j^{\text{th}}$  MSO is of minus spin ( $s = -$ ) or of plus spin ( $s = +$ ) respectively. Similarly, the Fock operator is defined

$$F^s(\mu) = H^c(\mu) + \sum_j [\phi_j \phi_j] - \sum_j^s [\phi_j \cdot | \phi_j] \quad (14)$$

Thus it is immediately apparent that when the exchange terms are properly accounted for, the two MSO's derived from a particular MO species are no longer degenerated in a molecule or atom having unpaired electrons.

Specifically, using  $\text{FeF}_6^{-3}$ , say, as an example, this means that every doubly occupied bonding and non-bonding MO of the

complex is split into two non-degenerate levels, one for each spin. Furthermore, it develops that within each MO the electron whose spin is parallel to the net spin of the whole complex is distributed differently from the electron whose spin is antiparallel. The differences are determined from solution of the requisite secular equations.

It is in this connection, then, that the SCF calculations of Wood (77) upon atomic iron are particularly relevant to the present discussion; he has indeed found that the radial wave functions for the electrons of one spin are different from those of the opposite spin.

(c) Magnetic effects. At this stage of the development, one important class of interactions has been neglected, namely, the spin and orbit interactions and all their manifestations which yield many of the interesting properties of transition-metal complexes. This omission is necessary, in order to allow the factoring out of the spin part of the MSO. Such interactions are considered as perturbations upon the set of zero-order wave functions and energies to be derived for the molecular system. The theory of the spin-orbit and other magnetic perturbations has already been worked out by writers on the crystalline field theory. It has been pointed out, that because of the one-to-one correspondence between the MO and crystalline field approaches, there is a formal equivalence between the calculations of both in regard to the 3d levels. Therefore, these further effects will not be specifi-

cally considered in this thesis.

(d) The self-consistency procedure. If the molecule under consideration possesses sufficient symmetry so as to completely determine all the coefficients in the LCAO MO's,  $\phi_j$ , then all terms in  $F$  which depend upon the  $\phi$ 's (the exchange and coulomb operators) are fixed, and the energy of the  $j^{\text{th}}$  MO is found directly from

$$E_j = \int \lambda_j F \lambda_j d\tau = \int \phi_j F^S \phi_j dv . \quad (15)$$

If, on the other hand, the MO's under consideration (as in all transition-metal complexes) contain undetermined coefficients, the usual variational calculation must be performed, resulting in the familiar secular equation already discussed. In the present case, however, not only does  $\phi_j$  contain variable parameters, but so also does  $F^S$ , since it contains terms (the exchange and coulomb operators) depending upon those same parameters. Thus a self-consistent procedure is necessary, wherein a set of coefficients is assumed, the  $F^S$  evaluated and the resulting secular equation solved to derive a new set of coefficients. These form the basis for a new choice of  $F^S$ . The process is repeated until the calculated and assumed coefficients agree satisfactorily.

It is to be emphasized again that, with half-filled shells electronic states as in  $\text{FeF}_6^{-3}$ , there will be one set of secular equations corresponding to MSO's of plus spins and another set corresponding to those of minus spins.

### 3. Simplification of the Fock operator

It is convenient to introduce approximations into the problem in two stages, first into the Fock operator and then into the final energy expressions. The first step will now be taken; the next will be considered in the section following.

(a) Expansion of the Fock operator. If the  $F^S$  of Equation 14 is assumed, then the spin conditions upon Equations 10a and 10b are satisfied and the coulomb and exchange operators become

$$\{[\bar{\varphi}_j(\nu)\varphi_j(\nu)]\} \varphi_i(\mu) = \left\{ \int \bar{\varphi}_j(\nu)\varphi_j(\nu) \frac{1}{r_{\mu\nu}} d\nu(\nu) \right\} \varphi_i(\mu) \quad (16a)$$

$$\{[\bar{\varphi}_j(\nu) \cdot |\varphi_j(\nu)]\} \varphi_i(\mu) = \left\{ \int \bar{\varphi}_i(\nu)\varphi_j(\nu) \frac{1}{r_{\mu\nu}} d\nu(\nu) \right\} \varphi_j(\mu) \quad (16b)$$

In the molecular problem at hand, the  $\varphi$ 's are real MO's which have been approximated in LCAO form. Thus the coulomb and exchange operators are reducible ultimately to other operators of similar form but containing only AO's. For simplicity, and only for the present, it will be assumed that each MO of the system can be constructed from only one or two SO's. Extensions to more complicated MO's will appear obvious.

For convenience and brevity, the coulomb and exchange operators will be abbreviated

$$[\varphi_j(\nu)\varphi_j(\nu)] \equiv [\varphi_j\varphi_j] \quad (17a)$$

$$[\varphi_j(\nu) \cdot |\varphi_j(\nu)] \equiv [\varphi_j \cdot |\varphi_j] \quad (17b)$$

Thus the coulomb and exchange integrals, Equations 6a and 6b may be written again

$$\int \varphi_i \{ [\varphi_j \varphi_j] \} \varphi_i dv = [\varphi_j \varphi_j | \varphi_i \varphi_i] \quad (18a)$$

$$\int \varphi_i \{ [\varphi_j \cdot | \varphi_j] \} \varphi_i dv = [\varphi_j \varphi_i | \varphi_j \varphi_i] \quad (18b)$$

Now setting  $\varphi_j = a_j \chi_j + b_j \rho_j$ , the coulomb and exchange operators in  $F^S$ , Equation 14, are easily expanded so that  $F^S$  becomes

$$\begin{aligned} F^S &= H^C + \sum_j [\varphi_j \varphi_j] - \sum_j^s [\varphi_j \cdot | \varphi_j] \quad (14) \\ &= H^C + \sum_j \{ a_j^2 [\chi_j \chi_j] + b_j^2 [\rho_j \rho_j] + 2a_j b_j [\chi_j \rho_j] \} \\ &\quad - \sum_j^s \{ a_j [\chi_j \cdot | \chi_j] + b_j^2 [\rho_j \cdot | \rho_j] + 2a_j b_j [\chi_j \cdot | \rho_j] \}. \end{aligned} \quad (19)$$

If the  $\rho$ 's themselves are combinations of AO's (as in most MO's of the transition-metal complexes), then further reduction is necessary. This is only a slight complication, and ignoring it for the present will not affect the validity of the remainder of the discussion.

(b) The Mulliken approximation. The whole subject of approximation techniques in molecular quantum mechanical problems has recently been reviewed critically by Ellison (110). Of all the available methods, most use will be made of Mulliken's for three reasons: (a) it is a widely accepted method, (b) it allows further useful approximations to be made

and (c) its application leads to interpretations of chemical utility.

If  $u_a, u_b, u_c$  and  $u_d$  are  $\Delta O$ 's at centers a, b, c, d, respectively, then the integral  $[u_a u_b | u_c u_d]$  is approximated, according to Mulliken's method, by

$$[u_a u_b | u_c u_d] \simeq \frac{S(u_a, u_b)}{2} \{ [u_a^2 | u_c u_d] + [u_b^2 | u_c u_d] \} \quad (20)$$

$$\simeq \frac{S(u_a, u_b) S(u_c, u_d)}{4} \times$$

$$\{ [u_a^2 | u_c^2] + [u_a^2 | u_d^2] + [u_b^2 | u_c^2] + [u_b^2 | u_d^2] \} \quad (21)$$

Equation 20 may be rewritten

$$[u_a u_b | u_c u_d] \simeq [S(u_a, u_b) \left\{ \frac{u_a^2}{2} + \frac{u_b^2}{2} \right\} | u_c u_d] \quad (22)$$

That is, in calculating electrostatic effects by Mulliken's approximation, a charge distribution  $(u_a u_b)$  is equally divided between the two charge distributions  $u_a^2$  centered on a and  $u_b^2$  centered on b, the total magnitude of the charge distribution  $(u_a u_b)$  being equal to the overlap integral,  $S(u_a, u_b)$ .

Turning back to the cross term in the coulomb operators  $[\chi_j \rho_j]$ ,  $(\chi_j \rho_j)$  represents just such a charge distribution as  $(u_a u_b)$ . Therefore, it will be approximated as above described. Although no similar argument is possible to approximate the cross term in the exchange operators, it is exceedingly tempting to effect an analogous reduction of them. The error



introduced is of uncertain magnitude, and could of course be assessed only by actual computation. In the complete absence of such calculations, the choice of Mulliken (94) will be made here also:

$$[\chi_j \cdot | \rho_j] \approx \frac{G(\chi_j, \rho_j)}{2} \{ [\chi_j \cdot | \chi_j] + [\rho_j \cdot | \rho_j] \} \quad (23)$$

Making these substitutions into Equation 19, there is obtained

$$\begin{aligned} F^S = H^C + \sum_j \{ \underline{a}_j^2 [\chi_j \chi_j] + \underline{b}_j^2 [\rho_j \rho_j] \} \\ - \sum_j^S \{ \underline{a}_j^2 [\chi_j \cdot | \chi_j] + \underline{b}_j^2 [\rho_j \cdot | \rho_j] \} \end{aligned} \quad (24)$$

where

$$\begin{aligned} \underline{a}_j^2 &= a_j^2 + a_j b_j G(\chi_j, \rho_j) \\ \underline{b}_j^2 &= b_j^2 + a_j b_j G(\chi_j, \rho_j) \end{aligned} \quad (25)$$

(c) The simplified Fock operators. Taking  $F^S$  to represent the Fock operator for the complex molecule  $ML_6$ , the operators in Equation 24 may now be interpreted in terms of their physical significance.  $F^S$  represents the total energy of one electron associated with  $ML_6$ ; it is composed of the following kinetic and potential energy terms:

Kinetic	Potential	Potential	Exchange
	energy	energy due	energy due
	+ due to	+ to electrons	+ to electrons
	nucleus	associated	associated
energy	of M	with M	with M

$$\begin{array}{rcl}
 \text{Potential} & & \text{Potential} & & \text{Exchange} \\
 \text{energy due} & & \text{energy due} & & \text{energy due} \\
 + \text{ to six} & + & + \text{ to electrons} & + & + \text{ to electrons (26)} \\
 \text{nuclei of} & & \text{associated} & & \text{associated} \\
 \text{L} & & \text{with the six} & & \text{with the six} \\
 & & \text{L} & & \text{L}
 \end{array}$$

The electrons associated with the metal atom are given by the  $a_j^2$  coefficients; whereas those associated with the ligand atoms are obtained from the  $b_j^2$  coefficients.

The sum of the first four terms is equivalent to the Fock operator for a metal atom with electronic configuration given by the  $a_j^2$ . Call this operator  $F_M^S$ . Extracting all the terms from  $F^S$ , Equation 24, which belong also in  $F_M^S$  there is obtained

$$F^S = F_M^S + U_L \quad (27)$$

where<sup>a</sup>

$$U_L = \sum_j b_j^2 [\rho_j \rho_j] - \sum_j^s b_j [\rho_j \cdot |\rho_j - \frac{1}{Z_L} \sum_{\pm} \delta_{\pm}] \quad (28)$$

and  $Z_L$  is the nuclear charge of the ligand atom. Similarly,  $Z_M$  will be the nuclear charge of the metal.

Furthermore,  $\rho_j \rho_j$  is the charge distribution within the  $j^{\text{th}}$  ligand SO.

Since the discussion is limited to totally symmetric electronic states, it necessarily follows that the sum over

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<sup>a</sup> Notice that the subscripts on the ligand AO's (corresponding to the index  $\pm$ ) indicate the position of the AO around the metal (according to the convention of Table 2) and not to the numbering of the MSO's. There is no need for confusion, which only a third alphabet would eliminate, if it is remembered that there is no occasion to identify particular ligand AO's with MSO's.

all  $\rho_j \rho_j$  produces a net charge distribution which is also totally symmetric. Thus, as is immediately obvious, equal charge densities are associated with each ligand atom. Hence, the electronic configuration of each of the six ligand atoms is given by the numbers  $\frac{1}{6}b_j^2$ , if overlap charge distributions such as  $K_1 K_2$  (which arise from the expansion of  $\rho_j \rho_j$ ) are neglected. Actually, these overlap functions are quite small indeed for the systems to be investigated.

Except for similarly specifying the exchange operators  $[\rho_j \cdot | \rho_j]$ , it is now clear that terms may also be extracted from  $F^S$  which form the Fock operator for an isolated ligand atom, say ligand atom numbered one. Call this operator  $F_L^S$ . In analogy with Equation 27 there is obtained

$$F^S = F_L^S + U_M + \sum_{\pm > 1} U_{\pm} \quad (29)$$

where

$$U_M = \sum_j \underline{a}_j^2 [\chi_j \chi_j] - \sum_j^S \underline{a}_j^2 [\chi_j \cdot | \chi_j] + Z_M [\delta_M] \quad (30)$$

and

$$U_{\pm} = (1/6) \sum_j \underline{b}_j^2 [K_{\pm} K_{\pm}] - Z_L [\delta_{\pm}] + \begin{array}{l} \text{exchange operator} \\ \text{yet to be investi-} \\ \text{gated.}^a \end{array} \quad (31)$$

Equations 27 to 31 specify the simplified Fock operator to be used in the remainder of the discussion.

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<sup>a</sup> See page 119.

### C. Expansion of the Energy Integrals

#### 1. General considerations

Hereafter, the discussion will specifically consider only the MO's derived from valence-shell AO's. Thus the MO's will be given according to Table 2, and numbered according to previously established conventions, i.e., odd numbered MO's are occupied by electrons with plus spins and even numbered MO's by minus spins.

For the ground states of the complex ions  $\text{FeF}_6^{-3}$  and  $\text{Fe}(\text{NH}_3)_6^{+3}$  the occupied MO's are:

- (a) the inner shell AO's
- (b) all bonding and non-bonding MO's as listed in Table 2
- (c) the odd-numbered anti-bonding  $e_g$  and  $f_{2g}$  MO's.

The coefficients in the normalized  $k^{\text{th}}$  MO

$$\phi_k = a_k \chi_k + b_k \sigma_k + c_k \pi_k \quad (32)$$

are determined by the self-consistent minimization of the orbital energy  $E_k$

$$E_k = \int \lambda_k F \lambda_k d\tau = \int \phi_k F^S \phi_k dv, \quad (33)$$

Substituting Equation 32 in Equation 33 gives the general expansion

$$E_k = a_k^2 \int \chi_k F^S \chi_k dv + b_k^2 \int \sigma_k F^S \sigma_k dv + c_k^2 \int \pi_k F^S \pi_k dv \\ + 2a_k b_k \left\{ (1/2) \int \chi_k F^S \sigma_k dv + (1/2) \int \sigma_k F^S \chi_k dv \right\} \quad (34)$$

$$\begin{aligned}
& + 2a_k c_k \left\{ (1/2) \int \chi_k F^S \pi_k dv + (1/2) \int \pi_k F^S \chi_k dv \right\} \\
& + 2b_k c_k \left\{ (1/2) \int \sigma_k F^S \pi_k dv + (1/2) \int \pi_k F^S \sigma_k dv \right\} \\
& = a_k^2 F^S(\chi, \chi) + b_k^2 F^S(\sigma, \sigma) + c_k^2 F^S(\pi, \pi) \\
& + 2a_k b_k F^S(\chi, \sigma) + 2a_k c_k F^S(\chi, \pi) + 2b_k c_k F^S(\sigma, \pi) \quad (35)
\end{aligned}$$

The energy quantities  $F^S(m, n)$  are those which occur in the secular equation

$$\det \left| F^S(m, n) - G(m, n) E \right| = 0 \quad (36)$$

The remaining problem is to expand each of the energy quantities,  $F^S(m, n)$ , into a form which ultimately allows their evaluation in terms of elementary integrals.

It is sufficient to derive here three of the quantities in detail in order to illustrate the expansion and approximation techniques employed. The  $a_{1g}$  MO is selected;  $F^S(4s, 4s)$ ,  $F^S(\sigma, \sigma)$  and  $F^S(4s, \sigma)$  are therefore considered. Final results for the other MO's will then be given.

## 2. Approximation of one-center integrals

Direct use is now made of the two forms for  $F^S$  as given in Equations 27 and 29. Putting

$$F^S(4s, 4s) = \int (4s) F^S(4s) dv = \int (4s) \left\{ F_M^S + U_L \right\} (4s) dv \quad (37a)$$

$$\begin{aligned}
F^S(\sigma, \sigma) &= \int (\sigma) F^S(\sigma) dv \\
&= \int (\sigma) \left\{ F_L^S + U_M + \sum_{\pm > 1} U_{\pm} \right\} (\sigma) dv \quad (37b)
\end{aligned}$$

$$F^S(4s, \sigma) = (1/2) \left\{ \int (4s) F^S(\sigma) dv + \int (\sigma) F^S(4s) dv \right\} \quad (37b)$$

$$= (1/2) \int (4s) \left\{ F_L^S + U_M + \sum_{\pm > 1} U_{\pm} \right\} (\sigma) dv \quad (37c)$$

$$+ (1/2) \int (\sigma) \left\{ F_M^S + U_L \right\} (4s) dv,$$

the energy terms become

$$F^S(4s, 4s) = \int (4s) F_M^S(4s) dv + [(4s)^2 | U_L] \quad (38a)$$

$$F^S(\sigma, \sigma) = \int (\sigma) F_L^S(\sigma) dv + [(\sigma)^2 | U_M + \sum_{\pm > 1} U_{\pm}] \quad (38b)$$

$$F^S(4s, \sigma) = (1/2) \left\{ \int (4s) F_L^S(\sigma) dv + \int (\sigma) F_M^S(4s) dv \right\} \quad (38c)$$

$$+ (1/2) [(4s)(\sigma) | U_M + U_L] + [(4s)(\sigma) | \sum_{\pm > 1} U_{\pm}]$$

Substituting the ligand  $a_{1g}$  SO for  $\sigma$  and taking advantage of the molecular symmetry, it is found that

$$\int (\sigma) F_L^S(\sigma) dv = \int (\psi_1) F_L^S(\psi_1) dv \quad (39)$$

$$\int (4s) F_L^S(\sigma) dv = \sqrt{6} \int (4s) F_L^S(\psi_1) dv \quad (40)$$

$$\int (\sigma) F_M^S(4s) dv = \sqrt{6} \int (\psi_1) F_M^S(4s) dv \quad (41)$$

Now it is presumed that the metal and ligand AO's have been chosen such that they are eigenfunctions of the operators  $F_M^S$  and  $F_L^S$ , respectively. Thus in Equations 39, 40, and 41 those operators may be replaced by their eigenvalues. From Koopman's theorem, these eigenvalues may be approximated by valence state ionization potentials,  $Q^S(4s)$  and  $Q^S(\psi)$ , respectively. Making all these substitutions and integrating when possible,

there is obtained finally

$$F^S(4s, 4s) = Q^S(4s) + [(4s)^2 | U_L] \quad (42a)$$

$$F^S(\sigma, \sigma) = Q^S(\psi) + [(\psi)^2 | U_M + \sum_{\pm > 1} U_{\pm}] \quad (42b)$$

$$F^S(4s, \sigma) = (1/2)G(4s, \sigma) \{ Q(4s) + Q(\psi) \} \\ + \frac{\sqrt{6}}{2} [(4s)(\psi) | U_M + U_1 + 2 \sum_{\pm > 1} U_{\pm}], \quad (42c)$$

where the U's have been defined in Equations 28, 30 and 31.

Essentially what has been done is to approximate all the integrals required to evaluate the one-centered nuclear and electronic interactions by appropriate ionization potentials, which are experimentally known. This approximation tremendously reduces the complexity and tediousness of the calculation. How valid an approximation this is remains to be seen; nevertheless, in view of the difficulties experienced by Duncan (105) in computing the one-center effects in  $SF_6$  and in view of the quite poor results to be obtained thereby, the approximation probably is the best practical one currently available.

At this point one can see the source of the Wolfsberg and Helmholz approach, and at the same time its limitations. They essentially neglect, or give minor importance to the electrostatic (both coulomb and exchange effects in  $F(4s, 4s)$  and  $F(\sigma, \sigma)$ ; but in  $F(4s, \sigma)$  estimate them as some fraction (the  $F^\sigma$  and  $F^\pi$  factors) of the atomic terms. This neglect is partially justifiable if (a) each atom in the molecule is effectively

uncharged, such that the sums of the coulomb potential terms in the U's are relatively small, or (b) any excess charge is rather evenly distributed throughout the molecule, in which event all F's would be shifted by roughly the same amount. Apparently it is this latter situation which prevails in the tetrahedral ions considered by Wolfsberg and Helmholtz.

The remainder of the development of the energy terms involves expansion and simplification of the U's. It is convenient to consider the coulomb part separate from the exchange part. For definiteness, the former will be called  $C(4s,4s)$  and the latter  $K^S(4s,4s)$ . Thus  $F^S(m,n)$  in general will be written

$$F^S(m,n) = \frac{1}{2} G(m,n) \{ Q^S(m) + Q^S(n) \} + C(m,n) - K^S(m,n) \quad (43)$$

Notice that  $C(m,n)$  is independent of the spin of the electron under consideration.

