

This dissertation has been 65-8424
microfilmed exactly as received

DUMKE, Warren Lloyd, 1928-
A VALENCE BOND CALCULATION OF OCTA-
HEDRAL TITANIUM (III) COMPLEX IONS.

The University of Nebraska, Ph.D., 1965
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

A VALENCE BOND CALCULATION OF OCTAHEDRAL
TITANIUM (III) COMPLEX IONS

by

Warren Lloyd Dumke

A THESIS

Presented to the Faculty of
The Graduate College in the University of Nebraska
In Partial Fulfillment of Requirements
For the Degree of Doctor of Philosophy
Department of Chemistry

Under the Supervision of Dr. Gordon Gallup

Lincoln, Nebraska

December 1964

TITLE

A VALENCE BOND CALCULATION OF OCTAHEDRAL TITANIUM(III)

COMPLEX IONS

BY

Warren L. Dumke

APPROVED

DATE

Gordon A. Gallup

January 22, 1965

Robert B. Johnston

January 22, 1965

James H. Looker

January 22, 1965

Edgar A. Pearlstein

January 22, 1965

Hubert H. Schneider

January 22, 1965

SUPERVISORY COMMITTEE

GRADUATE COLLEGE

UNIVERSITY OF NEBRASKA

TABLE OF CONTENTS

	Page
INTRODUCTION	1
CALCULATION OF THE ENERGY PROCESS	6
SPECTRUM OF Ti^{+3} ($3d^3 4s^1 4p^3$) ION AND THE ENER- GETICS OF FORMATION OF THE ION	12
HAMILTONIAN AND WAVEFUNCTIONS	18
MATRIX ELEMENTS OF THE HAMILTONIAN	26
DERIVATION OF THE SPIN STATE EIGENFUNCTIONS	32
CALCULATION OF THE ENERGY	44
PROJECTION OPERATORS	55
ONE ELECTRON SYMMETRY ADAPTED EIGENFUNCTIONS	63
DERIVATION OF THE MOLECULAR EIGENFUNCTIONS AND VALENCE BOND FUNCTIONS	74
DERIVATION OF THE ENERGY MATRIX TERMS	95
EXPRESSIONS FOR THE ENERGY MATRIX ELEMENTS OF THE WAVE FUNCTIONS	128
NUMERICAL EVALUATION OF THE MATRIX ELEMENTS OF THE HAMILTONIAN	137
ENERGY OF D_5 AND D_6 AND INTERACTION ENERGY OF THE UNBONDED ELECTRON	147
DISCUSSIONS AND CONCLUSIONS	149
ACKNOWLEDGEMENT	158
Appendix I	A-1
Appendix II	A-14
Appendix III	A-19
Appendix IV	A-47
REFERENCES	

INTRODUCTION

The calculations of Heitler and London¹ provided the first successful quantum mechanical explanation of the stability of molecules by means of which they were able to account for a large part of the binding energy of the hydrogen molecule and showed why some of the molecular systems with only a few electrons were stable and others not. Slater² and Pauling³ later devised methods of extending these principles to more complex molecular systems and thus were able to correlate the stability and geometrical arrangements of many molecules with their electronic configurations. Application of the principles derived from the valence bond theory (abbreviated VB) led to the semi-quantitative definition of many energy changes connected with chemical reactions and were able to account for some of the physical properties of molecules such as dipole moment. In spite of this success, however, the valence bond method has largely remained a reference point for qualitative explanations of molecular phenomena and few actual numerical calculations have been attempted in contrast to other approximation schemes.

One of the areas of success of the valence bond theory has been the explanation of the physical and chemical properties of complex metal ions. Pauling⁴ showed on the basis of the valence bond theory that a transition metal ion is able to form a stable sigma bond system with an octahedral

arrangement of ligand ions if the central metal ion has available a d^2sp^3 orbital configuration which electron pairs from the ligands can occupy to form covalent bonds between the ligands and the central ion. In addition he showed that other geometrical arrangements of ligand ions could be stable with other orbital configurations of the central ion.

Kimball,⁵ using group theoretical methods, was able to derive criteria for the stability of certain geometrical metal-ligand configurations. Pauling also was able to make correlations between the geometry of complex ions and their magnetic moments on the basis of their electronic configurations.

