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I am submitting herewith a thesis written by Bradley Douglas Snow entitled "The Applicability of the MSX α Method to the Lanthanides." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

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THE APPLICABILITY OF THE MSX α METHOD
TO THE LANTHANIDES

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Presented for the
Master of Science
Degree
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Bradley Douglas Snow

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ABSTRACT

Multiple scattering X α (MSX α) calculations have been performed on the lanthanide trihalide molecules: LaF₃, LaCl₃, CeF₃, CeCl₃, PrCl₃, EuCl₃, GdCl₃, TbCl₃, YbCl₃, and LuCl₃. Both spin restricted (SR) and spin polarized (SP) calculations were done for all of the open shell molecules except CeF₃ for which only SR results were obtained. The closed shell molecules were treated only in an SR format. An overlapping atomic sphere model was used in all cases except EuCl₃, for which both overlapping sphere and nonoverlapping sphere models were employed. Both neutral molecule calculations and transition state calculations (0.5 an electron removed) were carried out for all molecules except the nonoverlapping sphere EuCl₃ and the SP YbCl₃, for which results were obtained only for the neutral molecules. The primary emphasis of the work was to assess the effectiveness of the MSX α method in adequately describing the behavior of the 4f electrons. These electrons are expected to exhibit: (1) valence region energies, (2) only small crystal field splittings, and (3) only slight participations in bonding.

The SR calculations predicted the above type of behavior for the 4f electrons in molecules containing zero or only one or two unpaired 4f electrons. However, in molecules containing six or seven unpaired 4f electrons the SR results indicated a rather substantial involvement in bonding and significant crystal field splittings for these electrons. For these molecules the SP calculations greatly improved the results by reducing both the participation in bonding and the crystal field splittings of the 4f electrons.

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CHAPTER I

EXPERIMENTAL BACKGROUND

A. Lanthanide Elements

The lanthanides, taken here to denote the elements lanthanum through lutetium, once considered rare, are now known to be quite abundant and are finding wide application in science and industry.¹ They are characterized by a progressive filling of the 4f subshell, ranging from $4f^0$ for La through $4f^{14}$ for Yb and Lu. The open 4f subshell exhibited by all of the lanthanides, except the previously mentioned three, gives rise to a variety of interesting electronic and magnetic properties. These 4f electrons are strongly screened by the completed $5s^2 5p^6$ subshells and thus do not influence the valency forces to any great extent. However they are important to properties such as magnetism and spectra.²

The probable electronic structure of the elements 58 through 70 may be denoted as $\text{Ln}: (\text{Xe}) 6s^2 5d^0 4f^n$ where n progresses sequentially from 2 for Ce through 14 for Yb, with the exception of Gd which has the configuration $6s^2 5d^1 4f^7$.³ Lanthanum and Lu have the configurations $6s^2 5d^1 4f^0$ and $6s^2 5d^1 4f^{14}$ respectively.³ Experiments on the electronic structures of the lanthanides provide information concerning the 4f electrons' energy levels and the splitting of these levels. These data have been determined through: (1) optical spectroscopy, (2) X-ray spectroscopy, and (3) photoelectron spectroscopy.

The technique of optical spectroscopy involves either the emission or absorption of radiation by a gaseous species. Emission is accomplished by first exciting electrons to higher energy levels with

an input of energy. Radiation of a characteristic wavelength is emitted when the electron drops back to a lower level, the wavelength being dependent upon the difference in energy between the levels involved. Absorption involves the excitation of electrons to higher levels, the absorbed wavelengths are detected, and again the energy difference between the levels is determined. In both the absorption and emission techniques an atomic selection rule of $\Delta l = \pm 1$ is operating, l being the angular momentum quantum number. The lines obtained in the spectra often converge in a Rydberg series representing the complete loss of an electron and thus ionization energies may be obtained. Ionization energies as derived through the analysis of optical spectra of the lanthanides have been compiled by Moore⁴ and by Reader and Sugar.⁵

Substances may absorb X-rays in a process involving the transfer of the photon's energy to an electron which is then ejected. The incident and resultant X-ray intensities are measured. Enhanced absorption corresponds to an ionization energy, because the phenomenon occurs with considerable intensity when the X-ray energy is equivalent to the energy required to remove the electron. An alternative technique involves the irradiation of a sample with electrons or photons of sufficient energy to eject an inner orbital electron. An outer electron may drop into the hole, subject to $\Delta l = \pm 1$, resulting in the emission of an X-ray. The energy of the emitted X-ray is determined and is characteristic of the difference in energy between the inner and outer orbitals. Most of the X-ray absorption and emission data have been obtained for solids, corrections being necessary to obtain values for the free gaseous species. To obtain data for the free atom the corrections applied are: (1) allowing

for the work function of the solid and (2) adjusting the valence state to zero charge. Burr⁶ has compiled X-ray data for the lanthanides.

In recent years photoelectron spectroscopy (PES) has emerged as a powerful technique for obtaining ionization energies. Experimentally a gaseous or solid sample is bombarded with monoenergetic photons, causing the ejection of electrons. Common photon sources include He(I) and He(II) discharges (21.22 eV and 40.81 eV respectively) and AlK α and MgK α X-rays (1486.6 eV and 1253.6 eV respectively). The kinetic energies of the electrons are measured and the ionization energies are obtained by subtracting the kinetic energies from the energy of the incident photons. The technique thus has the advantage of directly analyzing the energy of ejected electrons. The spectrum produced is generally given as intensity versus kinetic energy (or ionization energy), ideally each peak in the spectrum corresponding to one atomic or molecular orbital. Two types of ionization energies are generally recognized for molecules. The adiabatic ionization energy is the minimum energy required to remove the electron from a molecule in its ground vibrational state to form a molecular ion in its ground vibrational state. The vertical ionization energy, corresponding to the peak of maximum intensity in the photoelectron spectrum band, is the energy associated with the process of ionizing a molecule in its ground vibrational state to form the molecular ion in the most probable vibrational state.⁷ The X-ray photoelectron spectra of several lanthanide metal solids have been obtained by Baer and Busch,⁸ and by Heden, Lofgren, and Hagström.⁹ The same corrections mentioned earlier are necessary to obtain data for the gaseous atoms.

The previously discussed methods may be mutually employed to obtain the one electron ionization energies. Table I, taken from

TABLE I

ELECTRON BINDING ENERGIES (-ev)

OF THE LANTHANIDES

	$4f_{5/2,7/2}$	5s	$5p_{1/2}$	$5p_{3/2}$	$5d_{3/2}$	$5d_{5/2}$	6s
57 La	-	36	22	19	5.75	--	5.58
58 Ce	6	39	25	22	6	--	5.65
59 Pr	6	41	27	24	--	--	5.42
60 Nd	6	42	28	25	--	--	5.49
61 Pm	6	43	28	25	--	--	5.55
62 Sm	6	44	29	25	--	--	5.63
63 Eu	6	45	30	26	--	--	5.68
64 Gd	6	46	31	27	6	--	6.16
65 Tb	6	48	32	28	6	--	5.85
66 Dy	6	50	33	28	--	--	5.93
67 Ho	6	52	34	29	--	--	6.02
68 Er	6	54	35	30	--	--	6.10
69 Tm	7	56	36	30	--	--	6.18
70 Yb	8	58	37	31	--	--	6.25
71 Lu	13	62	39	32	6.6	--	7.0

Lotz,¹⁰ gives such energies for the 4f, 5s, 5p, 5d, and 6s levels of the lanthanide atoms.

B. Lanthanide Compounds

As previously mentioned the 4f electrons are well shielded by the completed $5s^2 5p^6$ subshells and are therefore not expected to be appreciably affected by the chemical environment of the lanthanide. This section presents some of the experimental evidence supporting the essential atomicity of the 4f electrons in lanthanide compounds.

The most common oxidation state of the lanthanides is 3+, for which the ionic configuration is $\text{Ln}^{3+}: (\text{Xe}) 6s^0 5d^0 4f^n$, where n progresses sequentially from 0 for La^{3+} through 14 for Lu^{3+} .¹¹ The electronic configurations and ground state terms for these trivalent ions are shown in Table II. The electropositive character of the lanthanides coupled with the contracted nature of the 4f orbitals and the resulting small overlap with ligand orbitals usually lead to highly ionic complexes.

The 4f electronic structures of lanthanide ions are characterized by large spin-orbit coupling and small crystal field splittings.¹² These are in sharp contrast to the d-transition series of elements in which the relative magnitudes of perturbations acting on the otherwise degenerate orbitals are:

$$\begin{aligned} \text{electron-electron repulsion (of the order of 1.0 ev)} & \quad (1) \\ & \approx \text{crystal field splitting} \\ & > \text{spin orbit coupling (about 0.3 ev)} \\ & > kT \text{ (about 0.03 ev).} \end{aligned}$$

where the values in parentheses relate to the 3d series. The relative magnitudes of the corresponding factors for the 4f orbitals of the

TABLE II
ELECTRONIC CONFIGURATION AND GROUND
STATE TERM FOR THE TRIPOSITIVE
LANTHANIDE CATIONS

Ion	Electronic Configuration	Ground State Term
La ³⁺	(Xe) 4f ⁰	1S ₀
Ce ³⁺	(Xe) 4f ¹	2F _{5/2}
Pr ³⁺	(Xe) 4f ²	3H ₄
Nd ³⁺	(Xe) 4f ³	4I _{9/2}
Pm ³⁺	(Xe) 4f ⁴	5I ₄
Sm ³⁺	(Xe) 4f ⁵	6H _{5/2}
Eu ³⁺	(Xe) 4f ⁶	7F ₀
Gd ³⁺	(Xe) 4f ⁷	8S _{7/2}
Tb ³⁺	(Xe) 4f ⁸	7F ₆
Dy ³⁺	(Xe) 4f ⁹	6H _{15/2}
Ho ³⁺	(Xe) 4f ¹⁰	5I ₈
Er ³⁺	(Xe) 4f ¹¹	4I _{15/2}
Tm ³⁺	(Xe) 4f ¹²	3H ₆
Yb ³⁺	(Xe) 4f ¹³	2F _{7/2}
Lu ³⁺	(Xe) 4f ¹⁴	1S ₀

lanthanides are:¹²

electron-electron repulsion (of the order of 1.0 eV) (2)

> spin orbit coupling (about 1.0 eV)

> crystal field splitting (about 0.03 eV)

$\approx kT$ (about 0.03 eV)

The large spin-orbit coupling reflects the high atomic numbers while the small crystal field splitting reflects the very effective shielding of the 4f orbitals.

The paramagnetic properties of the trivalent lanthanide ions also provide evidence for the small influence by ligands on the 4f electrons.¹³ If the splitting of the J levels is large compared to kT, the magnetic moment of the ion in Bohr Magnetons is closely approximated by the Hund equation

$$\mu = g [J (J + 1)]^{1/2}, \quad (3)$$

where the Lande' g factor is

$$g = 1 + [S (S + 1) + J(J + 1) - L(L + 1)] [2J(J + 1)]^{-1} \quad (4)$$

In the previous equations L is the orbital angular momentum quantum number, S is the spin angular momentum quantum number, and J is the total angular momentum quantum number. The magnetic moments calculated with the above equations are in very good agreement with experiment for all of the lanthanides except Sm^{3+} and Eu^{3+} , in which the separation of J levels is very small.¹⁴ This agreement is attributed to the screening of the unpaired 4f electrons.¹³ The same equations do not reproduce experimental values for the 3d transition metals, because of the perturbation of the 3d electrons by the ligands and the resultant quenching of the orbital angular momenta of the electrons.¹³ Also the magnetic moments

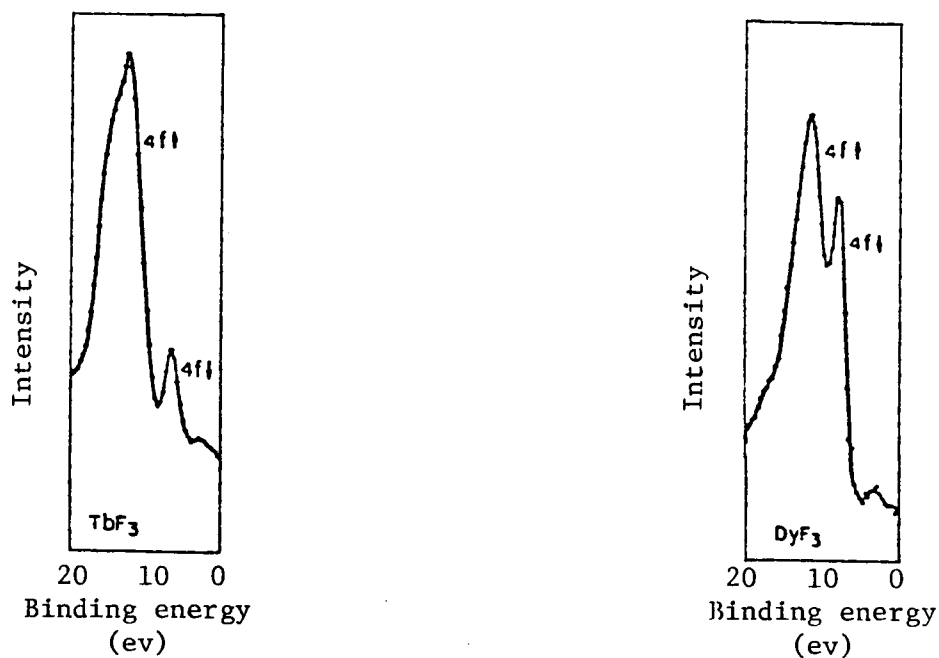
of the lanthanide ions are essentially independent of the nature of the ligand groups associated with them, which is not the case with the transition metal ions.¹⁴ Again the difference is ascribed to the lack of participation in bonding of the 4f electrons.

The colors of the trivalent lanthanide cations are also indicative of the non-bonding character of the 4f electrons. The colors of both crystalline salts and solutions are characteristic of the metal ion regardless of the ligands present.¹⁴ Qualitatively the color of the ion may be correlated with the number of unpaired electrons and thus associated with the ground state terms which differ only in the inversion of J values. It is also to be noted that the magnetic properties and colors indicate that all of the trivalent lanthanide ions exist in the high spin configuration.

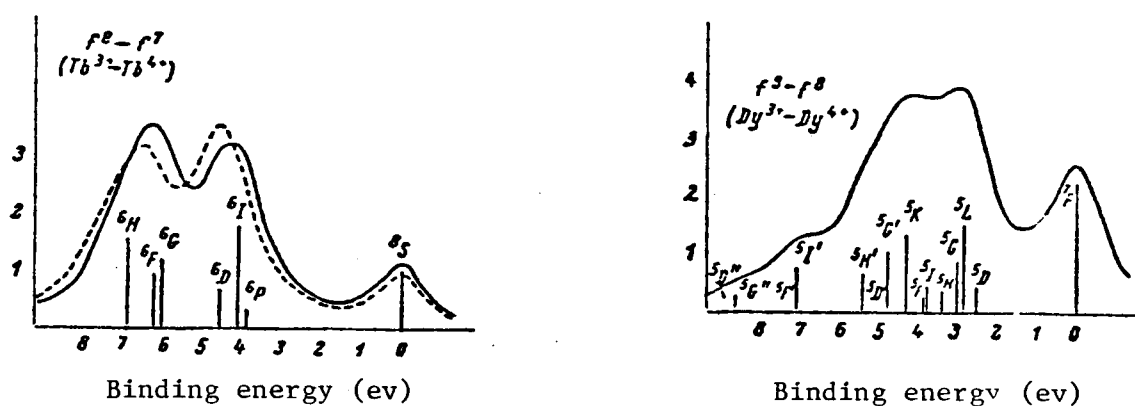
Optical spectra of lanthanide compounds, in solids and in solution, provide further evidence for the atomicity of the 4f electrons. The most interesting feature of the spectra of the lanthanide ions is the sharpness of the bands. These narrow bandwidths are in sharp contrast to the spectra characteristic of the 3d transition metal compounds, which exhibit strong vibrational broadening of the bands due to the perturbation of the 3d electrons by ligand vibrations. The lack of this feature in the lanthanide spectra leads to the conclusion that the 4f electrons are not appreciably affected by ligand vibrations, thus reflecting the strong screening and contracted nature of the 4f orbitals.¹⁵ Also, as would be expected, the energies and intensities of the f-f spectral lines are rather insensitive to changes in the ligand associated with the metal ion.¹⁶

Photoelectron spectra of lanthanide compounds also support the non-bonding properties of 4f electrons. The X-ray photoelectron spectra of several lanthanide trifluoride solids have been obtained by Wertheim.¹⁷ The spectrum of PrF_3 shows the 4f ionization energy clearly more shallow than the ligand valence band. With GdF_3 the 4f shell is half full and the 4f band coincides with the valence band. A new peak appears in the spectrum of TbF_3 approximately 5 eV more shallow than the 4f band, and may be thought of as representing ionization of the eighth 4f electron which has a different spin from the others. As the series is crossed this new structure becomes more intense and moves toward greater binding energy as evidenced by the spectra of DyF_3 and TmF_3 .

Successful interpretation of these spectra requires a final state approach, wherein the various states populated on ionization give rise to the observed peaks. Calculations on the free lanthanide ions¹⁸ based on a final state analysis result in excellent correlation with the experimental spectra. These calculations involve determining the intensities of the peaks (states arising on ionization) by a fractional parentage method. Their energies are obtained through optical spectral data. The facts that the calculations are performed on the free ions, and that the results are in agreement with the spectra of lanthanide compounds, indicate that the 4f electrons remain predominately atomic. Comparisons of the experimental spectra with the theoretical predictions, based on the above type of calculation, for TbF_3 and DyF_3 are shown in Figure 1. Further examples of the spectra of lanthanide compounds¹⁹ show similarly good agreement with free ion calculations.