### 3. Expansion of the coulomb terms, $C(m,n)$

(a) Expansion of  $C(4s,4s)$ . From Equations 28 to 31 plus the inclusion of  $\pi$ -SO's it appears directly that

$$C(4s,4s) = \sum_j [ \underline{b}_j^2 \psi_j^2 + \underline{c}_j^2 \xi_j^2 ] (4s)^2 - 6Z_L [ \delta_1 | (4s)^2 ] \quad (44)$$

Having assumed that inner shells will be neglected,  $Z_L$  must now be taken as the core charge of each ligand atom.

(b) Expansion of  $C(\sigma,\sigma)$ . Similarly, it is directly shown



that

$$\begin{aligned}
 C(\sigma, \sigma) = & \sum_j a_j^2 [\chi_j^2 | \psi_1^2] - [Z_M \delta_M + Z_L \sum_{\pm > 1} \delta_{\pm} | \psi_1^2] \\
 & + \frac{1}{6} \sum_{\pm > 1} \left[ \left( \sum_j b_j^2 \right) \psi_{\pm}^2 + \left( \sum_j c_j^2 \right) \xi_{\pm}^2 | \psi_1^2 \right]
 \end{aligned} \tag{45}$$

Each summation over  $\pm > 1$  contains four equal contributions from the ligands nearest  $\psi_1$  and one from the ligand diametrically opposed. As with  $Z_L$ ,  $Z_M$  is the core charge of the metal atom.

(c) Expansion of  $C(4s, \sigma)$ . Since  $F^S$  is an hermitian operator and all SO's  $\chi_j$  and  $\rho_j$  are real,  $\int \chi_j F^S \rho_j dv = \int \rho_j F^S \chi_j dv$ ; therefore, the cross terms of the energy expression as given in Equation 34 actually are redundant. In view of the approximations to be made, however, it may be better to consider the form given there. In other words, it seems better to average the two results than to place full weight upon one form or the other.

From Equations 30, 31 and 42c there obtains

$$\begin{aligned}
 C(4s, \sigma) = & \frac{\sqrt{6}}{2} \left\{ \sum_j a_j^2 [\chi_j^2 | (4s) \psi_1] \right. \\
 & - [Z_M \delta_M + Z_L \delta_1 + 2Z_L \sum_{\pm > 1} \delta_{\pm} | (4s) \psi_1] \\
 & + \frac{1}{6} \left[ \left( \sum_j b_j^2 \right) \psi_1^2 + \left( \sum_j c_j^2 \right) \xi_1^2 | (4s) \psi_1 \right] \\
 & \left. + \frac{1}{3} \sum_{\pm > 1} \left[ \left( \sum_j b_j^2 \right) \psi_{\pm}^2 + \left( \sum_j c_j^2 \right) \xi_{\pm}^2 | (4s) \psi_1 \right] \right\}
 \end{aligned} \tag{46}$$

(d) Summary of expansions of coulomb terms for all MO's.

Expansions of all the remaining  $C(m,n)$  for the other MO's proceeds almost as rapidly as for the  $a_{1g}$  MO. For purposes of summarizing, it is convenient to introduce two abbreviations:

$$\Omega_M = \sum_j \bar{a}_{jM}^2 \chi_j^2 - Z_M \delta_M \quad (47a)$$

$$\Omega_{\pm} = (1/6) \sum_j \{ \bar{b}_{j\pm}^2 \psi_{\pm}^2 + \bar{c}_{j\pm}^2 \xi_{\pm}^2 \} - Z_L \delta_{\pm} \quad (47b)$$

$\Omega_M$  is therefore the charge density distribution associated with the metal;  $\Omega_{\pm}$  is similarly defined for the  $\pm^{\text{th}}$  ligand.

The remaining  $C(\chi, \chi)$  are slightly more complicated because the metal AO's other than the 4s do not present the same appearance to every ligand. For instance, the  $4p_z$  AO is  $\sigma$  with respect to ligands 3 and 6, but  $\pi$  with respect to ligands 1, 2, 4, and 5, as an inspection of Figure 3 reveals. Hence, the general expression for  $C(\chi, \chi)$

$$C(\chi, \chi) = \sum_{\pm} [\Omega_{\pm} | \chi^2 ] \quad (48)$$

must be specialized for every symmetry species. The particular forms are obvious from the geometries given in Figure 3. It is convenient to refer all integrals to a single ligand, say 3, and consider the metal AO to be transformed in space.

The derived formulas for the  $C(\chi, \chi)$  are:

$$C(4s, 4s) = 6 [ \Omega_3 | (4s)^2 ] \quad (49)$$

$$C(4p, 4p) = 2[\Omega_3|(4p\sigma)^2 + 2(4p\pi)^2] \quad (49b)$$

$$C(3d\sigma, 3d\sigma) = 3[\Omega_3|(3d\sigma)^2 + (3d\delta)^2] \quad (49c)$$

$$C(3d\pi, 3d\pi) = 2[\Omega_3|(3d\delta)^2 + 2(3d\pi)^2] \quad (49d)$$

Because the metal AO's, for convenience in integration, have been transformed in space, they are now distinguished by their symmetry about the axis between the metal atom and ligand 3; thus in Equations 51a to 51d:  $4p\sigma = 4p_z$ ,  $4p\pi = 4p_x$  or  $4p_y$ ;  $3d\sigma = 3d_{z^2}$ ,  $3d\pi = 3d_{xz}$  or  $3d_{yz}$ ; and  $3d\delta = 3d_{xy}$  or  $3d_{x^2-y^2}$ .

The  $C(\rho, \rho)$  are simpler, the formulas being:

$$Q(\rho, \rho) = [\Omega_M + 2\Omega_1 + 2\Omega_2 + \Omega_6](K_3)^2 \quad (50)$$

The  $C(\chi, \rho)$  are again somewhat complicated like the  $C(\chi, \chi)$ ; they are:

$$C(4s, \sigma) = \sqrt{3/2} [\Omega_M + \Omega_3 + 4\Omega_1 + 2\Omega_6](4s)\psi_3 \quad (51a)$$

$$C(4p\sigma, \sigma) = \sqrt{1/2} [\Omega_M + \Omega_3 + 4\Omega_1 + 2\Omega_6](4p\sigma)\psi_3 \quad (51b)$$

$$C(4p\pi, \pi) = [\Omega_M + \Omega_3 + 4\Omega_1 + 4\Omega_2 + 2\Omega_6](4p\pi)\xi_3 \quad (51c)$$

$$C(3d\sigma, \sigma) = (2/3) \sqrt{3} [\Omega_M + \Omega_3 + 8\Omega_1 + 2\Omega_6](3d\sigma)\psi_3 \quad (51d)$$

$$C(3d\pi, \pi) = [\Omega_M + \Omega_3 + 4\Omega_1 + 4\Omega_2 + 2\Omega_6](3d\pi)\xi_3 \quad (51e)$$

#### 4. Expansion of the exchange terms

Unfortunately, the expansion of the exchange terms proceeds with none of the ease and dispatch of the coulomb term

expansions. Rather, it is necessary to expand each exchange integral in each sum for each MO. However, despite its complexity, the process is merely algebraic. There are no inherent difficulties and no detailed example will be given here. Instead, there will be indicated: (a) the exchange terms as obtained from the energy integral, Equation 33, using the simplified  $F^S$  of Equations 27 and 29; (b) the types of integrals neglected; and (c) the final results of the expansions.

(a) The exchange integrals considered. Again from Equations 28 to 31 after distinguishing between and ligand SO's, it appears directly that, for all MO's,

$$K^S(\chi_k, \chi_k) = \sum_j^S \left\{ \underline{a}_j^2 [\chi_k \sigma_j | \chi_k \sigma_j] + \underline{c}_j^2 [\chi_k \pi_j | \chi_k \pi_j] \right\} \quad (52)$$

$$K^S(\sigma_k, \sigma_k) = \sum_j^S \left\{ \underline{a}_j^2 [\sigma_k \chi_j | \sigma_k \chi_j] + \underline{b}_j^2 [\sigma_k \sigma_j | \sigma_k \sigma_j] + \underline{c}_j^2 [\sigma_k \pi_j | \sigma_k \pi_j] \right\} \quad (53)$$

$$K^S(\pi_k, \pi_k) = \sum_j^S \left\{ \underline{a}_j^2 [\pi_k \chi_j | \pi_k \chi_j] + \underline{b}_j^2 [\pi_k \sigma_j | \pi_k \sigma_j] + \underline{c}_j^2 [\pi_k \pi_j | \pi_k \pi_j] \right\} \quad (54)$$

$$K^S(\chi_k, \rho_k) = \sum_j^S \left\{ \underline{a}_j^2 [\chi_k \chi_j | \rho_k \chi_j] + \underline{b}_j^2 [\chi_k \sigma_j | \rho_k \sigma_j] + \underline{c}_j^2 [\chi_k \pi_j | \rho_k \pi_j] \right\} \quad (55)$$

$$K^S(\sigma_k, \pi_k) = \sum_j^S \left\{ \underline{a}_j^2 [\sigma_k \chi_j | \pi_k \chi_j] + \underline{b}_j^2 [\sigma_k \sigma_j | \pi_k \sigma_j] + \underline{c}_j^2 [\sigma_k \pi_j | \pi_k \pi_j] \right\} \quad (56)$$

It is to be noted that  $K^S(\sigma_k, \sigma_k)$  and  $K^S(\pi_k, \pi_k)$  still contain exchange terms properly belonging in  $Q^S(\psi)$  and  $Q^S(\xi)$ . Their removal will be effected in the next paragraph.

(b) Integrals neglected. Of the exchange integrals contained in Equations 52 to 56, some are assuredly quite small

and may be safely neglected. Some will be shown to belong in the  $Q(k)$  terms. Others are susceptible to the Mulliken or related approximations. But still there remain some integrals for which no approximation techniques are available.

These last-mentioned integrals are of a type such as  $[4s\xi_1|4s\xi_1]$ ; that is, integrals between charge distributions, one or both of which present equivalent positive and negative regions to the other. Since the integral of such distributions (the overlap integral) over all space is identically zero, it is immediately obvious that the Mulliken approximation, Equations 20 and 21, fails. Nevertheless, these exchange integrals are not necessarily zero; in fact, it is possible that a few may be significant. An alternative method for estimating these integrals was suggested by Mulligan (98) for  $CO_2$ . Even there, however, knowledge of the exact values for some of the integrals was necessary in order to establish the validity of the technique. Since the calculation of such exchange integrals as occur in this work would be exceedingly laborious, the decision was made to neglect this sort of integral entirely. Certainly this neglect remains among the lesser approximations of the present treatment.

This approximation eliminates roughly half the terms in  $K^S(\chi_k, \chi_k)$ , all of  $K^S(\sigma_k, \pi_k)$ , and many parts of the other  $K$ 's.

A much better approximation is the neglect of all exchange integrals containing charge distributions such as  $(\psi_1\xi_2)$  or

$(\psi_1 \psi_4)^a$ , which are very small.

Finally, direct expansion and summation of the exchange integrals which are the coefficients of  $b_j^2$  and  $c_j^2$  in Equations 55 and 56 reveal that they are very nearly equal to the exchange integrals which properly occur in  $\int \psi_1 F_L^S \psi_1 dv$  and  $\int \xi_1 F_L^S \xi_1 dv$ ; thus they really belong in  $Q^S(\psi)$  and  $Q^S(\xi)$ . Since these particular terms are the result of the "exchange operators yet to be investigated" in Equation 31,  $U_{\pm}$  is properly defined there without those operators.

(c) Summary of the expansion of the exchange terms for all MO's. For convenience as well as clarity in presenting the results of the expansions, the coefficients of the SO's within each MO will be identified by the irreducible representation symbol, instead of the index of the MSO. Thus, for example, both  $a_9^2$  to  $a_{12}^2$  are replaced by  $a^2(e_g)^b$ ;  $a_3^2$  to  $a_8^2$  are replaced by  $a^2(f_{1u})$ ; etc. Furthermore, it is to be understood here that no explicit notation for the spin state ( $s = +$  or  $-$ )

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<sup>a</sup> See footnote, p. 107.

<sup>b</sup> In this connection, it is noted that Duncan (105) states that the coefficients for the  $d_{z^2}$ -type eg MO are different from those in the  $d_{x^2-y^2}$ -type because of the difference in the shapes of the orbitals. This cannot be so, provided the SO's are each properly normalized, not only because they are degenerate, but also because the MO's must transform under the symmetry operations of the group in exactly the same manner as do the individual SO's. This is impossible if the coefficients are not identical.

will be indicated; the formulas for both  $s$  are identical, except for the inclusion of terms from anti-bonding  $\underline{MO}$ 's. In interpreting the formulas for  $s = +$ , coefficients applicable to the plus spins will be used, for  $s = -$ , coefficients applicable to the minus spins will be used, which means that the anti-bonding coefficients, given as  $\underline{a}^2(c_g^+)$ ,  $\underline{b}^2(e_g^+)$ ,  $\underline{a}^2(f_{2g}^+)$  and  $\underline{c}^2(f_{2g}^+)$ , are to be omitted.

$K(\chi, \chi)$ :

First define

$$B = \underline{b}^2(a_{1g}) + 3\underline{b}^2(f_{1u}) + 2\underline{b}^2(e_g) + 2\underline{b}^2(e_g^+) \quad (57)$$

$$C = \underline{c}^2(f_{1u}) + \underline{c}^2(f_{2g}) + \underline{c}^2(f_{2g}) + 2 \quad (58)$$

Then for each  $\underline{MO}$ ,  $K(\chi, \chi)$  is

$$a_{1g}: \quad (59)$$

$$B[4s\psi_1 | 4s\psi_1] + 6[4s\psi_1' | 4s\psi_1'] + \underline{b}^2(e_g) \{ 2[4s\psi_1 | 4s\psi_4] - 4[4s\psi_1 | 4s\psi_2] \}$$

$$e_g: \quad (60)$$

$$(1/2)B[3d\sigma\psi_1 | 3d\sigma\psi_1] + 3[3d\sigma\psi_1' | 3d\sigma\psi_1'] + (B - 3\underline{b}^2(f_{1u})) [3d\sigma\psi_1 | 3d\sigma\psi_2]$$

$$f_{2g}: \quad (61)$$

$$C[3d\pi\xi_1 | 3d\pi\xi_1] + 2\{\underline{c}^2(f_{2g}) + \underline{c}^2(f_{2g}^+)\} [3d\pi\xi_1 | 3d\pi\xi_2] \\ + \underline{c}^2(f_{2g}) [3d\pi\xi_1 | 3d\pi\xi_4]$$

$$f_{1u}: \quad (62)$$

$$(1/3)B[4p\sigma\psi_1 | 4p\sigma\psi_1] + 2[4p\sigma\psi_2' | 4p\sigma\psi_1'] + C[4p\pi\xi_1 | 4p\pi\xi_1] \\ + (1/3)\{B - 2\underline{b}^2(f_{1u})\} [4p\sigma\psi_1 | 4p\sigma\psi_4]$$

$$+ 2\underline{c}^2(f_{1u})\{2[4p\pi\xi_1 | 4p\pi\xi_2] + [4p\pi\xi_1 | 4p\pi\xi_4]\} \\ - \underline{c}^2(f_{2g})[4p\pi\xi_1 | 4p\pi\xi_4]$$

K(\sigma, \sigma):

$$\begin{aligned} & a_{1g} \\ & \underline{a}^2(a_{1g}) [4s\psi_1 | 4s\psi_1] + \underline{a}^2(f_{1u}) [4p\sigma\psi_1 | 4p\sigma\psi_1] \\ & + \{\underline{a}^2(e_g) + \underline{a}^2(e_g^+)\} [3d\sigma\psi_1 | 3d\sigma\psi_1] \end{aligned} \quad (63)$$

$$\begin{aligned} & e_g : \\ & \underline{a}^2(a_{1g}) \{ [4s\psi_1 | 4s\psi_1] - 2[4s\psi_1 | 4s\psi_2] \} \underline{a}^2(f_{1u}) [4p\pi\psi_2 | 4p\sigma\psi_1] \\ & + \{\underline{a}^2(e_g) + \underline{a}^2(e_g^+)\} \{ [3d\sigma\psi_1 | 3d\sigma\psi_1] + [3d\sigma\psi_1 | 3d\sigma\psi_2] + [3d\sigma\psi_1 | 3d\sigma\psi_4] \} \end{aligned} \quad (64)$$

$$\begin{aligned} & f_{1u}: \\ & \underline{a}^2(a_{1g}) \{ [4s\psi_1 | 4s\psi_1] + [4s\psi_1 | 4s\psi_4] \} \\ & + \{\underline{a}^2(e_g) + \underline{a}^2(e_g^+)\} \{ [3d\sigma\psi_1 | 3d\sigma\psi_1] - [3d\sigma\psi_4 | 3d\sigma\psi_4] \} \end{aligned} \quad (65)$$

K(\pi, \pi):

$$\begin{aligned} & f_{2g}: \\ & \{ \underline{a}^2(f_{2g}) + \underline{a}^2(f_{2g}^+) \} \{ [3d\pi\xi_1 | 3d\pi\xi_1] + 2[3d\pi\xi_1 | 3d\pi\xi_2] \\ & + [3d\pi\xi_1 | 3d\pi\xi_4] \} \\ & + \underline{a}^2(f_{1u}) \{ [4p\pi\xi_1 | 4p\pi\xi_1] - [4p\pi\xi_1 | 4p\pi\xi_4] \} \end{aligned} \quad (66)$$

$$\begin{aligned} & f_{1u}: \\ & \underline{a}^2(f_{1u}) \{ [4p\pi\xi_1 | 4p\pi\xi_1] + 2[4p\pi\xi_1 | 4p\pi\xi_2] + [4p\pi\xi_1 | 4p\pi\xi_4] \} \\ & + \{ \underline{a}^2(f_{2g}) + \underline{a}^2(f_{2g}^+) \} \{ [3d\pi\xi_1 | 3d\pi\xi_1] - [3d\pi\xi_4 | 3d\pi\xi_4] \} \end{aligned}$$



K( $\chi, \sigma$ ): $a_{1g}$ :

(68)

$$\begin{aligned}
& (\sqrt{5}/2) \{ \underline{a}^2(a_{1g}) [(4s)^2 | 4s\psi_1] + \underline{a}^2(f_{1u}) [4s4p\sigma | 4p\sigma\psi_1] \} \\
& + (\sqrt{5}/2) \{ \underline{a}^2(e_g) + \underline{a}^2(e_g^+) \} [4s3d\sigma | 3d\sigma\psi_1] \\
& + (\sqrt{5}/2) [4s\psi_1 | \psi_1 \psi_1'] \\
& + (2/\sqrt{5}) B [4s\psi_1 | \psi_1^2] \\
& + (1/\sqrt{5}) \underline{b}^2(e_g) \{ [4s\psi_1 | \psi_4^2] - 2[4s\psi_1 | \psi_4^2] \}
\end{aligned}$$

 $e_g$ :

(69)

$$\begin{aligned}
& (\sqrt{3}/2) \{ \underline{a}^2(a_{1g}) [3d\sigma 4s | 4s\psi_1] + \underline{a}^2(f_{1u}) [3d\sigma 4p\sigma | 4p\sigma\psi_1] \} \\
& + \sqrt{3} \{ \underline{a}^2(e_g) + \underline{a}^2(e_g^+) \} \{ [(3d\sigma)^2 | 3d\sigma\psi_1] + [3d\sigma\psi_1' | \psi_1 \psi_3'] \} \\
& + (\sqrt{3}/24) \{ 2B + \underline{b}^2(e_g) + \underline{b}^2(e_g^+) \} [3d\sigma\psi_1 | \psi_1^2] \\
& + (\sqrt{3}/3) \{ 2\underline{b}^2(a_{1g}) + 6\underline{b}^2(e_g) + 6\underline{b}^2(e_g^+) \} [3d\sigma\psi_1 | \psi_2^2]
\end{aligned}$$

 $f_{1u}$ :

(70)

$$\begin{aligned}
& (\sqrt{2}/2) \{ \underline{a}^2(a_{1g}) [4p\sigma 4s | 4s\psi_1] + \underline{a}^2(f_{1u}) [(4p\sigma)^2 | 4p\sigma\psi_1] \} \\
& + (\sqrt{2}/2) \{ \underline{a}^2(e_g) + \underline{a}^2(e_g^+) \} [4p\sigma 3d\sigma | 3d\sigma\psi_1] \\
& + (7/6\sqrt{2}) [4p\sigma\psi_1' | \psi_1 \psi_1' + \psi_4 \psi_4'] \\
& + 3/2 \{ B + 2\underline{b}^2(e_g) + 2\underline{b}^2(e_g^+) \} \{ [4p\sigma\psi_1 | \psi_1^2] - [4p\sigma\psi_1 | \psi_4^2] \}
\end{aligned}$$

K( $\chi, \pi$ ): $f_{2g}$ :

(71)

$$\begin{aligned}
& \underline{a}^2(f_{1u}) [3d\pi 4p\pi | 4p\pi\xi_1] + \underline{a}^2(f_{2g}) [(3d\pi)^2 | 3d\pi\xi_1] \\
& + (1/4)C [3d\pi\xi_1 | \xi_1^2] + (1/4) \{ C - 2\underline{c}^2(f_{1u}) \} [3d\pi\xi_1 | \xi_4^2]
\end{aligned}$$

 $f_{1u}$ :

(72)

$$\begin{aligned}
& (1/4) \underline{a}^2(f_{1u}) [(4p\pi)^2 | 4p\pi\xi_1] + (1/4) \{ \underline{a}^2(f_{2g}) + \\
& + \underline{a}^2(f_{2g}^+) \} [4p\pi 3d\pi | 3d\pi\xi_1]
\end{aligned}$$

$$+(1/4)C[4p\pi\xi_1|\xi_1^2] + (1/4)\{2c^2(f_{1u})-C\}[4p\pi\xi_1|\xi_4^2]$$

In all the K integrals, the charge distributions to the left of the vertical line are defined independently of those on the right. For example,  $[3d\sigma\psi_1|3d\sigma\psi_2]$  is computed as  $[3d_{x^2}\sigma\psi_1|3d_{y^2}\sigma\psi_2]$ .