Although most complex ions seem to fit the predictions made on the basis of the valence bond theory, there are apparent exceptions which do not obviously fit these predictions. This has led some authorities to state that the valence bond theory is of limited validity. An example of this is the recent debate between Liehr and Pauling³² over the interpretation of McGarvey's paramagnetic measurements of square planar complexes of Cu^{+2} ions and the type of electron configuration implied by these measurements in the view of the various theoretical interpretations including the valence bond and molecular orbital theories. Thus the question of which of the theoretical approaches is superior for interpretation of complex ion phenomena remains largely unresolved.

A survey of the literature shows that few actual numerical

evaluations of energy states in molecules have been based on the valence bond method, since they usually encounter obstacles formidable enough to prevent its use. Although it has shown itself in many ways a superior simple theory for the description of ground state phenomena, the simple molecular orbital theory has proven to be the better approach for the description of the excited states. Since a refined valence bond theory requires a large number of ionic terms to give a good description, the calculation task then becomes rapidly overwhelming. The refinement of the molecular orbital treatment also requires a similar configuration interaction if it is to give acceptable results especially for the ground state. However, these limitations have prevented the wide spread use of the valence bond approach to describe molecular energy states.

Not all of the problems in using the valence bond theory have been connected with these difficulties alone. One of the most formidable problems in the application of the valence bond theory has been in the calculation of pure spin state eigenfunctions. Rumer⁶ gave guidelines for accomplishing this by trial and error in conjugated molecular systems of the ground state. McWeeney⁷ later showed how this could be done in a more systematic manner and applied the rules he derived to a simple conjugated system. However, these rules proved rather cumbersome to apply and they have not been widely used. In 1962 Lowdin⁸ pointed out that the problem

of calculating the energies of valence bond functions had not been solved by conventional techniques and suggested that a projection operator could be used to attack this problem. The spin projection operator may be used to derive the eigenfunctions of pure spin states by following a method suggested by Lowdin in 1955.⁹

In the past few years some valence bond calculations have been made for simple molecular systems. An extended valence bond theory was proposed by Hurley, Lennard-Jones, and Pople¹⁰ in 1953 but it has not been applied to any numerical calculations; Slater¹¹ however, shows how its principles can be applied to several simple molecules. In 1962 Ellison¹² reported the results of applying a semi-empirical valence bond treatment to certain hydrogen compounds of boron, carbon, and nitrogen.

However, a search of the literature has revealed no theoretical or semi-empirical calculations based on the valence bond theory for transition metal complexes. Even the crystal field and molecular orbital treatments seem to rely largely on the empirical correlations made between the spectral and magnetic data of the complex ions and the corresponding free metal ion.¹³ In view of the success of both the valence bond theory and the crystal field theory in explaining some of the same phenomena in spite of their widely different bonding pictures, this investigation was initiated to calculate theoretically the magnitude of covalent bonding in a simple

transition metal complex ion. Because of the simple electronic configuration of the free ion and the bonding species, a complex ion of Ti^{+3} with an octahedrally arranged system of ligands was chosen for this purpose. Because sigma bonds seem to give the largest contribution to the energy of the complex ion, the effects of pi bonding were neglected. Methods of deriving and evaluating the energies of symmetry adapted eigenfunctions in more straightforward ways were investigated and applied where feasible. Since there are a large number of states actually possible in the derivation given here, the calculation will be confined to the evaluation of those states arising as a result of deriving the theoretical expressions for the energy of the ground state.

CALCULATION OF THE ENERGY PROCESS

The binding energy of a complex ion is defined to be the energy released in a reaction between a free central metal ion, M^{+m} , and n ligand ions, $L^{-\ell}$, to form the molecular species, $(ML_n)^{+m-n\ell}$. This energy will be the sum of the energy due to the electrostatic attractions and repulsions between the unreacted ions and the energy due to the changes in the electronic energy of the system as the reaction takes place. It is the change in the electronic energy of the system which is regarded as the covalent binding energy of the complex ion.