X-ray photoemission spectra of TbF_3 and DyF_3 .¹⁷



Calculated spectra of 4f electrons (bars) with a broadening of 1.6 eV. (The dashed curve incorporates spin orbit interaction).¹⁸

Figure 1. Comparison of experimental and calculated photoelectron spectra for TbF_3 and DyF_3 .

The X-ray photoelectron spectra of the solid trifluorides, trichlorides, and tribromides of La and Ce have been obtained by Sato.²⁰ These spectra allow the unambiguous identification of the ionization energy of the first 4f electron in the series, as its peak is the only qualitative difference between spectra of the La and Ce compounds. This 4f peak appears on the low binding energy side of the ligand valence band and its binding energy remains virtually constant regardless of which halide ligand (F, Cl, or Br) is present. In CeF_3 the F valence band appears at higher binding energy than the 4f peak and this X np band gradually moves toward the 4f peak in CeCl_3 and CeBr_3 such that in CeBr_3 the 4f peak appears only as a shoulder on the low energy side of the X np band. The constancy in binding energy of the 4f electron provides further evidence for its being nonbonding.

These studies on lanthanide compounds elucidate three important properties of the lanthanide 4f electrons. These may be summarized as: (1) the 4f electrons are valence region electrons, (2) their energies are perturbed only slightly by the ligands, and, (3) they remain virtually atomic.

C. The 4f Wave Functions

The behavior of 4f electrons is one of the primary objectives in undertaking this study of the lanthanides. Therefore a brief presentation of the 4f wave functions is given. These functions are obtained, as usual, by multiplying a radial factor, $R_{4,3}(r)$, by an appropriate spherical harmonic function, $Y_{3,m}(\theta, \phi)$:

$$\psi_{4f} = R_{4,3}(r)Y_{3,m}(\theta, \phi). \quad (5)$$

The subscript 4 and 3 denote the values of the principal quantum number $n = 4$ and angular momentum quantum number $\ell = 3$. Substituting the values for the magnetic quantum number $m = -3$ through $m = 3$ by integers into the spherical harmonic function²¹ gives seven equations in the form of equation (5). Seven real 4f orbitals are obtained by taking appropriate linear combinations to eliminate the factor $e^{im\phi}$ to yield:

$$\begin{aligned}
 \psi_{z^3} &= R_{4,3} Y_{3,0} \\
 \psi_{xz^2} &= 2^{-1/2} R_{4,3} (Y_{3,1} + Y_{3,-1}) \\
 \psi_{yz^2} &= -i 2^{-1/2} R_{4,3} (Y_{3,1} - Y_{3,-1}) \\
 \psi_{z(x^2-y^2)} &= 2^{-1/2} R_{4,3} (Y_{3,2} + Y_{3,-2}) \\
 \psi_{xyz} &= -i 2^{-1/2} R_{4,3} (Y_{3,2} - Y_{3,-2}) \\
 \psi_{x(x^2-3y^2)} &= 2^{-1/2} R_{4,3} (Y_{3,3} + Y_{3,-3}) \\
 \psi_{y(3x^2-y^2)} &= -i 2^{-1/2} R_{4,3} (Y_{3,3} - Y_{3,-3})
 \end{aligned} \tag{6}$$

The explicit forms of the angular factors in the above equations are shown in Table III.

The above set of seven equations is referred to as the "general set" and is appropriate for problems requiring no more than double degeneracy. Another set, the "cubic set", which is obtained by taking linear combinations of the functions in equation (6) is used when triply degenerate functions are required.²³ An excellent discussion of the angular functions is given by Waber and Hockett.²⁴

In C_{3v} symmetry, which is applicable to the gaseous rare earth trihalides (see page 31), only double degeneracy is required. The f functions form a basis for the irreducible representations of the C_{3v}

TABLE III

THE f ORBITAL ANGULAR FACTORS

True Polynomial	Simplified Polynomial	Angular Function
$z(5z^2-3r^2)$	z^3	$7^{1/2}(5\cos^3\theta-3\cos\theta)/4\pi^{1/2}$
$x(5z^2-r^2)$	xz^2	$(42)^{1/2}\sin\theta(5\cos^2\theta-1)\cos\theta/8\pi^{1/2}$
$y(5z^2-r^2)$	yz^2	$(42)^{1/2}\sin\theta(5\cos^2\theta-1)\sin\theta/8\pi^{1/2}$
xyz	xyz	$(105)^{1/2}\sin^2\theta\cos\theta\sin 2\theta/4\pi^{1/2}$
$z(x^2-y^2)$	$z(x^2-y^2)$	$(105)^{1/2}\sin^2\theta\cos\theta\cos 2\theta/4\pi^{1/2}$
$x(x^2-3y^2)$	$x(x^2-3y^2)$	$(70)^{1/2}\sin^3\theta\cos 3\theta/8\pi^{1/2}$
$y(3x^2-y^2)$	$y(3x^2-y^2)$	$(70)^{1/2}\sin^3\theta\sin 3\theta/8\pi^{1/2}$

point group as shown below:

$$\Gamma_f = 2a_1 + 2e + a_2. \quad (7)$$

The specific functions belonging to each particular irreducible representation are:²⁵

$$\begin{aligned} a_1: & f_{z^3} \\ a_1: & f_{x(x^2-3y^2)} \\ e: & (f_{xz^2}, f_{yz^2}) \\ e: & (f_{xyz}, f_{z(x^2-y^2)}) \\ a_2: & f_{y(3x^2-y^2)} \end{aligned} \quad (8)$$

A crystal field splitting diagram for these seven f functions in a C_{3v} environment is shown in Figure 2. As indicated in equation (2), the magnitude of this splitting is approximately equal to kT.

As discussed in the previous sections, the 4f orbitals are usually thought not to be affected appreciably by the ligands. This is primarily due to the radial factor in the wave function. For purposes of comparing the radial extension of the 4f orbitals with the 5s, 5p, 5d, and 6s orbitals the hydrogenic radial factors are qualitatively instructive.²³ This is only an approximation since electron-electron repulsions are ignored. Consideration of the radial probability distribution function, $r^2 R_{nl}^2(r)$, shows that the maximum probability of finding the electron at a distance r from the nucleus is as follows:²³

$$r_{\max 4f} < r_{\max 5s} \cong r_{\max 5p} \cong r_{\max 5d} < r_{\max 6s}. \quad (9)$$

A plot of $r^2 R_{nl}^2(r)$ versus r for the hydrogenic 4f, 5d, and 6s functions of Gd is shown in Figure 3. The plot and equation (9) explain why the

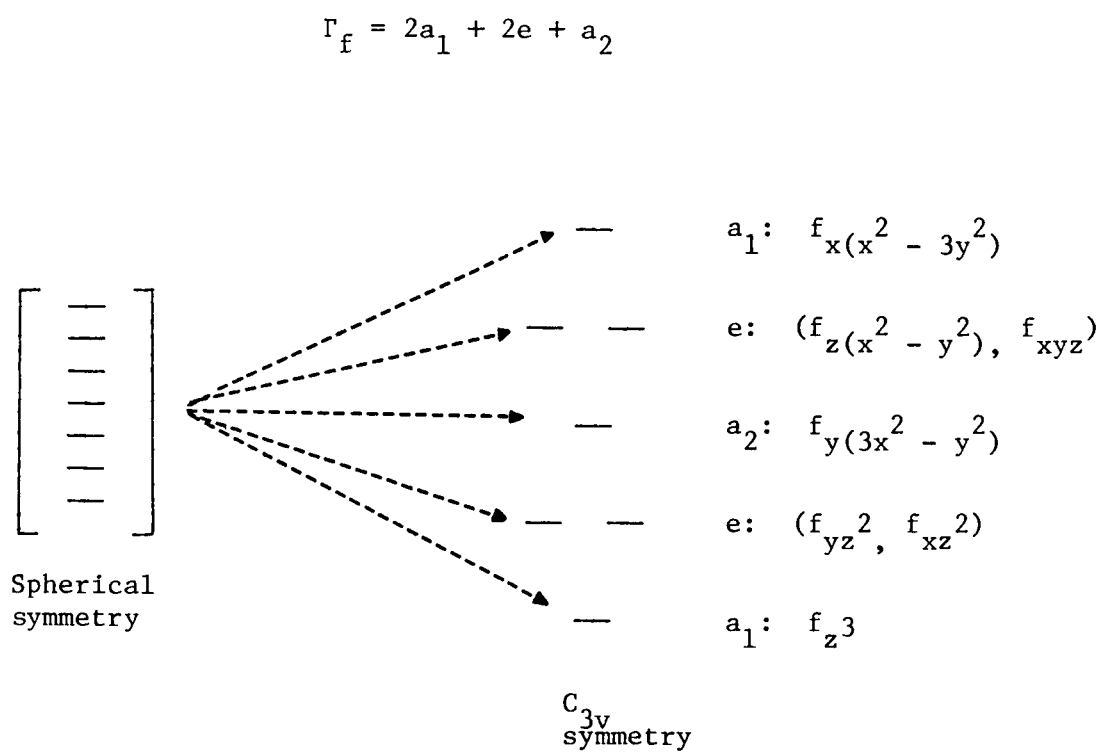
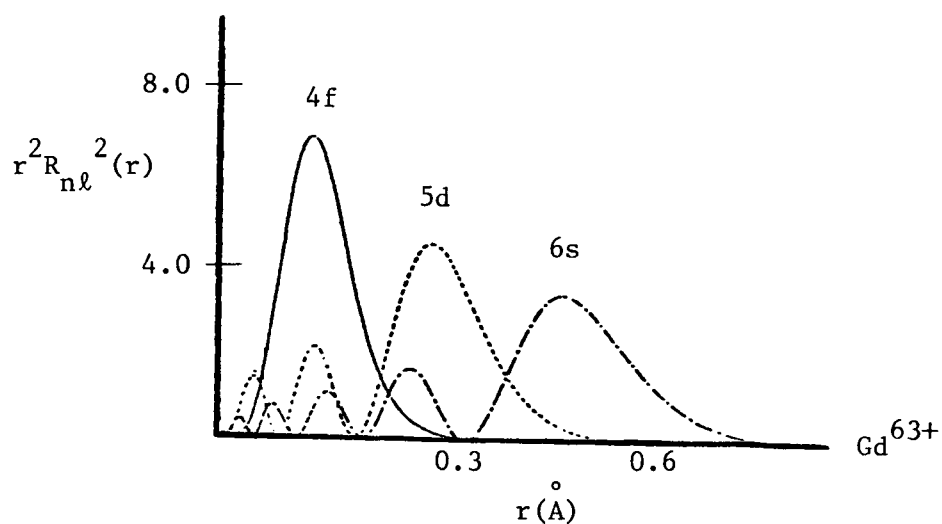
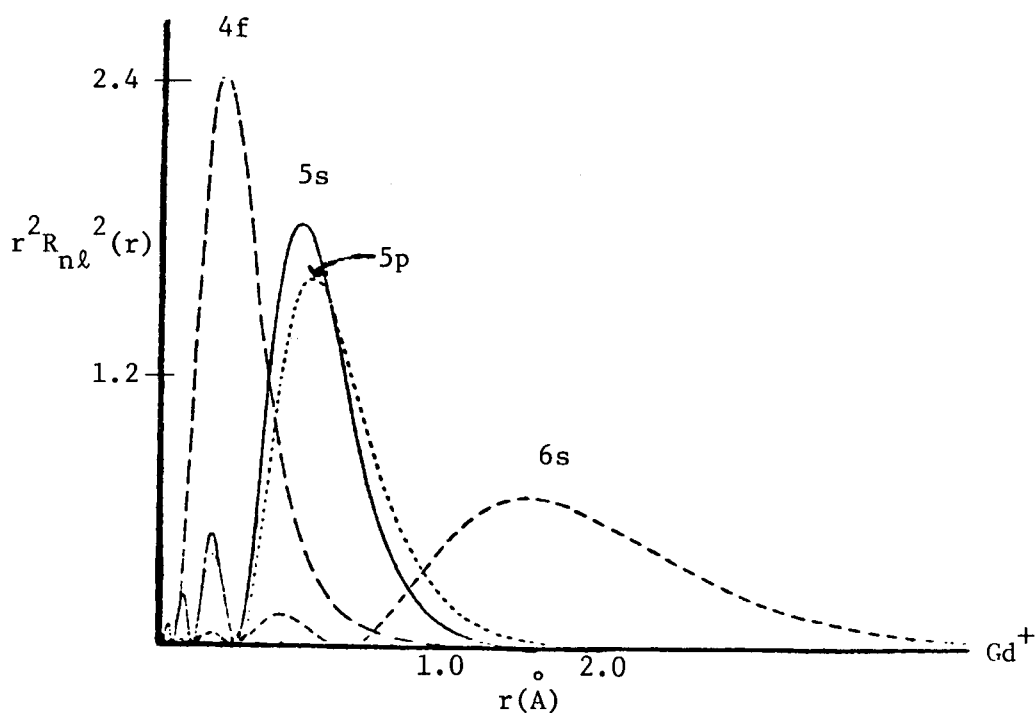


Figure 2. Splitting diagram for the seven f functions in a C_{3v} environment.



Hydrogenic Radial Probability Distribution Function



Radial Probability Distribution Function

Figure 3. Radial probability distribution functions for the $4f$ orbitals.

4f electrons of the lanthanides do not participate extensively in bonding as well as why the crystal field splitting of the 4f levels is small. They are unavailable spatially and well shielded from ligand effects by the 5s, 5p, 5d, and 6s orbitals. Inclusion of electron-electron repulsion expands the hydrogenic plot, but the trends in equation (9) remain, as shown by the calculation of more precise radial eigenfunctions for Gd^{+} .²⁶ A plot of these radial factors for the 4f, 5s, 5p, and 6s orbitals of Gd^{+} , including electron-electron repulsion, is shown in Figure 3.²⁶

D. The Proposed Problem

The calculation of ionization energies for even first-row transition-metal compounds by ab initio SCF techniques has proven to be a formidable task. The large basis sets required to handle d orbitals, coupled with a large number of configuration interaction terms, leads to great expenditures in computer time. In spite of the effort involved in such a calculation, the best results so far obtained are not very satisfactory.²⁷ It would seem a reasonable assumption that similar difficulties would be encountered with the more complicated f orbitals.

The Multiple Scattering $X\alpha$ (MS $X\alpha$) technique has been shown to be effective in predicting ionization energies and thus assigning molecular orbital origins to the bands in the gas phase photoelectron spectra of first row transition metal dihalides.²⁸ However, the applicability of this method in adequately describing the behavior of the 4f electrons in the lanthanides is relatively uninvestigated. The few previous studies will be discussed in Chapter II.

It is proposed, therefore, to perform both spin restricted and spin polarized MS $X\alpha$ calculations on several of the lanthanide trihalides to

assess its effectiveness in this area, particularly with respect to the 4f electrons. If the method is to be useful in the correlation of theoretical results with the experimental spectra it should, at a minimum, satisfy the three criteria mentioned earlier regarding the 4f electrons. These were: (1) the 4f energies must turn out to be shallow in energy, (2) the 4f energies must remain essentially degenerate with respect to crystal field splitting, and (3) the 4f electrons must remain virtually atomic. The results of the calculations will be examined in light of these criteria, and correlations will be drawn with existing photoelectron spectra of lanthanide compounds.

CHAPTER II

THEORETICAL CONSIDERATIONS

A. History of the MSX α Method

The X α theoretical method may be thought of as occupying a position between the traditional extremes of the ab initio and the semiempirical techniques. It overcomes many of the inherent disadvantages of the LCAO ab initio calculation while avoiding most of the defects of the semiempirical approach. The principal difference between the Hartree-Fock (H-F) ab initio equations and the X α equations is the treatment of the exchange energy, which has no simple classical interpretation, but arises because of the requirement that the wave function be antisymmetric with respect to electron permutation. The X α method was formulated by Slater²⁹ and involves approximating the exchange term as being proportional to the one-third power of the charge density. The advantage is that, through this approximation, the environment of an electron is simulated by a single local potential. This is in contrast to an H-F ab initio method in which a different local potential is required for each electron due to the exchange term. The multiple scattering (MS) technique of Johnson³⁰ is widely used for self consistently solving the molecular X α equations. It is the combination of Johnson's MS technique and Slater's X α equations that is known as the MSX α method.

B. Theory of the MSX α Method

As previously stated, the X α equations result from the replacement of the nonlocal exchange term of H-F formalism by an averaged local

exchange term of the form²⁹

$$V_{X\alpha} = -6\alpha (3\rho/4\pi)^{1/3}, \quad (10)$$

where ρ is the charge density. The factor α is an adjustable parameter which varies between 2/3 and 1. It is normally optimized in atomic calculations so that the total X α energy equals the total H-F energy.³¹

In molecular calculations a weighted average may be employed.

With the approximation in equation (10) the one electron Schrödinger equation is (in Rydberg units)³²

$$[-\nabla_1^2 + V_c(1) + V_{X\alpha}(1)] U_i(1) = \epsilon_i U_i(1) \quad (11)$$

where ∇_1^2 is the kinetic energy operator, $V_c(1)$ is the potential energy due to electronic and nuclear charges, and the $U_i(1)$ factor represents the orbitals with eigenvalues ϵ_i . Equation (11) is very similar to the H-F equations, with the exception that the term $V_{X\alpha}(1)U_i(1)$ is replaced by³³ $-\sum_j \hat{K}_j(1)U_i(1)$ where $\hat{K}_j$ is an exchange operator.

The charge density, ρ , may be represented as the sum of the charge densities of electrons with spins up and spins down.³⁴ The exchange term, $V_{X\alpha}$, is then written as either $V_{X\alpha\uparrow}$ or $V_{X\alpha\downarrow}$ corresponding to $\rho_\uparrow$ or $\rho_\downarrow$, respectively. Equation (11) may then be rewritten in a spin polarized form, in which the spin orbitals U_i become either $U_{i\uparrow}$ or $U_{i\downarrow}$.