#### E. Evaluation of the Energy Integrals for $\text{FeF}_6^{-3}$

The next step in the treatment of the two complex ions is, of course, the evaluation, by exact calculation or further approximation, of the energy terms derived in Section C. That is, numerical values must be obtained for the  $Q^S$  terms, for the coulomb terms (Equations 49a through 51e), and for the exchange terms (Equations 59 through 72). The three sets of terms will be considered in that order.

Throughout these calculations of the electronic levels of the  $\text{FeF}_6^{-3}$  complex ion, the same interatomic parameters will be used as were used in the Wolfsberg and Helmholz treatment. Also, the inner shell electrons will be considered point charges and therefore will serve only to reduce the nuclear charge. Furthermore, the 2s AO of the fluoride will be neglected so far as participation in bonding is concerned. That is, allowance for incomplete nuclear screening as well as exchange effects will be admitted, but the six MO's arising from these AO's are restrained to be strictly non-bonding.

Some justification for this procedure will be indicated. Effectively, this restriction amounts to the neglect of polarization of fluoride, previously mentioned.

As for the choices of AO's to be used, Slater orbitals were retained for the fluoride. Since the particular 3d functions available from curve-fitting have been found to depend upon the electronic configuration assumed for the iron, and since within the self-consistent procedure, the assumed charge distribution is a variable of the calculation,<sup>a</sup> some original assumption was necessary. Rather than calculate all integrals for each cycle, a rough approximate calculation of the whole problem was made in order to arrive at some reasonable choice of 3d functions. The initial guess was for  $\text{Fe}^{+1.5}$  with configuration  $3d)^{5.5} 4s, 4p)^1$ . However, because of the relative "screening" abilities of 4s and 4p electrons as against 3d, the wave function selected is applicable through a range of configurations and total charge. Hence, recalling the systematic curve-fitting results, the radial function for the  $d^6 (3d^5 s^2)$  configuration was used throughout all the computations, except that the overlap integrals were varied to agree with the charge distribution assumed for each cycle.

The 4s and 4p wave functions will be commented upon below.

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<sup>a</sup> Throughout the development of the energy terms, atomic units are used. In the presentation of numerical results for integrals and formulas for energy terms, however, energy units are converted to ev.

### 1. Valence state ionization potentials

The  $Q$  values, previously derived from the calculations of Skinner and Pritchard (82) and of Moore (81) as used for the Wolfsberg and Helmholz calculations, are applicable here also, but, with some further interpretation and revision. The appropriate quantities are the  $Q^S$ , which differ from the  $Q$  by the exclusion or inclusion of certain exchange integrals. For the ligand atoms, it turns out that the net charge distribution finally derived is very nearly evenly divided between electrons of both spins. Thus  $Q^+(K) \simeq Q^-(K) \simeq Q(K)$ ; and the values given by Figure 7 will be used for both spin states.

A similar situation, however, does not hold for the metal atom, since there are five unpaired electrons (approximately) on the metal. Thus the  $Q(\chi)$  previously used must be adjusted. The magnitude of this adjustment may be estimated from atomic spectra by observing the average energy to invert the spin of a 3d, 4s or 4p electron, i.e. to transfer it from a plus-spin AO to a minus-spin orbital. Atomic spectra indicate that the  $3d^+ \text{ AO}$  is about 3.5 ev lower than the  $3d^- \text{ AO}$  and that  $4s^+$  and  $4p^+$  are roughly 1.5 lower than  $4s^-$  and  $4p^-$ , respectively. These quantities also appear in the calculations of Wood (77) upon the  $d^6 s^2$  configuration of Fe. His  $3d^+$  to  $3d^-$  separation was larger, being reported as 6.24 ev. Compromising between an uncertain interpretation of an exact quantity and an exact interpretation of an uncertain quantity, the  $3d^+$  to  $3d^-$  separation was set at 4.0 ev.

Thus, the  $Q^S(\chi)$  values are obtained from the previous  $Q(\chi)$  values by inclusion of the corrections of 4.0 ev and 1.5 ev for the 3d and the 4s,4p AO's, respectively.

## 2. Coulomb terms

(a) Reduction of the  $\Omega$  charge distributions. Inspection of Equations 49a through 51a reveals that there are four main classes of integrals of this character. These are (a) the two- and three-center nuclear attraction integrals of the type  $[\delta_M | k^2]$ ,  $[\chi^2 | \delta_1]$  and  $[\chi K_1 | \delta_2]$ , (b) the two-center coulomb integrals of the type  $[\chi^2 | K_1^2]$  and  $[K_1^2 | K_2^2]$ , (c) the two-center hybrid integrals of the type  $[\chi K | \chi^2]$  and  $[\chi K_1 | K_1^2]$ , and (d) the three-center hybrid integrals  $[\chi K_1 | K_2^2]$ .

The nuclear attraction integrals turn out to be relatively easy to evaluate, since integration proceeds only over the coordinates of one electron. On the other hand, each of the remaining (two-electron) integrals might seem to cause difficulty. Much of the expected trouble is circumvented, however, by taking full advantage of the symmetry of the molecule.

Consider  $C(\rho, \rho)$ , for example:

$$[\Omega_M | K_1^2] = \sum_j a_j^2 [\chi_j^2 | K_1^2] - Z_M [\delta_M | K_1^2] \quad (73)$$

Now integrating separately each of the  $[\chi_j^2 | K_j^2]$  would be exceedingly tedious, but it can be made unnecessary from the following observations. If, before integrating, the functions  $\chi_j^2$  are first summed, then it can be verified that the sum of

the squares of the 4p AO's is spherically symmetric, as is also the sum of the squares of the 3d AO's. Therefore,

$$\sum_j a_{jk}^2 \simeq q(f_{1u}) \cdot 4s^2(\delta_{4p}) + q(a_{1g}) \cdot 4s^2(\delta_{4s}) \\ \{q(e_g) + q(f_{2g})\} R_{3d}^2, \quad (74)$$

where the  $q$ 's indicate the total electron density assigned to the metal atom within the MO symmetry species specified, and where  $R_{3d}$  is a normalized Fe 3d radial wave function derived in Chapter IV. If  $3q(e_g) = 2q(f_{2g})$ , the equality would be exact. This means that  $\Omega_M$  is very nearly equal to the point (core) potential  $Z_M \delta_M$  plus a sum of  $(ns)^2$  functions, both of which are much easier to integrate.

At this point it was felt desirable to respecify the form of the 4s and 4p iron AO's. It will be recalled that they were obtained as a sum of 1s, 2s, 3s and 1p, 2p, 3p Slater-type AO's, but that great uncertainty surrounds their origin and applicability to the problem. It was decided to replace these previous combinations by single 3s and 3p Slater functions which are selected to reproduce as closely as possible the values obtained for the overlap integrals with the ligand. Thus hereafter, the 4s and 4p AO's are to be replaced by 3s(2.00) and 3p(2.00), respectively, whenever actual computations are made. The 3d functions are retained as previously derived.

These considerations suggest that it might not be a bad approximation to replace the whole valence shell electronic

distribution by a single function. This, in fact, was done. It is justifiable for two reasons: (a) the greater part of total valence shell charge distribution arises from the 3d electrons and (b) since 4s and 4p, are intermediate between the orbital exponents in the functions representing the 3d AO's, the radial distributions of the three sets of AO's probably will be rather similar.

Hence, finally,  $\Omega_M$  reduces to

$$\Omega_M = q_M R_{3d}^2 + Z_M \delta_M \quad (75)$$

where  $R_{3d}$  is the normalized 3d radial function derived in Chapter IV and  $q_M$  is the total valence shell charge density assigned to the metal atom.

In an exactly similar manner, and probably to an even better approximation,

$$\Omega_L = q_L R_{2s}^2 + Z_L \delta_L, \quad (76)$$

where  $R_{2s}$  is the Slater 2s AO for a ligand and  $q_L$  is the total valence shell charge density assigned to the ligand atom.

(b) The nuclear attraction integrals. All two-center nuclear attraction integrals occurring in the present cases can be evaluated analytically by methods given, e.g., by Roothaan (66). Formulas for all needed integrals, either derived here or obtained from the literature, are collected in Appendix B. Evaluation of all three-center integrals is especially difficult. Hence they were calculated by the

Mulliken approximation in terms of the two-center integrals already evaluated, and which are tabulated in Appendix C.

(c) The two-center coulomb integrals. Coulomb integrals between AO's belonging only to the first and second quantum shells have been expressed in analytical form by a number of people; see Roothaan (66) for such a listing as well as a review of earlier literature. Also, these integrals have been tabulated with a wide range of parameters by Roothaan (111) among others. Thus all these integrals may be computed exactly or interpolated from tables, as desired.

On the other hand, third quantum shell coulomb integrals have not been investigated at all. In order to obtain an estimate of the magnitude of such integrals occurring in the present cases, the analytic expression for the coulomb integral  $[R_{3d}^2 | (2s_L)^2]$  was derived and evaluated for the relevant parameters. For the fluoride case, the results were obtained

$$\begin{aligned} [R_{3d}^2 | (2s_L)^2] &= 6.850 \text{ ev} \\ &= 0.9944 [R_{3d}^2 | \delta_L] = 0.9896 [\delta_M | 2s_L]^2 \\ &= 0.9896 [\delta_M | \delta_L] \quad . \end{aligned}$$

These results are interesting, for they imply that at the internuclear distances encountered in the transition-metal complexes, the metal and ligand orbitals appear much like point charges, with respect to this type of integral. (That is, the correct value is almost 99 per cent of the value obtained if



the two AO's each were shrunk down to point charges.) These results, then, imply that a semi-point charge approximation (see the discussion of Ellison (110)) is rather good for these integrals, and it was adopted, in principle, for these calculations.

Another useful interpretation of these results is that, for the coulomb integrals, the valence-shell electronic charge distributions of the metal is effectively a point charge 0.9896 times as large in magnitude. Similarly, that of the ligand atom (fluorine) is effectively a point charge 0.9944 times as large in magnitude. Based upon this reasoning, a modified semi-point charge approximation was adopted:

$$[\Omega_M | k^2] \simeq \{0.9896q_M - Z_L\} [\delta_M | k^2] \quad (77a)$$

$$[\chi^2 | \Omega_L] \simeq \{0.9944q_L - Z_L\} [\chi^2 | \delta_L] , \quad (77b)$$

where  $\chi$  or  $k$  now may be any valence-shell AO of the metal or ligand respectively. Although the correction per valence-shell electron is comparatively small, the net result is, effectively, to increase the positiveness of the charge on the metal relative to that on the ligand. Put in another way, from a distance of 2.07 Å (the metal-fluorine distance), a neutral iron atom would appear to have a positive fractional charge of about one-twelfth.

(d) The two-center hybrid integrals. At first thought, it might seem that the semi-point charge approximation could be carried over equally well to the case of the hybrid

integrals. However, the reason that such good results were obtained for the two-center coulomb integrals is that the two charge distributions are sufficiently separated so that they do not overlap to any great extent. Thus, in fact, they appear as point charges. In the hybrid integral  $[\chi\kappa|\chi^2]$ , the situation is different. Although the  $\chi^2$  distribution is relatively closely drawn in toward the metal, the charge distribution  $\chi\kappa$ , unlike  $\kappa^2$ , is largest somewhere between the metal and ligand atom. (Near the metal,  $\chi$  is large, but  $\kappa$  very small; near the ligand, the reverse is true. It is only where both are moderately large that  $\chi\kappa$  is most important.) Therefore,  $\chi^2$  as well as  $\kappa^2$  will be overlapped to a relatively greater extent in the hybrid integrals than in the coulomb. Furthermore, it is to be expected that the accuracy of a semi-point charge approximation will depend quite sensitively upon the nature of the AO's involved.

In order to semi-quantitatively assess the nature of the magnitude of the hybrid integrals and the errors of approximation, four hybrid integrals were considered analytically, using a method of solution similar to that used for the coulomb integrals. The precise calculations were carried, not through to completion, but only to the inclusion of the major contributors to the total values of the integrals. The integrals considered, and the approximate values are

$$[(R_{3d})(2s_L)^2|2s_L^2] = 0.845 [(R_{3d})2s_L|\delta_L] = 3.03 \text{ ev}$$

$$[(R_{3d})(2s_L)|R_{3d}^2] = 0.983 [(R_{3d})(2s_L)|\delta_M] = 1.26$$

$$[(R_{3d})(2p\sigma_L)|(2s_L)^2] = 0.955 [(R_{3d})(2p\sigma_L)|\delta_L] = 1.91$$

$$[(R_{3d})(2p\sigma_L)|R_{3d}^2] = 0.970 [(R_{3d})(2p\sigma_L)|\delta_M] = 1.23 \quad .$$

It is seen that the semi-point charge approximation is not quite so good here; nevertheless, rather than compute all hybrid integrals, the assumption was made and a factor of 0.95 was used for the point charge representation of both metal and ligand valence electrons.

(e) The three-center hybrid integrals. If the evaluation of the three-center nuclear attraction integrals is difficult, then the three-center hybrid integrals are very nearly impossible, at least with hand calculation. Thus, also, for these integrals, the Mulliken approximation was used without further consideration. Thereby,

$$[\chi_{K_1}|\kappa_{\pm}^2] \simeq \frac{S(\chi, \kappa_1)}{2} [\chi^2 + \kappa_1^2|\kappa_{\pm}^2] \quad (\text{for } \pm = 1) \quad (78)$$

The necessary two-center coulomb integrals have already been discussed.

(f) Summary of results for coulomb terms. It is now apparent that the results expressed in Equations 77 through 79b are now in such forms as to allow very good approximation of all integrals by means of the simple one-electron nuclear attraction integrals. To utilize these formulas for the C

terms, it is merely necessary to substitute the new approximations for the  $\Omega$ 's and to integrate, with due regard, however, to the geometry of the molecule. The  $\Omega$ 's are:

for all  $C(\rho, \rho)$  terms

$$\Omega_M = (0.9896q_M - 8)\delta_M \quad (Z_M = 8 \text{ for Fe}); \quad (79a)$$

for all  $C(\chi, \chi)$  terms

$$\Omega_{\pm} = (0.9944q_L - 7)\delta_{\pm} \quad (Z_L = 7 \text{ for F}); \quad (79b)$$

for all  $C(\chi, \rho)$  terms

$$\Omega_M = (0.95q_M - 8)\delta_M \quad (79c)$$

$$\Omega_3 = (0.95q_L - 7)\delta_3 \quad (79d)$$

and for all  $C(\rho, \rho)$  and  $C(\chi, \rho)$  terms

$$\Omega_{\pm} = (q_L - 7)\delta_{\pm} \quad \text{for } \pm \neq 3. \quad (79e)$$

Inserting the  $\Omega$ 's given by Equation 79 into Equations 75 through 77b gives the C's as functions of  $q_M$  and  $q_L$ , in terms of integrals, the formulas and values for which, are given in the Appendices. It is important, when evaluating certain ligand-ligand interactions, to note that the ligand orbital must be transformed into sums of other functions, which are defined according to the ligand-ligand axis. Thus, for example, the integral

$$[\delta_1 | \psi_3^2] = (1/2)[\delta_1 | (2p\sigma_3)^2 + (2p\pi_3)^2]$$

for  $R = \sqrt{2}R_{Fe-F}$ . The 2p functions are here defined with respect to the  $F_1-F_3$  axis which is at  $45^\circ$  to the metal ligand axis.

From all this results these equations, with energy units of ev,

$$C(\sigma, \sigma) = 7.065q_M + 23.150q_L - 219.251 \quad (80)$$

$$C(\pi, \pi) = 6.732q_M + 23.106q_L - 216.265 \quad (81)$$

$$C(4s, 4s) = 41.055q_L - 290.611 \quad (82a)$$

$$C(4p, 4p) = 41.055q_L - 290.611 \quad (82b)$$

$$C(3d\sigma, 3d\sigma) = 41.512q_L - 293.817 \quad (82c)$$

$$C(3d\pi, 3d\pi) = 40.146q_L - 284.148 \quad (82d)$$

$$C(4s, \sigma) = 1.354q_M + 8.664q_L - 73.013; G(4s, \sigma) = 0.242 \quad (83a)$$

$$C(4p, \sigma) = 1.188q_M + 9.857q_L - 81.594; G(4p, \sigma) = 0.297 \quad (83b)$$

$$C(4p, \pi) = 0.333q_M + 3.854q_L - 30.774; G(4p, \pi) = 0.122 \quad (83c)$$

$$C(3d\sigma, \sigma) = 1.073q_M + 7.913q_L - 66.413; G(3d\sigma, \sigma) = 0.217 \quad (83d)$$

$$C(3d\pi, \pi) = 0.692q_M + 6.801q_L - 55.181; G(3d\pi, \pi) = 0.182 \quad (83e)$$

The group overlap integrals are also listed, corresponding to the particular choices of metal AO's assumed for the starting calculations.

### 3. Exchange terms

An examination of the exchange terms listed in Equations 57 through 72 reveals that some are very similar to the hybrid integrals already discussed. This sort of integral occurs in the  $K(\chi, \rho)$  terms and is of the form  $[\chi^2|\chi\kappa]$  or  $[\kappa^2|\chi\kappa]$ . The already computed modified semi-point charge approximation to

these integrals has been used here also. For the remaining exchange integrals, essentially the Mulliken approximation was employed.

The one-center coulomb integrals arising from the approximated two-center exchange integrals were obtained analytically for the ligand orbitals ( $\sim 0.4\delta_L$ ), and were estimated from ionization potentials for the metal orbitals. Neither method of estimation furnishes better than a rough estimate; but the net possible error is quite small.

Numerical values for the exchange integrals, evaluated on this basis, are given in Appendix C. Upon substituting those values in Equation 57 through 72 there results the following formulas for the exchange terms. Recall that the coefficients with the plus signs are to be set equal to zero when the substitutions for  $K^-(m,n)$  are made.

for  $a_{1g}$ :

$$K(4s,4s) = 3.78 - 0.87\underline{a}^2(a_{1g}) - 0.61\underline{a}^2(f_{1u}) - 0.74\underline{a}^2(e_g) + 0.12\underline{b}^2(e_g^+) \quad (84a)$$

$$K(\sigma,\sigma) = 0 + 0.13\underline{a}^2(a_{1g}) + 0.13\underline{a}^2(f_{1u}) + 0.17\underline{a}^2(e_g) + 0.17\underline{a}^2(e_g^+) \quad (84b)$$

$$K(4s,\sigma) = 3.37 - 1.12\underline{a}^2(a_{1g}) + 0.39\underline{a}^2(f_{1u}) + 0.07\underline{a}^2(e_g) + 0.37\underline{a}^2(e_g^+) + 0.30\underline{b}^2(e_g^+) \quad (84c)$$

for  $e_g$ :

$$K(3d\sigma, 3d\sigma) = 3.26 - 0.18\underline{a}^2(a_{1g}) - 0.74\underline{a}^2(f_{1u}) - 0.64\underline{a}^2(e_g) \\ + 0.36\underline{b}^2(e_g^+) \quad (85a)$$

$$K(\sigma, \sigma) = 0 + 0.01\underline{a}^2(a_{1g}) + 0.15\underline{a}^2(f_{1u}) + 0.30\underline{a}^2(e_g) \\ + 0.30\underline{a}^2(e_g^+) \quad (85b)$$

$$K(3d\sigma, \sigma) = 3.20 - 0.22\underline{a}^2(a_{1g}) + 0.01\underline{a}^2(f_{1u}) + 1.82\underline{a}^2(e_g) \\ + 1.95\underline{a}^2(e_g^+) \\ + 0.87\underline{b}^2(e_g^+) \quad (85c)$$

for  $f_{2g}$ :

$$K(3d\pi, 3d\pi) = 2.22 - 0.89\underline{a}^2(f_{1u}) - 0.77\underline{a}^2(f_{2g}) \\ + 0.27\underline{c}^2(f_{2g}^+) \quad (86a)$$

$$K(\pi, \pi) = 0 + .03\underline{a}^2(f_{1u}) + 0.27\underline{a}^2(f_{2g}) \\ + 0.27\underline{a}^2(f_{2g}^+) \quad (86b)$$

$$K(d\pi, \pi) = 2.40 - .64\underline{a}^2(f_{1u}) - .06\underline{a}^2(f_{2g}) \\ + 0.73\underline{a}^2(f_{2g}) \\ + 0.21\underline{c}^2(f_{2g}) \quad (86c)$$

for  $f_{1u}$ :

$$K(\sigma, \sigma) = 0.18\underline{a}^2(a_{1g}) + 0.16\underline{a}^2(f_{1u}) - 0.03\underline{a}^2(e_g) \\ - 0.03\underline{a}^2(e_g^+) \quad (87a)$$

$$K(\pi, \pi) = .13\underline{a}^2(f_{1u}) + .02\underline{a}^2(f_{2g}) + 0.02\underline{a}^2(f_{2g}^+) \quad (87b)$$

$$\begin{aligned} K(4p, 4p) &= 0.04\underline{b}^2(a_{1g}) + 0.13\underline{b}^2(f_{1u}) + 0.08\underline{b}^2(e_g) \\ &+ 0.14\underline{b}^2(e_g^+) + 0.42 \\ &+ 0.08\underline{c}^2(f_{1u}) + 0.08\underline{c}^2(f_{2g}) + 0.08\underline{c}^2(f_{2g}^+) \end{aligned} \quad (87c)$$

$$\begin{aligned} K(4p, \sigma) &= 0.21\underline{a}^2(a_{1g}) + 1.25\underline{a}^2(f_{1u}) + 0.21\underline{a}^2(e_g) \\ &+ 0.21\underline{a}^2(e_g^+) + 0.54 \\ &+ 0.17\underline{b}^2(a_{1g}) + 0.50\underline{b}^2(f_{1u}) + 0.67\underline{b}^2(e_g) \\ &+ 0.67\underline{b}^2(e_g^+) \end{aligned} \quad (87d)$$

$$\begin{aligned} K(4p, \pi) &= 0.09\underline{a}^2(a_{1g}) + 0.02\underline{a}^2(f_{2g}) + 0.02\underline{a}^2(f_{2g}^+) + 0.26 \\ &+ 0.37\underline{c}^2(f_{1u}) + 0.07\underline{c}^2(f_{2g}) + 0.07\underline{c}^2(f_{2g}^+) \end{aligned} \quad (87e)$$

#### 4. Numerical values of the $F^S(m, n)$

The values of the  $F^S(m, n)$ , for any given electronic distribution on the iron atom, can now be obtained from the valence state ionization potentials of Figure 7, and upon substitution of the proper coefficients into the formulas for the  $C(m, n)$  and  $K^S(m, n)$  of Equations 80 through 87c. There remains one final point, however, in connection with the  $F^S(\chi, \rho)$ .

