MAGNETIC FORM FACTORS OF RARE EARTH IONS

Harry William Deckman

Ph.D. Thesis Submitted to Iowa State University

Ames Laboratory, ERDA

Iowa State University

Ames, Iowa 50011

Date Transmitted: February 1977

PREPARED FOR THE U.S. ENERGY RESEARCH AND DEVELOPMENT
ADMINISTRATION UNDER CONTRACT NO. W-7405-eng-82

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

—NOTICE—

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Available from: National Technical Information Service
U. S. Department of Commerce
P.O. Box 1553
Springfield, VA 22161

Price: Microfiche \$3.00

Magnetic form factors of rare earth ions

by

Harry William Deckman

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Physics
Major: Solid State Physics

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1976

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

TABLE OF CONTENTS

	Page
Abstract	vi
CHAPTER I. INTRODUCTION	1
CHAPTER II. THE GENERAL THEORY	8
Nonrelativistic Formulation	11
Multipole Moment Operators	17
Nonrelativistic Current Density	20
Relativistic Formulation	23
CHAPTER III. REVIEW OF ATOMIC CALCULATIONS	27
Racah Algebra	28
Atomic Structure	39
Classification of States	43
Matrix Elements of Racah Double Tensors	55
CHAPTER IV. MAGNETIC SCATTERING BY A NONRELATIVISTIC ATOM	68
Extreme Nonrelativistic Limit	72
Elastic Scattering by an Atom in a Single Russel-Saunders	
State of the ℓ^n Configuration	79
Elastic Scattering by Rare Earth Ions	84
CHAPTER V. MAGNETIC SCATTERING BY A RELATIVISTIC ATOM	95
Nonrelativistic Limit	105
Elastic Scattering by an Atom in a Single Russell-Saunders	
State	107
Elastic Scattering By Rare Earth Ions	110
Discussions and Conclusions	124

APPENDIX A	129
APPENDIX B	133
APPENDIX C	138
3-j Symbols	138
6-j Symbols	140
9-j Symbols	140
APPENDIX D	145
BIBLIOGRAPHY	147
ACKNOWLEDGMENTS	152

Magnetic form factors of rare earth ions[†]

Harry William Deckman

Under the supervision of C. Stassis
 From the Department of Physics
 Iowa State University

The magnetic scattering of neutrons by atoms has been investigated by exploiting its similarity to the radiation problem in spectroscopy. Expressions for the magnetic scattering amplitude have been developed for cases in which an atom in the ℓ^n electronic configuration is described either by a relativistic or nonrelativistic Hamiltonian. For each of these cases, it has been shown that the magnetic scattering amplitude can be expressed in terms of relativistic or nonrelativistic matrix elements of magnetic and electric multipole operators. For a nonrelativistic atom, the calculation of these matrix elements has been separated into evaluating radial matrix elements and matrix elements of Racah tensors $W^{(0,k)}k$ and $W^{(1,k')}k$. For a relativistic atom the effective operator approach has been used to define effective multipole operators so that a relativistic result is obtained by taking matrix elements of these effective operators between nonrelativistic states of the atom. The calculation of matrix elements of these effective operators has been reduced to evaluating relativistic radial integrals and matrix elements of the Racah tensors taken between nonrelativistic states of the atom.

[†]USERDA Report IS-T-729. Work performed for the U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.

It is shown that for the case of elastic scattering by either a relativistic or nonrelativistic atom in single Russell-Saunders state, the magnetic scattering amplitude can be written in the conventional form $p(\vec{q})\vec{q}_m \cdot \vec{\sigma}$. General expressions for $p(\vec{q})$ as well as elastic magnetic form factors have been obtained. The formalism has been illustrated throughout by applying it to the case of scattering by rare earth ions.

Detailed calculations for the form factors of Er and Gd ions are presented. These form factors have been compared with measurements performed by Moon et al.¹ and Stassis et al.² It has been found that using the nonrelativistic formalism to analyze these experiments overestimates the conduction electron polarization by approximately ten percent.

¹R. M. Moon, W. C. Koehler, J. W. Cable and H. R. Child, Phys. Rev. B5, 997 (1972).

²C. Stassis, G. R. Kline, A. J. Freeman and J. P. Desclaux, Phys. Rev. B13, 3916 (1976).