It is in theory possible to calculate the changes in the electronic energy of the system completely from first principles; this may be done by calculating the energy of all the species before binding takes place and then calculating the energy of all species after bonding takes place and taking the difference to obtain the covalent binding energy. However, in practice the known methods require such a large amount of labor to solve even the simplest systems that it is usually necessary to restrict the problem in such a manner as to be able to use as much empirical data as possible. Since the purpose of this dissertation is to examine the changes that take place in the energy levels of the spectrum of the central ion as covalent bonding takes place to form the complex ion, a completely theoretical treatment of a complex ion's electronic energy is not necessary if an experimentally measurable

energy state can be found or calculated to which the energy changes may be referred. In this work it is found convenient to use for this state the spectrum of the electron configurations of the central ion which has been built up from half of the electrons of the ligands as well as its own, so that definite electronic states may be present. In this work the effects of covalent bonding on the Ti^{+3} ion by an octahedrally arranged system of ligands will be calculated. Extensions to other transition metal-ligand systems may logically be made.

It may be assumed that the Ti^{+3} ion is in the presence of an octahedrally arranged system of ligand ions, $L^{-\ell}$, as shown in figure 1. If the ligands are placed at an infinite distance from the central ion, the states of the Ti^{+3} ion will be identical to those of the free ion. If the ligands are then brought close to the central ion without any chemical reaction taking place, the degenerate levels of the energy spectrum will split and shift with respect to each other with a magnitude that depends upon the charges on the ligands and the distance from the central ion. For the case of the Ti^{+3} ion, the 2D ground state will split into a lower triply degenerate F_{2g} state and a higher doubly degenerate E_g upper state.¹⁴ If covalent bonding also takes place, the energy structure of the complex ion will no longer be so simple and another picture must be used. The effects of covalent bonding may be calculated by means of the valence bond method in which changes are noted in the energy pattern when singly occupied

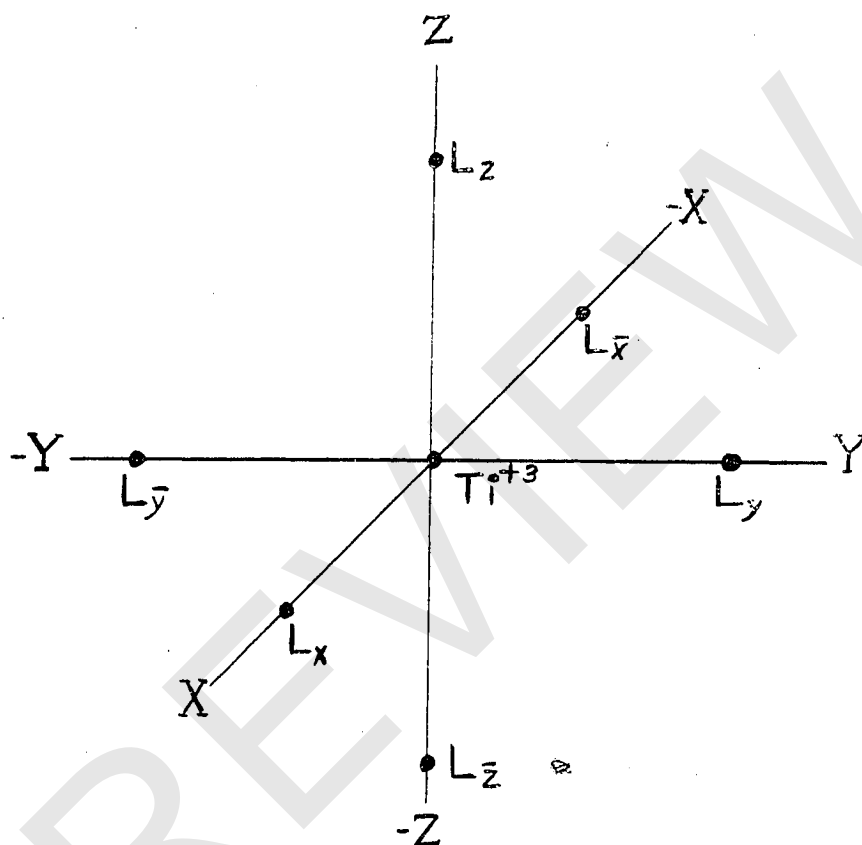


FIGURE 1

OCTAHEDRAL LIGAND $-Ti^{+3}$
COMPLEX ION SYSTEM

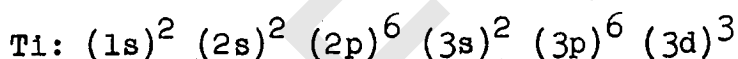
electron orbitals of the central ion are allowed to interact with the singly occupied electron orbitals of the ligand ions. Although the central ion does not possess enough singly occupied orbitals to account for all the bonds formed in a complex ion and the ligands only possess doubly occupied orbitals, it is possible to build up such components in a systematic manner such that the relative energies of the unreacted system may be calculated from experimental data.