Throughout all the discussion of the hybrid integrals, which occur in the  $F^S(\chi, \rho)$  part of the total energy expression, it has been pointed out that the overlap function  $\chi\rho$  is to be considered as a charge distribution of total integrated



magnitude equal to the particular overlap integral defined in terms of those same two SO's,  $\chi$  and  $\rho$ . In the cases where is either  $3d\sigma$  or  $3d\pi$ , however, it is possible to assess the variation of the radial  $3d$  AO's with changing configuration of the iron atom. Thus, as the overlap integrals vary so also do the hybrid integrals. It has been found by Mulliken, (94), that it is indeed a good approximation to factor out the group overlap integral from  $F^S(\chi, \rho)$ . Hence, to compute  $F^S(\chi, \rho)$  for any electronic configuration of the iron from the formulas given above, it is only necessary to divide out the  $G(\chi, \rho)$  given in Equations 83a through 83e and then multiply by the appropriate group overlap integrals.

It is instructive to examine the variations of the  $F^S(m, n)$  with assumed charge distribution. From the definition of  $q_M$  and  $q_L$ , it holds that  $Z_M + 6Z_L - q_M - 6q_L$  must equal the net charge upon the whole complex ion, namely -3. Furthermore, if it is assumed, for purposes of illustration, that the polarities of all MO's are the same, then all the  $a_k^2$  will be determined. Hence it is possible to graph the variations of the various  $F^S(m, n)$  as functions of assumed charge,  $q_M$ , on the metal atom. Graphs such as this are helpful not only in making the initial guess for beginning the self-consistent solutions of the secular equations, but also in analyzing the nature of the interaction between metal and ligand. More will be made of this feature in the next chapter.

The graphs described are given in Figure 11 for the  $F^+(m,n)$  and in Figure 12 for the  $F^-(m,n)$ .

#### E. Evaluation of the Energy Integrals

for  $\text{Fe}(\text{NH}_3)_6^{+3}$

##### 1. Preliminary considerations

It is much more difficult to consider the ammonia complex upon the same basis as the fluoride because of the additional variabilities introduced by the presence of hydrogens also attached to the nitrogen. Thus, aside from the fact that there are no good zero-order wave functions for the isolated ammonia molecule, there must be considered the polarization of the N—H system by the field of the metal. The magnitude of this polarization effect is not known, although some recent infra-red spectral data of Kobayashi and Fujita (112) indicate that the hydrogens do become significantly more positive upon being complexed with the metal, as one might expect. Crystalline field theorists have resorted to large polarization effects in order to account for the observed splitting of the 3d level. Where polarization ends and chemical bonding begins, however, is another matter.

Without further questioning in the Wolfsberg and Helmholz treatment the lone-pair electrons were assumed to be described by tetrahedral orbitals, and no further specification of the remainder of the ammonia molecule was made. This simplification cannot be justified here, since the polarization effects

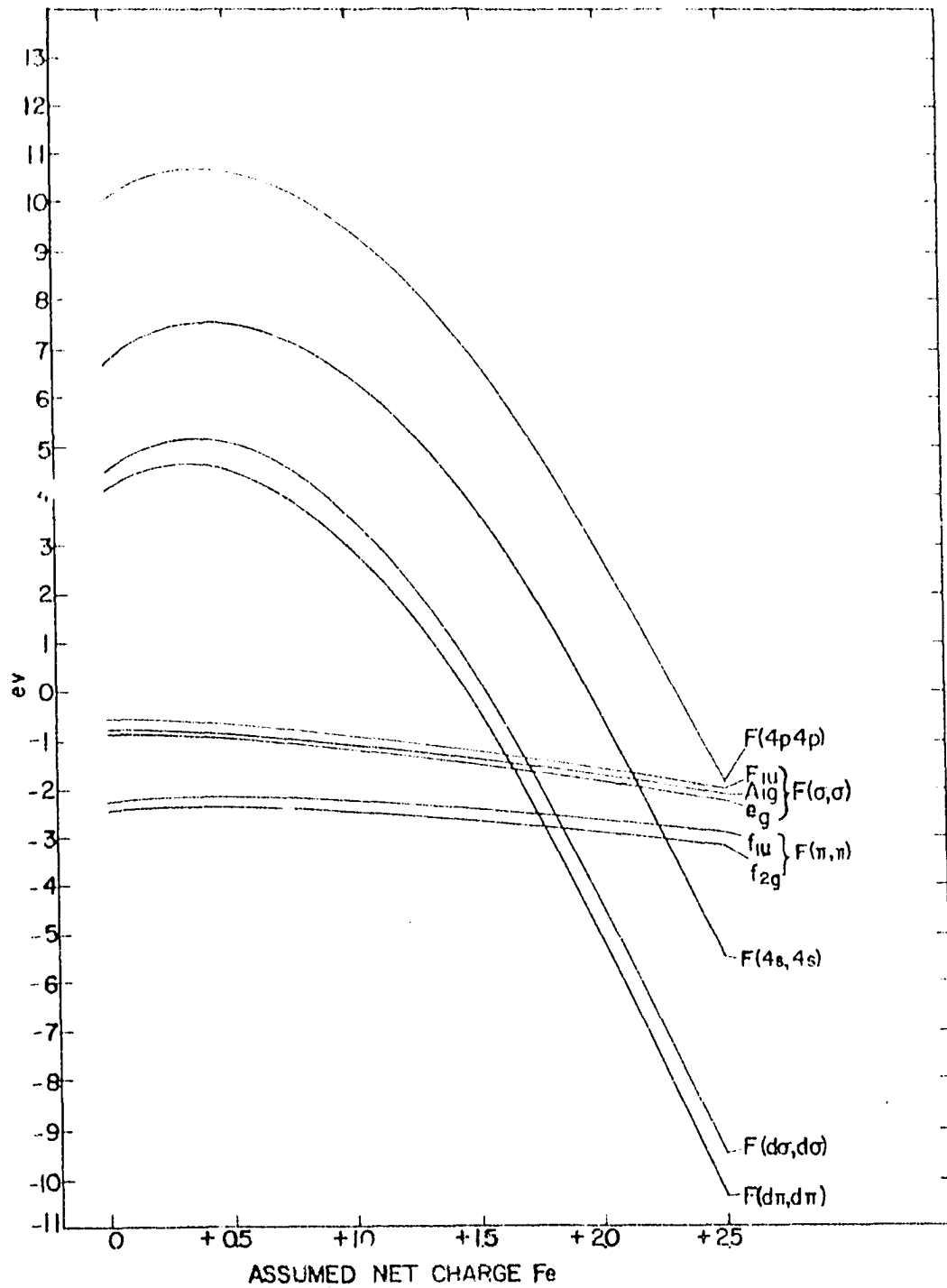


Figure 11.  $F^+(m,n)$  for  $\text{FeF}_6^{-3}$

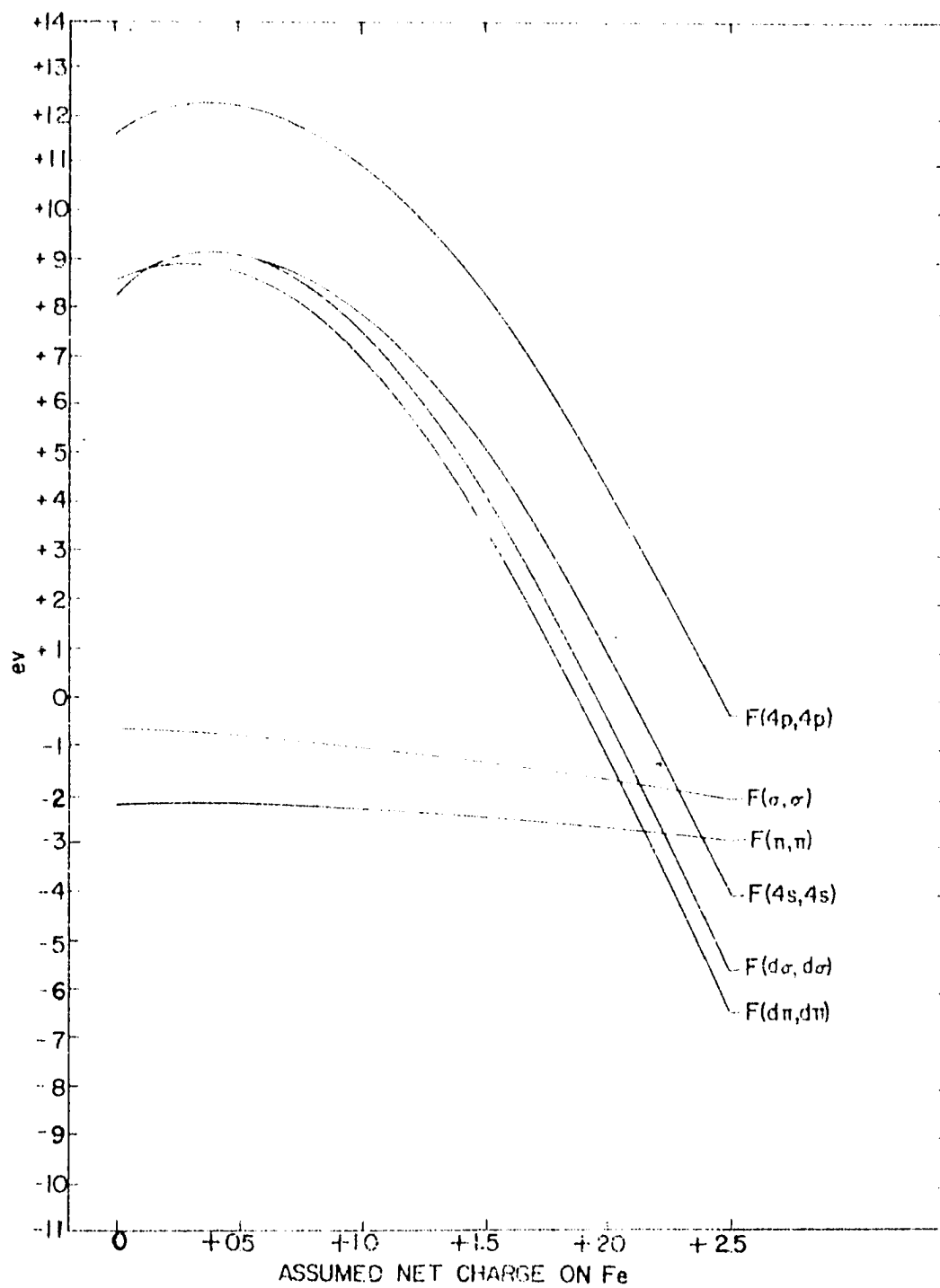


Figure 12.  $F^-(m,n)$  for  $\text{FeF}_6^{3-}$

(permanent or induced) enter explicitly into the coulomb terms of the energy expressions.

Thus there are present from the start two more major variables in the ammonia case than there were in the fluoride case. These two variables are (a) the amount of s,p hybridization present in the lone pair orbitals and (b) the polarity of the N—H<sub>3</sub> bonding system. Actually, as is clear from Mulliken's discussion of the bonding, there surely are two polarities of relevance -- the polarity of the  $\sigma$ -type N—H interaction and that of the  $\pi$ -type. Obviously, the most correct approach to the problem would be to include all the valence-shell AO's of the NH<sub>3</sub> groups into the secular equations. This procedure, if adequate approximations could be made, would automatically take care of hybridization and polarization problems. Not only that, but surely such an approach would reveal that the hybridization and polarization would be different for every MSO.

To make the discussion of the electronic structure of Fe(NH<sub>3</sub>)<sub>6</sub><sup>+3</sup> tractable, however, all such considerations were neglected. Rather, two cases were investigated, assuming the lone pair electrons to be in (a) pure 2p $\sigma$  nitrogen AO's and (b) in tetrahedral hybrid AO's. For both cases the following model of NH<sub>3</sub> was assumed. The electronic charge distribution was approximated by a sum of (1s)<sup>2</sup> functions centered on the hydrogens and squares of appropriate AO's on the nitrogen (for case (a) by (2s)<sup>2</sup>, (2p $\sigma$ )<sup>2</sup> and (2p $\pi$ )<sup>2</sup>; for case (b) by

squares of tetrahedral hybrids). The comparative amounts of the hydrogen and nitrogen functions are, of course related to the polarity of the N—H bonds. In fact, a parameter specifying this ratio was introduced at this point. The fractional distribution of one bonding electron between the N and one H was set as  $a'$  on N and  $(1 - a')$  on H, each fraction in its appropriate AO.

An additional complication arises from the presence of the hydrogen atoms off the four-fold axes of the octahedron. (Actually, because of the hydrogens, the ammonia complex is not strictly octahedral, only very nearly so). This complication could be accommodated in the calculations, but without much reward. Accordingly, the model of  $\text{NH}_3$  was simplified further by projecting, radially from the metal, each hydrogen to the nearest four-fold axis. Thus, the metal-hydrogen distance is preserved and made colinear with the M—N distance. Although the N—H distance is thereby shortened, this is of no consequence, since whenever effects within a given  $\text{NH}_3$  group are assessed, the correct distance can then be used.

Thus the  $\text{NH}_3$  is taken to be a diatomic species with the metal on the axis. Polarity of the N—H system is specifically included in an approximate fashion.<sup>a</sup> Other geometric

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<sup>a</sup> Compare the model assumed by Kleiner (28) for his calculations on  $\text{Cr}(\text{H}_2\text{O})^{+3}$ . He first selected  $(\text{H}^{+1})_2\text{O}^{-2}$ , and smeared the protons out into a ring by rotating the water molecules about the metal-oxygen axis; later in the calculations, he also allowed for less charge on the oxygen. Keliner's model is more realistic, geometrically, than the model adopted here, but

specifications of the molecules were identical to those used in the Wolfsberg and Helmholz treatment. The new 4s and 4p iron AO's, introduced during the  $\text{FeF}_6^{-3}$  calculations, were retained.

## 2. Valence state ionization potentials

Valence state ionization potentials for the iron atom were retained exactly as they were used in the  $\text{FeF}_6^{-3}$  calculations.

There are two processes by which the ionization potential of the lone-pair electrons of the ammonia molecule may change: (a) by alteration of the electron density associated with the nitrogen atom through loss to the metal or through gain (via polarization) from the hydrogens, and (b) by alteration of the coulomb effect of the three hydrogen atoms upon the nitrogen electrons.

The changes due to process (a) may be estimated from interpolation of valence state ionization potentials of atomic nitrogen. Those due to process (b) might be estimated from computing the change in the coulomb interaction between the 1s-electron density on the three hydrogens and the lone-pair electron density on the nitrogen (i.e., making the hydrogens more positive by loss of electron density tends to stabilize, or lower the energy of, the lone-pair electrons). Direct

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(Footnote a, p.143 continued) computing ligand-ligand interactions by his model would be very difficult.

evaluation of the relevant quantities reveals that process (a) may lower the energy of the lone-pair electrons by about 16 ev per electron lost; process (b) may lower the energy by about 13 ev per electron lost.

### 3. Coulomb terms

For the ammonia case it is necessary to include the hydrogen atoms into the  $\Omega_{\pm}$  charge distributions. This addition is easily made, and there is obtained

$$\begin{aligned} \Omega_{\pm} = & \left(\frac{1}{6} \sum_k b_R^2\right) \psi_{\pm}^2 + \left(\frac{1}{2} + a'\right) \left\{4\tilde{\chi}_{\pm}^2 + 2\psi_{\pm}^2\right\} + 6\left(\frac{1}{2} - a'\right) 1s_{H,\pm}^2 \\ & - 5\delta_{\pm} - 3\delta_{H,\pm} \end{aligned} \quad (88)$$

The  $1s_{H,\pm}^2$  function was immediately reduced to a point charge. Reduction of the other two charge distributions depends somewhat upon the nature of the lone-pair AO in the following way. If the lone pair is in a pure  $2p\sigma$  AO, then  $\psi^2 = (2p\sigma)^2$  and  $\psi'^2 = (2s)^2$ . But, on the other hand, if the lone pair is in a tetrahedral AO, then

$$\psi^2 = (1/4) \left\{ (2s)^2 + 3(2p)^2 + 2\sqrt{3}(2s2p\sigma) \right\}, \text{ and } (89a)$$

$$\psi'^2 = (1/4) \left\{ (2s)^2 + 3(2p)^2 - 2\sqrt{3}(2s2p\sigma) \right\}. \quad (89b)$$

If the lone pair is  $2p\sigma$ , then the electronic charge distribution on the nitrogen can be approximated rather well by the function  $R_{2s}^2$ , as well as in the fluoride case. But, for the tetrahedral hybrid case, not only is there obtained the same  $R_{2s}^2$  function, but also the  $2s$ - $2p$  mixing terms. These



latter terms have a not negligible effect upon the metal orbitals, and so they were considered. Integrated over all space, the  $2s2p\sigma$  function vanishes, thus it is composed equally of positive and negative regions. A closer examination reveals that this particular charge distribution resembles a dipole directed toward the metal atom. Qualitatively, then, the effective dipole of the overall charge distribution of the  $\text{NH}_3$  molecule is augmented by the  $2s-2p\sigma$  hybridization.

Applying these considerations, Equation 90 becomes

$$\begin{aligned} \Omega_{\pm} = & (q_L - 6a')(2s_N)^2 + (5/4)(q_L - 2a')(2s2p\sigma) \\ & + (3 - 6a')\delta_{H,\pm} - 5\delta_{\pm}, \end{aligned} \quad (90)$$

for the tetrahedral hybrid case; for the pure  $2p\sigma$  case, the  $(2s2p\sigma)$  terms are omitted. Here  $q_L$  is the charge on the nitrogen arising through the  $\sigma$ -type bonding to the metal; it does not include charge shifted from the hydrogens.

In order to again simplify the calculation of the coulomb terms, the two-center coulomb integrals  $[R_{3d}^2 | (2s_L)^2]$  were evaluated exactly:

$$\begin{aligned} [R_{3d}^2 | (2s_L)^2] &= 7.239 \text{ ev} \\ &= 0.9821[R_{3d}^2 | \delta_L] = 0.9699[\delta_M | (2s_L)^2] \end{aligned}$$

The same 0.95 factor was retained for the hybrid integrals approximations.

Hence, the  $\Omega$  charge distributions, for  $\text{Fe}(\text{NH}_3)_6^{+3}$ , becomes: for all  $C(\rho, \rho)$  terms

$$\Omega_M = (0.9699q_M - 8)\delta_M \quad (91a)$$

for all  $C(\chi, \chi)$  terms

$$\begin{aligned} \Omega_{\pm} = & (0.9821q_L - 5)\delta_{\pm} + (3 - 6a')\delta_{H, \pm} + \\ & + (5/4)(q_L - 2a')(2s2p\sigma) \end{aligned} \quad (91b)$$

for all  $C(\chi, \rho)$  terms

$$\Omega_M = (0.95q_M - 8)\delta_M \quad (91c)$$

$$\begin{aligned} \Omega_3 = & (0.95q_L - 5)\delta_{\pm} + (3 - 6a')\delta_{H, \pm} \\ & + (5/4)(q_L - 2a')(2s2p\sigma) \end{aligned} \quad (91d)$$

and for all  $C(\rho, \rho)$  and  $C(\chi, \rho)$  terms

$$\Omega_{\pm} = (q_L - 5)\delta_{\pm} + (3 - 6a')\delta_{H, \pm} + (5/4)(q_L - 2a')(2s2p\sigma) \quad (91e)$$

As for approximating the integrals arising from the  $(2s2p\sigma)$  function, considerable investigation revealed that the following simple substitution gives very good results, at least when applied to integrals involving only second quantum shell AO's:

$$(2s2p\sigma) \simeq (1/6)\delta_{\pm} \quad (92)$$

Upon substituting these expressions for the  $\Omega$ 's into Equations 75 through 77b gives the C's as functions of  $q_M$ ,  $q_L$ , and  $a'$ . Values for the resulting integrals are collected in Appendix C. Proper substitution of these gives two sets of formulas for the C's, depending upon the nature of the lone-

pair.