CHAPTER I. INTRODUCTION

Slow thermal neutrons interacting with an arbitrary system of particles may be scattered either by virtue of the nuclear interaction¹⁻⁴ or by the electromagnetic interaction between the neutron magnetic moment and the charge and current densities of the scattering system. There are three separate contributions to the electromagnetic interaction Hamiltonian; (i) the magnetic dipolar interaction between the magnetic moment of the neutron and the magnetic field produced by the microscopic current density in the scattering system⁵⁻⁹; (ii) the coupling of the electric field of the moving neutron magnetic moment with the charge density of the scattering system (neutron-spin-neutron-orbit)¹⁰; and (iii) the Foldy interaction due to the zitterbewegung motion of the anomalous magnetic moment of the neutron.¹¹ In most magnetic scattering problems of practical interest, the magnetic dipolar interaction is of the order of 1000 times greater than either the neutron-spin-neutron-orbit or Foldy interactions. In the present work, only the contribution to the scattering cross section from the magnetic dipolar interaction will be considered and the corresponding scattering will be referred to as magnetic scattering.

The problem of magnetic scattering has been examined by many authors over the last 40 years. Bloch⁵ and Schwinger⁶ brilliantly initiated the work in articles which showed that the magnetic scattering of neutrons should be an observable effect. These articles were limited to polarization effects in ferromagnetic bodies which could be used to distinguish

between nuclear and magnetic scattering. Approximately three years after the work was initiated, Halpern and Johnson⁷ published an article examining in detail the magnetic scattering of neutrons by an atom with zero orbital magnetic moment. In such a system the current density connected with the quasi-classical motion of an electron in an atomic orbit (the orbital current density) can be ignored and only the current density due to the electron spin (magnetization current) need be considered. They were able to show that the magnetic scattering cross section could be written in terms of a magnetic scattering amplitude which was simply related to the Fourier transform of the magnetization current. The expression for the magnetic scattering amplitude could then be evaluated if the radial wavefunctions of the electrons in the unfilled atomic shells were known.

Some fourteen years later, Trammell⁸ extended Halpern and Johnson's treatment to the case of magnetic scattering by atoms possessing both spin and orbital magnetic moments. More recently, Odier and Saint-James⁹ reviewed and extended Trammell's treatment to include the scattering from crystal field levels. To handle the orbital current, Trammell evaluated matrix elements of the interaction Hamiltonian using the traditional Condon and Shortley¹² formalism. Using the techniques of Condon and Shortley to evaluate matrix elements in many electron atoms requires involved calculation which offers little physical insight into the problem.

In 1966, Johnston¹³, using tensor algebra to simplify the evaluation of the required matrix elements, gave a treatment of magnetic scattering of neutrons by atoms. His work was expanded upon in articles

by Johnston and Rimmer¹⁴, Lovesey and Rimmer¹⁵, Balcar and Lovesey¹⁶, Balcar¹⁷, Lovesey¹⁸, Balcar, Lovesey and Wedgewood¹⁹, and Mahendra and Khan.²⁰ A review of this work can be found in the book written by Marshall and Lovesey.²¹ Although the theory of magnetic scattering as formulated in articles based on Johnston's work does produce some calculational simplification, it is not gauge invariant. According to these papers and much to the surprise of an atomic physicist, there would be no contribution to a general inelastic scattering process from an electric multipole term in the scattering cross section. For an atom whose Hamiltonian contains no momentum dependent terms other than the kinetic energy, the theory of magnetic scattering as formulated in these papers does give the correct numerical expressions for the elastic magnetic scattering cross section. However, the final expression for the cross section is a complex collection of coefficients which are devoid of any physical significance, and a practical evaluation of the cross section requires the writing of complex computer programs.^{15,22}

The aim of the work discussed in this thesis, has been to formulate an accurate theory of magnetic scattering which can be used to interpret several recent experiments which utilized the sensitivity of polarized neutron techniques to obtain precise measurements of rare earth form factors.²³⁻²⁵ Of principal interest among these experiments are the measurements performed by Moon et al.²³ and Stassis et al.²⁴ on Gd and Er metals, respectively. For the rare earth metals, the observed scattering is due both to the highly localized 4f electrons and the polarized conduction band. By subtracting a theoretical expression for the 4f electron

contribution to the scattering, the form factor and thus the spatial distribution of the conduction electrons can be resolved. This subtraction produces uncertainties in the conduction electron form factor because even changes as small as a few parts per thousand in the theoretical 4f electron form factor can be of importance in the quantitative analysis of the conduction electron polarization. However, the results can be compared directly with theoretical calculations of the band wavefunctions, such as the spin-polarized augmented-plane wave calculation of the conduction electron polarization in ferromagnetic Gd performed by Harmon and Freeman.²⁶ Such a comparison provides fundamental knowledge about the conduction electron wavefunctions which are necessary for our understanding of the electronic properties of the rare earth metals.