If one electron is removed from each of the ligand electron pairs capable of forming sigma type bonds with the central ion, the energy required, if the ligands are at an infinite distance from any other ion, will be equal to the ionization constant of the ligand times the number of ligands. This quantity may or may not be experimentally known; but if only the relative energies of the complex ion system are desired, its actual value need not be known. If these electrons are now added to the central ion, the new central ion formed will assume the energy spectrum of the atomic system with a Ti nucleus and 25 external electrons. Although this spectrum has never been measured experimentally, the energy levels of interest in studying the covalent bonding effects in Ti^{+3} complexes may be estimated by relating them to the $\text{Ti}^{+1}(3d^3)$ atomic energy levels. Richardson¹⁵ has mentioned that Watson's calculations¹⁶ showed that in an atom containing only 3d or lower level electrons the addition of 4s and 4p electrons results in insignificant changes in the relative separations

of the energy levels; this is true because an electron in the 4s or 4p state will be located outside the sphere of the atom in which the electron density of the 3d electrons are the highest and thus the 4s and 4p electrons will have little influence on the potential energy of 3d electrons. A comparison of the spectra¹⁷ of two ions of the same atom with different 4s-4p electron systems shows the same change in the 3d electron subshell system will result in approximately the same energy change, thus confirming Watson's observations. Thus the relative positions of a titanium ion with the electronic structure:



should show about the same energy spectrum as the ion:



if changes only take place in the 3d electron arrangement. Since group theory shows that octahedral transition metal complex ions usually have a $3d^2 4s^1 4p^3$ electronic arrangement for the central ion, the effect of covalent bonding for the Ti^{+3} ion may thus be related to the energy spectrum of (1) as a reference state of the energy. It should then be possible to calculate the energy changes in the spectrum of ion (1) as covalent bonding takes place with the octahedrally arranged ligand ions by applying the valence bond method. Each level

of ion (1) will then be split and shifted as the interaction occurs, resulting in the spectrum of the complex ion.

The spectrum of ion (1) will be evaluated and a discussion of the role of ionization of the ligands will be given in the next section. The various aspects of the valence bond calculations will then be treated in the succeeding sections.

PREVIEW

SPECTRUM OF $Ti^{+1} (3d^3 4s^1 4p^3)$ ION AND THE
ENERGETICS OF FORMATION OF THE ION.

The energy level spectrum of the unperturbed ion:

$$Ti: (1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (3d)^3 \quad (2)$$

contains the following spectral terms in the order of their energies above the ground state:

$${}^4F, {}^2G, {}^4P, {}^2P, {}^2D, {}^2H, {}^2F, \quad (3)$$

where the capital letters designate the total azimuthal quantum number, L, according to the scheme:

$$\begin{array}{ll} L = 0, 1, 2, 3, 4, 5, 6, 7, \dots\dots\dots & (4) \\ S, P, D, F, G, H, I, K, \dots\dots\dots \end{array}$$

and the superscript before the capital letter is equal to the spin multiplicity, $2S + 1$, for the term, where S is the total spin quantum number. An energy diagram of this spectrum in terms of the energy in cm^{-1} above the lowest observed state, is given in figure 2.¹⁷ Since there are several spin levels for each term and the spectra of complex ions are not so clearly defined that the individual spin states may be detected, the various energies of the spin states were averaged for each term.