Another major difference between the X α method and the H-F method is the relationship between the eigenvalues, ϵ_i , and the total energy E . The H-F eigenvalues, ϵ_{iHF} , are the difference between the total energy evaluated at $n_i = 1$ and $n_i = 0$ where the n_i are the occupations of the orbitals.³² However, the X α eigenvalues, ϵ_i , are given by the partial derivatives of the total energy, $E_{X\alpha}$, with

respect to the i th occupation number,²⁹

$$\epsilon_i = \partial E_{X\alpha} / \partial n_i. \quad (12)$$

Equation (12) is the basis for a significant result with respect to $X\alpha$ ionization energies. Koopman's theorem, often used in H-F theory, wherein the ionization energies are set equal to the negative of the eigenvalues, does not apply. Instead, to a high degree of approximation, the energy required to remove the K th electron may be shown to be³⁵

$$\begin{aligned} I_K &= E_{X\alpha}(n_K = n-1) - E_{X\alpha}(n_K = n) \\ &\cong - \partial E_{X\alpha} / \partial n_K \big|_{n_K = n - 1/2} \\ &= -\epsilon_K \big|_{n_K = n - 1/2} \end{aligned} \quad (13)$$

Therefore the ionization energy, I_K , is approximated as the negative of the K th eigenvalue calculated in a state where one-half an electron has been removed. This state is referred to as the transition state. Because the eigenvalues evaluated at $n_K = n$ and at $n_K = n - 1/2$ are different, the transition state method automatically includes a relaxation effect, and in this respect is an improvement over Koopman's theorem.

As indicated earlier, Johnson's MS formalism is widely used in conjunction with the $X\alpha$ equations. This method involves the "muffin tin" approximation in which a molecule is partitioned into three types of regions: I, II, and III.³⁶ Regions I are the atomic regions surrounding the constituent atoms, wherein the potential, $V_c(1) + V_{X\alpha}(1)$, is spherically averaged. Region II is the interatomic volume, between the atomic regions

and an outer boundary surrounding the molecule. Generally, in this region the potential is taken to be a constant volume average. Region III is the extramolecular space in which the potential is again spherically averaged. The initial molecular potential is obtained from free atom or free ion charge densities generated through a solution to an atomic, $X\alpha$ radial Schrödinger equation.

It has been shown³⁶ that, through the muffin tin approximation, the molecular orbital wave functions of equation (11) may be represented in regions I and III by the expansions

$$U_I(1) = \sum_{\ell, m} C_{\ell m j} R_{\ell j} Y_{\ell m}, \quad (14)$$

and

$$U_{III}(1) = \sum_{\ell, m} C_{\ell m} R_{\ell} Y_{\ell m}. \quad (15)$$

In equations (14) and (15) j represents the j th atomic sphere, $Y_{\ell m}$ are spherical harmonics, and the C are constants. The functions $R_{\ell j}$ and R_{ℓ} are solutions to radial Schrödinger equations within the specific regions for the appropriate spherically averaged potentials. This procedure has the important consequence that the $MSX\alpha$ wave functions are not dependent upon an analytic basis set, but rather they are obtained by a direct numerical solution of the radial Schrödinger equation. In the intersphere region II, equation (11) reduces to form³²

$$(\nabla_1^2 + \epsilon - \bar{V}_{II})U_{II}(1) = 0, \quad (16)$$

where $\bar{V}_{II}$ is the constant volume average. The solutions to equation (16) and their first derivatives are required to be continuous with the wave functions in equations (14) and (15). This requirement leads to^{35,36} a set of secular equations which have solutions only for certain eigenvalues. For a symmetrical molecular system, the size of the secular equations may be reduced using group theoretical procedures.³⁷

In summary, the MSX α technique involves two simplifications of the H-F method: (1) the exchange terms of H-F theory are replaced by an averaged local exchange, and (2) the actual potential, $V_c + V_{X\alpha}$, is replaced by either a spherically averaged one or a constant average. One resultant advantage of these approximations is a great reduction in computational time compared with an H-F ab initio technique.

C. Applications of the MSX α Method

The MSX α method is applicable to a variety of problems,³² however only the electronic structures of atoms and molecules will be considered in this discussion. The earliest applications of the X α equations were to atomic systems. An X α study of all the atoms in the periodic table was conducted by Herman and Skillman,³⁸ giving results which were generally in good agreement with X-ray spectra when an appropriate value of α was selected and the transition state approximation employed.³⁵ Also, because of the simplicity of the method, the results of atomic X α calculations may be used to initiate a more rigorous treatment. For example, the X α orbitals have been used as a starting point for ab initio calculations.³⁹

Since the application to molecular systems was suggested by Slater⁴⁰ the MSX α method has been applied to a large number of molecular systems.^{35,36}

The computed electronic structure of a considerable number of diatomic molecules³⁶ and several triatomic molecules³⁵ have been successfully correlated with X-ray, photoelectron, and optical spectra. In general, better results are obtained using overlapping atomic spheres rather than the strict muffin tin approximation. Further attention will be devoted to this overlapping sphere model in the following chapter; here it suffices to mention that the general formalism remains the same except the atomic spheres are no longer tangent to one another.

Perhaps the most important application of the MSX α method is in the treatment of transition metal compounds and complexes^{35,36} since it is very difficult to otherwise obtain reliable theoretical results for these species. The MSX α results have been useful in the analysis of optical and photoelectron spectra for many d electron containing compounds. A recent application²⁸ represents an extensive MSX α study of the first row transition metal dihalides. The results were used in conjunction with the photoelectron spectra of the vapor to make ground state and molecular orbital assignments.

As stated in Chapter I, the MSX α method has not yet been applied extensively to lanthanide compounds. Salleh and Copland⁴¹ have used the method to evaluate crystal field parameters for PrCl₃ in the solid state. Their model consisted of Pr³⁺ surrounded by nine chloride ions in D_{3h} symmetry. Nonoverlapping spheres were used and the calculations were spin restricted. The crystal field parameters, $A_n^m \langle r^n \rangle$, were determined using relations developed by Ellis and Newman⁴² involving the splitting of the 4f energies. The results of the calculations were dependent upon the choice of Watson sphere models, and in the most favorable

case the computed crystal field parameters show reasonable agreement with those extracted from experiment. These results also show a very small splitting of the 4f energies, the maximum splitting in the most favorable model being only about 0.06 ev.

Weber, et al.⁴⁴ have performed MSX α calculations on the free molecules LaF_3 , Ce(IV)F_3^+ , CeF_3 , and YbF_3 . The calculations were performed on the planar molecules, employing a nonoverlapping sphere, spin restricted format. The negatives of the eigenvalues in ev for the fluorine 2p electrons in neutral LaF_3 were found to be: 9.74 (e'), 9.86 (a_2''), 9.90 (a_2'), 9.95 (e''), 10.04 (e'), 10.09 (a_1'). These are in reasonable agreement with those obtained in the present work. The differences are that the two lowest orbitals are inverted and the splitting of the levels obtained in the present work is 0.9 ev compared with 0.35 ev for those shown above. Similar comments are applicable to the CeF_3 molecule. The maximum splitting of the fluorine 2p orbitals of CeF_3 obtained by Weber, et al. is 0.39 ev while those obtained in this work exhibit a splitting of 1.0 ev. The 4f electron of neutral CeF_3 has an energy of -8.20 ev as obtained by Weber, et al., as compared to -6.9 ev obtained in the present work. However the most notable differences between the present work and those of Weber, et al., are for the Yb compound. The differences are largely attributable to the fact that Weber has treated neutral YbF_3 as an f^{14} compound due to the fact that the 4f orbitals exhibit lower energy than the 2p orbitals of fluorine. The 4f eigenvalues thus obtained are slightly less than -10 ev and show a splitting of 0.26 ev. In this thesis YbCl_3 was treated as an f^{13} compound which leaves an empty orbital at lower energy than the chlorine 3p orbitals, and result in 4f

eigenvalues which are all -20.6 ev.

The X α discrete variational method⁴⁵ has been employed⁴⁶ to compute the electronic structure of some lanthanide oxyfluorides. It should be noted that this method is an LCAO procedure and, as such, the results obtained are very dependent on the atomic orbital basis set used.⁴⁶ The calculations were performed on the molecules LaOF, PrOF, NdOF, and EuOF. These were spin restricted for LaOF and spin polarized for the other three. The 4f orbitals are vacant in LaOF and appear at higher energy than the O 2p and F 2p orbitals for PrOF and NdOF. In EuOF the 4f orbitals have energies between the F 2p and O 2p orbitals. The most prevalent interaction occurred between the O 2p and metal 4f orbitals. For LaOF the orbitals containing O 2p character were quite atomic, with other states contributing less than 5%, but significant interaction between the 4f orbitals and 2p orbitals appeared in PrOF and reached a maximum of 18% in EuOF. The energies of the 4f orbitals were crystal field split by about 0.5 ev in all the calculations.

Similar calculations employing the X α discrete variational method have been applied to LnVO₄ where Ln = Ce, Nd, Eu, Tb, Dy, Gd, and Yb.⁴⁷ All of the calculations were spin polarized, and were not iterated to self consistency. The model consisted of VO₄³⁻ and LnO₈¹³⁻ clusters characteristic of the orthovanadate crystal lattice.⁴⁷ The results indicate a significant mixing of the metal 4f orbitals and the oxygen 2p orbitals. This mixing is a maximum for compounds in the middle of the lanthanide series where, for example, the O 2p contributed up to 30% to the Eu 4f orbitals. The crystal field splitting is also large for the metal 4f orbitals of these compounds where again, for example, the

occupied 4f levels of Eu are split by approximately 0.3 eV. These results are in sharp contrast to the results presented in this thesis with respect to the metal 4f orbitals.

D. Theoretical Considerations for the Lanthanides

Much of the theoretical work for lanthanide compounds has been concerned with crystal field parameters. As seen in equation (2) the spin orbit splitting exceeds the crystal field splitting for the 4f orbitals of lanthanide compounds. Figure 4 shows a typical absorption spectrum of a lanthanide compound.⁴⁸ Typically such spectra show groups of very sharp lines with an overall group spacing of about 300 cm^{-1} , and the various groups of lines are generally separated by at least 1000 cm^{-1} . The transitions are all from the ground term $^4I_{15/2}$ to the excited terms by which the various line groups are designated. The lower portion of the figure shows three of the transitions at much greater resolution and clearly demonstrates the sharpness of the optical absorption lines. The spectra suggest that the various groups of lines are due to transitions between free ion states which are crystal field split through the electrostatic interaction of the cation with the ligands. The fine structure therefore provides a measure of the magnitude of the interaction of the 4f electrons with the crystal field. The high resolution required is not generally obtainable through PES or X-ray experiments and thus the optical spectra provide the usual means of experimentally determining the crystal field parameters.

The crystal field problem has two aspects. First, the number of levels into which the free ion state is split may be deduced from the

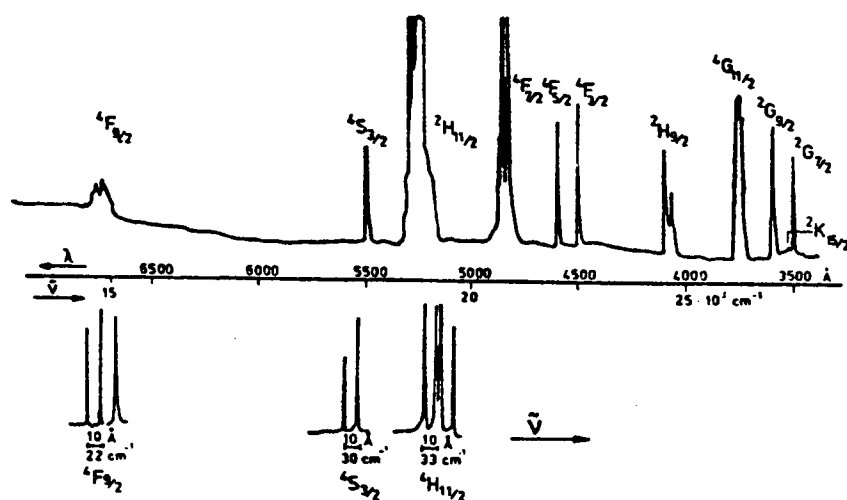


Figure 4. Typical absorption spectrum of a lanthanide compound:
 $\text{Er}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.

symmetry of the problem. Secondly, and much more complicated, is the question of the magnitude of the splitting. The crystal field interactions are proportional to the expectation values $\langle r^n \rangle$ and from Figure 3, it is seen that these values are relatively small. Since the 4f shell of the lanthanides is not affected to as great an extent by the ligands as the nd shell of the transition metal groups, it was often assumed that the electrostatic approach of crystal field theory would be more appropriate for treating lanthanide compounds than transition metal compounds. This assumption, however, has proved to be inadequate.⁴⁹ Instead, it has been discovered that overlap and covalency contribute significantly to the lanthanide crystal field parameters.^{49,50} This should not be taken to imply that overlap and covalency are large in lanthanide compounds, but rather that small amounts of overlap and covalency may greatly affect small crystal field parameters. One approach which has been developed to take into account the weak covalent bonding in lanthanide compounds is the angular overlap model.⁵¹ This technique has been successfully applied to the calculation of lanthanide crystal field parameters.⁵²

One way of estimating the degree of covalency is by consideration of the magnitude of the overlap integrals. These integrals represent the amount of overlap between a ligand ns or np function and a metal 4f function and are of an order of magnitude of 10^{-2} .⁵³ The values for these overlap integrals have been used in conjunction with the nephelauxetic ratio to estimate a percent covalency for some Pr^{3+} complexes.⁵⁴ These values are very small, for example less than 0.36% for $\text{Pr}(\text{OH}_2)_9^{3+}$.

Another important consideration with respect to the 4f electrons is their relative energies, as compared to the energies of the valence levels of the ligands. In some 4f group compounds, the ionization energies of the partly filled 4f shell are larger than the fully occupied molecular orbitals, this phenomenon being referred to as the "third revolution in ligand field theory."⁵⁵ There are essentially two explanations for this occurrence. First, the 4f orbital energies themselves may be deeper than the ligand orbital energies, whereby assuming comparable relaxation of the 4f orbitals and ligand orbitals upon ionization, the ionization energy from a 4f level will be greater. Secondly, the 4f level may be more shallow than the ligand level, but, upon ionization relaxes to a greater extent, thus again resulting in a greater ionization energy. This second case will obviously result in a violation of Koopman's theorem in the ordering of the orbital ionization energies. These ionization energies will be elaborated on further in Chapter III.

A third point of theoretical importance is the relativistic treatment of the 4f electrons. Relativistic f charge distributions are expanded compared to nonrelativistic ones,⁵⁶ resulting in crystal field expectation values, $\langle r^n \rangle$, which are larger in relativistic calculations, leading to a greater crystal field interaction. Ratios of the corresponding relativistic versus nonrelativistic expectation values vary from 1.10 to 1.50.⁵⁶ In addition, the L-S splitting of the 4f energies in a relativistic calculation⁵⁷ averages about 1.0 ev.

CHAPTER III

MSX α CALCULATIONS FOR LANTHANIDE TRIHALIDES

This chapter presents the results obtained from treating several lanthanide trihalide molecules by the MSX α method. First the data necessary to set up to calculations are presented, followed by a description of the computations performed.

A. The Input Parameters

The majority of the experimental data favor a pyramidal geometry for the lanthanide trihalide vapors,⁵⁸ although there are some data which support a planar triangular structure.⁵⁹ Pertinent bond distances and angles were taken from the electron diffraction data⁶⁰ for the trichlorides of La, Pr, Gd, Tb, Ho, and Lu which indicated C_{3v} symmetries for all of the compounds. To obtain the necessary data for the other lanthanide trichlorides a linear variation of bond distance with atomic number was assumed. A linear least squares treatment gave the following equations:

$$r_{\text{Ln-Cl}} = [-0.0230906Z + 6.19317](\text{a.u.}) \quad (17)$$

and

$$r_{\text{Cl-Cl}} = [-0.0403376Z + 10.3805](\text{a.u.}) \quad (18)$$

where $r_{\text{Ln-Cl}}$ is the Ln-Cl bond distance, $r_{\text{Cl-Cl}}$ is the non-bonded distance between two chlorines, and Z is the atomic number of Ln. The Cl-Ln-Cl bond angle, α , was computed from

$$\sin(\alpha/2) = r_{\text{Cl-Cl}} / 2r_{\text{Ln-Cl}} \quad (19)$$

To approximate the bond distances for the lanthanide trifluorides the difference between the radius of a chloride ion ($1.67 \text{ \AA}$)⁶¹ and a fluoride ion ($1.19 \text{ \AA}$)⁶¹ was subtracted from the corresponding Ln-Cl distance. The F-Ln-F angle was taken to be the same as in the corresponding tri-chloride.

As indicated in Chapter II, better results are normally obtained by allowing the atomic spheres to overlap. One theoretical justification usually given for doing so is that the volume of region II is decreased, and it is in this region that the potential approximation is the weakest (taken as a constant). This overlapping sphere method, however, necessitates a reliable method of choosing atomic radii, $r_{X\alpha}$, such that the sum of the $r_{X\alpha}$ values for the metal and ligand is greater than the bond distance. Several methods have been proposed for choosing these radii.⁶²⁻⁶⁴ These often involve the fitting of an experimental quantity⁶² or the satisfying of a theoretical criterion.⁶³ The disadvantage of both of these approaches is that in order to apply them numerous calculations for different amounts of overlap have to be performed resulting in a significant increase in computational time. A nonempirical method for obtaining the atomic radii, $r_{X\alpha}$, that does not increase the computational time is to utilize the atomic density from Herman-Skillman atomic calculations. The procedure, developed by Sherrod,⁶⁴ is to choose the radii, $r_{X\alpha}$, such that the total electronic charge in a sphere of radius $r_{X\alpha}$ is equal to $Z - |n|$, where Z is the atomic number and $|n|$ is the magnitude of the charge on the ion.