An analysis of the experiments on Er and Gd metals^{23,27,28} indicates the 4f electron wavefunctions are most accurately represented by the solutions of the relativistic Dirac equation for the tripositive ion. The previous formulations of magnetic scattering which have been discussed^{5-9,13-19}, cannot be easily generalized to treat the case of scattering by an atom described by a relativistic Hamiltonian. By formulating the theory of the magnetic scattering of neutrons on sound physical grounds, Stassis and Deckman²⁹⁻³² have presented a new theory which can be applied to evaluate the scattering by an atom described by either a non-relativistic or relativistic Hamiltonian. In this work the theory formulated by Dr. Stassis and myself will be reviewed and applied to the interpretation of the conduction electron form factor in the rare earth metals.

The theory of the magnetic scattering of neutrons has been formulated on sound physical grounds by treating it like a specific problem in the general theory of atomic collisions. The atomic and nuclear physicists have developed many elegant and powerful techniques with which to treat atomic collisions and thus much of their work can be used in treating the magnetic scattering of neutrons. This fact was not fully recognized by previous workers in the field and thus many previous formulations of magnetic scattering are unnecessarily complicated.

In Chapter II, it will be shown that a fundamental property of magnetic scattering is the fact that the magnetic moment of the neutron couples only to the Fourier transform of the component of the current density transverse to the scattering vector. It is well known that the probability of emission or absorption of a photon by an atom is determined by the Fourier transform of the component of the atomic current density transverse to the wavevector of the emitted photon. Thus there is a direct analogy between the problem of magnetic scattering of neutrons and the radiation problem in atomic spectroscopy. By exploiting this fact a general theory of magnetic scattering of neutrons by atoms described by relativistic and nonrelativistic Hamiltonians is presented in Chapter II.

The differential cross section for scattering by an atom will be written quite generally in terms of a magnetic scattering amplitude. The advantage of calculating a scattering amplitude is the natural way in which the coherent and incoherent cross sections can be derived. Since it is well known that the radiation problem can be formulated in terms of the multipole moment operators, we expect that the magnetic scattering

amplitude can also be expressed in terms of these operators. It will be shown that an exact calculation of the magnetic scattering amplitude requires the evaluation of transition matrix elements of the multipole operators.

The evaluation of these matrix elements can be considerably simplified by using techniques commonly employed in atomic spectroscopy, which take full advantage of the symmetries of the atomic states. Since many of these techniques are unfamiliar to the solid state physicist, a brief review of these techniques will be presented in Chapter III.

In Chapter IV, the magnetic scattering amplitude of an atom or ion described by a nonrelativistic Hamiltonian will be evaluated. The general techniques outlined in Chapter III will be used to evaluate the required matrix elements. The theory will be illustrated by applying it to analyze scattering by rare earth ions. Previous relativistic generalizations of this theory which were used to obtain 4f electron form factors will be discussed. The tables presented will allow one to evaluate the "nonrelativistic" magnetic scattering amplitude for rare earth ions by using simple algebraic manipulations.

In Chapter V, the magnetic scattering amplitude of an atom described by a relativistic Hamiltonian will be discussed. The necessary matrix elements will be evaluated using the effective operator approach along with the general techniques outlined in Chapter III. The theory will again be illustrated by applying it to the analysis of rare earth form

factors. Using this theory the conduction electron form factors in Er and Gd metal will be reanalyzed.

CHAPTER II. THE GENERAL THEORY

To obtain the differential magnetic scattering cross section, we will treat the neutron as a plane-wave and calculate the transition probability from a plane-wave state $|\vec{k}\rangle$ of the incident beam to $|\vec{k}'\rangle$ of the scattered beam. Plane-wave states $|\vec{k}\rangle$ and $|\vec{k}'\rangle$ of the incident and scattered neutron beams are defined by wavevectors $\vec{k}$ and $\vec{k}'$, respectively, have energies E and E' , respectively (which are determined by $E = \frac{\hbar^2 k^2}{2M}$), and the states, $|\vec{k}\rangle$, can be written in the form

$$|\vec{k}\rangle = e^{i\vec{k} \cdot \vec{r}_n}, \quad (1)$$

with $\vec{r}_n$ and M being the position vector and mass, respectively, of the neutron. The plane wave states are normalized by the condition

$$\langle \vec{k} | \vec{k}' \rangle = (2\pi)^3 \delta(\vec{k} - \vec{k}'), \quad (2)$$

and the difference between the incident and scattered wavevectors is defined to be the neutron scattering vector,

$$\vec{q} = \vec{k} - \vec{k}'. \quad (3)$$

While the neutron is scattered, the atom or scattering system will undergo a transition from some initial state $|i\rangle$ of energy E_i to a final state $|f\rangle$ of energy E_f . The transition probability is given by Fermi's Golden rule[†], namely