Since the covalent bonding of an octahedral ligand system with a central transition metal ion seems to require that the electronic structure of the central ion have at least a $3d^2 4s^1 4p^3$ arrangement for sigma type bonding,¹⁸ the spectrum of the ion:

$$Ti: (1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (3d)^3 (4s)^1 (4p)^3 \quad (1)$$

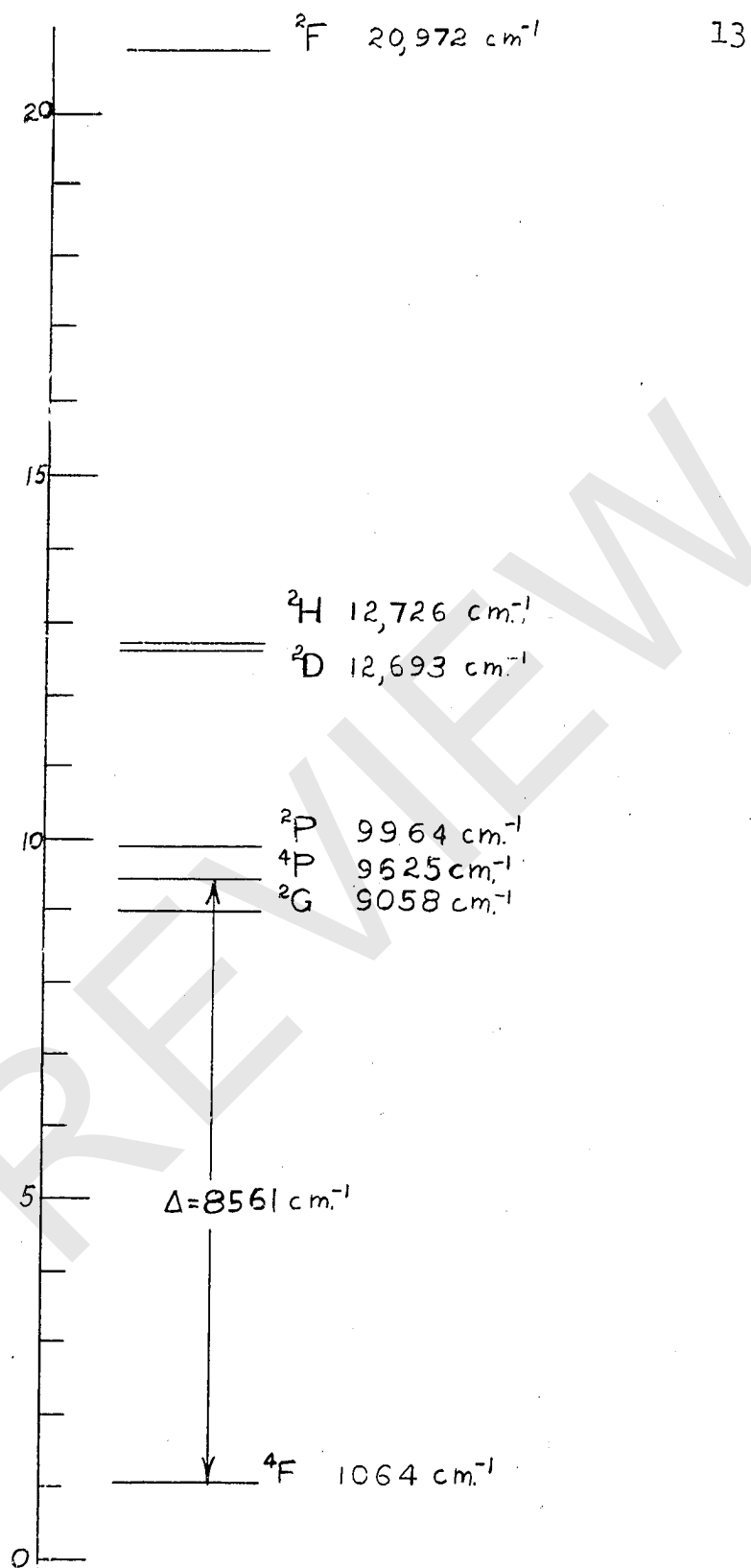


FIGURE 2
SPECTRUM OF Ti^{+1} ION FOR $3d^3$ ELECTRON CONFIGURATION

should contain states which will bond with an octahedral ligand system. It was pointed out in the previous section that the separations between energy levels of ion (1) for any specific $(4s)^1(4p)^3$ electronic arrangement should be approximately those between the energy levels of ion (2) with the same $3d^3$ electronic arrangements.