The bond lengths, $r_{\text{Ln-X}}$, ($X = \text{Cl}, \text{F}$) computed from equation (17) for the LnCl_3 and obtained as explained earlier for the LnF_3 , the angles, α ,

computed from equation (19) and taken to be the same for the corresponding LnF_3 , and the atomic radii obtained from the $Z-|n|$ method are shown in Table IV. These data were used to compute the coordinates of the atoms in the appropriate molecular geometry to generate an initial molecular potential.

The α value chosen was a weighted average, obtained by employing approximate atomic values,⁶⁵ and then taking three parts ligand to one part metal. This gave an approximate α value of 0.72 which was used in all calculations in order to more readily compare the results. Also, this same value was used in all atomic spheres as well as in the inter-sphere and extramolecular regions so that the virial ratio could be used as a viable theoretical criterion for the quality of the calculations.⁶⁶

B. The Format for the Calculations

The following molecules were studied: LaF_3 , CeF_3 , LaCl_3 , CeCl_3 , PrCl_3 , EuCl_3 , GdCl_3 , TbCl_3 , YbCl_3 , and LuCl_3 . In accordance with the MSX α summary in Chapter II, Herman-Skillman atomic calculations were performed to generate initial charge densities for the constituent atoms of the above molecules. The atomic charge densities were then placed in the appropriate molecular geometry to create an initial molecular potential via the muffin tin approximation. All molecules were assumed to have a C_{3v} geometry, with the exception of LaF_3 , for which results were obtained in both planar (D_{3h}) and pyramidal (C_{3v}) configurations. As will be pointed out later in this chapter, there seems to be little difference between the results obtained in the two

TABLE IV

INPUT DATA

LnX_3	$r_{\text{X}\alpha\text{Ln}}$ (a.u.)	r_{LnX} (a.u.)	$\angle \text{X-Ln-X}$ (degrees)
LaF_3	2.554	4.000	120.00
LaF_3	2.554	4.000	111.89
CeF_3	2.392	3.944	111.85
LaCl_3	2.554	4.877	111.89
CeCl_3	2.392	4.854	111.85
PrCl_3	2.379	4.832	111.80
EuCl_3	2.221	4.739	111.62
GdCl_3	2.315	4.717	111.58
TbCl_3	2.162	4.693	111.53
YbCl_3	2.041	4.577	111.29
LuCl_3	2.134	4.554	111.24

$$r_{\text{X}\alpha\text{F}} = 1.728 \text{ a.u.}$$

$$r_{\text{X}\alpha\text{Cl}} = 2.720 \text{ a.u.}$$

geometries. In all cases the atomic spheres have been permitted to overlap, with the exception of EuCl_3 , for which both overlapping spheres and nonoverlapping spheres models were employed. Symmetry calculations were performed in order that the MSX α secular equations would be symmetry factorized into the appropriate irreducible representations. Spherical harmonics up to $\ell_{\text{max}} = 4$ were included for the outer sphere and for the metal sphere, and up to $\ell_{\text{max}} = 2$ for the ligand spheres.

The muffin tin potentials were used to initiate self consistent MSX α calculations for the ten molecules listed. Both spin restricted (SR) and spin polarized (SP) results were obtained for each of the open shell molecules except CeF_3 which was only treated in an SR format. Only SR calculations were performed for the closed shell molecules. Transition state (TS) calculations were done for all molecules except, for reasons to be explained later, the nonoverlapping sphere EuCl_3 calculation and the SP YbCl_3 calculation. The TS calculations were applied to both the metal 4f level and to the ligand p level. Thus two TS calculations were required except for the lanthanum compounds. The potential convergence was set at 10^{-2} . The computer program employed was developed by Sherrod and is similar to the one listed by Liberman and Batra.⁶⁷

C. Results

Throughout the discussion that follows the eigenvalues obtained in a neutral molecule calculation will be referred to as NM eigenvalues, while those obtained in a TS calculation will be referred to as TS

eigenvalues, the negatives of which are approximately equal to the ionization energies. The results of the MSX α calculations are shown in Tables V through XXII, each of which contains the following information. The molecular orbitals (MOS), classified according to symmetry type, with the electron occupation numbers as right superscripts, and the negatives of the NM eigenvalues (in electron volts) appear in the first two columns. The SP MOS are denoted by an α or β on the right representing spin up or spin down respectively. The MOS contain major contributions from the s, p, and f atomic orbitals of the metal, and from the s and p atomic orbitals of the ligands. These are indicated in the tables as Ms, Mp, Mf, Xs, and Xp respectively, along with their corresponding percent contributions in the MOS. The 1s, 2s, 2p 3s, 3p, 3d, 4s, 4p, and 4d atomic orbitals of the metals were treated as core levels and do not appear in the tables. The 1s orbital of fluorine and the 1s, 2s, and 2p orbitals of chlorine were also treated as core orbitals and do not appear in the tables. Therefore the major contribution to the metal s orbital is largely attributable to the metal 5s, since the s orbitals higher in energy than the 5s are unoccupied in the tripositive cation. Similarly, the major contributions to the metal p and f orbitals are largely the metal 5p and 4f orbitals. An analogous argument shows that the principal ligand contributors are the 2s and 2p orbitals in fluorine and the 3s and 3p orbitals in chlorine. Smaller contributions occur from the metal d orbitals and an occasional one percent contribution is due to the chlorine d orbitals. The metal g functions did not contribute to any of the MOS even though they were included in the calculations. The percentage contributions were taken

TABLE V

SPIN RESTRICTED ENERGIES FOR $\text{MX}_3 = \text{LaF}_3(\text{D}_{3h})$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1')^2$	35.2	Ms 94, Xs 5, Xp 1	38.6	3.4
$1(e')^4$	29.3	Xs 93, Mp 6, Md 1	32.7	3.4
$2(a_1')^2$	28.5	Xs 93, Ms 6	31.9	3.4
$3(e')^4$	21.0	Mp 87, Xs 6, Xp 6	24.3	3.3
$1(a_2')^2$	21.1	Mp 99	24.4	3.3
$3(e')^4$	10.8	Xp 94, Md 6	14.1	3.3
$3(a_1')^2$	10.7	Xp 86, Mf 8, Md 4, Ms 2	14.1	3.4
$1(e'')^4$	10.6	Xp 97, Md 2, Mf 1	14.0	3.4
$1(a_2')^2$	10.5	Xp 96, Mf 4	13.9	3.4
$2(a_2')^2$	10.4	Xp 97, Mf 2, Mp 1	13.7	3.3
$4(e')^4$	9.7	Xp 86, Mp 7, Mf 4, Md 3	13.1	3.4

virial ratio = 1.0004223

total energy = -17049.152 Rydbergs

metal charge = 1.91

ligand charge = -0.64

TABLE VI

SPIN RESTRICTED ENERGIES FOR $\text{MX}_3 = \text{LaF}_3(\text{C}_{3v})$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^2$	35.2	Ms 94, Xs 5, Xp 1	38.6	3.4
$1(e)^4$	29.3	Xs 94, Mp 5, Md 1	32.7	3.4
$2(a_1)^2$	28.6	Xs 92, Ms 6, Mp 1	32.1	3.5
$2(e)^4$	21.0	Mp 88, Xs 6, Xp 6	24.3	3.3
$3(a_1)^2$	21.1	Mp 97, Xp 2, Xs 1	24.4	3.3
$3(e)^4$	10.9	Xp 93, Md 5, Mf 1	14.2	3.3
$4(a_1)^2$	10.7	Xp 92, Mf 4, Md 3, Ms 1	14.1	3.4
$4(e)^4$	10.7	Xp 96, Md 2, Mf 2	14.0	3.3
$1(a_2)^2$	10.5	Xp 97, Mf 3	13.9	3.4
$5(a_1)^2$	10.2	Xp 91, Mf 6, Mp 2, Ms 1	13.6	3.4
$5(e)^4$	9.9	Xp 88, Mp 6, Md 4, Mf 2	13.3	3.4

virial ratio = 1.0004179

total energy = -17049.246 Rydbergs

metal charge = 1.91

ligand charge = -0.64

TABLE VII

SPIN RESTRICTED ENERGIES FOR $\text{MX}_3 = \text{LaCl}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^2$	36.5	Ms 98, Xs 1, Xp 1	39.0	2.5
$1(e)^4$	23.3	Mp 79, Xs 17, Xp 2, Xd 1	25.8	2.5
$2(a_1)^2$	22.7	Mp 93, Xs 6, Xp 1	25.2	2.5
$3(a_1)^2$	20.6	Xs 94, Mp 5, Ms 1	23.2	2.6
$2(e)^4$	20.2	Xs 83, Mp 16, Xp 1	22.8	2.6
$2(e)^4$	9.4	Xp 93, Md 5, Mf 2	11.9	2.5
$4(a_1)^2$	9.3	Xp 89, Mf 7, Md 3	11.8	2.5
$4(e)^4$	9.2	Xp 96, Md 2, Mf 2	11.7	2.5
$1(a_2)^2$	9.1	Xp 96, Mf 4	11.6	2.5
$5(a_1)^2$	9.1	Xp 92, Mf 6, Mp 1, Ms 1	11.6	2.5
$5(e)^4$	8.9	Xp 91, Mp 3, Md 3, Mf 3	11.4	2.5

virial ratio = 1.003654

total energy = -19209.832 Rydbergs

metal charge = 2.00

ligand charge = -0.67

TABLE VIII

SPIN RESTRICTED ENERGIES FOR $\text{MX}_3 = \text{CeF}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^2$	36.5	Ms 95, Xs 4, Xp 1	40.5 (39.9) ^a	4.0 (3.4) ^a
$1(e)^4$	29.6	Xs 94, Mp 5, Md 1	33.1	3.5
$2(a_1)^2$	29.0	Xs 94, Ms 5, Mp 1	32.4	3.4
$3(a_1)^2$	21.7	Mp 97, Xp 2, Xs 1	25.6 (25.1) ^a	3.9 (3.4) ^a
$2(e)^4$	21.6	Mp 88, Xs 6, Xp 6	25.5 (25.0) ^a	3.9 (3.4) ^a
$3(e)^4$	11.2	Xp 95, Md 4, Mf 1	14.5	3.3
$4(a_1)^2$	11.0	Xp 93, Mf 4, Md 2, Ms 1	14.4	3.4
$4(e)^4$	11.0	Xp 96, Md 2, Mf 2	14.4	3.4
$1(a_2)^2$	10.9	Xp 96, Mf 4	14.3	3.4
$5(a_1)^2$	10.5	Xp 89, Mf 7, Mp 2, Md 1, Ms 1	14.0	3.5
$5(e)^4$	10.2	Xp 88, Mp 6, Md 4, Mf 3	13.6	3.4
$6(a_1)^1$	6.9	Mf 99, Xp 1	11.5 (10.3) ^a	4.6 (3.4) ^a

virial ratio = 1.0005091

total energy = -17741.078 Rydbergs

metal charge = 2.03

ligand charge = -0.68

^a0.5 electron removed from 5(e) MO

TABLE IX

SPIN RESTRICTED ENERGIES FOR $\text{MX}_3 = \text{CeCl}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^2$	37.7	Ms 98, Xp 1	40.6 (40.3) ^a	2.9 (2.6) ^a
$1(e)^4$	23.8	Mp 82, Xs 14, Xp 2, Xd 1	26.5 (26.3) ^a	2.7 (2.5) ^a
$2(a_1)^2$	23.3	Mp 95, Xs 4, Xp 1	26.1 (25.8) ^a	2.8 (2.5) ^a
$3(a_1)^2$	20.9	Xs 96, Mp 4	23.5	2.6
$2(e)^4$	20.6	Xs 87, Mp 12	23.2	2.6
$3(e)^4$	9.6	Xp 96, Md 2, Mf 1	12.1	2.5
$4(a_1)^2$	9.5	Xp 92, Mf 6, Md 1	12.1	2.6
$4(e)^4$	9.5	Xp 96, Mf 3, Md 1	12.0	2.5
$1(a_2)^2$	9.4	Xp 95, Mf 5	12.0	2.6
$5(a_1)^2$	9.3	Xp 89, Mf 9, Ms 1, Mp 1	11.9	2.6
$5(e)^4$	9.1	Xp 90, Mf 4, Mp 3, Md 3	11.7	2.6
$6(a_1)^1$	7.6	Mf 99, Xp 1	10.6 (10.2) ^a	3.0 (2.6) ^a

virial ratio = 1.0004673

total energy = -19901.621 Rydbergs

metal charge = 2.07

ligand charge = -0.69

^a0.5 electron removed from 5(e) MO

TABLE X

SPIN POLARIZED ENERGIES FOR $\text{MX}_3 = \text{CeCl}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^1\beta$	38.0	Ms 99, Xp 1	40.8 (40.6) ^a	2.8 (2.6) ^a
$1(a_1)^1\alpha$	37.4	Ms 99, Xp 1	40.2 (39.9) ^a	2.8 (2.5) ^a
$1(e)^2\beta$	23.9	Mp 84, Xs 13, Xp 2, Xd 1	26.6	2.7
$1(e)^2\alpha$	23.5	Mp 80, Xs 17, Xp 2, Xd 1	26.3 (26.0) ^a	2.8 (2.5) ^a
$2(a_1)^1\beta$	23.5	Mp 96, Xs 4, Xp 1	26.2	2.7
$2(a_1)^1\alpha$	23.0	Mp 93, Xs 6, Xp 1	25.7 (25.5) ^a	2.7 (2.5) ^a
$2(e)^2\beta$	20.6	Xs 88, Mp 11	23.2	2.6
$2(e)^2\alpha$	20.6	Xs 84, Mp 15, Xp 1	23.3	2.7
$3(a_1)^1\beta$	20.9	Xs 96, Mp 3	23.4 (23.6) ^a	2.5 (2.7) ^a
$3(a_1)^1\alpha$	20.9	Xs 94, Mp 5	23.6	2.7
$3(e)^2\beta$	9.6	Xp 95, Md 3, Mf 2	12.1	2.5
$3(e)^2\alpha$	9.6	Xp 97, Md 2, Mf 1	12.2	2.6
$4(a_1)^1\beta$	9.5	Xp 88, Mf 10, Md 2, Ms 1	12.1	2.6
$4(a_1)^1\alpha$	9.6	Xp 96, Mf 3, Md 1	12.2	2.6
$4(e)^2\beta$	9.5	Xp 95, Mf 4, Md 1	12.0	2.5
$4(e)^2\alpha$	9.5	Xp 97, Mf 2, Md 1	12.1	2.6
$1(a_2)^1\beta$	9.4	Xp 93, Mf 7	11.9	2.5
$1(a_2)^1\alpha$	9.4	Xp 97, Mf 3	12.0	2.6
$5(a_1)^1\beta$	9.4	Xp 88, Mf 11, Ms 1, Mp 1	11.9	2.5
$5(a_1)^1\alpha$	9.3	Xp 90, Mf 7, Ms 1, Mp 1, Md 1	12.0	2.7
$5(e)^2\beta$	9.1	Xp 88, Mf 6, Md 3, Mp 2	11.7	2.6
$5(e)^2\alpha$	9.1	Xp 92, Mp 3, Md 3, Mf 3	11.8	2.7
$6(a_1)^1\beta$	7.9	Mf 99, Xp 1	10.9 (10.5) ^a	3.0 (2.6) ^a

virial ratio = 1.0004607

total energy = -19901.770 Rydbergs

metal charge = 2.05

ligand charge = -0.68

^a0.5 electron removed from 5(e) α MO

TABLE XI

SPIN RESTRICTED ENERGIES FOR $\text{MX}_3 = \text{PrCl}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^2$	38.5	Ms 98, Xp 1	41.2 (41.0) ^a	2.7 (2.5) ^a
$1(e)^4$	24.1	Mp 85, Xs 12, Xp 2, Xd 1	26.8 (26.6) ^a	2.7 (2.5) ^a
$2(a_1)^2$	23.6	Mp 96, Xs 3, Xp 1	26.3 (26.1) ^a	2.7 (2.5) ^a
$3(a_1)^2$	20.9	Xs 96, Mp 3	23.5	2.6
$2(e)^4$	20.6	Xs 89, Mp 10	23.2	2.6
$3(e)^4$	9.6	Xp 96, Md 2, Mf 2	12.1	2.5
$4(a_1)^2$	9.5	Xp 90, Mf 8, Md 2, Ms 1	12.1	2.6
$4(e)^4$	9.5	Xp 95, Mf 4, Md 1	12.0	2.5
$1(a_2)^2$	9.4	Xp 94, Mf 6	11.9	2.5
$5(a_1)^2$	9.4	Xp 88, Mf 10, Ms 1, Mp 1	11.9	2.5
$5(e)^4$	9.1	Xp 89, Mf 5, Md 3, Mp 2	11.7	2.6
$6(a_1)^1$	7.8	Mf 99, Xp 1	10.7 (10.3) ^a	2.9 (2.5) ^a
$6(e)^1$	7.7	Mf 94, Xp 5	10.7 (10.3) ^a	3.0 (2.6) ^a