[†] See for example, the quantum mechanics book by Schiff.³³

$$w_{\vec{k} \rightarrow \vec{k}'} = \frac{2\pi}{\hbar} |\langle \vec{k}', f | H_{int} | \vec{k}, i \rangle|^2 \rho(E') \quad (4)$$

where $\rho(E')$ is the density of final states per unit energy range and H_{int} is the perturbing interaction causing the scattering, which is of course taken to be the magnetic dipolar interaction between the magnetic moment of the neutron and atom. By substituting Equation 1 into Equation 4, we can see that the transition probability can be written in terms of the Fourier transform of the interaction Hamiltonian,

$$w_{\vec{k} \rightarrow \vec{k}'} = \frac{2\pi}{\hbar} |\langle f | \int d\vec{r}_n e^{i\vec{q} \cdot \vec{r}_n} H_{int} | i \rangle|^2 \rho(E'). \quad (5)$$

The density of scattered neutron-plane wave states can be expressed in terms of a unit element of solid angle $d\Omega$,

$$\rho(E') = \frac{Mk'}{\hbar^2 (2\pi)^3} d\Omega, \quad (6)$$

and thus a differential scattering cross section can be obtained from the transition probability (Equation 5) by utilizing the relation

$$d\sigma = w_{\vec{k} \rightarrow \vec{k}'} / \text{Incident flux}. \quad (7)$$

The incident flux of the neutron wave is determined by the neutron velocity,

$$\text{incident flux} = \frac{\hbar k}{M}. \quad (8)$$

Substituting Equations 5, 6 and 8 into Equation 7, we obtain an expression for the partial differential scattering cross section which is commonly referred to as the first Born approximation,

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k} |f(\vec{q})|^2 \delta(E_i - E_f - \hbar\omega) \quad (9)$$

where

$$f(\vec{q}) = -\frac{M}{2\pi\hbar^2} \langle f | \int d\vec{r}_n e^{i\vec{q} \cdot \vec{r}_n} H_{int} | i \rangle \quad (10)$$

is called the scattering amplitude. The sign of the scattering amplitude has been fixed by requiring that an attractive potential have a positive scattering amplitude. The delta function in the first Born approximation to the scattering cross section contains the conditions for energy conservation in the scattering process, since $\hbar\omega$ is the energy transferred to the neutron. Although the first Born approximation has been derived from perturbation theory (Fermi's Golden rule), it provides an excellent approximation to the magnetic scattering cross section for thermal neutrons.

In the first Born approximation, the magnetic scattering amplitude is simply related to a matrix element of the Fourier transform of the interaction Hamiltonian. In obtaining this result we have not specified whether or not the initial and final state atomic wavefunctions are solutions of relativistic or nonrelativistic Hamiltonians. In the remainder of this chapter we will give separate derivations of the magnetic scattering amplitudes of atoms described by relativistic and nonrelativistic Hamiltonians. The common convention of denoting a nonrelativistic state by an angular ket $| \rangle$, and a relativistic state by a rounded ket $| \rangle$ will be adopted throughout the rest of this work.

Nonrelativistic Formulation

Nonrelativistically, the interaction Hamiltonian between the vector potential due to the magnetic moment of the neutron and the spin and convection currents of the atom can be written as

$$H_{int} = - \frac{1}{c} \int \vec{j}(\vec{r}) \cdot \vec{A}_n(\vec{r}) d\vec{r} \quad (11)$$

where $\vec{j}(\vec{r})$ is the current density of the atom. For slow neutrons, $\vec{A}_n(\vec{r})$, the vector potential due to the magnetic moment of the neutron, is given by

$$\vec{A}_n(\vec{r}) = \frac{\vec{\mu}_n \times (\vec{r} - \vec{r}_n)}{|\vec{r} - \vec{r}_n|^3} \quad (12)$$

and thus the magnetic scattering amplitude can be written as

$$f(\vec{q}) = \frac{M}{2\pi\hbar^2 c} \langle f | \int d\vec{r} d\vec{r}_n e^{i\vec{q} \cdot \vec{r}} \vec{j}_n(\vec{r}) \cdot \frac{\vec{\mu}_n \times (\vec{r} - \vec{r}_n)}{|\vec{r} - \vec{r}_n|^3} | i \rangle \quad (13)$$