The term designations for ion (1) can be found from the terms of the ion (2) by the vector coupling method in which the components of the $4s\ 4p$ system are added vectorially to those of the $3d$ electron system. The possible term designations for the $4s^1$ and $4p^3$ electron systems are listed below:

<u>Electron subshell</u>	<u>Spectral Terms</u>
$4s^1$	2S
$4p^3$	$^4S, ^2D, ^2P.$ (5)

By applying the vector coupling method to the azimuthal and spin quantum numbers of the above terms the following spectral terms are derived for the $4s^1 4p^3$ electron arrangement:

$$^5S, ^3S, ^3D, ^1D, ^3P, ^1P. \quad (6)$$

These spectral terms can now be coupled with the $3d^3$ spectral terms to form a set of terms belonging to ion (1). Since not all terms of this ion have the electron configuration required for sigma type octahedral bonding with the ligands, only the terms with the necessary configuration need be considered. This requires that the $4s4p$ electron system of the central ion have four unpaired electrons which occupy one and only

one orbital each and combine with the now unpaired ligand electrons to bond because Pauli's principle states that no two electrons may occupy the same space orbital and have the same spin. Since only four orbitals are available before bonding in the $4s4p$ system (even if hybrid orbitals are formed), each orbital will have one and only one electron and only the $5S$ term will permit this condition. Thus only the coupling of this term with the $3d$ electron system of the ion will be of any importance for octahedral sigma bonding in complex ions.

The coupling of the $5S$ term of the $4s4p$ system with the terms of the $3d$ electron system will give rise to several spin multiplicities for each term, but the quantum number will remain unchanged. Since total spin number $S = 2$ for the $5S$ term of the $4s4p$ system and the terms of the $3d$ system have either $S = 3/2$ or $S = 1/2$, the overall possible total spin quantum number can be:

$S = 7/2, 5/2, 3/2, 1/2$ for $S = 3/2$ in the $3d$ system.

$S = 5/2, 3/2$ for $S = 1/2$ in the $3d$ system.

Thus the spectrum of interest in the bonding scheme will include the terms:

$8F \quad 6G \quad 8P \quad 6P \quad 6D \quad 6H \quad 6F$

$6F \quad 4G \quad 6P \quad 4P \quad 4D \quad 4H \quad 4F$

$4F \quad 4P$

$2F \quad 2P$

Hund's rule states that the lowest energy state for any system

of equivalent orbitals possessing a specific L value is the one with the highest multiplicity. Since there are six equivalent ligand orbitals, six unpaired electrons will span these orbitals which will include the state with the maximum total spin component S_z (i.e. all spins parallel) in the lowest energy state. If covalent bonding is to occur between the ligand system and the central atom for all possible total spin components, S_z , then the central atom must be able to have at least six electrons with parallel spins in its bonding orbitals to allow them to bond with the possible six electrons with parallel spins in the ligand system. The electron in the nonbonding orbital of the central ion must also be free, however, to take on either of the two possible spin orientations. The only terms which possess the spin multiplicity necessary for these possibilities are the 8F and 8P terms, and therefore only these can contribute to maximum bonding within the complex ion. Any of the other terms listed above will only contribute to partial covalent bonding and therefore to less bonding energy. Thus only the 8F and 8P terms need be considered initially to study the effects of covalent bonding on the energy levels of ion (1) and its complex ion. The energy differences between the 8F and 8P state of ion (1) and between the 4F and the 4P states of ion (2) will be equal to 8370 cm^{-1} . The spectrum of the octahedrally bonded complex of ion (1) can then be calculated by evaluating the energy changes which occur in the 8F and 8P terms as a result of covalent bonding.

The transition from a system of a Ti^{+3} ion in an octahedral arrangement of ligands with one bonding electron pair each to a system of ion (1) in an octahedral arrangement of ligands having one unpaired electron each is straightforward. The energy necessary for removing one electron from each ligand in the ground state will result in a total energy change of E_I in the system, whose magnitude will be unaffected by the electronic arrangement of the Ti^{+3} ion if the ligands are at infinity. The electrons are then placed on Ti^{+3} ion to form ion (1). If the energy necessary to place the electrons in the 8F state of ion (1) is called E_A , then the energy required to arrange the electrons in state 8P is:

$$E_A + \Delta \quad (8)$$

where Δ is the energy separation between the 8F and 8P states. Similar calculations may be made for all the other states of ion (1), but since the absolute values of the quantities E_I and E_A are not required for the study of the spectrum which is the main problem of this thesis, only the values of Δ need be considered. Starting from this point and applying the valence bond method to the 8F and 8P states of ion (1) in order to follow the energy changes as the ligands are brought within bond distances of the central ion should give a means of deriving the energy spectrum of the complex ion to at least a first approximation.