virial ratio = 1.0004422

total energy = -20610.762 Rydbergs

metal charge = 1.96

ligand charge = -0.65

^a0.5 electron removed from 5(e) MO

TABLE XII

SPIN POLARIZED ENERGIES FOR $\text{MX}_3 = \text{PrCl}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^1\beta$	38.8	Ms 99, Xp 1	41.5	2.7
$1(a_1)^1\alpha$	37.6	Ms 99, Xp 1	40.2	2.6
$1(e)^2\beta$	24.3	Mp 87, Xs 10, Xp 2, Xd 1	26.9	2.6
$1(e)^2\alpha$	23.4	Mp 77, Xs 19, Xp 2, Xd 1	26.1	2.7
$2(a_1)^1\beta$	23.8	Mp 97, Xs 3, Xp 1	26.5	2.7
$2(a_1)^1\alpha$	22.9	Mp 92, Xs 7, Xp 1	25.5	2.6
$3(a_1)^1\beta$	20.8	Xs 97, Mp 2	23.4 (23.6) ^a	2.6 (2.8) ^a
$3(a_1)^1\alpha$	21.0	Xs 93, Mp 6	23.7	2.7
$2(e)^2\beta$	20.6	Xs 90, Mp 9	23.1 (23.3) ^a	2.5 (2.7) ^a
$2(e)^2\alpha$	20.6	Xs 82, Mp 17, Xp 1	23.4 (23.2) ^a	2.8 (2.6) ^a
$3(e)^2\beta$	9.5	Xp 94, Mf 4, Md 3	12.0	2.5
$3(e)^2\alpha$	9.7	Xp 98, Md 2	12.3	2.6
$4(a_1)^1\beta$	9.5	Xp 80, Mf 18, Md 2	12.1	2.6
$4(a_1)^1\alpha$	9.6	Xp 97, Md 1, Mf 1	12.2	2.6
$4(e)^2\beta$	9.4	Xp 92, Mf 7, Md 1	11.9	2.5
$4(e)^2\alpha$	9.5	Xp 98, Md 1, Mf 1	12.2	2.7
$1(a_2)^1\beta$	9.4	Xp 88, Mf 12	11.9	2.5
$1(a_2)^1\alpha$	9.4	Xp 98, Mf 2	12.1	2.7
$5(a_1)^1\beta$	9.3	Xp 88, Mf 11, Mp 1	11.8 (12.0) ^a	2.5 (2.7) ^a
$5(a_1)^1\alpha$	9.3	Xp 93, Mf 5, Ms 1, Mp 1, Md 1	12.0	2.7
$5(e)^2\beta$	9.1	Xp 84, Mf 11, Mp 2, Md 2	11.6	2.5
$5(e)^2\alpha$	9.2	Xp 93, Mp 3, Md 3, Mf 1	11.8	2.6
$6(a_1)^1\beta$	8.3	Mf 98, Xp 2	11.0	2.7
$6(e)^1\beta$	8.2	Mf 94, Xp 6	11.0 (10.8) ^a	2.8 (2.6) ^a

virial ratio = 1.0004387

total energy = -20610.879 Rydbergs

metal charge = 1.92

ligand charge = -0.64

^a0.5 electron removed from 5(e) α MO

TABLE XIII

SPIN RESTRICTED ENERGIES FOR $\text{MX}_3 = \text{EuCl}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^2$	41.9	Ms 99	44.6	2.7
$1(e)^4$	25.5	Mp 91, Xs 6, Xp 2, Xd 1	28.0	2.5
$2(a_1)^2$	25.1	Mp 98, Xs 2, Xp 1	27.7	2.6
$3(a_1)^2$	21.2	Xs 98, Mp 1	23.8	2.6
$2(e)^4$	21.0	Xs 94, Mp 6	23.6	2.6
$3(e)^4$	9.8	Xp 97, Mf 2, Md 1	12.3	2.5
$4(a_1)^2$	9.8	Xp 84, Mf 14, Md 1	12.3	2.5
$4(e)^4$	9.7	Xp 92, Mf 7, Md 1	12.2	2.5
$1(a_2)^2$	9.6	Xp 88, Mf 12	12.2	2.6
$5(a_1)^2$	9.6	Xp 84, Mf 15, Mp 1	12.2	2.6
$5(e)^4$	9.4	Xp 82, Mf 15, Mp 2, Md 2	11.9	2.5
$6(a_1)^1$	8.7	Mf 98, Xp 2	11.4	2.7
$6(e)^2$	8.7	Mf 94, Xp 5	11.3	2.6
$2(a_2)^1$	8.6	Mf 90, Xp 10	11.3	2.7
$7(e)^1$	8.6	Mf 86, Xp 13	11.2	2.6
$7(a_1)^1$	8.4	Mf 78, Xp 21	11.1	2.7

virial ratio = 1.0004552

total energy = -23617.047 Rydbergs

metal charge = 1.69

ligand charge = -0.56

TABLE XIV

SPIN RESTRICTED ENERGIES FOR $\text{MX}_3 = \text{EuCl}_3$
(NONOVERLAPPING SPHERES)

MO	-E(ev)	% Constituency
$1(a_1)^2$	42.3	Ms 99
$1(e)^4$	25.3	Mp 90, Xs 7, Xp 2, Xd 1
$2(a_1)^2$	25.0	Mp 97, Xs 2, Xp 1
$3(a_1)^2$	21.7	Xs 98, Mp 2
$2(e)^4$	21.5	Xs 93, Mp 6
$3(e)^4$	10.2	Xp 99, Md 1, Mf 1
$4(a_1)^2$	10.2	Xp 95, Mf 5
$4(e)^4$	10.1	Xp 94, Mf 6
$1(a_2)^2$	10.1	Xp 91, Mf 9
$5(a_1)^2$	10.0	Xp 76, Mf 23
$5(e)^4$	9.8	Xp 80, Mf 17, Mp 2
$6(a_1)^1$	9.2	Mf 99, Xp 1
$6(e)^2$	9.1	Mf 95, Xp 4
$2(a_2)^1$	9.1	Mf 92, Xp 8
$7(e)^1$	9.0	Mf 84, Xp 15
$7(a_1)^1$	8.9	Mf 78, Xp 21

virial ratio = 1.0007220

total energy = -23615.910 Rydbergs

metal charge = 1.86

ligand charge = -0.62

TABLE XV

SPIN POLARIZED ENERGIES FOR $\text{MX}_3 = \text{EuCl}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^1\beta$	44.5	Ms 99	47.3	2.8
$1(a_1)^1\alpha$	42.2	Ms 99	44.8	2.6
$1(e)^2\beta$	27.6	Mp 95, Xs 3, Xp 2, Xd 1	30.3	2.7
$1(e)^2\alpha$	25.8	Mp 92, Xs 5, Xp 2, Xd 1	28.3	2.5
$2(a_1)^1\beta$	27.3	Mp 99, Xs 1	30.1	2.8
$2(a_1)^1\alpha$	25.4	Mp 98, Xs 1	28.0	2.6
$3(a_1)^1\beta$	21.2	Xs 99, Mp 1	24.0	2.8
$3(a_1)^1\alpha$	21.1	Xs 98, Mp 1	23.5	2.4
$2(e)^2\beta$	21.1	Xs 97, Mp 3	23.9	2.8
$2(e)^2\alpha$	20.9	Xs 95, Mp 5	23.4	2.5
$4(a_1)^1\beta$	12.9	Mf 99, Xp 2	15.7 (15.9) ^a	2.8 (3.0) ^a
$3(e)^2\beta$	12.8	Mf 99, Xp 1	15.7 (15.9) ^a	2.9 (3.1) ^a
$1(a_2)^1\beta$	12.8	Mf 99, Xp 1	15.7 (15.9) ^a	2.9 (3.1) ^a
$4(e)^1\beta$	12.8	Mf 100	15.7 (15.9) ^a	2.9 (3.1) ^a
$5(a_1)^1\beta$	12.8	Mf 100	15.6 (15.9) ^a	2.8 (3.1) ^a
$5(e)^2\beta$	9.8	Xp 98, Md 2	12.5	2.7
$5(e)^2\alpha$	9.7	Xp 97, Mf 2, Md 1	12.1	2.4
$6(a_1)^1\beta$	9.7	Xp 99, Md 1	12.4	2.7
$6(a_1)^1\alpha$	9.7	Xp 86, Mf 12, Md 1	12.1	2.4
$6(e)^2\beta$	9.6	Xp 98, Md 1, Mf 1	12.3	2.7
$6(e)^2\alpha$	9.6	Xp 93, Mf 7, Md 1	12.0	2.4
$2(a_2)^1\beta$	9.5	Xp 99, Mf 1	12.2	2.7
$2(a_2)^1\alpha$	9.5	Xp 89, Mf 11	11.9	2.4
$7(a_1)^1\beta$	9.4	Xp 95, Mf 3, Md 1, Ms 1	12.1	2.7
$7(a_1)^1\alpha$	9.5	Xp 84, Mf 15, Mp 1	11.9	2.4
$7(e)^2\beta$	9.4	Xp 94, Mp 2, Md 2, Mf 1	12.1	2.7
$7(e)^2\alpha$	9.3	Xp 84, Mf 12, Mp 2, Md 2	11.7	2.4

virial ratio = 1.0004949

total energy = -23617.731 Rydbergs

metal charge = 1.99

ligand charge = -0.66

^a0.5 electron removed from $4(e)\beta$ MO

TABLE XVI

SPIN RESTRICTED ENERGIES FOR $\text{MX}_3 = \text{GdCl}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^2$	42.4	Ms 99, Xp 1	45.1	2.7
$1(e)^4$	25.7	Mp 91, Xs 6, Xp 2, Xd 1	28.3	2.6
$2(a_1)^2$	25.3	Mp 98, Xs 1, Xp 1	28.0	2.7
$3(a_1)^2$	20.9	Xs 98, Mp 1	23.6	2.7
$2(e)^4$	20.8	Xs 94, Mp 5	23.4	2.6
$4(a_1)^2$	9.6	Xp 75, Mf 23, Ms 1, Md 1	12.2	2.6
$3(e)^4$	9.5	Xp 94, Mf 4, Md 2	12.1	2.6
$4(e)^4$	9.4	Xp 90, Mf 9, Md 1	12.0	2.6
$5(a_1)^2$	9.4	Xp 89, Mf 10, Mp 1	12.0	2.6
$1(a_2)^2$	9.4	Xp 84, Mf 16	11.9	2.5
$5(e)^4$	9.2	Xp 80, Mf 16, Mp 2, Md 2	11.8	2.6
$6(a_1)^1$	8.6	Mf 97, Xp 3	11.3	2.7
$6(e)^2$	8.5	Mf 92, Xp 8	11.2	2.7
$2(a_2)^1$	8.5	Mf 87, Xp 13	11.2	2.7
$7(e)^2$	8.4	Mf 83, Xp 15, Md 1	11.1	2.7
$7(a_1)^1$	8.3	Mf 76, Xp 23	10.9	2.6

virial ratio = 1.0003319

total energy = -24412.613 Rydbergs

metal charge = 1.52

ligand charge = -0.51

TABLE XVII

SPIN POLARIZED ENERGIES FOR $\text{MX}_3 = \text{GdCl}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^1\beta$	45.0	Ms 99	48.3	3.3
$1(a_1)^1\alpha$	42.6	Ms 99, Xs 1	45.4 (45.6) ^a	2.8 (3.0) ^a
$1(e)^2\beta$	27.8	Mp 95, Xs 3, Xp 2	31.0	3.2
$1(e)^2\alpha$	26.0	Mp 92, Xs 5, Xp 2, Xd 1	28.7 (28.9) ^a	2.7 (2.9) ^a
$2(a_1)^1\beta$	27.6	Mp 99, Xs 1	30.8	3.2
$2(a_1)^1\alpha$	25.6	Mp 98, Xs 1, Xp 1	28.4 (28.6) ^a	2.8 (3.0) ^a
$3(a_1)^1\beta$	21.0	Xs 99, Mp 1	23.7	2.7
$3(a_1)^1\alpha$	20.8	Xs 98, Mp 1	23.5	2.7
$2(e)^2\beta$	20.9	Xs 97, Mp 3	23.6	2.7
$2(e)^2\alpha$	20.6	Xs 95, Mp 4	23.1 (23.3) ^a	2.5 (2.7) ^a
$4(a_1)^1\beta$	12.9	Mf 97, Xp 2	16.5 (16.7) ^a	3.6 (3.8) ^a
$3(e)^2\beta$	12.9	Mf 100	16.5	3.6
$1(a_2)^1\beta$	12.9	Mf 99, Xp 1	16.5	3.6
$4(e)^2\beta$	12.9	Mf 99, Xp 1	16.5	3.6
$5(a_1)^1\beta$	12.9	Mf 100	16.5	3.6
$5(e)^2\beta$	9.6	Xp 97, Md 2	12.2	2.6
$5(e)^2\alpha$	9.4	Xp 95, Mf 3, Md 2	12.0	2.6
$6(a_1)^1\beta$	9.5	Xp 98, Md 1, Mf 1	12.1	2.6
$6(a_1)^1\alpha$	9.4	Xp 82, Mf 16, Md 2	12.0	2.6
$6(e)^2\beta$	9.5	Xp 97, Md 2, Mf 1	12.0	2.5
$6(e)^2\alpha$	9.3	Xp 92, Mf 7, Md 1	11.9	2.6
$2(a_2)^1\beta$	9.3	Xp 99, Mf 1	11.8	2.5
$2(a_2)^1\alpha$	9.2	Xp 89, Mf 11	11.8	2.6
$7(a_1)^1\beta$	9.2	Xp 95, Mf 2, Ms 1, Mp 1, Md 1	11.8	2.6
$7(a_1)^1\alpha$	9.3	Xp 89, Mf 10, Mp 1	11.8	2.5
$7(e)^2\beta$	9.2	Xp 94, Md 3, Mp 2, Mf 1	11.8	2.6
$7(e)^2\alpha$	9.0	Xp 85, Mf 10, Mp 2, Md 2	11.7	2.7

virial ratio = 1.0003229

total energy = -24413.352 Rydbergs

metal charge = 1.93

ligand charge = -0.64

^a0.5 electron removed from $5(a_1)\beta$ MO

TABLE XVIII

SPIN RESTRICTED ENERGIES FOR $\text{MX}_3 = \text{TbCl}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^2$	43.8	Ms 99	46.5	2.7
$1(e)^4$	26.3	Mp 93, Xs 4, Xp 2, Xd 1	28.9	2.6
$2(a_1)^2$	26.0	Mp 98, Xs 1, Xp 1	28.6	2.6
$3(a_1)^2$	21.3	Xs 99, Mp 1	23.9	2.6
$2(e)^4$	21.1	Xs 96, Mp 4	23.8	2.7
$3(e)^4$	9.8	Xp 97, Mf 2, Md 1	12.4	2.6
$4(a_1)^2$	9.8	Xp 80, Mf 18, Md 1	12.4	2.6
$4(e)^4$	9.7	Xp 90, Mf 9, Md 1	12.3	2.6
$5(a_1)^2$	9.7	Xp 83, Mf 16, Mp 1	12.3	2.6
$1(a_2)^2$	9.7	Xp 85, Mf 15	12.3	2.6
$5(e)^4$	9.4	Xp 76, Mf 21, Mp 2, Md 2	12.1	2.7
$6(a_1)^2$	8.9	Mf 98, Xp 2	11.7 (11.5) ^a	2.8 (2.6) ^a
$6(e)^2$	8.9	Mf 93, Xp 7	11.6	2.7
$2(a_2)^1$	8.8	Mf 87, Xp 12	11.6	2.8
$7(e)^2$	8.8	Mf 80, Xp 19, Md 1	11.5	2.7
$7(a_1)^1$	8.6	Mf 74, Xp 25	11.3	2.7

virial ratio = 1.0033430

total energy = -25225.519 Rydbergs

metal charge = 1.57

ligand charge = -0.52

^a0.5 electron removed from 5(e) MO

TABLE XIX

SPIN POLARIZED ENERGIES FOR $\text{MX}_3 = \text{TbCl}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^1\beta$	45.9	Ms 99	49.0	3.1
$1(a_1)^1\alpha$	43.9	Ms 99	46.6	2.7
$1(e)^2\beta$	28.1	Mp 95, Xs 3, Xp 2	31.0	2.9
$1(e)^2d$	26.5	Mp 93, Xs 4, Xp 2, Xd 1	29.2	2.7
$2(a_1)^1\beta$	27.9	Mp 99, Xs 1	30.8	2.9
$2(a_1)^1\alpha$	26.2	Mp 98, Xs 1	28.9	2.7
$3(a_1)^1\beta$	21.5	Xs 99	24.1	2.6
$3(a_1)^1\alpha$	21.2	Xs 99, Mp 1	23.6	2.4
$2(e)^2\beta$	21.4	Xs 97, Mp 4	24.0	2.6
$2(e)^2\alpha$	21.0	Xs 96, Mp 4	23.5	2.5
$4(a_1)^1\beta$	12.7	Mf 97, Xp 3	16.1 (15.9) ^a	3.4 (3.2) ^a
$3(e)^2\beta$	12.7	Mf 99, Xp 1	16.1 (15.9) ^a	3.4 (3.2) ^a
$1(a_2)^1\beta$	12.7	Mf 99, Xp 1	16.1 (15.9) ^a	3.4 (3.2) ^a
$4(e)^2\beta$	12.7	Mf 100	16.0	3.3
$5(a_1)^1\beta$	12.6	Mf 100	16.0	3.4
$5(e)^2\beta$	10.0	Xp 99, Md 1	12.5	2.5
$5(e)^2\alpha$	9.8	Xp 97, Mf 2, Md 1	12.1	2.3
$6(a_1)^1\beta$	10.0	Xp 99, Md 1	12.5	2.5
$6(a_1)^1\alpha$	9.7	Xp 86, Mf 13, Md 1	12.2	2.5
$6(e)^2\beta$	9.9	Xp 98, Md 1, Mf 1	12.4	2.5
$6(e)^2\alpha$	9.7	Xp 93, Mf 8	12.0	2.3
$2(a_2)^1\beta$	9.8	Xp 99, Mf 1	12.3	2.5

TABLE XIX (continued)

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$2(a_2)^1\alpha$	9.6	Xp 88, Mf 12	12.0	2.4
$7(a_1)^1\beta$	9.6	Xp 95, Mf 3, Ms 1, Md 1	12.2	2.6
$7(a_1)^1\alpha$	9.6	Xp 82, Mf 17, Mp 1	12.0	2.4
$7(e)^2\beta$	9.6	Xp 94, Md 3, Mp 2, Mf 1	12.1	2.5
$7(e)^2\alpha$	9.4	Xp 81, Mf 16, Mp 2, Md 2	11.8	2.4
$4(a_1)^1\alpha$	8.7	Mf 98, Xp 2	11.3	2.6

virial ratio = 1.0006494

total energy = -25225.840 Rydbergs

metal charge = 1.93

ligand charge = -0.64

^a0.5 electron removed from $7(e)\alpha$ mo.