In these equations, $\vec{\mu}_n = \gamma \mu_N \vec{\sigma}$ is the magnetic moment of the neutron, $\gamma = -1.91$, μ_N is the nuclear magneton, and $\vec{\sigma}$ is the Pauli matrix. If the current density of the atom is independent of the magnetic moment of the neutron (this amounts to neglecting terms quadratic or of higher order in $\vec{A}_n(\vec{r})$ in the interaction Hamiltonian), the integration over the neutron coordinates can be performed²⁹, and the magnetic scattering amplitude can be written in the simple form

$$f(\vec{q}) = (|\gamma| r_0) \vec{\sigma} \cdot \vec{\mathcal{J}}_{\perp} \quad (14)$$

The operator $\vec{\mathcal{J}}_{\perp}$ is dimensionless[†] and is simply related to the Fourier transform of the transverse component of the current density operator,

$$\vec{\mathcal{J}}_{\perp} = -i\left(\frac{m}{e\hbar q}\right) \hat{q} \times \langle f | \int \vec{j}(\vec{r}) e^{i\vec{q} \cdot \vec{r}} d\vec{r} | i \rangle . \quad (15)$$

In these equations, m is the electronic mass, $r_0 = e^2/mc^2$ is the classical electron radius, and $e = -|e|$ denotes the electronic charge.

Thus the calculation of the magnetic scattering amplitude has been reduced to the evaluation of the Fourier transform of the transverse component of the current density, which is exactly the quantity calculated in the radiation problem in atomic and nuclear spectroscopy. This means that the problem of magnetic scattering can be handled using many of the elegant and powerful techniques that have been developed by atomic physicists studying general atomic radiation and collision problems. The importance of this conclusion cannot be overstated. The general problem of magnetic scattering can be formulated by direct analogy with the radiation problem in atomic spectroscopy.

It is well known that the radiation problem in atomic spectroscopy can be formulated in terms of the multipole operators characterizing the atom. There are several ways in which to expand the magnetic scattering amplitude in terms of the multipole operators.^{29,30} In this work the multipole expansion shall be derived using the same approach as that used in the radiation problem when the long wavelength approximation is not

[†] It may be shown that if the electronic velocity operator is equal to $\vec{p}/m$, the operator $\vec{\mathcal{J}}_{\perp}$ is equal to the operator $\vec{Q}_{\perp}$ defined by Marshall and Lovesey.²¹

made.³¹⁻³⁵ To do this, we first express the current operator in Equation 15 as,

$$\vec{J} = \sum_p (\vec{J} \cdot \vec{e}_p) \vec{e}_p^* , \quad (16)$$

where $\vec{e}_p$ is a spherical unit vector³⁶ defined by

$$\vec{e}_p = -\frac{p}{\sqrt{2}} (\vec{e}_1 + ip\vec{e}_2) , \quad p = \pm 1 \quad (17)$$

$$\vec{e}_0 = \vec{e}_3 .$$

and $\vec{e}_1, \vec{e}_2, \vec{e}_3$ are an arbitrary set of orthonormal unit vectors. Then using Equations 15 and 16 we obtain

$$\vec{J}_\perp = -i \left(\frac{m}{e\hbar q} \right) \hat{q} \times \sum_p \langle f | \int (\vec{J} \cdot \vec{e}_p) \vec{e}_p^* e^{i\vec{q} \cdot \vec{r}} d\vec{r} | i \rangle , \quad (18)$$

and the polarized wave $\vec{e}_p^* e^{i\vec{q} \cdot \vec{r}}$ can be expanded in vector spherical harmonics using the identity

$$\vec{e}_p^* e^{i\vec{q} \cdot \vec{r}} = 4\pi \sum_{k,L,m} i^L [\vec{e}_p^* \cdot \vec{Y}_{k,L,1}^{m*}(\hat{r})] j_L(qr) \vec{Y}_{k,L,1}^m(\hat{q}) , \quad (19)$$