For tetrahedral case:

$$C(\sigma, \sigma) = 8.827q_M + 55.554q_L + 17.823a' - 137.276 \quad (93)$$

$$C(4s, 4s) = 105.839q_L + 21.314a' - 111.477 \quad (94a)$$

$$C(4p, 4p) = 105.839q_L + 21.314a' - 111.477 \quad (94b)$$

$$C(3d\sigma, 3d\sigma) = 102.322q_L + 30.410a' - 114.818 \quad (94c)$$

$$C(3d\pi, 3d\pi) = 98.156q_L + 26.961a' - 109.160 \quad (94d)$$

$$C(4s, \sigma) = 3.834q_M + 48.451q_M + 30.542a' - 103.534$$

$$G = 0.604 \quad (95a)$$

$$C(4p, \sigma) = 2.734q_M + 36.654q_L + 19.682a' - 75.315$$

$$G = 0.441 \quad (95b)$$

$$C(3d\sigma, \sigma) = 2.655q_M + 38.701q_L + 23.901a' - 76.210$$

$$G = 0.533. \quad (95c)$$

For the pure 2p case:

$$C(\sigma, \sigma) = 7.658q_M + 50.064q_L + 14.184a' - 120.332 \quad (96)$$

$$C(4s, 4s) = 91.589q_L + 35.564a' - 111.477 \quad (97a)$$

$$C(4p, 4p) = 91.589q_L + 35.564a' - 111.477 \quad (97b)$$

$$C(3d\sigma, 3d\sigma) = 92.194q_L + 40.538a' - 114.818 \quad (97c)$$

$$C(3d\pi, 3d\pi) = 88.500q_L + 36.617a' - 109.160 \quad (97d)$$

$$C(4s, \sigma) = 3.834q_M + 46.934q_L + 32.059a' - 103.534$$

$$G = 0.208 \quad (98a)$$

$$C(4p, \sigma) = 2.734q_M + 35.750q_L + 20.586a' - 75.315$$

$$G = 0.123 \quad (98b)$$

$$C) 3d\sigma, \sigma) = 2.655q_M + 37.728q_L + 24.874a'$$

$$G = 0.301. \quad (98c)$$

#### 4. Exchange terms

Exchange terms for the ammonia complex were evaluated on exactly the same basis as those for the fluoride case; numerical results for each integral are listed in Appendix C. Because of their close variation with the group overlap integrals, formulas for the exchange terms are listed here only for the tetrahedral case. Formulas for the pure  $2p\sigma$  case may be obtained directly by proper inclusion of overlap factors. In the latter case,  $\psi'$  will overlap the metal orbitals much more, so that exchange terms arising from this AO will arise. Estimation of this additional uncertainty is again difficult; but these terms are not too important. Hence they were neglected.

$$\frac{a^2(a_{1g})}{a^2(f_{1u})} \frac{a^2(e_g)}{a^2(e_g^+)} \frac{a^2(e_g^+)}{b^2(e_g^+)} \text{ const.}$$

$a_{1g}$ :

$$K(4s, 4s) = -0.84 \quad -2.52 \quad -1.68 \quad +0.84 \quad +5.04 \quad (99a)$$

$$K(\sigma, \sigma) = +0.84 \quad +1.36 \quad +0.97 \quad +0.97 \quad (99b)$$

$$K(4s, \sigma) = +3.11 \quad -1.72 \quad -0.89 \quad +0.76 \quad +0.83 \quad +5.01 \quad (99c)$$

$f_{1u}$

$$K(4p, 4p) = -0.45 \quad -1.36 \quad -0.91 \quad 1.28 \quad +2.72 \quad (100a)$$

$$K(\sigma, \sigma) = +1.18 \quad +1.91 \quad +0.57 \quad +0.57 \quad (100b)$$

$$K(4p, \sigma) = -0.06 \quad +0.95 \quad -1.92 \quad +0.56 \quad +2.98 \quad +4.97 \quad (100c)$$

$e_g$ :

$$K(3d\sigma, 3d\sigma) = -0.94 \quad -1.46 \quad -1.87 \quad -1.87 \quad +4.27 \quad (101a)$$

$$K(\sigma, \sigma) = +0.08 \quad +1.36 \quad +1.82 \quad +1.82 \quad (101b)$$

$$K(3d\sigma, \sigma) = -1.90 \quad -1.90 \quad +1.75 \quad +5.45 \quad +3.67 \quad +8.56 \quad (101c)$$

### 5. Numerical values of the $F^S(m,n)$

All that remains in order to calculate the  $F^S(m,n)$  for the ammonia case is to specify the value of  $a'$ , the polarization parameter. A value of  $a' = 0.70$  was selected; this gives a slightly greater polarity to the N—H bond than the estimate by Mulliken (89), which placed a formal charge of +0.3 on each of the hydrogens. It is interesting to note from Equations 93 through 98c that small changes in  $a'$  produce only small changes in the separation between the  $C(\chi, \chi)$  and  $C(\sigma, \sigma)$ .

It has been found that the effect of polarization upon the valence state ionization potential of the lone pair electrons is relatively small; in preparing graphs of the  $F^S(m,n)$ , analogous to Figures 11 and 12, this factor has been neglected. See Figures 13, 14, 15 and 16.

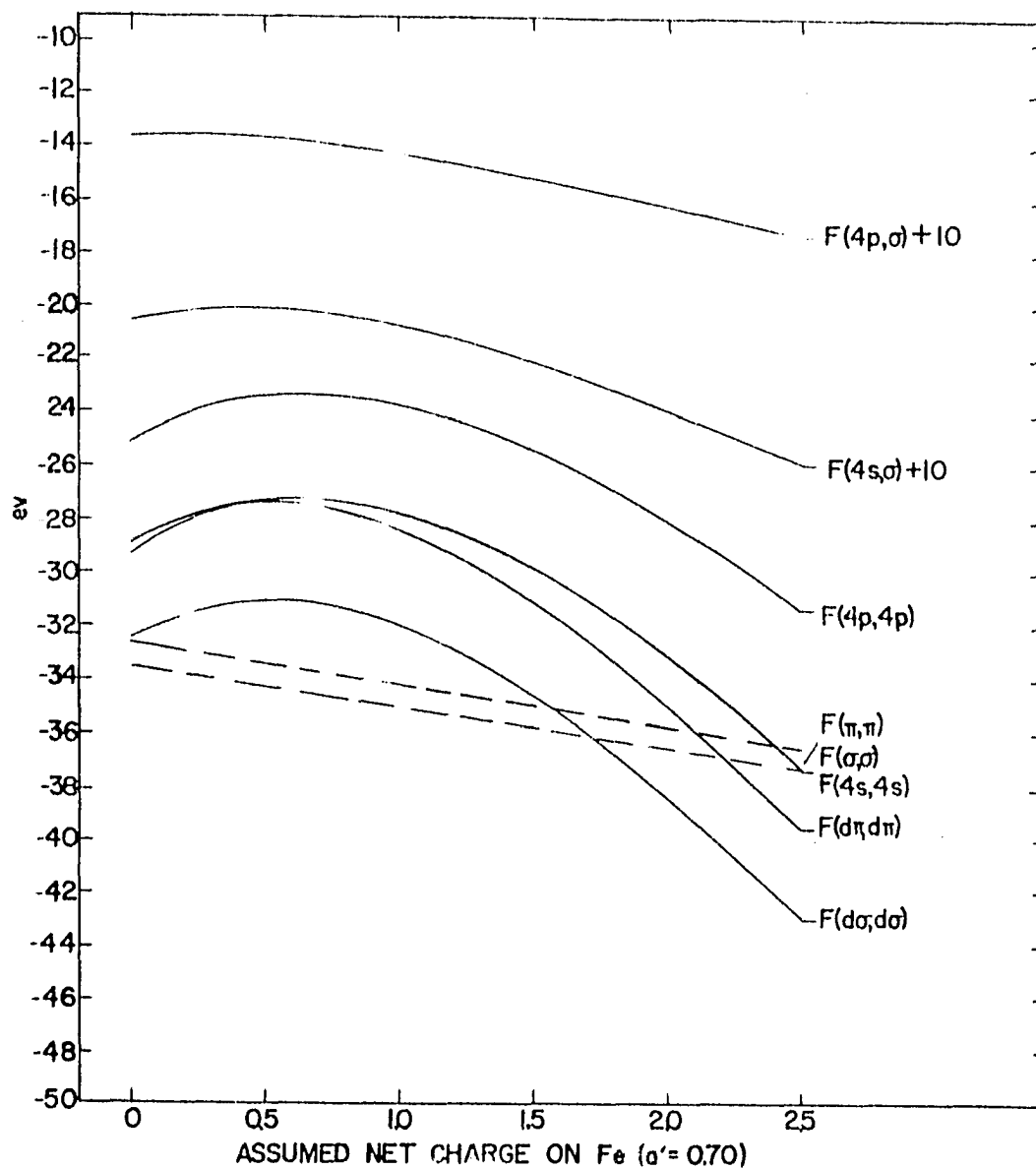


Figure 13.  $F^+(m,n)$  for  $\text{Fe}(\text{NH}_3)_6^{+3}$  assuming  $s, p\sigma$  hybrid

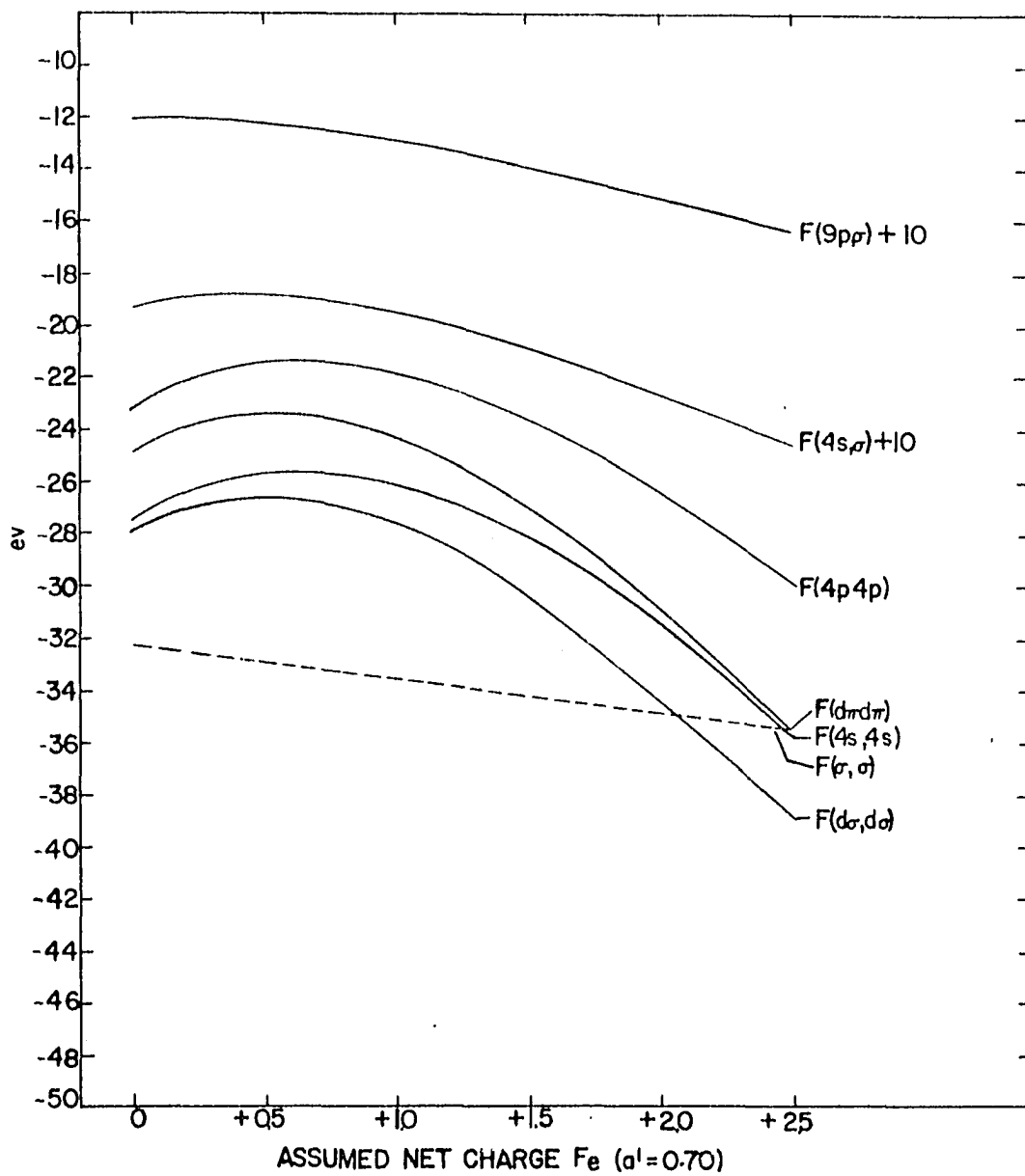


Figure 14.  $F^-(m,n)$  for  $\text{Fe}(\text{NH}_3)_6^{+3}$  assuming s,p $\pi$  hybrid

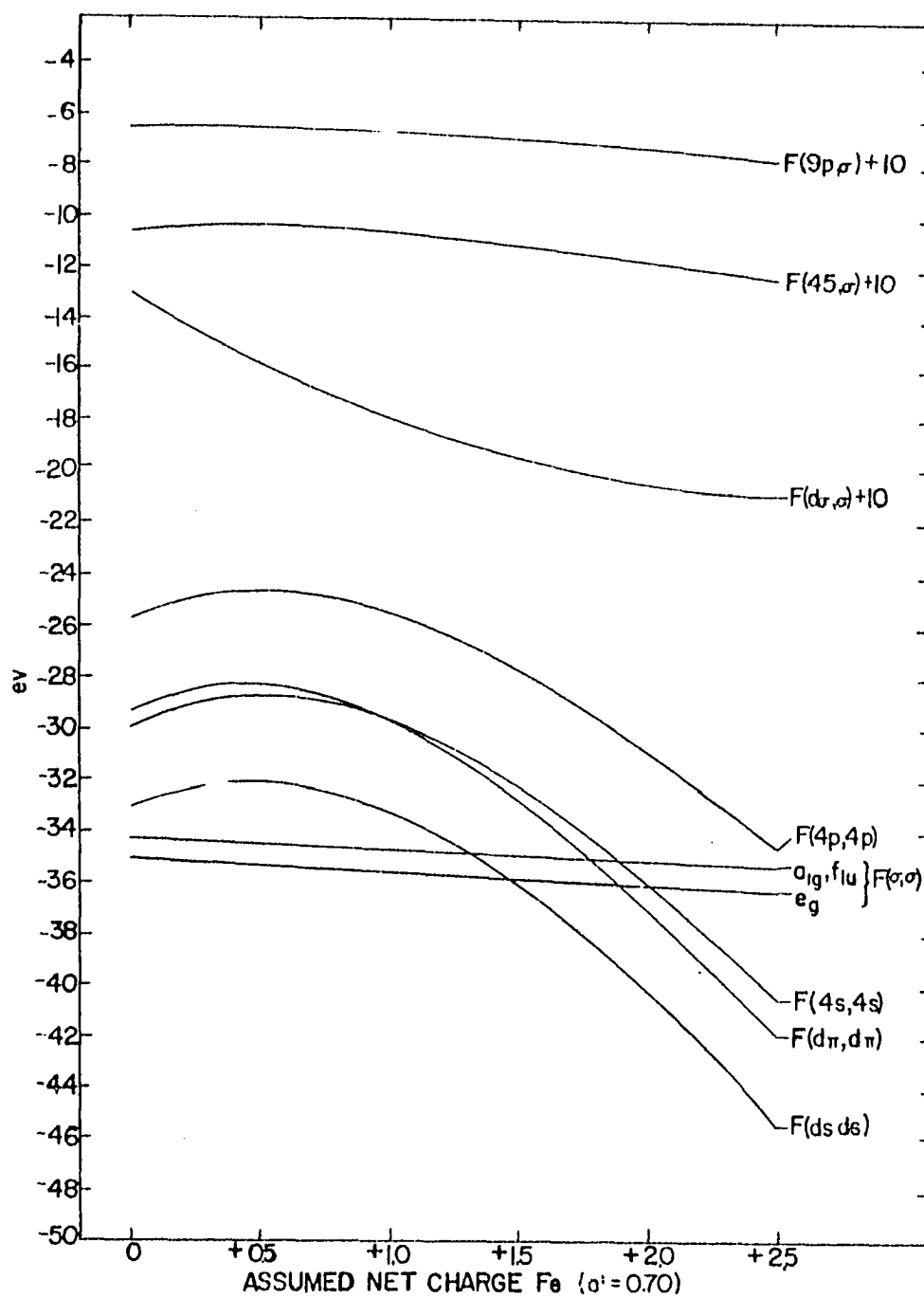


Figure 15.  $F^+(m,n)$  for  $\text{Fe}(\text{NH}_3)_6^{+3}$  assuming pure  $p\sigma$



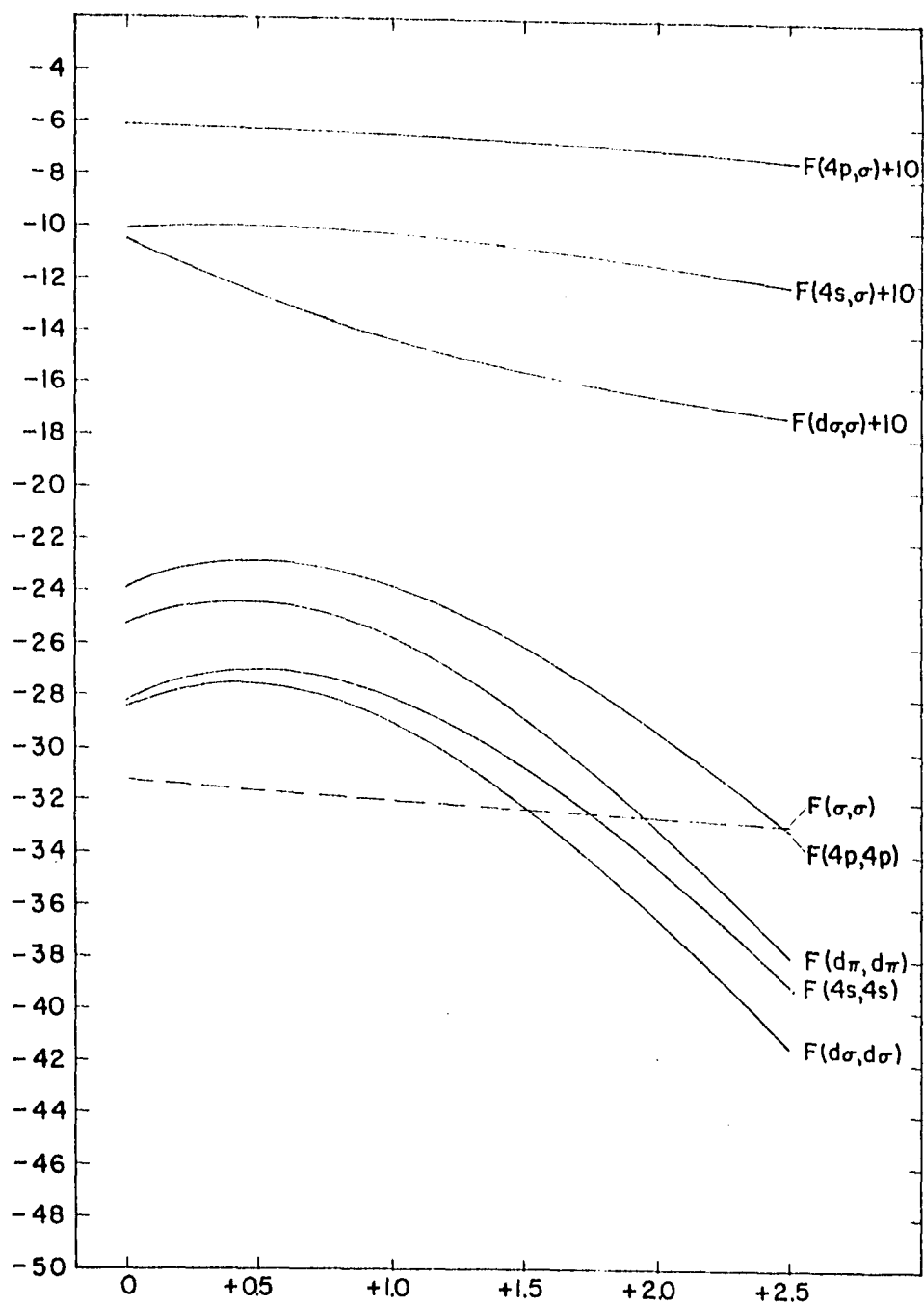


Figure 16.  $F^-(m,n)$  for  $\text{Fe}(\text{NH}_3)_6^{+3}$  assuming pure  $p\sigma$

## VII. RESULTS AND DISCUSSION

## A. Wave Functions and Energy Levels

1. Results for  $\text{FeF}_6^{+3}$ 

Using the formulas for the energy terms derived in the last chapter, the secular equations were solved according to the self-consistency requirement. The numerical values of the energy terms derived for construction of Figures 11 through 16 were used to bracket the region within which the correct coefficients lay. From there on, reasonable estimates were made to determine choices of coefficients for succeeding cycles, until satisfactory agreement was obtained between calculated and assumed coefficients.