TABLE XX

SPIN RESTRICTED ENERGIES FOR $\text{MX}_3 = \text{YbCl}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^2$	55.8	Ms 99	58.5 (58.8) ^a	2.7 (3.0) ^a
$1(e)^4$	34.9	Mp 98, Xs 1, Xp 1, Xd 1	37.6 (37.8) ^a	2.7 (2.9) ^a
$2(a_1)^2$	34.7	Mp 99	37.4 (37.7) ^a	2.7 (3.0) ^a
$3(a_1)^2$	21.4	Xs 92, Mf 8	24.1	2.7
$2(e)^4$	21.3	Xs 96, Mf 3, Mp 1	24.0	2.7
$4(a_1)^2$	20.6	Mf 100	23.3 (23.9) ^a	2.7 (3.3) ^a
$3(e)^4$	20.6	Mf 100	23.3 (23.9) ^a	2.7 (3.3) ^a
$1(a_2)^2$	20.6	Mf 100	23.3 (23.9) ^a	2.7 (3.3) ^a
$4(e)^4$	20.6	Mf 97, Xs 3	23.3 (23.8) ^a	2.7 (3.2) ^a
$5(a_1)^1$	20.6	Mf 92, Xs 7	23.3 (23.7) ^a	2.7 (3.1) ^a
$5(e)^4$	10.0	Xp 98, Md 2	12.6	2.6
$6(a_1)^2$	9.9	Xp 99, Md 1	12.5	2.6
$6(e)^4$	9.8	Xp 97, Md 3	12.4	2.6
$7(a_1)^2$	9.7	Xp 97, Ms 1, Md 1	12.3	2.6
$7(e)^4$	9.7	Xp 95, Md 4, Mp 1	12.2	2.5
$2(a_2)^2$	9.6	Xp 100	12.2	2.6

virial ratio = 1.0003807

total energy = -29558.047 Rydbergs

metal charge = 2.51

ligand charge = -0.84

^a0.5 electron removed from $5(a_1)$ MO

TABLE XXI

SPIN POLARIZED ENERGIES FOR $\text{MX}_3 = \text{YbCl}_3$

MO	-E(ev)	% Constituency
$1(a_1)^1\beta$	55.8	Ms 99
$1(a_1)^1\alpha$	55.8	Ms 99
$1(e)^2\beta$	34.9	Mp 98, Xs 1, Xp 1, Xd 1
$1(e)^2\alpha$	34.9	Mp 98, Xs 1, Xp 1, Xd 1
$2(a_1)^1\beta$	34.8	Mp 99
$2(a_1)^1\alpha$	34.7	Mp 99
$3(a_1)^1\beta$	21.4	Xs 91, Mf 9
$3(a_1)^1\alpha$	21.4	Xs 92, Mf 8
$2(e)^2\beta$	21.3	Xs 95, Mf 4, Mp 1
$2(e)^2\alpha$	21.3	Xs 96, Mf 3, Mp 1
$4(a_1)^1\beta$	20.7	Mf 100
$4(a_1)^1\alpha$	20.6	Mf 100
$3(e)^2\beta$	20.7	Mf 100
$3(e)^2\alpha$	20.6	Mf 100
$1(a_2)^1\beta$	20.7	Mf 100
$1(a_2)^1\alpha$	20.6	Mf 100
$4(e)^2\beta$	20.7	Mf 96, Xs 3
$4(e)^2\alpha$	20.6	Mf 97, Xs 3
$5(a_1)^1\beta$	20.6	Mf 92, Xs 8
$5(a_1)^0\alpha$	20.6	---
$5(e)^2\beta$	10.0	Xp 98, Md 2
$5(e)^2\alpha$	10.0	Xp 98, Md 2
$6(a_1)^1\beta$	9.9	Xp 99, Md 1
$6(a_1)^1\alpha$	9.9	Xp 99, Md 1
$6(e)^2\beta$	9.8	Xp 97, Md 3
$6(e)^2\alpha$	9.8	Xp 97, Md 2
$7(a_1)^1\beta$	9.7	Xp 97, Ms 1, Md 1

TABLE XXI (continued)

MO	-E(ev)	% Constituency
$7(a_1)^1\alpha$	9.7	Xp 97, Ms 1, Md 1
$2(a_2)^1\beta$	9.7	Xp 100
$2(a_2)^1\alpha$	9.6	Xp 100
$7(e)^2\beta$	9.7	Xp 95, Md 4, Mp 1
$7(e)^2\alpha$	9.7	Xp 95, Md 4, Mp 1

virial ratio = 1.0003597

total energy = -29558.273 Rydbergs

metal charge = 2.51

ligand charge = -0.84

TABLE XXII

SPIN RESTRICTED ENERGIES FOR $\text{MX}_3 = \text{LuCl}_3$

MO	-E(ev)	% Constituency	IE(ev)	Relaxation(ev)
$1(a_1)^2$	56.4	Ms 99	59.3 (59.7) ^a	2.9 (3.3) ^a
$1(e)^4$	35.3	Mp 97, Xs 1, Xp 1, Xd 1	38.1 (38.4) ^a	2.8 (3.1) ^a
$2(a_1)^2$	35.1	Mp 99	38.0 (38.3) ^a	2.9 (3.2) ^a
$3(a_1)^2$	21.3	Xs 81, Mf 19	24.0 (23.8) ^a	2.7 (3.1) ^a
$2(e)^4$	21.1	Xs 88, Mf 11, Mp 1	23.9 (23.8) ^a	2.8 (3.2) ^a
$4(a_1)^2$	20.8	Mf 100	23.7 (24.4) ^a	2.9 (3.5) ^a
$3(e)^4$	20.8	Mf 100	23.7 (24.3) ^a	2.9 (3.0) ^a
$1(a_2)^2$	20.8	Mf 100	23.7 (24.3) ^a	2.9 (3.5) ^a
$4(e)^4$	20.7	Mf 90, Xs 10	23.6 (24.3) ^a	2.9 (3.6) ^a
$5(a_1)^2$	20.7	Mf 83, Xs 17	23.5 (24.3) ^a	2.8 (3.1) ^a
$5(e)^4$	9.8	Xp 95, Md 5	12.4	2.6
$6(a_1)^2$	9.7	Xp 97, Md 3	12.3	2.6
$6(e)^4$	9.7	Xp 94, Md 5	12.3	2.6
$7(a_1)^2$	9.6	Xp 97, Ms 1, Md 1	12.2	2.6
$7(e)^4$	9.5	Xp 97, Md 2, Mp 1	12.1	2.6
$2(a_2)^2$	9.4	Xp 100	12.0	2.6

virial ratio = 1.0002603

total energy = -30480.207 Rydbergs

metal charge = 2.39

ligand charge = -0.80

^a0.5 electron removed from $5(a_1)$ MO

from calculations on neutral molecules rather than TS calculations. The fourth column in the tables contains the negative of the TS eigenvalues, which, according to equation (13), are approximately equal to the ionization energies. In all instances except for SR TbCl_3 these TS calculations were performed with one-half an electron removed from the last MO in the left column. For the SR TbCl_3 calculation, one-half an electron was removed from the $6(a_1)$ MO. Earlier in this chapter it was indicated that two TS calculations were included for each molecule except the lanthanum compounds. In most cases, however, the ionization energies agreed within 0.1 ev regardless of whether the one-half an electron was removed from the ligand p level or from the metal f level. If the ionization energies differed by more than 0.1 ev, the additional energy is shown in parentheses and the level from which the one-half an electron was removed is indicated. The right column contains the MO relaxation upon ionization, taken as the difference between the NM eigenvalues and the TS eigenvalues. Each table also includes the virial ratio ($|T/E|$, T being the kinetic energy and E the total energy), the total energy, the metal charge, and the ligand charge, all taken from the neutral molecule calculations.

D. Discussion of Results

The results of the calculations will now be discussed with particular emphasis being placed on the behavior of the metal 4f electrons with respect to the three criteria indicated in Chapter I. These were: (1) the energies of the 4f electrons, (2) the crystal field (CF) splitting of the 4f eigenvalues, and (3) the atomicity of

the 4f orbitals. With respect to the third criterion, it was decided to consider an atomic orbital as one that is comprised of 90% or greater constituents from one atom. An orbital containing less than 90% contribution from constituents of any one atom is considered to be a molecular orbital.

Tables V and VI show the results for the planar and pyramidal configurations of LaF_3 . These results were used to ascertain if one geometry was decidedly preferable over the other. Inspection of the tables clearly shows that the results in both geometries are quite similar in all respects. The total energy is about 0.1 Rydbergs lower in the C_{3v} calculation, however, this difference is not considered large enough to definitely favor the pyramidal geometry. However, as indicated previously in this chapter, electron diffraction data favor C_{3v} symmetry and all of the subsequent calculations were performed on pyramidal molecules. These results may be compared with those for LaCl_3 in Table VII. While none of these results yields information concerning the 4f electrons, qualitatively correct conclusions may be drawn with respect to the ligand p levels in that the chlorine 3p electrons show ionization energies approximately 2 ev more shallow than the fluorine 2p electrons. This is in good agreement with the photoelectron data for solid LaF_3 and LaCl_3 ²⁰ which show a 2-3 ev difference in binding energy between the fluorine and chlorine p electrons. Also, the LaCl_3 ionization energies for the chlorine p electrons are in quantitative agreement with recent photoelectron spectra obtained for LaCl_3 vapor.⁶⁸ The spectra show two peaks attributable to the Cl 3p electrons with binding energies of about 11.5 ev and 12.3 ev, the peak

at 11.5 ev being the more intense.

Tables VIII, IX, and X show, respectively, the SR results for CeF_3 , and the SR and SP results for CeCl_3 . All three of the calculations show that the $6(a_1)$ [$6(a_1)\beta$ in the SP calculation] orbital is 99% Ce f, implying negligible involvement in bonding. Again, the fluorine 2p electrons are predicted to have ionization energies about 2 ev larger than the chlorine 3p electrons. Comparing the SR CeF_3 results with the SR CeCl_3 results shows that the ionization energy of the 4f electron is about 1 ev more shallow in CeCl_3 than in CeF_3 . This predicts that the photoelectron spectra would have the f band and p band closer together in the trichloride than in the trifluoride, in agreement with the spectra discussed for these compounds in Chapter I.²⁰ However, the calculated difference in the ionization energy of the 4f electron in the two compounds appears to be slightly larger (about 0.5 ev) than the experimental difference, although comparison of solid spectra must be done with caution since differences in work functions and charging can cause difficulty. The principal differences between the SR and SP results for CeCl_3 are the 0.3 ev lower NM eigenvalue and the resultant 0.3 ev higher ionization energy for the Ce 4f electron in the SP calculation. This similarity is expected in a molecule with only one unpaired electron.

The results of the SR and SP calculation for PrCl_3 are shown in Tables XI and XII. The two 4f electrons are in the $6(a_1)$ and $6(e)$ [$6(a_1)\beta$ and $6(e)\beta$ in the SP calculation] orbitals. The NM eigenvalues corresponding to these orbitals are CF split by only 0.1 ev in both the SR and SP calculations and are 0.5 ev lower in energy in the SP results.

The two orbitals are 99% Pr f and 94% Pr f, respectively, in the SR calculation while the SP results show 98% Pr f and 94% Pr f. Thus, again, no substantial involvement in bonding is indicated in either of the calculations.

Tables XIII and XV contain the SR and SP results for EuCl_3 . Table XIV gives SR nonoverlapping sphere results for EuCl_3 . The SR overlapping sphere calculation shows the six 4f electrons have NM eigenvalues that are CF split from -8.7 ev to -8.4 ev. The corresponding ionization energies indicate a similar splitting. Although the $6(a_1)$, $6(e)$, and $2(a_2)$ orbitals may be classified as atomic, the $7(e)$ and $7(a_1)$ orbitals are less than 90% Eu f and are thus classified as molecular. The nonoverlapping sphere calculation shows no significant improvement, and thus ionization energies were not obtained for the non overlapping sphere model. Therefore, while both of these calculations give acceptable energies for the 4f electrons, they do not predict as small a CF splitting for the 4f orbitals nor as little mixing with ligand electrons as is expected. The SP results, however, show impressive differences. In this calculation the 4f NM eigenvalues are split by only 0.1 ev and a similar splitting occurs for the 4f ionization energies. Equally important is the fact that the 4f orbitals have become very atomic. All of the 4f orbitals are either 99% or 100% Eu f. Therefore the SP calculation has given much more desirable results than the SR calculations, which might be expected considering the six unpaired electrons. Another important fact emerges when comparing the SR and SP results. The SP calculation places the 4f NM eigenvalues lower than the chlorine 3p NM eigenvalues, and the resulting 4f

ionization energies are larger than the chlorine 3p ionization energies. This phenomenon leaves an empty orbital at lower energy than the fully occupied ligand orbitals, and, as discussed in Chapter II, has been labeled as the "third revolution in ligand field theory." A calculation was performed in which the empty 4f orbital was occupied with one of the higher energy electrons leaving the ligand 3p level incomplete. In this configuration more mixing occurred (about 20% ligand contribution), the 4f NM eigenvalues were split to a greater degree (about 0.3 ev), and the total energy was about 0.1 Rydbergs lower. This small change in total energy did not seem enough to override the otherwise poor results. Furthermore, in the MSX α method, because of the relationship between the total energy, E , and the eigenvalues, ϵ_i , the lowest levels must be occupied in order to minimize the total energy.⁶⁹

The results for GdCl_3 are shown in Tables XVI and XVII. As with EuCl_3 , the SR results show that the 4f NM eigenvalues are higher than the chlorine 3p NM eigenvalues, and are split by 0.3 ev. Also, four of the seven 4f orbitals are less than 90% Gd f, thus indicating too great a participation in bonding. Again, the SP results are considerably better. The SP calculation indicates that the 4f NM eigenvalues are all degenerate to 0.1 ev and places these electrons lower than the ligand 3p electrons. Moreover, the considerable mixing present in the SR results has disappeared, all of the SP 4f orbitals being at least 97% Gd f.

Tables XVIII and XIX contain the TbCl_3 results. As with the f^6 and f^7 systems, this f^8 molecule shows a remarkable difference between the SR and SP results. The SR calculation shows that the eight 4f

electrons have NM eigenvalues higher than the chlorine 3p electrons and a 0.3 ev splitting is indicated for the 4f orbitals. A comparable situation occurs for the 4f ionization energies. Also, similar to the SR calculations for EuCl_3 and GdCl_3 four of the seven 4f orbitals contain less than 90% Tb f. However, the SP calculation again substantially improves the results. The seven 4f β NM eigenvalues are lower than the chlorine 3p level and are split by only 0.1 ev. All seven 4f orbitals are at least 97% Tb f. The remaining 4f orbital $[4(a_1)\alpha]$ is 98% Tb f and corresponds to an NM eigenvalue higher than the ligand 3p level. Similar trends hold for the SP ionization energies, and thus the predicted photoelectron spectrum shows two 4f peaks, separated by almost 5 ev due to the spin splitting. The chlorine 3p band appears between them. The 4f separation predictions compare quite favorably with the experimental spectrum for solid TbF_3 shown in Figure I.

The results for YbCl_3 are in Tables XX and XXI. The NM eigenvalues are very similar in the SR and SP calculations, and thus ionization energies were not obtained in the SP calculation. In the SR calculation the 4f NM eigenvalues are all -20.6 ev. This result places them considerably lower than the chlorine 3p level. Similar energies were obtained for the SP 4f electrons, the 4f α orbitals being equal to 0.1 ev and the 4f β orbitals being split by 0.1 ev. In both calculations all of the 4f orbitals are at least 96% Yb f, except the $5(a_1)$ $[5(a_1)\beta]$ in the SP calculation which is 92% Yb f. As with EuCl_3 , an empty orbital again appears at lower energy than the fully filled ligand orbitals.

The SR energies for LuCl_3 are in Table XIX. The 4f NM eigenvalues are split by only 0.1 ev, as are the 4f ionization energies.

Four of the seven 4f orbitals are 100% Lu f, two are 90% Lu f, and one is only 83% Lu f. Thus one of the seven orbitals must be considered as molecular according to the 90% criterion. Since there are no unpaired electrons in LuCl_3 , it is not believed that a SP calculation would improve this result.

All of the NM eigenvalues and ionization energies were rounded to the nearest 0.1 ev in the previous tables and therefore the splitting of energy levels was reported to 0.1 ev. However, as pointed out earlier, the 4f energies are split by less than 0.1 ev ($\approx 800 \text{ cm}^{-1}$) in experimental measurements on lanthanide compounds. Closer analysis of the theoretical data shows that in all cases the NM eigenvalue splitting was actually less than 0.1 ev, and thus the 0.1 ev splits were all rounded up to 0.1 ev rather than down to 0.1 ev. Table XXIII shows the maximum 4f NM eigenvalues, the minimum 4f NM eigenvalues, and the maximum splits for the occupied α and β spin orbitals of the f electrons, all to three decimal places.

TABLE XXIII
CALCULATED SPLITTING OF THE 4f NM EIGENVALUES

Molecule	-[Maximum 4f NM eigenvalue] (e.v.)		-[Minimum 4f NM eigenvalue] (e.v.)		Split (e.v.)	
	β	α	β	α	β	α
PrCl ₃	8.209	---	8.254	---	0.045	---
EuCl ₃	12.822	---	12.895	---	0.073	---
GdCl ₃	12.869	---	12.940	---	0.071	---
TbCl ₃	12.642	---	12.718	---	0.076	---
YbCl ₃	20.638	20.589	20.692	20.609	0.054	0.020

CHAPTER IV

CONCLUSIONS

A. Summary

In all of the molecules studied (LaF_3 , CeF_3 , LaCl_3 , CeCl_3 , PrCl_3 , EuCl_3 , GdCl_3 , TbCl_3 , YbCl_3 , and LuCl_3) the SR and the SP calculations indicated that the 4f NM eigenvalues are in the valence region. These were most shallow in CeF_3 , appearing at about -7 ev, and were progressively lowered to almost -21 ev in LuCl_3 . An average relaxation of about 3 ev occurred for the 4f orbitals when 0.5 an electron was removed, and the 4f ionization energies were, therefore, approximately 3 ev larger than the magnitude of the NM eigenvalues.