HAMILTONIAN AND WAVEFUNCTIONS

The energy states of atomic or molecular systems are described in terms of wave functions Ψ_n belonging to the total energy E_n , which are eigen solutions of the Schroedinger wave equation with total Hamiltonian operator H :

$$H\Psi_n = E_n\Psi_n. \quad (9)$$

The total energy E_n of a molecule consists of contributions from electronic motion within the molecule, translational motion of the molecule, and internal molecular motions such as vibrations and rotations as well as interactions between these. However, the Born, Oppenheimer expansion shows that as a first approximation the electronic energy may be calculated as if the nuclei were infinitely massive.

Since the effects of spin interactions on the total energy are usually small in polyelectronic systems when compared with those due to electronic motion, the total wave function Ψ_n is usually assumed to be the solution of the Schroedinger equation with no spin interaction terms in the Hamiltonian. In a molecule having N electrons and a number of nuclei which shall be designated by subscript a , H may be written (in atomic units) as follows:

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_a \sum_{i=1}^N (Z_a/r_{ai}) + \sum_{i=1}^N \sum_{j>i=1}^N (1/r_{ij}) \quad (10)$$

where ∇_i^2 is the Laplacian operator for the system,

Z_a is the nuclear charge of the a^{th} nucleus,

r_{ai} is the distance between the a^{th} nucleus and the i^{th} electron,

r_{ij} is the distance between the i^{th} and j^{th} electrons.

The first term on the right of (10) represents the kinetic energy of the electrons, the second term the attraction between the nuclei and the electrons, and the third term the inter-electronic repulsion. Since techniques for obtaining exact analytic expressions for Ψ_n are unavailable at present for cases where H includes interelectronic repulsion terms, it is a common practice to neglect these terms and to solve the resulting Schroedinger equation. The result of applying this approximation is to reduce the Hamiltonian H to a sum of one electron Hamiltonian operators H_i :

$$H = \sum_{i=1}^N H_i \quad (11)$$

where

$$H_i = -\frac{1}{2} \nabla_i^2 - \sum_a \frac{Z_a}{r_{ai}} \quad (12)$$

The Schroedinger equation (9) thus becomes:

$$H' \Psi_n = H'_i \Psi_n = E_n \Psi_n \quad (13)$$

where each term of the sum in (13) has an operator involving coordinates of one electron only and H' is the Hamiltonian without the electron repulsion term. Under these conditions it is possible to separate the effects of electron i from the others and E_n can be expressed in terms of the energies of

individual electrons i . Under the condition of separability of the Hamiltonian into one electron parts, a product of eigenfunctions ψ_{nj} , which depend only on the coordinates of one electron, may be used as a trial eigenfunction of Ψ_n

$$\Psi_n = \sum_{j=1}^n \psi_{nj} \quad (14)$$

which will lead to the expression

$$\sum_i H_i \Psi_n = \sum_i H_i \prod_j \psi_{nj} = E_n \prod_j \psi_{nj} \quad (15)$$

Since operator H_i will operate only on the coordinates of electron i , dividing the last expression by the product $\prod_j \psi_{nj}$ on both sides, will lead to the equation

$$\sum_i \frac{1}{\psi_{nk}} H_i \psi_{ni} = E_n \quad (16)$$

Since each part of this equation must hold for all possible values of the coordinates of ψ_{nj} , each term of the sum on the left of equation (16) must be a constant, say e_{ni} for term z , which will result in $E_n = \sum_i e_{ni}$. However, since the electrons in a molecule are indistinguishable, the products of the same wave functions having different assignments of electrons are also particular solutions of equation (13). General solutions of equation (13) may be expressed in terms of linear combinations of products such as containing all possible permutations of electrons

$$\Psi_n = \sum_P c_n^P \{ \psi_{n1}(b_1) \psi_{n2}(b_2) \dots \psi_{nN}(b_N) \} \quad (17)$$