where $j_L(qr)$ is a spherical Bessel function. The vector spherical harmonics $\vec{Y}_{k,L,1}^{m*}$ are vector fields which are generalizations of the spherical harmonics, Y_{km} . They transform under a rotation of coordinates like the Y_{km} , and are commonly used in the multipole expansion of the electromagnetic field³⁷⁻³⁹. Several of their most useful properties have been tabulated in Appendix A. Substituting the expression for the polarized wave given in Equation 19 into Equation 18, and performing the sum over $L (L = k, k \pm 1)$ we find

$$\begin{aligned}
\vec{J}_\perp = & -4\pi i \left(\frac{m}{e\hbar q}\right) \sum_{p,k,m} (\hat{q} \times \vec{X}_{km}(\hat{q})) \langle f | \int i^k j_k(qr) [\vec{e}_p^* \cdot \vec{X}_{km}^*(\hat{r})] (\vec{J} \cdot \vec{e}_p) d\vec{r} | i \rangle \\
& - 4\pi i \left(\frac{m}{e\hbar q}\right) \sum_{p,k,m} \vec{X}_{k,m}(\hat{q}) \langle f | \int [i^{k+2} \left(\frac{k}{2k+1}\right)^{\frac{1}{2}} j_{k+1}(qr) [\vec{e}_p^* \cdot \vec{Y}_{k,k+1,1}^m(\hat{r})] (\vec{J} \cdot \vec{e}_p) \\
& + i^k \left(\frac{k+1}{2k+1}\right)^{\frac{1}{2}} j_{k-1}(qr) [\vec{e}_p^* \cdot \vec{Y}_{k,k-1,1}^m(\hat{r})] (\vec{J} \cdot \vec{e}_p)] d\vec{r} | i \rangle, \quad (20)
\end{aligned}$$

where Equations A.11 and A.12 have been used to simplify this result and $\vec{X}_{km}$ has been used to denote[†] the vector spherical harmonic $\vec{Y}_{k,k,1}^m$. Equation 20 can be further simplified by using Equations A.7 and the fact that for any vector $\vec{A}$, $\vec{A}^* = [(\vec{e}_p^* \cdot \vec{A}) \vec{e}_p]$:

$$\begin{aligned}
\vec{J}_\perp = & -4\pi i \left(\frac{m}{e\hbar q}\right) \sum_{k,m} (\hat{q} \times \vec{X}_{km}^*(\hat{q})) \langle f | \int i^k j_k(qr) \vec{X}_{k,m}(\hat{r}) \cdot \vec{J}(\vec{r}) d\vec{r} | i \rangle \\
& + 4\pi i \left(\frac{m}{e\hbar q}\right) \sum_{k,m} \vec{X}_{k,m}^*(\hat{q}) \langle f | \int i^k \\
& \times \left[\left(\frac{k+1}{2k+1}\right)^{\frac{1}{2}} j_{k-1}(qr) \vec{Y}_{k,k-1,1}^m(\hat{r}) - \left(\frac{k}{k+1}\right)^{\frac{1}{2}} j_{k+1}(qr) \vec{Y}_{k,k+1,1}^m(\hat{r}) \right] \cdot \vec{J} d\vec{r} | i \rangle, \quad (21)
\end{aligned}$$

Using Equation A.13 to simplify the last term in Equation 21, we find that the multipole expansion of the operator $\vec{J}_\perp$ is

$$\vec{J}_\perp = \sum_{k,m} \left(\frac{8\pi}{2k+1}\right)^{\frac{1}{2}} \{ \vec{X}_{km}^*(\hat{q}) \langle f | T_{km}^{(e)} | i \rangle - i (\hat{q} \times \vec{X}_{km}^*(\hat{q})) \langle f | T_{km}^{(m)} | i \rangle \}, \quad (22)$$