The occupied MO's, their energies (in ev) and the  $\underline{a}_k^2$  coefficients were derived as follows, with  $\sigma$  and  $\pi$  indicating the proper ligand SO's:

$\phi(1a_{1g}^+) = (0.315)4s + (0.876)\sigma$	$E = -2.19 \underline{a}^2 = 0.17$
$\phi(1a_{1g}^-) = (0.241)4s + (0.914)\sigma$	$E = -1.66 \underline{a}^2 = .11$
$\phi(1f_{1u}^+) = (0.302)4p + (0.740)\sigma + (0.445)\pi$	$E = -2.23 \underline{a}^2 = .19$
$\phi(1f_{1u}^-) = (0.246)4p + (0.780)\sigma + (0.437)\pi$	$E = -1.85 \underline{a}^2 = .00$
$\phi(2f_{1u}^+) = (0.044)4p - (0.526)\sigma + (0.852)\pi$	$E = -0.79 \underline{a}^2 = .15$
$\phi(2f_{1u}^-) = (0.055)4p - (0.504)\sigma + (0.859)\pi$	$E = -0.78 \underline{a}^2 = .00$
$\phi(1e_g^+) = (0.527)3d\sigma + (0.751)\sigma$	$E = -4.48 \underline{a}^2 = 0.36$
$\phi(1e_g^-) = (0.322)3d\sigma + (0.884)\sigma$	$E = -2.17 \underline{a}^2 = 0.16$
$\phi(2e_g^+) = (0.874)3d\sigma - (0.691)\sigma$	$E = +7.24 \underline{a}^2 = 0.64$

$$\begin{array}{lll}
\varphi(1f_{2g}^+) = (0.486)3d\pi + (0.782)\pi & E = -2.32 & \underline{a}^2 = 0.31 \\
\varphi(1f_{2g}^-) = (0.197)3d\pi + (0.940)\pi & E = -1.15 & \underline{a}^2 = 0.08 \\
\varphi(2f_{2g}^+) = (0.898)3d\pi - (0.656)\pi & E = +3.97 & \underline{a}^2 = 0.09
\end{array}$$

Values of the  $\underline{a}_k^2$  for successive cycles were used as the criterion for self-consistency. The maximum difference between the final calculated and assumed coefficients was 0.02. The final calculated net charge on the iron is +1.09, compared to the assumed value of +1.27. The energy level diagram is given in Figure 17.

The calculated separation between the  $2e_g^+$  and the  $2f_{2g}^+$  MO's is 3.26 ev, as compared to a splitting parameter  $Dq$  of somewhat less than 2.5 ev, which results from the spectral analyses of Orgel (30). The agreement between these two values is remarkably good, it is felt, in view of all the approximations made in the theoretical treatment as well as in the spectral analyses.

Notice, also, that the correct ordering of the two levels is given by these calculations, in contrast to the results from the Wolfsberg and Helmholz approximations.

The delocalization of 36 per cent of the  $2e_g$  and 16 per cent of the  $2f_{2g}$  electrons is consistent with the optical and paramagnetic resonance spectra interpreted by Owen (47), although, it is true, no data are available for the fluoride complex.

It is interesting to observe that the most non-polar (*i.e.* most covalent) MO's turn out to be those involving the metal

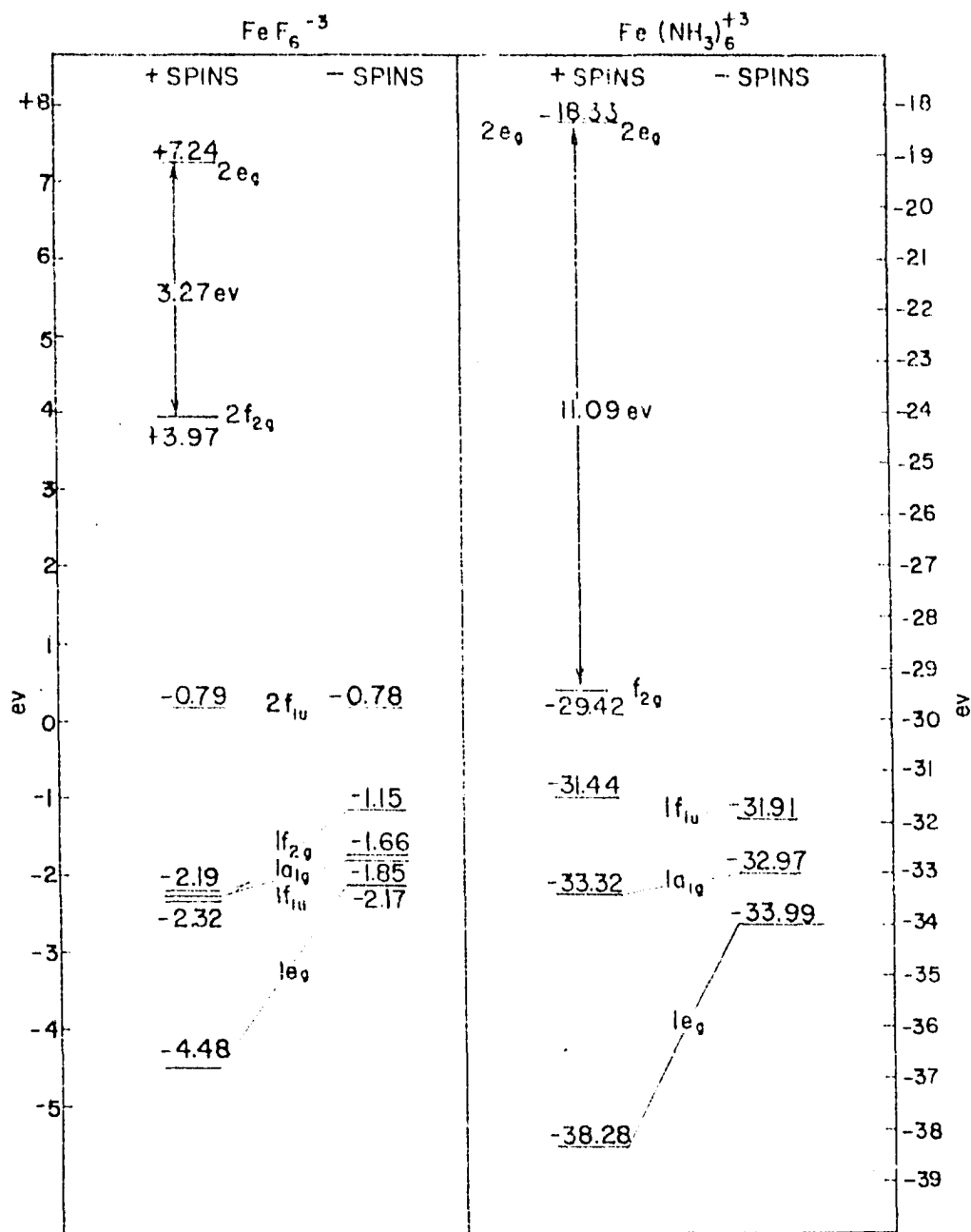


Figure 17. SCF MSO energy levels derived for FeF<sub>6</sub><sup>3-</sup> and Fe(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>

3d orbitals. That is, the magnetic electrons are found to be the ones most involved in exchange with the ligand. This conclusion may be somewhat surprising in view of the previous thoughts on the subject, both of the crystalline field and of the ionic versus covalent hybrid orbital varieties. But this conclusion seems inescapable.

## 2. Results for $\text{Fe}(\text{NH}_3)_6^{+3}$

The situation with regard to the ammonia complex is less pleasing. In brief, the difficulty arises from the fact that the  $F^+(\rho, \rho)$  terms all appear to lie too high with respect to the  $F^+(\chi, \chi)$ , particularly the  $F^+(3d, 3d)$ . This situation results in two undesirable features. First, the  $2e_g$ — $2f_{2g}$  separation is increased greatly, and second, the anti-bonding  $2e_g$  electrons are shifted out too much onto the ligands, as estimated from the experimental results reported by Owen (47).

The case in which the lone-pair electrons were assumed to be described by a tetrahedral hybrid ammonia AO produced extremely unsatisfactory results, i.e., a  $3d_{e_g}$ — $3d_{f_{2g}}$  separation of about 23 ev. This is to be compared to the corresponding results obtained in the Wolfsberg and Helmholtz calculations, before the empirical factor was introduced.

On the other hand, the case in which the lone-pair electrons were assumed to be in pure 2p AO's produced somewhat better results. But still the calculated separation turns out to be about 11 ev, which exceeds Orgel's and Owen's estimates

by a factor of four. It is interesting to note that the disparities arising in this theoretical calculation are quite opposite to those encountered by Hartmann, et al., namely that too great a separation is computed, as well as too much chemical bonding.

Because of these obvious deficiencies, no attempt was made to carry the ammonia calculations to self-consistency. The results of the first cycle for the latter case, however, are presented for their interest.

$\phi(1a_{1g}^+) = (0.526)4s + (0.748)\sigma$	$E = -33.32$	$\underline{a}^2 = 0.36$
$\phi(1a_{1g}^-) = (0.422)4s + (0.823)\sigma$	$E = -32.97$	$\underline{a}^2 = .25$
$\phi(1e_g^+) = (0.621)3d\sigma + (0.618)\sigma$	$E = -38.28$	$\underline{a}^2 = .50$
$\phi(1e_g^-) = (0.477)3d\sigma + (0.747)\sigma$	$E = -33.99$	$\underline{a}^2 = .50$
$\phi(2e_g^+) = (0.846)3d\sigma - (0.848)\sigma$	$E = -18.33$	$\underline{a}^2 = .34$
$\phi(f_{2g}^+) = 3d\pi$	$E = -29.42$	$\underline{a}^2 = 1.00$
$\phi(1f_{1u}^+) = (0.369)4p + (0.885)\sigma$	$E = -31.44$	$\underline{a}^2 = .18$
$\phi(1f_{1u}^-) = (0.261)4p + (0.934)\sigma$	$E = -31.91$	$\underline{a}^2 = .10$

The derived net charge on the iron is +0.9 compared to the assumed value +1.2. The 50 per cent delocalization of the  $2e_g^+$  electron is in fair agreement with the 60 per cent estimate of Owen (47). But the 11.1 ev separation between the  $2e_g^+$  and  $f_{2g}^+$  MO's is much too large. The calculated energy level diagram is given in Figure 17.

In both the  $FeF_6^{-3}$  and the  $Fe(NH_3)_6^{+3}$  results, it is observed that the plus spin MO's are always lower in energy and more covalent in character than are the minus spin MO's. This is a

consequence of the exchange interactions of the unpaired anti-bonding electrons.

### 3. Resume of the calculations

Before commenting upon these results, it might be well to review briefly the nature of the calculations presented.

In contrast to the crystalline field theory assumption of no electronic exchange between metal and ligand, the electronic structures of two transition-metal complexes,  $\text{FeF}_6^{-3}$  and  $\text{Fe}(\text{NH}_3)_6^{+3}$ , have been discussed on the basis of modern chemical valence theory. These calculations are intended to augment the existing qualitative hybrid AO and MO theories in two ways: (a) to establish, on a reasonably sound theoretical basis, the nature of the interactions within such a complex ion. (b) to simplify, in a reasonable and justifiable fashion, the calculational approach so that drawing semi-quantitative conclusions is practical, while retaining as much of the qualitative virtue of the naive MO approach as is possible.

The ferric complexes were discussed for several reasons. The ground states are totally symmetric,  ${}^6A_{1g}$ , so that the usual Hartree-Fock equations are applicable. There are no nearby excited states of the same symmetry to cause complications from configuration interaction. That the 3d shell is half-filled permits a very good approximation to be made for the net coulomb effect of the metal ion upon the ligands. And finally, it is of interest to investigate a system containing unpaired electrons, since this is a rare occurrence in other

kinds of chemical compounds.

Simplification of the Fock operator and the resulting energy terms proceeded along lines similar to those already used by others in simpler molecules. The derived expressions for the energy terms were obtained as sums of experimentally measured valence state ionization potentials and theoretically computed or estimated integrals, by means of relatively good approximation techniques. The major profit from the whole development lies in the exchange terms, for two reasons: (a) it is only through the correct inclusion of all exchange integrals that the differentiation between MSO's of plus spin and those of minus spin may be assessed; (b) the proper disposal of certain exchange integrals through inclusion within the  $Q$ 's, and the retention of others, has important consequences in the derived energy levels.

In connection with this last point, reference is made to the similar calculations made by Zaslow (95) on the  $\text{FeCl}_4^-$  ion. He did not explicitly include the exchange terms as such, but rather reduced the values of  $q_M$  and  $q_L$  by the charge density of the electron under consideration, assigned to the metal and to a ligand respectively. In other words, the repulsion of itself by the electron being considered is subtracted from the coulomb terms of  $F^S$ , as it surely must be. Where proper account is made of the exchange terms, however, this subtracting off proceeds in a different manner. It is found that in the  $K(\chi, \chi)$  and  $K(\rho, \rho)$  there are no analogues of coulomb terms,



these terms having been assigned to the Q's. On the other hand, in the  $K(\chi, \rho)$  only half the Coulomb analogues are found to belong with the Q's. The net effect is to make the  $F^S(\chi, \rho)$  larger (more negative) relative to the  $F(\rho, \rho)$ . And the result of this is to make the MO's more bonding. A number of Zaslow's bonding MO's looked antibonding (*i.e.* had the form  $a\chi - b\sigma$ ); and it is believed that the cause of this objectionable feature has now been eliminated.

Based upon these considerations and the AO's and distances previously obtained, the wave functions and energy levels of the two complex ions were derived. Of interest to the magnetic and spectral properties of these complexes, is the  $2e_g^+ - 2f_{2g}^+$  separation, identified with the Dq parameter of crystalline theory. Results for the fluoride complex are very satisfying, indeed, for an a priori calculation upon such a complicated system. The ammonia complex, however, has been found to be a much more complicated system to treat and furthermore the calculated energy levels are unreasonable.

Two possible alternative conclusions may be drawn at this point: (a) the excellence of the fluoride calculation is fortuitous and the theory is inadequate in its present form to deal with these systems or (b) the theory is sufficiently reliable to permit significant conclusions to be drawn. Doubtless, the truth lies between these extremes; but it is felt that the truth is nearer (b) than (a).

Granting this last assumption, the discussion proceeds with the expressed understanding that it is based upon the theories and approximations of Chapter VI.

#### 4. Errors

A theoretical study such as this is not properly complete without some consideration of the possible sources of errors present in the theoretical model, in the approximations necessary to make the theoretical development tractable, and in the actual calculations themselves.

Only the last-mentioned source of error is at all easy to discuss. In short, effort was made, of course, to keep calculations as free from numerical error as possible. In addition to the usual checking of numerical work, there was often present some other criterion of accuracy, such as comparison of parallel computations and also the general "reasonable-ness" of each result.

The other sources of error are much easily analyzed. General considerations on the subject have been given by Mulliken (94) and Slater (55), for example, and will not be elaborated upon here. Errors in estimation of certain multi-centered integrals could be evaluated by exact computation; this would be difficult, although quite desirable. The approximation of sums of one-center integrals by valence-state ionization potentials is at once a good and a doubtful approximation. It is good to the extent that it eliminates a great deal of the error that troubled Duncan (105) in his calculation

of the energy levels of  $\text{SF}_6$ . It is a doubtful approximation because it rests upon the somewhat arbitrary manner of dividing up the overlap charge distributions. This approximation technique is, of course, fundamental to the whole treatment. It certainly warrants further study, when the calculations are refined and extended.

The significance of the overlap integrals, and hence upon the analytic forms for the AO's, used, will be discussed below. Presumed deficiencies in the metal orbitals have been presented in Chapter IV. There is little more to be said here on the subject.

It is important to remember, when discussing the results of such a theoretical calculation as this, that all the conclusions are based upon the approximations inherent in any theory and are subject to all the errors mentioned and more. These limitations are implicitly included in all conclusions.

## B. Discussion

### 1. Significance of inner-shell orbitals

Neglect of inner shell-valence shell interactions has been assumed throughout the calculations, with little attempt at justification. As a partial check, however, the 3s AO of Fe derived by Wood (77) was approximated by a single Slater-type function and its overlap with a ligand was estimated to be about 0.04, which is small but not entirely negligible. On the

other hand, its coulomb effect upon a ligand AO is exceedingly close to that of a point charge.

The usual type of error introduced by such neglect is that the valence shells do not remain orthogonal to the inner shells. This neglect leads to a number of uncertainties in interpreting the results of the calculations. In the present case, however, the 3d AO's are, by virtue of the octrahedral symmetry, orthogonal to all inner shells of the metal. Thus, as far as the metal is concerned, it seems reasonable to conclude that the neglect of inner shells is a lesser assumption and one which will influence the  $e_g$  and  $f_{2g}$  MO's only through the  $a_{1g}$  and  $f_{1u}$  MO's.

The neglect of 2s,2p $\sigma$  mixing in the fluorine SO's is another matter, although rough inclusion of the 2s AO in a trial calculation did not alter the results to any major extent. The main reason for this lies in the fact that the 2s AO is about 15 ev below the 2p, and appreciable hybridization of the two is restricted by this large energy separation.

## 2. Significance of outer orbitals

It has been found that a reasonably adequate description of the bonding in these "ionic" complexes can be had without recourse to the "outer" 4d AO's of the metal; indeed, in the ammonia case, the difficulty is in too much bonding, not in too little.

It is certainly reasonable, and is easily theoretically verifiable, that the further apart are two interacting SO's

the less the interaction between them. Hence, if the ligand SO's are so far below the metal SO's that the bonds are highly polar ("ionic"), then, a fortiori, the outer orbitals are even less important in stabilizing the bonding MO's.

But it is also important to note that there is no reason to limit the discussion to outer AO's of the metal only. In fact, by including 3s AO's into the ligand SO's one may partially allow for the previously neglected polarization of the fluoride atoms in  $\text{FeF}_6^{-3}$ . Although even rough estimation of the energy terms for these SO's is filled with grave uncertainties, nevertheless a trial secular equation was solved for the  $e_g^+ \text{MO}$  system, in which the 3s AO was estimated at 10 ev above the 2p and other energy and overlap terms set at 1/2 the corresponding 2p terms. Inclusion of this type of ligand polarization decreases the  $2e_g^+ - 2f_{2g}^+$  separation by 1 ev (to 2.32 ev) and transferred an additional 0.2 unpaired electron to the fluorides in the antibonding MO's. Similar inclusion of fluorine 3p AO's in the  $f_{2g} \text{MO's}$  produced little change at all in either  $1f_{2g}^+$  or  $2f_{2g}^+$ . Presumably the 4d metal AO's would produce comparable effects, but it is impossible to estimate these at present.

Thus one is led to suspect that outer orbitals may indeed be significant, but that the ligand outer orbitals may be of even greater importance than those of the metal.

### 3. Significance of the group overlap integrals

If one solves a general  $2 \times 2$  secular equation and examines the dependence of the eigenvalues upon the group overlap integral, one finds an interesting conclusion, namely, that increasing the overlap integral raises the center of gravity of the bonding and antibonding MO's. That is to say, for example, that  $E(2e_g) + E(2e_g)$  is less negative than  $F^S(3d\sigma, 3d\sigma) + F^S(\sigma, \sigma)$  by an amount dependent upon the overlap. But  $E(1e_g)$  is always more negative than  $F^S(\sigma, \sigma)$ . Therefore, the major effect of changing the overlap integral is to change the energy of the antibonding level.

The magnitude of this factor may partially be judged from a calculation upon the eg MO of  $\text{Fe}(\text{NH}_3)_6^{-3}$ . Changing  $G(3d\sigma, \sigma)$  from 0.308 to 0.200 lowered the  $2e_g$  level 6 ev, while hardly affecting the  $1e_g$  level at all.

Thus the importance of the overlap integral to the electronic structure of transition-metal complexes re-emerges, though in a different manner than that discussed by Craig, et al., (6). The overlap integral, as well as the outer orbitals of both metal and ligand, appear to be of considerable significance in the description of the antibonding electrons.

These factors have two important effects: (a) reducing the antibonding repulsion of the five electrons in  $2e_g^+$  and  $2f_{2g}^+$ , thereby stabilizing the molecule and (b) influencing the separation between those two levels. Indeed, these two factors are at least as important, and may be more important in

determining the  $2e_g^+ - 2f_{2g}^+$  separation, than the electrostatic effect itself. If in ammonia or water complexes, for example, it is allowed that electron density is transferred from the ligand to the metal, the fractional positive charge on the ligand will surely reverse the splitting of the 3d AO's predicted by the crystalline field theory approximation.