In molecules containing zero, one, or two unpaired electrons, either the SR or the SP calculations gave desirable results with respect to the CF splitting of the 4f energies. For the f^6 , f^7 , and f^8 molecules the SR calculations overestimate the CF splitting. In these cases a SP calculation was necessary to adequately decrease the CF splitting, and as shown in Table XXIII this splitting was always less than 0.1 ev. Similarly, either SR or SP calculations gave satisfactory results with respect to atomicity for the f^1 , f^2 , f^{13} , and f^{14} molecules. All of the 4f orbitals for these molecules were at least 90% f with the exception of one orbital in LuCl_3 which was only 83% f. For the molecules containing six and seven unpaired electrons, the SR calculations indicated that either three or four of the seven 4f orbitals were less than 90% f, indicating a rather significant participation

of the 4f electrons in bonding. The SP calculations for the same molecules produced 4f orbitals which were all at least 97% f and thus greatly reduced the mixing of the 4f electrons. For all molecules studied, the SP 4f orbitals contained a minimum of 92% f character. These results show that the SP MSX α method appears to adequately describe the behavior of 4f electrons (in regard to energy region, crystal field splitting, and atomicity) in the lanthanide trihalides, and will hopefully prove to be a valuable theoretical method for treating lanthanide compounds.

B. Predicted Photoelectron Spectra

The results of the calculations have been used to produce theoretically predicted photoelectron spectra for LaCl_3 , CeCl_3 , PrCl_3 , EuCl_3 , GdCl_3 , TbCl_3 , YbCl_3 , and LuCl_3 . These spectra are shown in Figures 5 through 12. The energies of the peaks were taken as the ionization energies from the calculations, these being SR for LaCl_3 , YbCl_3 , and LuCl_3 and SP in the other cases. Each figure contains three sets of spectra representing line broadenings of 0.1, 0.2, and 0.3 eV, respectively. In addition, for those spectra containing 4f peaks, intensity ratios of $f/p = 1.0, 0.5, \text{ and } 0.1$ are shown superimposed upon one another within each set of spectra. For all of the above molecules except LuCl_3 only the metal 4f peak and Cl 3p peak are shown; for LuCl_3 the Cl 3s peak is also shown. The reader is reminded that these results are nonrelativistic, and, as such, any spin orbit splitting of the bands is not considered. For states of the same multiplicity this splitting may be approximately 5 eV (see Figures 1 and 4).

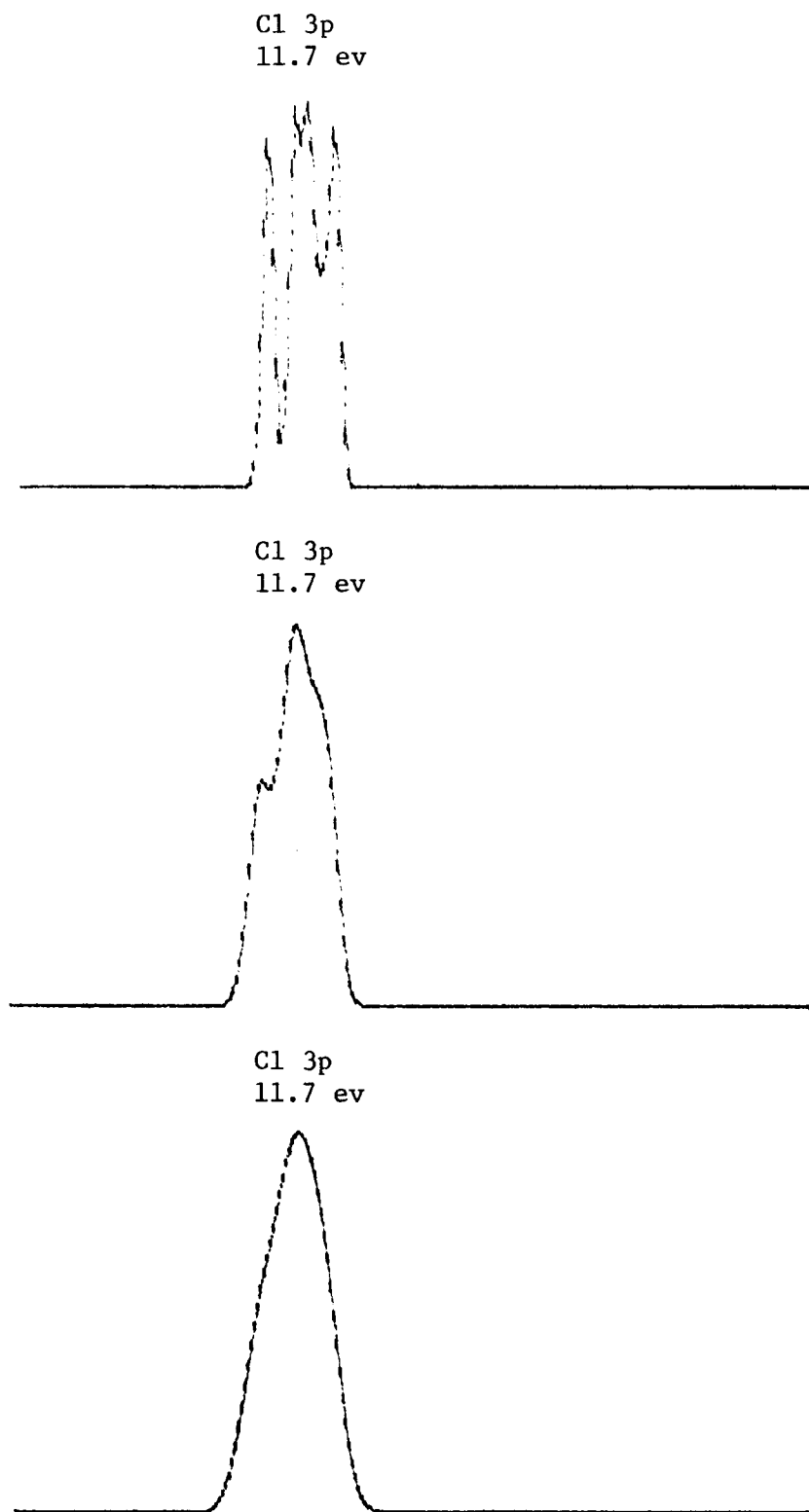


Figure 5. Predicted LaCl_3 spectra at broadenings of (a) 0.1, (b) 0.2, (c) 0.3 eV.

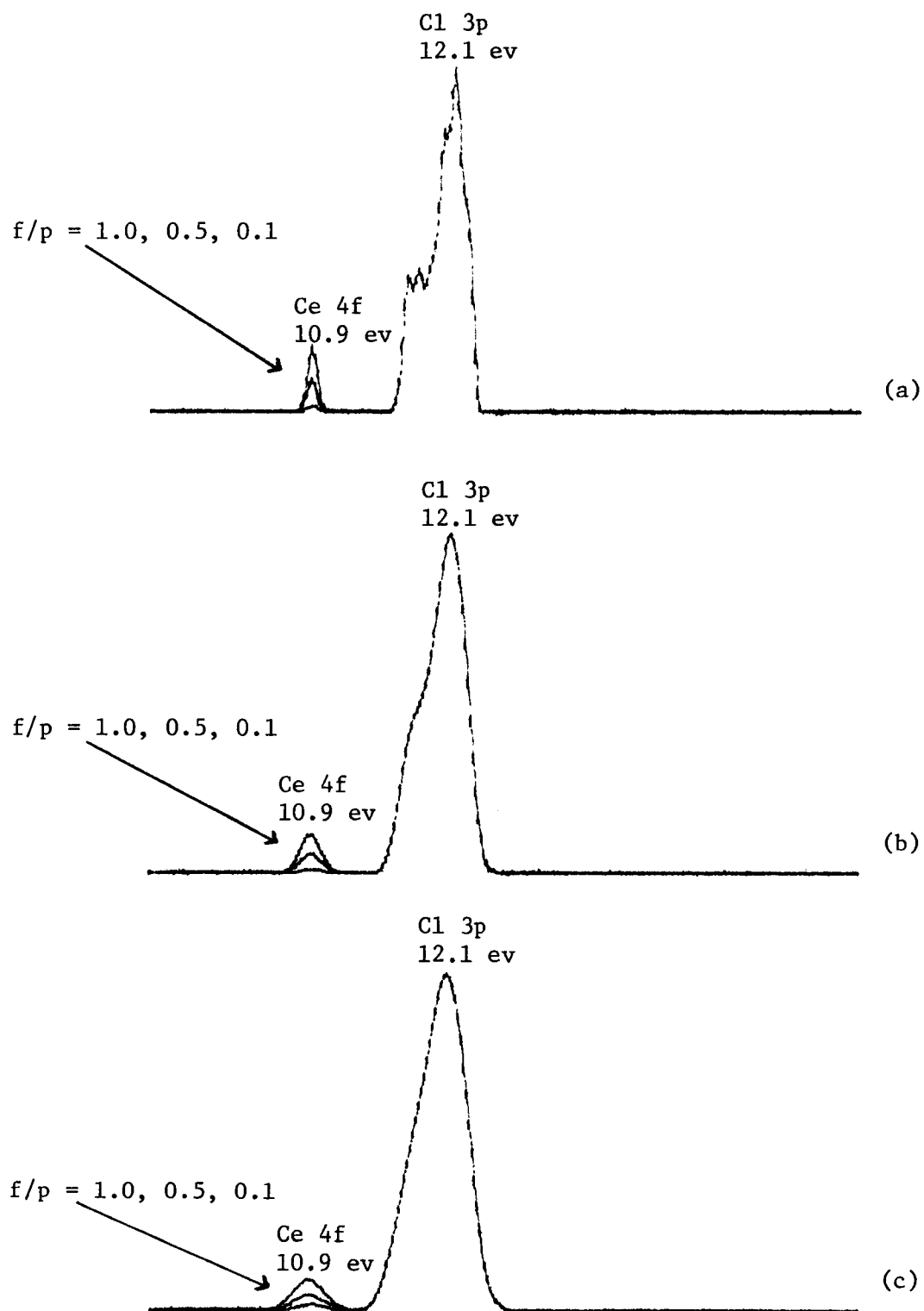


Figure 6. Predicted CeCl_3 spectra at broadenings of (a) 0.1, (b) 0.2, (c) 0.3 eV with f/p intensity ratios 1.0, 0.5, 0.1.

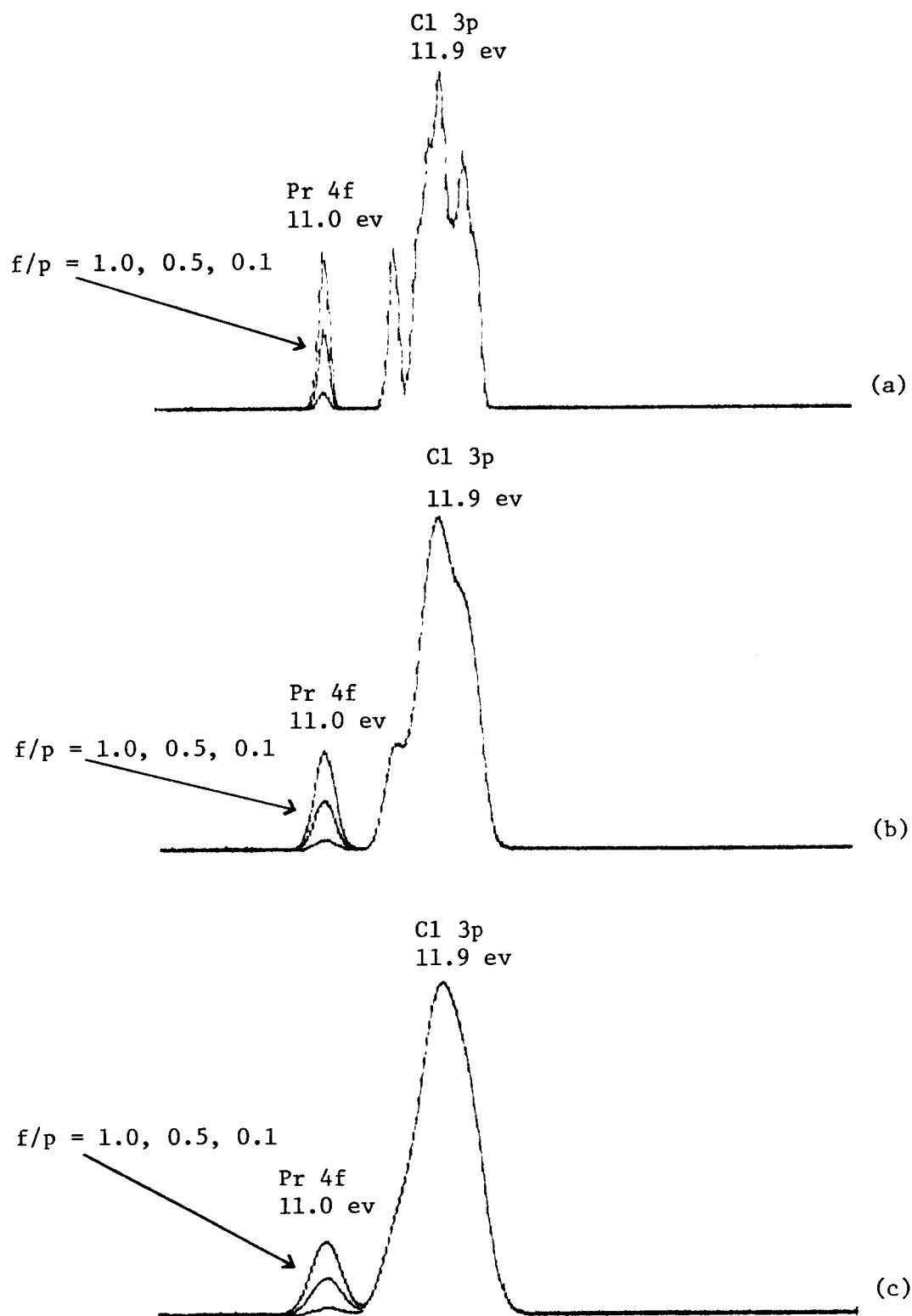


Figure 7. Predicted PrCl_3 spectra at broadenings of (a) 0.1, (b) 0.2, (c) 0.3 eV with f/p intensity ratios 1.0, 0.5, 0.1.

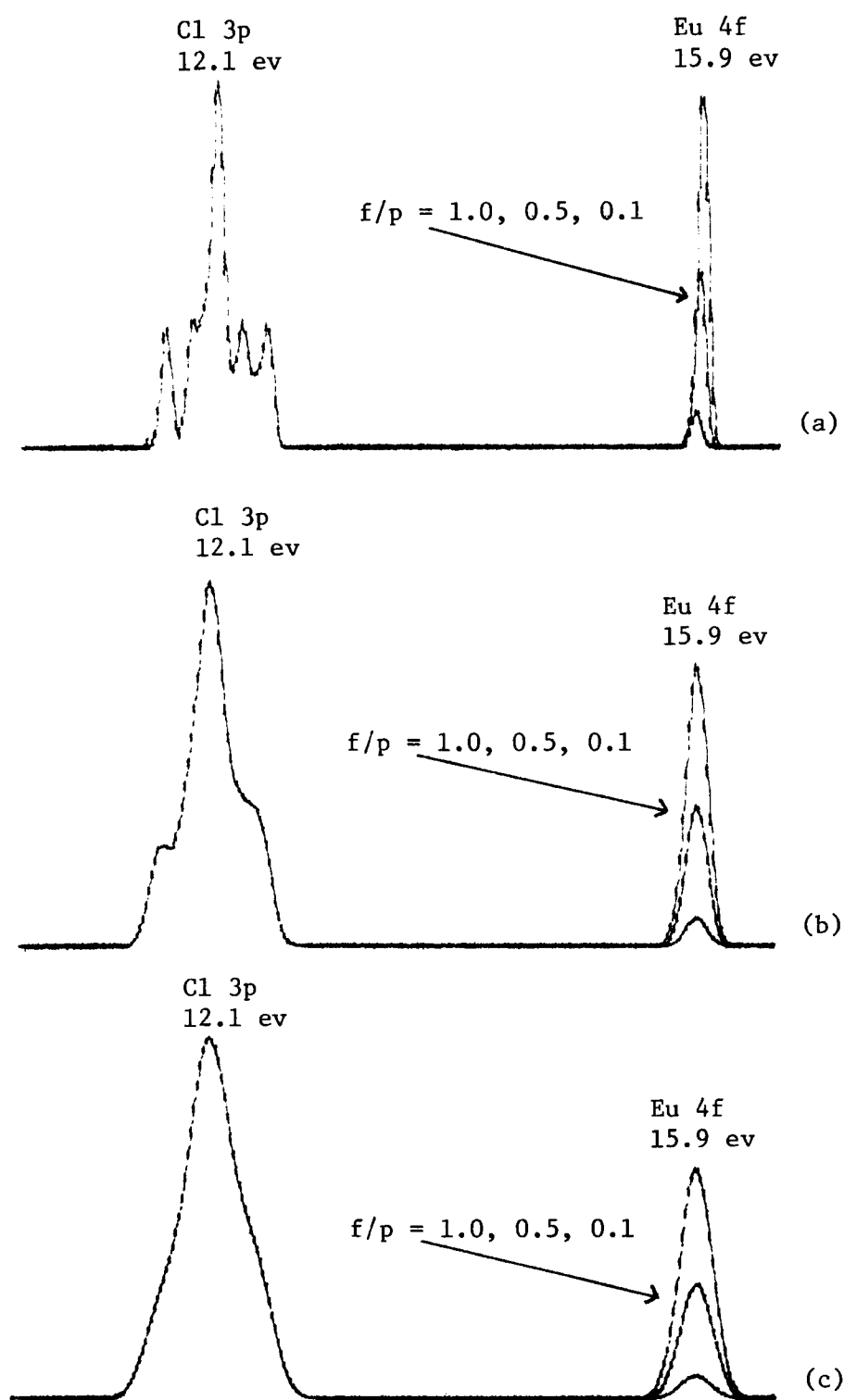


Figure 8. Predicted EuCl_3 spectra at broadenings of (a) 0.1, (b) 0.2, (c) 0.3 eV with f/p intensity ratios 1.0, 0.5, 0.1.