[†]The notation adopted for the vector spherical harmonics is that of Blatt and Weisskopf.³⁹

where T_{km}^e and T_{km}^m are the electric and magnetic multipole operators, respectively. The multipole operators

$$T_{km}^{(e)} = \frac{1}{\sqrt{2}} \left(\frac{m}{e\hbar q} \right) \int \vec{A}_{km}^{(e)} \cdot \vec{j} d\vec{r} \quad (23)$$

and

$$T_{km}^{(m)} = \frac{1}{\sqrt{2}} \left(\frac{m}{e\hbar q} \right) \int \vec{A}_{km}^{(m)} \cdot \vec{j} d\vec{r} \quad (24)$$

are determined by the current density of the atom and the multipole fields $\vec{A}_{km}^{(e)}$ and $\vec{A}_{km}^{(m)}$, familiar from the multipole expansion of the electromagnetic field.⁴⁰ The multiple fields,

$$\vec{A}_{km}^{(m)} = i^k (4\pi(2k+1))^{1/2} j_k(qr) \vec{X}_{km}(\hat{r}), \quad (25)$$

and

$$\vec{A}_{km}^{(e)} = i^k [4\pi(2k+1)]^{1/2} \frac{L}{q} \nabla \times (j_k(qr) \vec{X}_{km}(\hat{r})), \quad (26)$$

have parities $(-)^k$ and $(-)^{k+1}$, respectively. Since the parity of the current operator is $(-)$, the magnetic and electric multipole operators have parities $(-)^{k+1}$ and $(-)^k$, respectively. It may also be shown that the magnetic and electric multipole operators are irreducible tensors of order k (see Chapter III).

Then using Equation 14 we finally obtain an expression for the magnetic scattering amplitude in terms of the multipole moments characterizing the atom or scattering system,

[†]The multipole fields, as defined in this work, are dimensionless and differ from those defined by Ross and Brink⁴¹ by a factor of $\left(\frac{m}{e\hbar q}\right)$.

$$f(\vec{q}) = (|\gamma| r_o) \vec{\sigma} \cdot \left[\sum_{k,m} \left(\frac{8\pi}{2k+1} \right)^{\frac{1}{2}} \{ \vec{X}_{km}^*(\hat{q}) \langle f | T_{km}^{(e)} | i \rangle - i (\hat{q} \times \vec{X}_{km}^*(\hat{q})) \langle f | T_{km}^{(m)} | i \rangle \} \right]. \quad (27)$$

Since the mutually perpendicular vectors $\vec{X}_{km}^*$ and $\hat{q} \times \vec{X}_{km}^*$ are transverse to the scattering vector, Equation 27 explicitly exhibits the fundamental property of the magnetic scattering of neutrons, namely that only the transverse component of the atomic current density can couple with the magnetic moment of the neutron.

Since the multipole operators are irreducible tensor operators with definite parities, the number of multipole moments which contribute to the magnetic scattering amplitude is limited by selection rules based on parity and angular momentum conservation. The conservation of angular momentum produces the requirement that

$$|J_f - J_i| \leq k \leq J_f + J_i,$$

$$M_f = M_i + m.$$

where J is the total angular momentum and M is its projection along the z -axis. Parity conservation requires

$$P_f = (-)^k P_i \text{ for electric multipoles,}$$

$$P_f = (-)^{k+1} P_i \text{ for magnetic multipoles.}$$

where P_i and P_f are the parities of the initial and final states, respectively. The multipole moment operators given in Equations 23 and 24 are expressed only in terms of the current density of the atom. However, the charge and current density are connected by the continuity equation

$$\nabla \cdot \vec{j} = -\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H, \rho] \quad (28)$$

where H , is the Hamiltonian of the atom and ρ is the charge density. Thus we expect that the multipole operators are expressible in terms of both the charge and current densities.

Multipole Moment Operators

It is well known that most radiation problems in atomic and nuclear spectroscopy can be treated in the small q , or long wavelength, limit ($qR \ll 1$ where R characterizes the size of the system). In this limit the multipole moment operators are proportional to the static multipole moments of the system. However, in most neutron scattering problems, the wavelength of the neutron is of the same order as the characteristic size of the structure being studied, i.e. $qR \approx 1$. Thus exact expressions for the multipole operators in terms of the charge and current densities of the system must be obtained. The magnetic multipole operator (Equation 24) can be written in terms of the current density of the system by using Equation A.8 to obtain,

$$T_{km}^m = -\left(\frac{m}{e\hbar q}\right) \frac{i^{k-1}}{\sqrt{2}} \left[\frac{4\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \int d\vec{r} \vec{r} \times \vec{j} \cdot \nabla (j_k Y_{km}) d\vec{r} \quad (29)$$