Now one is in a position to assess the chemical implications of the  $Dq$  versus ligand series investigated by Orgel (30) among others. (See page 22.) For it is now apparent that any one of a number of factors other than the polarity of the bonding may influence the splitting of the 3d orbitals. Quantitative evaluation of all the factors is, of course, impossible. But it is not unreasonable to think that  $\pi$ -interactions increase relative to  $\sigma$ -interactions upon going down the halogen series. Comparison of the fluoride with the chloride overlaps calculated by Zaslow supports this view. Hence, the interpretation presented here implies that iodine causes the least splitting because the  $\sigma$  and  $\pi$  bonding are most equal in this sense, and not because iodide is the most ionic ligand. The splitting increase upon going to fluoride, then still more upon going to such complexes as the water and ammonia, where  $\pi$ -bonding is very small. Finally, in the complexes such as cyanide and other systems with conjugation, the  $\sigma$ -type interactions are much stronger than the  $\pi$ , first since the lone-pair electrons of the ligand are highly concentrated in the direction of the metal, as judged from the overlap integral, and second

since the  $\pi$ -type repulsions from the ligands are reduced by the delocalization of the ligand  $\pi$  electrons from the neighborhood of the metal-ligand linkage.

The nature of the overlap integral variations would seem to be well defined in broad outline, by the AO's used in the present work. More precise analyses, however, should wait consideration of such metal AO's as those reported by Wood (77), where the effect of spin orientation may be estimated.

#### 4. The $\text{Fe}(\text{NH}_3)_6^{+3}$ problem

Although speculation is hazardous on the possible causes for the poor results obtained for the  $\text{Fe}(\text{NH}_3)_6^{+3}$  complex, it appears that the difficulty stems from three sources, two of which are related to the assumed metal-ligand distance. It will be recalled that the sum of Pauling's covalent radii was used throughout the calculations. Direct computations show that if this assumed distance were to be increased by a few tenths of an Ångstrom, perhaps to 2.2 Å, not only would the  $F^S(\chi, \chi)$  become more positive relative to the  $F^S(\rho, \rho)$  but so also would the group overlap integrals decrease. Both results would tend to improve the calculated energies and wave functions considerably.

In addition, it is certainly true that with this complex, just as with  $\text{FeF}_6^{-3}$ , the outer orbitals of both the metal and the ligand may be quite significant in reducing the  $2e_g - f_{2g}^+$  separation. When good MO's for  $\text{NH}_3$  are available, it would be very profitable to investigate this possibility further.



Furthermore, possible effects of the environment of the complex ion as it occurs under experimental conditions must be considered. In solution, detailed examination of the environment would be exceedingly difficult. On the other hand, in the crystalline state, distances and orientations may be ascertained fairly accurately. Unfortunately, such crystallographic data are completely lacking, for the ammonia complex. Certainly careful crystalgraphic analyses of these compounds would facilitate further theoretical studies.

#### 5. Effects of localized excess charge

In the preceding paragraph, it was concluded that the electro-static effects of excess charge on the ligands may be of secondary importance in determining the splitting of the 3d AO's. Yet in discussing the results of the application of the Wolfsberg and Helmholtz approach to the complex ions considered here, it was stated that those same coulomb effects were critical. In this paragraph, the apparent conflict between these two comments will be resolved and, at the same time, some additional insight will be gained into the nature of the metal-ligand interaction in transition-metal complexes.

In developing this point it is helpful to resort to a specific example, namely, the  $\text{FeF}_6^{-3}$  ion and, of it, the electrons of plus spin in particular. The central column of Figure 18 is a reproduction of the MO energy levels for the plus spin electrons derived for  $\text{FeF}_6^{-3}$  and given in Figure 17. However, in addition, in this drawing are indicated the various factors

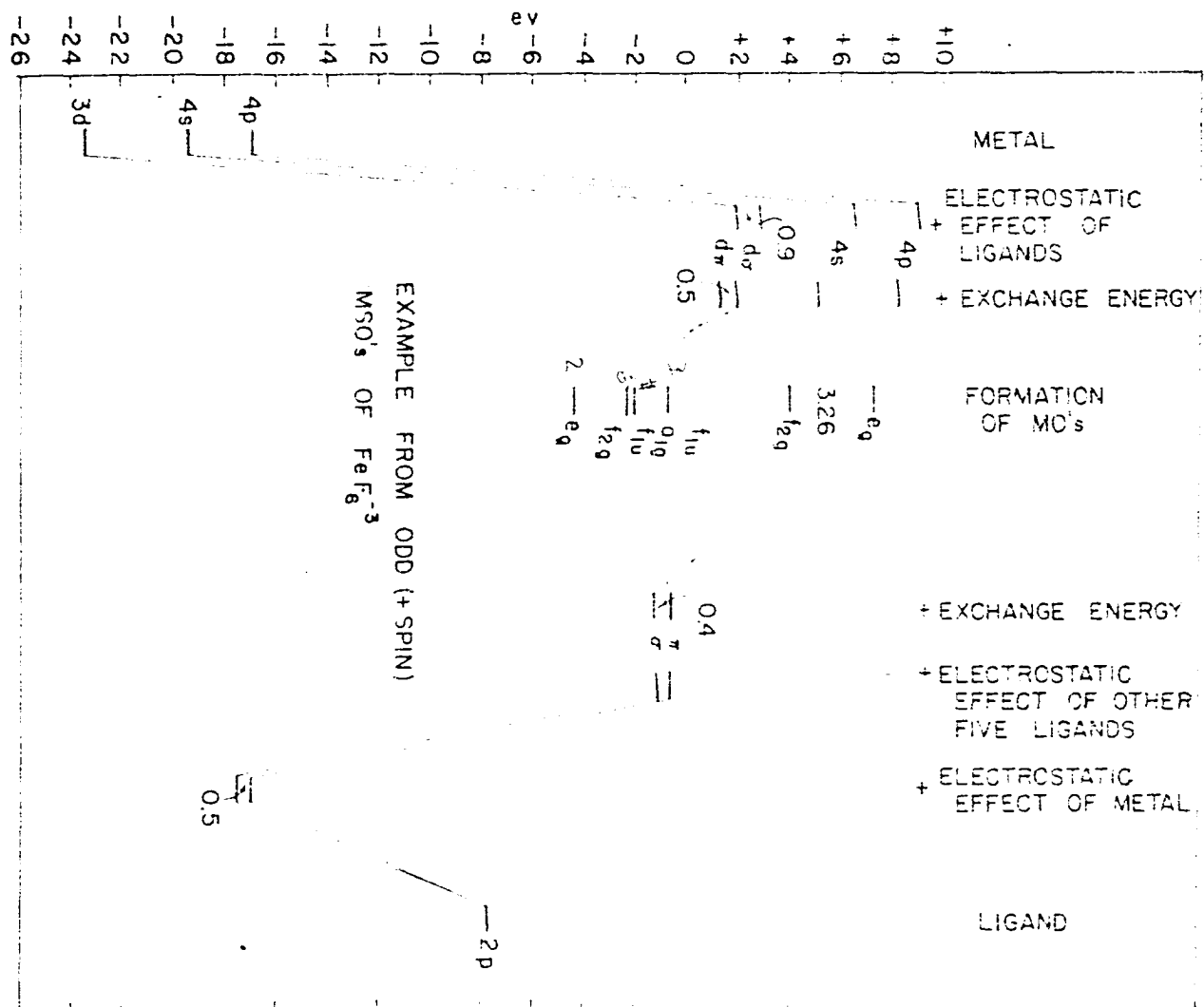


Figure 18. Analysis of origin of MSO energy levels.

which determine not only the energies of the final MO's but also, of more significance, the relative energy separation of the metal and the ligand SO's. The outermost columns of the figure indicate the orbital energies of the constituent atoms separated to infinity, but the each atom still allotted its share of the total electronic charge density according to Equation 25. It is seen that at this stage the metal SO's lie below those of the ligand.

When the electrostatic effects of the ligands upon the metal and of the metal and five ligands upon the remaining ligand are added, the orbital energy of the ligand is raised somewhat while that of the metal is raised by a considerable amount, such that the metal SO's lies above those of the ligand. Thus the negative charge on the ligands tends to stabilize the positive charge of the metal with respect to the ligands. In other words, by raising the relative energies of the electrons on the metal, the negative charge on the ligands helps maintain the proper polarity of the MO's in the self-consistency process. The positive charge on the metal has the complementary effect upon the electrons on the ligand atom.

Hence, it appears that the role of the excess net charges within the complex ion is to largely determine the equilibrium charge distribution (although the overlap integrals, through the  $F(\chi, \rho)$  terms, are also quite important). But also, as can be seen from Figure 18, these charges also serve to split the energies of the 3d AO's (but by only about 0.9 ev, less than

half the probable experimental value) and the  $\sigma$  and the  $\pi$  SO's of the ligand (but, again, by only half the value used in the Wolfsberg and Helmholtz approach). The first number quoted is the basis for judging the relative importance of electrostatic effects. But in this connection, the electrostatic effect has a secondary influence upon the overlap effect, as one can see by the following argument. The values of the relevant overlap integrals is seen to depend markedly upon the equilibrium electronic configuration of the complex ion (cf. Figure 8); but this electronic configuration has already been found to depend in turn upon the electrostatic factors as well as the overlap integrals. Thus the two effects are closely interdependent.

The discussion of the effects of local excesses of charge is also properly extended to cases wherein the excess is not located within the complex ion itself, i.e., to include the electrostatic effects of the environment of the complex ion when it is situated in a crystal or in solution. These particular factors are hereby recognized for their influence (which may be quite important) upon the electronic structure of the complex ion, but a study of them is postponed for further research.

#### 6. Summary of conclusions

In brief, in this thesis there has been developed a single theoretical approach to the understanding of the electronic structure and properties of transitional-metal complexes which

is applicable to any such system regardless of the experimentally measured magnetic properties. This approach combines the quantitative advantages of the physical or crystalline field theory with the intuitive advantages of the chemical or hybrid orbital theory.

If the calculated results of the semi-empirical LCAO MO SCF treatment presented for the octahedral  $\text{FeF}_6^{-3}$  complex ions can be accepted as significant, then it is not only possible to draw reasonably quantitative conclusions about those two complexes, but also to extend qualitative discussion to the electronic structure of transition-metal complexes in general.

In these rather detailed calculations there has been demonstrated a comparatively simple method to produce a semi-quantitative description of rather complicated electronic systems. In this process most of the approximations inherent in the theory and calculations are exposed for their bearing upon the conclusions. The major conclusions are:

- (a) That the outer d-orbitals of the metal are not necessary for a qualitative understanding of the complexes, but for a quantitative analysis.
- (b) That the outer orbitals of not only the metal, but very likely of the ligand as well, are of considerable significance in determining the magnetic (and other) properties of these complexes;
- (c) That a highly simplified semi-empirical approach, such as that of Wolfsberg and Helmholz, is

inadequate to discuss electronic systems wherein local excess of net charge may accumulate;

(d) That, contrary to the usual and necessary assumption of crystalline field theory, the overlap with the ligand orbitals is very important in determining the splitting of metal 3d orbitals.

As a concluding remark, it is quite appropriate to state that obviously the theory in its present development is still inadequate to deal completely and independently with these systems. As a final profit, then, to be gained from continuing theoretical studies such as this is the suggesting of useful experiments, experiments which remain essential for the advance of understanding the nature of these interesting chemical compounds - - the transition-metal complexes.

## VIII. ACKNOWLEDGMENTS

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## IX. GLOSSARY

Symbols used in Chapter VI.

- $\chi$  AO as well as SO on metal atom.
- $\psi$   $\sigma$ -type AO on ligand atom or molecule.
- $\xi$   $\pi$ -type AO on ligand atom or molecule.
- $\kappa$  either a  $\sigma$ -type or a  $\pi$ -type AO on ligand or molecule.
- $\sigma$   $\sigma$ -type ligand SO.
- $\pi$   $\pi$ -type ligand SO.
- $\rho$  either a  $\sigma$ -type or a  $\pi$ -type ligand SO.
- $\varphi$  MO, space parts of  $\lambda$ .
- $\lambda$  MSO .
- $\eta$  spin factor.
- $a_j^2, b_j^2, c_j^2$  coefficients of charge assignment within the  $j^{\text{th}}$  MO. See definition, Equation 25.
- H N-electron Hamiltonian operator.
- F generalized one-electron Fock operator, defined in terms MSO's, to operate on MSO's.
- $F^s$  one-electron Fock operator for a particular spin state ( $s = +$  or  $s = -$ ), defined in terms of MO's, to operate on MO's.
- $Q(\chi), Q^s(\chi)$  valence state ionization potential of the  $\chi$ -electron (of spin state indicated by  $s$ ) of a metal atom with appropriate charge distribution.
- $Q(\kappa), Q^s(\kappa)$  same for a  $\kappa$ -electron of a ligand atom.
- $\zeta$  orbital exponent of a Slater-type AO.
- $i, j, k$  -- indices numbering MSO's and, hence, MO's and SO's also.
- $\pm$  index specifying the position of a ligand about the metal atom.



## X. APPENDIX A. GROUP THEORETICAL DERIVATION OF THE SYMMETRY ORBITALS

Although it is possible to arrive at the proper linear combinations of ligand orbitals which form the set of symmetry orbitals by a process of inspection or by comparison with the metal orbitals, it is desirable to have a formal method available for this purpose. As a convenience and as a guide for extensions to systems of different symmetry, such a method will be outlined here. It differs somewhat from that given in Eyring, Walter and Kimball (20, Chapter 10 and pp. 252-253), in enabling one to construct a symmetry orbital which is to mix with another symmetry orbital of arbitrarily chosen form. It is assumed that the reader is familiar with the group theory terminology as given in such references as Eyring, Walter and Kimball.

For octahedral molecules, the nuclei, hence the MO's, transform according to the symmetry operations of the point group  $O_h$ , and therefore according to the irreducible representations of that group as well. The process begins by constructing the various irreducible representations. These are to be distinguished from the "characters" given in the character table. The non-degenerate representations are one-dimensional (that is they are represented by single numbers, or  $1 \times 1$  matrices); the characters of the representations are identical to the representations in this case. The doubly-

triply-degenerate representations are represented by  $2 \times 2$  and  $3 \times 3$  matrices, respectively; the characters are obtained, of course, from the sums of the diagonal elements.

The degenerate irreducible representations are not unique; but all possible choices are related by so-called "similarity transformations."

The non-degenerate representations ( $A_{1g}$ ,  $A_{1u}$ ,  $A_{2g}$ ,  $A_{2u}$ ) are obtained directly from the character table. The degenerate representations may be obtained from the following considerations. First note that the odd (u) representations differ from the even (g) merely in the alteration of sign for the terms which contain the factor of the inversion operator. Hence, it is necessary to consider only the degenerate representations  $E_g$  or  $E_u$ ,  $F_{1g}$  or  $F_{1u}$  and  $F_{2g}$  or  $F_{2u}$ . Next it is assumed that it has been established that

$$\begin{pmatrix} 3z^2 - r^2 \\ \sqrt{3}(x^2 - y^2) \end{pmatrix} \text{ belongs to } E_g, \quad \begin{pmatrix} x \\ y \\ z \end{pmatrix} \text{ to } F_{1u}, \text{ and } \begin{pmatrix} xz \\ yz \\ xy \end{pmatrix} \text{ to } F_{2g}.$$

Since these sets of functions correspond to the adopted atomic functions of the metal, one is assured of obtaining the appropriate representation matrices. Finally all matrices are constructed which transform the sets of functions in the same way as do the geometric operations of the point group. These matrices are the irreducible representations and have been constructed for  $O_h$  and are given in Table 8. (A similar table has been given by Matossi (113); however, there appears to be

an error in one set of matrices.)

For example, the operator  ${}^{111}C_3^+$  transforms  $\begin{pmatrix} x \\ y \\ z \end{pmatrix}$  into  $\begin{pmatrix} y \\ z \\ x \end{pmatrix}$ ;

the corresponding matrix for  $F_{1u}$ , is  $\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$  and

$$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} y \\ z \\ x \end{pmatrix}, \text{ by matrix multiplication.}$$

The correct symmetry orbitals may now be formed directly according to the following recipe. Take one of the ligand orbitals from which it is wished to construct a symmetry orbital. List the results of operating (geometrically) upon this orbital with each of the elements of the group. Multiply each result by the corresponding diagonal element of the matrix representation. (For the A representation, this number will be the character itself; for the E and  $\bar{F}$  representations, this number will be the diagonal element of the first row of the matrix for one symmetry orbital, the diagonal element of the second row for another and so on.) Add the results for each row of each representation. Each sum will be either identically zero or else one of the desired symmetry orbitals.

This method is perfectly general, and may be applied equally well to products of functions, such as encountered in the determination of antisymmetrized, many-electron wave functions. The method if used in detail for all the symmetry orbitals may become somewhat tedious. Some obvious simplifications are immediately recognized. These and others have been formalized by Melvin (114).

Table 8. Irreducible representation matrices for  
the point group  $O_h$

Only those symmetry operations and corresponding representation matrices are shown which do not contain the factor of the inversion operation. The remainder of the table is easily obtained by multiplying each symmetry operator by the inversion operator and the corresponding matrix of each irreducible representation by the following matrices:

$$A_{1g} \text{ by } 1, A_{1u} \text{ by } -1, A_{2g} \text{ by } 1, A_{2u} \text{ by } -1, E_g \text{ by } \begin{pmatrix} +1 & 0 \\ 0 & +1 \end{pmatrix},$$

$$E_u \text{ by } \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \quad F_{1g} \text{ and } F_{2g} \text{ by } \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{and}$$

$$F_{1u} \text{ and } F_{2u} \text{ by } \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

In the E representations,  $u = 1/2$ ,  $v = (\sqrt{3}/2)$ .

Table 8. Irreducible representation matrices for the point group  $O_h$ .

		<u>Symmetry operation</u>						
E		$111C_3^+$	$111C_3^-$	$\bar{1}\bar{1}\bar{1}C_3^+$	$\bar{1}\bar{1}\bar{1}C_3^-$	$111C_3^+$	$111C_3^-$	
$A_1$	1	1	1	1	1	1	1	
$A_2$	1	1	1	1	1	1	1	
E	1 0 0 1	-u v -v-u	-u-v v-u	-u v -v-u	-u v -v-u	-u-v v-u	-u v -v-u	
$F_1$	1 0 0 0 1 0 0 0 1	0 1 0 0 0 1 1 0 0	0 0 1 1 0 0 0 1 0	0 0 -1 -1 0 0 0 1 0	0 -1 0 0 0 1 -1 0 0	0 0 1 -1 0 0 0 -1 0	0 -1 0 0 0 -1 1 0 0	
$F_2$	1 0 0 0 1 0 0 0 1	0 1 0 0 0 1 1 0 0	0 0 1 1 0 0 0 1 0	0 -1 0 -1 0 0 0 -1 0 <i>mistake</i>	0 0 -1 0 0 -1 1 0 0 <i>mistake</i>	0 0 -1 1 0 0 0 -1 0	0 1 0 0 0 -1 -1 0 0	
<u>Symmetry operation</u>								
		$100C_4^+$	$100C_4^-$	$010C_4^+$	$010C_4^-$	$001C_4^+$	$001C_4^-$	$110C_2'$
$A_1$	1	1	1	1	1	1	1	1
$A_2$	-1	-1	-1	-1	-1	-1	-1	-1
E	-u-v -v u	-u-v -v u	-u v v u	-u v v u	1 0 0-1	1 0 0-1	1 0 0-1	
$F_1$	1 0 0 0 0 1 0-1 0	1 0 0 0 0 -1 0 1 0	0 0 -1 0 1 0 1 0 0	0 0 1 0 1 0 -1 0 0	0 1 0 -1 0 0 0 0 1	0 -1 0 1 0 0 0 0 1	0 1 0 1 0 0 0 0 -1	
$F_2$	0 0 1 0-1 0 -1 0 0	0 0 -1 0-1 0 1 0 0	0-1 0 1 0 0 0 0 -1	0 1 0 -1 0 0 0 0 -1	-1 0 0 0 0 -1 0 1 0	-1 0 0 0 0 1 0-1 0	1 0 0 0 0 -1 0-1 0	



the point group  $O_h$ .