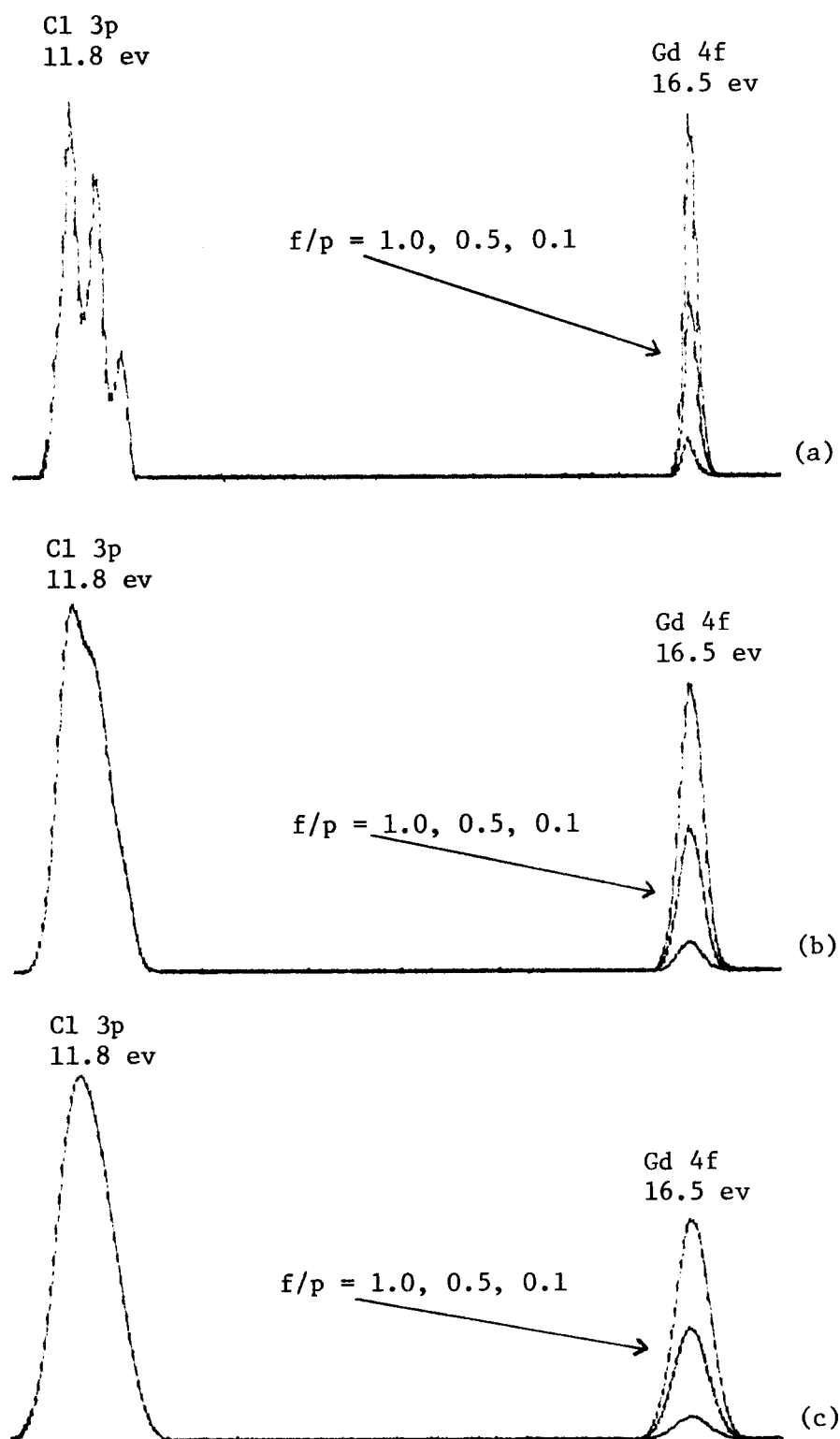


Figure 9. Predicted GdCl_3 spectra at broadenings of (a) 0.1, (b) 0.2, (c) 0.3 eV with f/p intensity ratios 1.0, 0.5, 0.1.

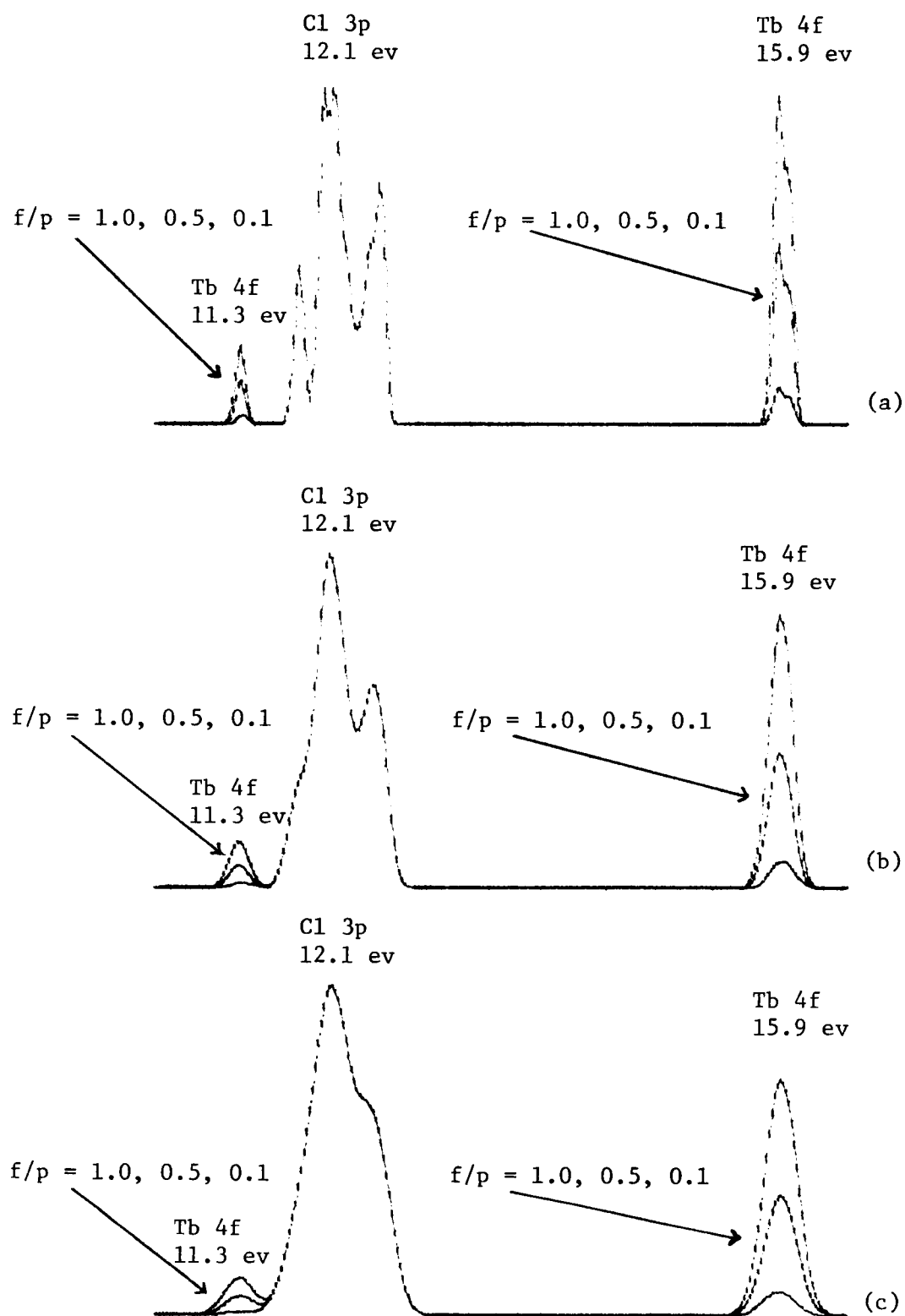


Figure 10. Predicted TbCl₃ spectra at broadenings of (a) 0.1, (b) 0.2, (c) 0.3 eV with f/p intensity ratios 1.0, 0.5, 0.1.

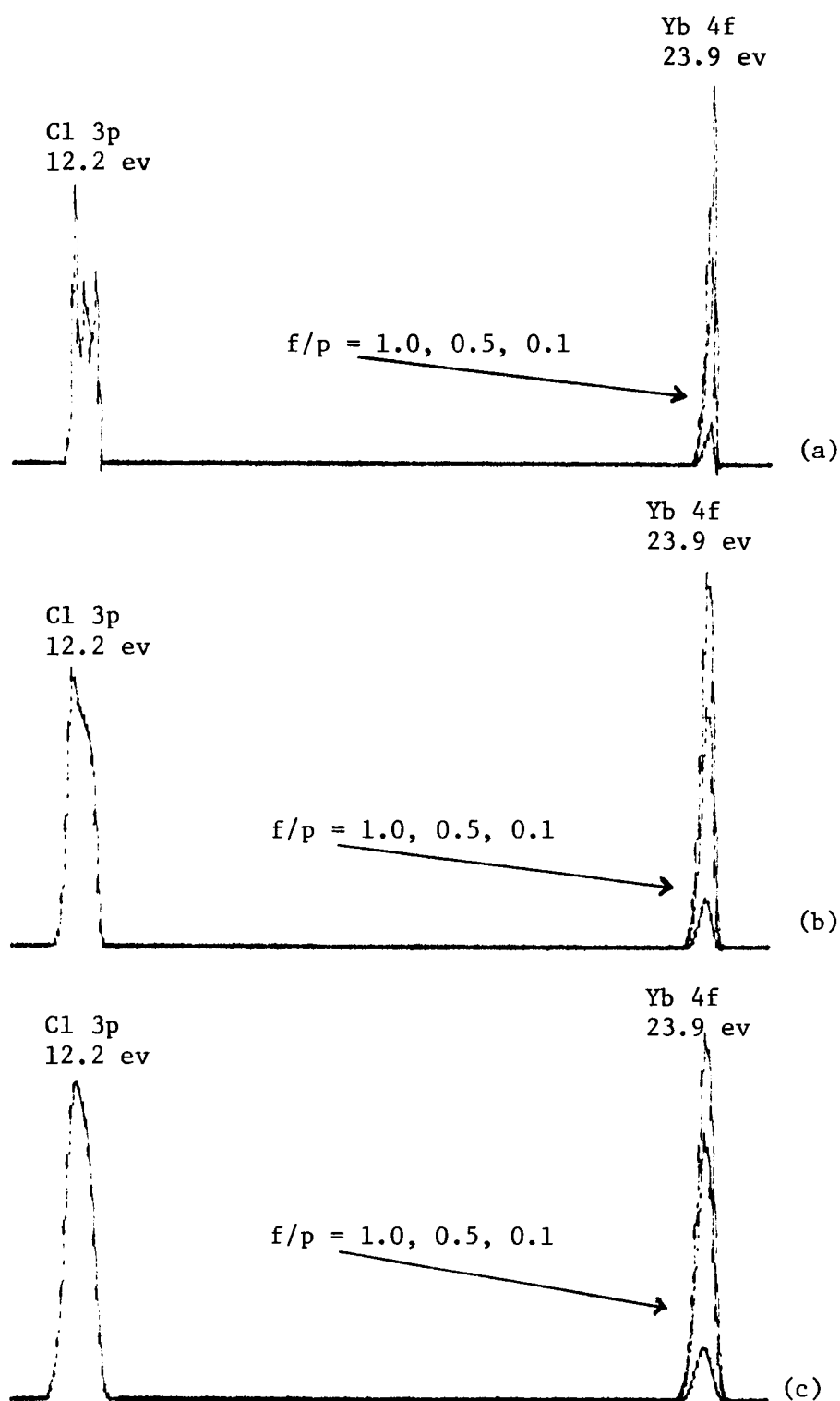


Figure 11. Predicted YbCl_3 spectra at broadenings of (a) 0.1 , (b) 0.2 , (c) 0.3 eV with f/p intensity ratios $1.0, 0.5, 0.1$.

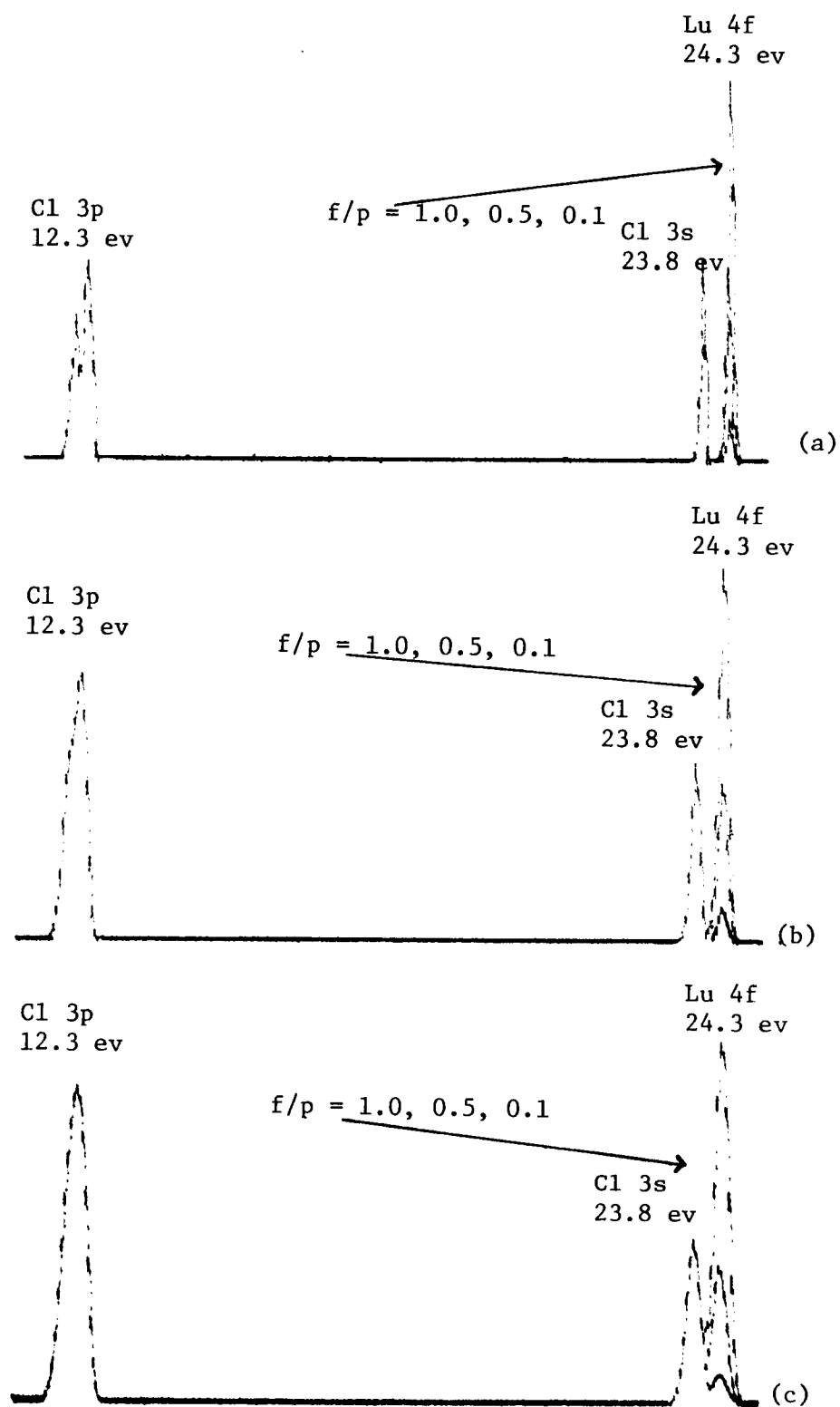


Figure 12. Predicted LuCl_3 spectra at broadenings of (a) 0.1, (b) 0.2, (c) 0.3 eV with f/p intensity ratios 1.0, 0.5, 0.1.

C. Suggestions for Further Work

The importance of relativistic effects for lanthanide compounds has been indicated, and their inclusion in the calculations may be accomplished by two methods. First, a relativistic core could be included and would likely raise the 4f eigenvalues, due to a contracting of the core around the nucleus. This may be necessary, particularly for the compounds YbCl_3 and LuCl_3 , which exhibited the lowest 4f NM eigenvalues. Secondly, a relativistic Hamiltonian could be employed, and this accomplishment would give the L-S splitting of the 4f energies. Either of the previous two suggestions would require a rather major modification of the approach taken thus far.

There has been some experimental evidence for the decomposition of MX_3 to MX_2 at high temperatures. It would therefore be desirable to obtain MSX α results for some of the MX_2 molecules and again study the behavior of the 4f electrons. An overall shift in energy of the 4f electrons might be expected in the dihalides, however the small CF splitting of the 4f eigenvalues and the essential atomicity of the 4f orbitals should remain preserved. Also, an MSX α study for the solid MX_3 would constitute an interesting problem, in that the 4f electrons in the solids should exhibit similar behavior to the 4f electrons in the free molecules. Furthermore, the very small CF splittings given in Table XXIII suggest that the MSX α method may be valuable in the interpretation of the fine structure observed in the optical spectra of lanthanide compounds.

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