Symmetry operation							
$\bar{3}$	$111C_3^+$	$111C_3^-$	$11\bar{1}C_3^+$	$11\bar{1}C_3^-$	$1\ 100C_2$	$010C_2$	$001C_2$
	1	1	1	1	1	1	1
	1	1	1	1	1	1	1
	-u-v v-u	-u v -v-u	-u-v v-u	-u v -v-u	1 0 0 1	1 0 0 1	1 0 0 1
	0 0 1 -1 0 0 0 -1 0	0 -1 0 0 0 -1 1 0 0	0 0 -1 1 0 0 0 -1 0	0 1 0 0 0 -1 -1 0 0	1 0 0 0 -1 0 0 0 -1	-1 0 0 0 0 1 0 0 -1	-1 0 0 0 -1 0 0 0 1
	0 0 -1 1 0 0 0 -1 0	0 1 0 0 0 -1 -1 0 0	0 0 -1 -1 0 0 0 1 0	0 -1 0 0 0 1 -1 0 0	-1 0 0 0 1 0 0 0 -1	-1 0 0 0 -1 0 0 0 +1	1 0 0 0 -1 0 0 0 -1

$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

Symmetry operation							
$4$	$001C_4$	$110C_2'$	$011C_2'$	$101C_2'$	$1\bar{1}0C_2'$	$01\bar{1}C_2'$	$10\bar{1}C_2'$
	1	1	1	1	1	1	1
	-1	-1	-1	-1	-1	-1	-1
	1 0 0 -1	1 0 0 -1	-u-v -v u	-u v v u	1 0 0 -1	-u-v -v u	-u v v u
	0 -1 0 1 0 0 0 0 1	0 1 0 1 0 0 0 0 -1	0 -1 0 -1 0 0 0 0 -1	-1 0 0 0 0 1 0 1 0	-1 0 0 0 0 -1 0 -1 0	0 0 1 0 -1 0 1 0 0	0 0 -1 0 -1 0 -1 0 0
	-1 0 0 0 0 1 0 -1 0	1 0 0 0 0 -1 0 -1 0	1 0 0 0 0 1 0 1 0	0 0 -1 0 1 0 -1 0 0	0 0 1 0 1 0 1 0 0	0 -1 0 -1 0 0 0 0 1	0 1 0 1 0 0 0 0 1





## XI. APPENDIX B. FORMULAS FOR THE ENERGY INTEGRALS

Table 9 give 11 formulas for integrals needed in the calculations of the electronic structures of fourth-period transition-metal complexes (as outlined in this thesis) except for the overlap integrals. Formulas for and tabulations of these integrals are found in Mulliken, Rieke, Orloff and Orloff (115), Jaffe (78), Jaffe and Doak (116), and Craig, et al. (6). The integrals were evaluated by standard methods (see Roothaan (66) for an outline). The list includes all integrals which would arise from complexes formed from first or second row ligand atoms in any arrangement about the metal atom—octahedral, tetrahedral, square-planar, or any lower symmetry. The parameters specifying the integrals are indicated at the beginning of each section.

For completeness and consistency in form, certain integrals have been repeated from Roothaan (66), although in somewhat modified form. These formulas are marked with an asterisk in the table. It has been reported that some of the formulas have also been given in a volume published in Japan in December, 1955 (117). This volume is not available for inspection at the time of writing.

The formulas were derived in duplicate by B. Zaslów; all discrepancies were corrected.

Since the integrals are all two-centered, the region of integration is cylindrically symmetrical. Thus it is appropriate

to classify the AO's with respect to symmetry about the axis, without reference to the manner in which they occur in the molecular problem. All the integrals may be transformed into integrals given in the table, plus more which are identically zero, by obvious algebraic manipulations. During these manipulations, however, it is necessary always to use normalized functions.

Table 9. Formulas for integrals.

(a) F(m,m) integrals			$[X_a X'_a   \delta_b]$	$z=1/2(r+r')$	$t=(r-r')(r+r')^{-1}$
				$p=2rab$	$w=(1-t^2)^{1/2}$
$X_a$	$X'_a$		$[X_a X'_a   \delta_b]$		
1	1s	1s'	$w z p^{-1} \{1-(1+p)e^{-2p}\}$		
2	2s	2s'	$w z p^{-1} \{1-(1+3/2p+p^2+1/3p^3)e^{-2p}\}$		
3	3s	3s'	$w z p^{-1} \{1-(1+5/3+4/3p^2+2/9p^4+2/45p^5)e^{-2p}\}$		
4	2p $\sigma$	2p $\sigma'$	$w z p^{-3} \{(3+p^2)-(3+6p+7p^2+11/2p^3+3p^4+p^5)e^{-2p}\}$		
5	3p $\sigma$	3p $\sigma'$	$1/15w z p^{-3} \{(84+15p^2)-(84+168p+183p^2+137p^3+76p^4+32p^5+10p^6+2p^7)e^{-2p}\}$		
6	2p $\pi$	2p $\pi'$	$w z p^{-3} \{(-3/2+p^2)+(3/2+3p+2p^2+1/2p^3)e^{-2p}\}$		
7	3p $\pi$	3p $\pi'$	$1/15w z p^{-3} \{(-42+15p^2)+(42+84p+69p^2+31p^3+8p^4+p^5)e^{-2p}\}$		
8	3d $\sigma$	3d $\sigma'$	$w z p^{-5} \{(90+4p^2+p^4)-(90+180p+184p^2+128p^3+69p^4+31p^5+12p^6+4p^7+10/9p^8+2/9p^9)e^{-2p}\}$		
9	3d $\pi$	3d $\pi'$	$w z p^{-5} \{(-60+2p^2+p^4)+(60+120p+118p^2+76p^3+35p^4+35/3p^5+8/3p^6+1/3p^7)e^{-2p}\}$		
10	3d $\delta$	3d $\delta'$	$w z p^{-5} \{(15-4p^2+p^4)-(15+30p+26p^2+12p^3+3p^4+1/3p^5)e^{-2p}\}$		
11	2s	2p $\sigma'$	$w z p^{-2} \{1-(1+2p+2p^2+6/5p^3+2/5p^4)e^{-2p}\} (5)(2/30)^{-1}$		
12	3s	3p $\sigma'$	$(30/3)^{-1} w z p^{-2} \{105-(105+210p+210p^2+136p^3+62p^4+20p^5+4p^6)e^{-2p}\}$		
13	2s	3s'	$(3/30)^{-1} w (1-t) z p^{-1} \{15-(15+24p+18p^2+8p^3+2p^4)e^{-2p}\}$		

Table 9. (Continued)

	$\chi_a$	$\chi'_a$	$[\chi_a \chi'_a   \delta_b]$
14	3d <sub>xy</sub>	3p <sub>z</sub>	$(\sqrt{15})^{-1} w^7 z p^{-4} \{90 - (90 + 180p + 180p^2 + 120p^3 + 60p^4 + 24p^5 + 8p^6 + 20/9p^7 + 4/9p^8) e^{-2p}\}$
15	3d $\sigma$	3s'	$(\sqrt{5})^{-1} w^7 z p^{-3} \{14 + (14 + 24p + 443/36p^2 + 183/9p^3 + 183/18p^4 + 11/3p^5 + 55/90p^6 + 2/9p^7) e^{-2p}\}$
16	2s	3p $\sigma$	$(3/\sqrt{10})^{-1} w^5 (1-t) z p^{-2} \{15 - (15 + 30p + 30p^2 + 19p^3 + 8p^4 + 2p^5) e^{-2p}\}$
17	2p $\sigma$	3s	same as 16, except replace t by -t
18	2p $\sigma$	3p $\sigma$	$(30)^{-1/2} w^5 (1-t) z p^{-3} \{(21 + 5p^2) - (21 + 42p + 47p^2 + 36p^3 + 20p^4 + 8p^5 + 2p^6) e^{-2p}\}$
19	2p $\pi$	3p $\pi$	$(2/\sqrt{30})^{-1} w^5 (1-t) z p^{-3} \{(21 + 10p^2) + (21 + 42p + 32p^2 + 12p^3 + 2p^4) e^{-2p}\}$

(b) F(m,n) integrals  $z = 1/2(\tau_a + \tau_b)$   $t = (\tau_a - \tau_b)(\tau_a + \tau_b)^{-1}$   $A_n \equiv A_n(p)$   
 $p = R_{ab}z$   $w = (1-t^2)^{1/2}$   $B_m \equiv B_m(tp)$

	$\chi_a$	$\chi'_b$	i	$[\chi_a \chi'_b   \delta_i]$
20	3d $\sigma$	2s	a	$(48/\sqrt{6})^{-1} w^5 (1+t) z p^5 \{A_4(3B_2 - B_0) + A_3(6B_1 - 6B_3) + A_2(3B_4 - 10B_2 + 3B_0) + A_0(B_4 - 3B_2)\}$
21	3d $\sigma$	2s	b	$(48/\sqrt{6})^{-1} w^5 (1+t) z p^5 \{A_4(3B_2 - B_0) + 4A_3B_1 + A_2(3B_0 - 3B_4) - 4A_1B_3 + A_0(B_4 - 3B_2)\}$

Table 9. (Continued)

$X_a$	$X'_b$	$i$	$[\chi_a \chi'_b / \delta_i]$	
22	3d $\sigma$	3s	a	$(288/5)^{-1} w^7 z p^6 \left\{ A_5(3B_2-B_0) + A_4(7B_1-9B_3) + A_3(9B_4-16B_2+3B_0) \right.$ $\left. + A_2(-3B_5+16B_3-9B_1) + A_1(9B_2-7B_4) + A_0(B_5-3B_3) \right\}$
23	3d $\sigma$	3s	b	$(288/5)^{-1} w^7 z p^6 \left\{ A_5(3B_2-B_0) + A_4(5B_1-3B_3) + A_3(3B_0-4B_2-3B_4) \right.$ $\left. + A_2(3B_5-4B_3-3B_1) + A_1(5B_4-3B_2) + A_0(3B_3-B_5) \right\}$
24	3d $\sigma$	2p $\sigma$	a	$(48/2)^{-1} w^5 (1+t) z p^5 \left\{ A_4(B_1-3B_3) + A_3(3B_4-2B_2-B_0) + A_2(2B_3+2B_1) \right.$ $\left. + A_1(-B_4-2B_2+3B_1) + A_0(B_3-3B_1) \right\}$
25	3d $\sigma$	2p $\sigma$	b	$(48/2)^{-1} w^5 (1+t) z p^5 \left\{ A_4(B_1-3B_3) - A_3(B_0+3B_4) + A_1(3B_0+B_4) + A_0(3B_1-B_3) \right\}$
26	3d $\sigma$	3p $\sigma$	a	$(96/15)^{-1} w^7 z p^6 \left\{ A_5(B_1-3B_3) - A_4(B_0+3B_2-6B_4) + A_3(3B_1+4B_3-3B_5) \right.$ $\left. + A_2(3B_0-4B_2-3B_4) + A_1(-6B_1+3B_3+B_5) + A_0(3B_2-B_4) \right\}$
27	3d $\sigma$	3p $\sigma$	b	$(96/15)^{-1} w^7 z p^6 \left\{ A_5(B_1-3B_3) - A_4(B_0+B_2) + A_3(B_1+3B_5) + A_2(3B_0+B_4) \right.$ $\left. - A_1(B_3+B_5) + A_0(B_4-3B_2) \right\}$
28	3d $\pi$	2p $\pi$	a	$(16/6)^{-1} w^5 (1+t) z_a p^5 \left\{ A_4(B_1-B_3) + A_3(B_0-2B_2+B_4) + 2A_2(B_3-B_1) \right.$ $\left. + A_1(-B_0+2B_2-B_4) + A_0(B_1-B_3) \right\}$
29	3d $\pi$	2p $\pi$	b	$(16/6)^{-1} w^5 (1+t) z_b p^5 \left\{ A_4(B_1-B_3) + A_3(B_0-B_4) + A_1(B_4-B_0) + A_0(B_3-B_1) \right\}$
30	3d $\pi$	3p $\pi$	a	$(96/5)^{-1} w^7 z_a p^6 \left\{ A_5(B_1-B_3) + A_4(B_0-3B_2+2B_4) + A_3(-B_5+4B_3-3B_1) \right.$ $\left. + A_2(-B_0+4B_2-3B_4) + A_1(2B_1-3B_2+B_5) + A_0(B_4-B_2) \right\}$

Table 9. (Continued)

	$\chi_a$	$\chi_b$	$i$	$[\chi_a \chi_b   \delta_i]$
31	3d $\pi$	3p $\pi$	b	$(96/5)^{-1} w^7 z_b p^6 \{A_5(B_1-B_3)+A_4(B_0-B_2)+A_3(B_5-B_1)+A_2(B_4-B_0)$ $+A_1(B_3-B_5)+A_0(B_2-B_4)\}$
32	3p $\pi$	2p $\pi$	b	$(16/30)^{-1} w^5 (1+t) z p^5 \{A_4(B_0-B_2)+2A_3(B_1-B_3)+A_2(-B_0+2B_2-B_4)$ $+2A_1(B_3-B_1)+A_0(B_4-B_2)\}$
33	3p $\sigma$	2p $\sigma$	b	$(8/30)^{-1} w^5 (1+t) z p^5 \{-A_4 B_2 - 2A_3 B_3 + A_2(B_0-B_4) + 2A_1 B_1 + A_0 B_2\}$
34	3s	2p $\sigma$	b	$(24/10)^{-1} w^5 (1+t) z p^5 \{A_4 B_1 + A_3(B_0-3B_2) + A_2(3B_1-3B_3)$ $+A_1(3B_2-B_4) + A_0 B_3\}$

(c) Integrals reducing to overlap integrals, formulas for which are given by Mulliken, Rieke, Orloff and Orloff, with parameters as defined by them.

$\chi_a$	$\chi_a$	$[\chi_a \chi_b   \delta_a]$	$\chi_a$	$\chi_b$	$[\chi_a \chi_b   \delta_a]$
35	3s	2s $2(30)^{-1/2} \int_a S(2s_a 2s_b)$	40	3p $\sigma$	2s $2(30)^{-1/2} \int_a S(2s_b 2p\sigma_a)$
36	2s	3s $(3)^{-1/2} \int_b S(1s_a 3s_b)$	41	2s	3p $\sigma$ $(3)^{-1/2} \int_a S(1s_a 3p\sigma_b)$
37	3s	3s $2(30)^{-1/2} \int_a S(2s_a 3s_b)$	42	3p $\sigma$	3s $2(30)^{-1/2} \int_a S(2p\sigma_a 3s_b)$
38	3p $\sigma$	2p $\sigma$ $2(30)^{-1/2} \int_a S(2p\sigma_a 2p\sigma_b)$	43	3s	3p $\sigma$ $2(30)^{-1/2} \int_a S(2s_a 3p\sigma_b)$
39	3p $\sigma$	3p $\sigma$ $2(30)^{-1/2} \int_a S(2p\sigma_a 3p\sigma_b)$	44	3p $\pi$	2p $\pi$ $2(30)^{-1/2} \int_a S(2p\pi_a 2p\pi_b)$
			45	3p $\pi$	3p $\pi$ $2(30)^{-1/2} \int_a S(2p\pi_a 3p\pi_b)$

XII. APPENDIX C. NUMERICAL VALUES FOR  
THE ENERGY INTEGRALS

Values for the energy integrals needed in the calculations are given here in terms of electron volts. Atomic units are retained for distances. The C integrals were computed exactly from the formulas given in Appendix B; the K integrals were approximated by methods described in Chapter VI.

C( $\chi, \chi$ ) integrals  $[\chi^2 | \delta_L]$  :

$\chi$	<u>Fe(NH<sub>3</sub>)<sub>6</sub></u>		<u>FeF<sub>6</sub></u>
	<u>R = 3.648</u>	<u>R = 4.370</u>	<u>R = 3.930</u>
3d $\sigma$	8.2110	6.6089	7.5668
3d $\pi$	7.4408	6.1454	6.9359
3d $\delta$	6.8617	5.7547	6.4245
4s	7.4506	6.2245	6.9193
4p $\sigma$	8.2219	6.6756	7.5418
4p $\pi$	7.0676	5.9930	6.6081

C( $\rho, \rho$ ) integrals for FeF<sub>6</sub><sup>-3</sup>:

<u>R<sub>ij</sub></u>	<u>[2p<math>\sigma_i^2</math>   <math>\delta_j</math>]</u>	<u>[2p<math>\pi_i^2</math>   <math>\delta_j</math>]</u>
3.930	7.1506	6.8076
$\sqrt{3}(3.930)$	4.9756	4.8543
2(3.930)	3.4897	3.4467

C( $\rho, \rho$ ) integrals for Fe(NH<sub>3</sub>)<sub>6</sub><sup>+3</sup>

$R_{ij}$	$[2s_i^2 \delta_j]$	$[2p\sigma_i^2 \delta_j]$	$[2p\pi_i^2 \delta_j]$	$[2s_i2p\sigma_i \delta_j]$
$R_1$	7.4784	7.8968	7.2363	1.5116
$\sqrt{2}R_1$	5.2730	5.4294	5.1949	0.7566
$2R_1$	3.7286	3.7838	3.7010	0.0378
$\sqrt{R_1^2+R_2^2}$	4.7789	4.8954	4.7207	0.6214
$R_1 + R_2$	3.3929	3.4345	3.3719	0.0313

where  $R_1 = R_{\text{Fe-N}} = 3.648$  and  $R_2 = R_{\text{Fe-H}} = 4.370$

C( $\chi, \rho$ ) integrals  $[\chi_M \psi_L|\delta_i]$  or  $[\chi_M \xi_L|\delta_i]$

$\chi$	$\psi_L, \xi_L$	$L'$	$\text{Fe}(\text{NH}_3)_6^{+3}$	$\text{FeF}_6^{-3}$
4s	2s	M	1.987	--
4s	2s	L	2.696	--
4s	2p $\sigma$	M	2.573	1.164
4s	2p $\sigma$	L	2.527	1.481
4p $\sigma$	2s	M	2.503	--
4p $\sigma$	2s	L	4.086	--
4p $\sigma$	2p $\sigma$	M	3.150	1.770
4p $\sigma$	2p $\sigma$	L	4.230	2.335
3d $\sigma$	2s	M	2.132	--
3d $\sigma$	2s	L	5.366	--
3d $\sigma$	2p $\sigma$	M	2.410	1.129
3d $\sigma$	2p $\sigma$	L	2.483	1.952
4p $\pi$	2p $\pi$	M	--	0.351
4p $\pi$	2p $\pi$	L	--	0.490
3d $\pi$	2p $\pi$	M	--	0.728
3d $\pi$	2p $\pi$	L	--	1.622

Some additional C integrals for  $\text{Fe}(\text{NH}_3)_6^{+3}$ :

for  $R_3 = R_{\text{N-H}} = 1.909$  a.u.

$$[2s_N^2|\delta_H] = 13.927$$

$$[2s_N^2|1s_H^2] = 8.378$$

$$[2p\sigma_N^2|\delta_H] = 14.211$$

$$[2p\sigma_N^2|1s_H^2] = 9.000$$



$$[2s_N 2p_N | \delta_H] = 3.330$$

$$[2s_N 2p_N | s_H^2] = 1.429$$

and

$$[1s_H^2 | \delta_j] \quad \begin{array}{ccccc} \frac{R_2}{6.225} & \frac{\sqrt{2}R_2}{4.402} & \frac{2R_2}{8.740} & \frac{R_1+R_3}{8.018} & \frac{\sqrt{R_1^2+R_3^2}}{5.693} \end{array}$$

In the exchange (K) integrals for  $\text{Fe}(\text{NH}_3)_6^{+3}$ ,  $\psi$  is assumed to be a tetrahedral orbital of nitrogen. Since these integrals were estimated by Mulliken's approximation, values relevant to the assumption of pure 2p character (or for any arbitrary hybrid orbital for the lone pair electrons on the ammonia) are obtained upon multiplying the values below by the proper ratios of overlap integrals.

K( $\chi, \rho$ ) and K( $\rho, \rho$ ) integrals  $[\chi\psi_i | \chi\psi_j]$  and  $[\chi\xi_i | \chi\xi_j]$  :

$\chi$	i	j	$\text{NH}_3$	F	$\chi$	i	j	$\text{NH}_3$	F
4s	1	1	0.84	0.13	4p	1	1	1.36	0.13
4s	1'	1'	0	.13	4p	1'	1'	0	.13
4s	1	2	.38	.06	4p	1	4	.55	.12
4s	1	4	.34	.05	4p	1	1	--	.05
d	1	1	.97	.17	4p	1	2	--	.03
d	1'	1'	0	.17	4p	1	4	--	.02
d	1	2	.45	.09	d	1	1	--	.11
d	1	4	.40	.06	d	1	2	--	.06
					d	1	4	--	.04

K( $\chi, \rho$ ) integrals  $[\chi\chi' | \chi'\psi_1]$  and  $[\chi\chi' | \chi'\xi_1]$

$\chi$	$\chi'$	$\text{NH}_3$	F	$\chi$	$\chi'$	$\text{NH}_3$	F
4s	4s	3.22	1.16	d	d	3.15	1.13
4s	4p	.64	.40	d	4s	.63	.23
4s	d	.64	.30	d	4p	.63	.23
4p	4s	.80	.30	d	d	--	.73
4p	4p	3.98	1.77	d	4p	--	.14
4p	d	.80	.30	4p	4p	--	.35
				4p	d	--	.07

$K(\chi, p)$  integrals  $[\psi_i^2 | \chi \psi_i]$  and  $[\xi_i^2 | \chi \xi_i] :$

$\chi$	$i$	$\text{NH}_3$	$\text{F}$	$\chi$	$i$	$\text{NH}_3$	$\text{F}$
4s	1	4.10	1.48	d $\sigma$	1	5.65	1.95
4s	2	1.57	.57	d $\sigma$	2	1.41	.62
4s	4	1.11	.42	d $\sigma$	1'	0	.40
4s	1'	0	.3	d $\pi$	1	--	1.62
4p $\sigma$	1	6.68	2.34	d $\pi$	4	--	.39
4p $\sigma$	4	1.40	.90	4p $\pi$	1	--	.49
4p $\sigma$	7	0	.47	4p $\pi$	2	--	.35
				4p $\pi$	4	--	.26

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