Using the simple vector identities, Equation 29 can be rewritten as

$$\begin{aligned} T_{km}^{(m)} &= -2\left(\frac{m}{e\hbar q}\right) i^{k-1} \left(\frac{2\pi(2k+1)}{k(k+1)}\right)^{\frac{1}{2}} \int d\vec{r} j_k(qr) \rho^{(m)}(\vec{r}) Y_{km}(\hat{r}) \\ &= -2\left(\frac{m}{e\hbar q}\right) i^{k-1} \left(\frac{2\pi(2k+1)}{k(k+1)}\right)^{\frac{1}{2}} \int d\vec{r} \vec{M}(\vec{r}) \cdot \nabla (j_k(qr) Y_{km}(\hat{r})) \end{aligned} \quad (30)$$

where

$$\vec{M}(\vec{r}) = \frac{1}{2c} \vec{r} \times \vec{j} , \quad (31)$$

and

$$\rho^{(m)} = -\nabla \cdot \vec{M}(\vec{r}) , \quad (32)$$

are the magnetization and magnetic pole densities, respectively, of the system. It is somewhat more difficult to express the electric multipole operator in terms of the charge and current densities of the system. By using Equation A.8, the electric multipole field may be written as

$$\vec{A}_{km}^{(e)} = i^{k+1} [4\pi(2k+1)]^{\frac{1}{2}} \left\{ \frac{\nabla \times \nabla \times (\vec{r} j_k Y_{km})}{q[k(k+1)]^{\frac{1}{2}}} \right\} , \quad (33)$$

which may be rewritten as⁴¹

$$\vec{A}_{km}^{(e)} = i^{k+1} \left(\frac{4\pi(2k+1)}{k(k+1)} \right)^{\frac{1}{2}} \left[q \vec{r} j_k(qr) Y_{km}(\hat{r}) + \frac{1}{q} \nabla \{ Y_{km}(\hat{r}) \frac{d}{dr} (r j_k(qr)) \} \right] . \quad (34)$$

Substituting this into Equation 23 and using the continuity equation (Equation 28), one obtains the following expression for the electric multipole operator in terms of the charge and current densities of the system,

$$\begin{aligned} T_{km}^{(e)} = i^{k+1} \left(\frac{m}{e\hbar q} \right) \left(\frac{2\pi(2k+1)}{k(k+1)} \right)^{\frac{1}{2}} & \left[\frac{i(E_f - E_i)}{\hbar q} \int d\vec{r} Y_{km}(\hat{r}) \rho(\vec{r}) \frac{d}{dr} (r j_k(qr)) + \right. \\ & \left. q \int d\vec{r} j_k(qr) Y_{km}(\hat{r}) \vec{r} \cdot \vec{j}(\vec{r}) \right] . \end{aligned} \quad (35)$$

These are exact expressions for the multipole operators. They are identical with the dimensionless multipole moment operators that would be

obtained in the radiation problem, if the long wavelength approximation were not made. As expected, the magnetic multipole operator is due solely to the magnetization of the system. On the other hand, the electric multipole operator has two contributions; one from changes in the charge density of the system, and a second which is an induced electric multipole moment due to the magnetization.

These exact expressions for the multipole operators are not always needed, for in some problems we can use the small q , or long wavelength, approximation familiar from atomic and nuclear spectroscopy. This limit can be obtained by substituting the small argument expression of the spherical Bessel function,

$$j_k(qr) \approx \frac{(qr)^k}{(2k+1)!!} \cdot qr \ll 1 \quad (36)$$

in Equations 30 and 35. The multipole operators then become proportional to the static multipoles characterizing the system and are given by,

$$\begin{aligned} T_{km}^{(m)} &= -\left(\frac{m}{e\hbar q}\right) \frac{2c i^{k-1} q^k}{(2k+1)!!} \left(\frac{2\pi(2k+1)}{k(k+1)}\right)^{\frac{1}{2}} \int d\vec{r} r^k \rho^{(m)}(\vec{r}) Y_{km}(\hat{r}), \quad qr \ll 1 \\ \text{and} \\ T_{km}^{(e)} &= -\left(\frac{m}{e\hbar q}\right) \frac{i^k q^k}{(2k+1)!!} \left(\frac{2\pi(2k+1)(k+1)}{k}\right)^{\frac{1}{2}} \frac{(E_f - E_i)}{\hbar q} \int d\vec{r} r^k \rho(\vec{r}) Y_{km}(\hat{r}), \\ &\quad qr \ll 1. \end{aligned} \quad (37)$$

In this limit, the magnetic multipole operator is connected with the magnetization of the system and the electric multipole operator is connected directly with the charge density of the system. Since $qr \ll 1$, only the lowest order multipoles will significantly contribute to the

scattering amplitude. In fact, if the initial and final states have the same parity, the magnetic dipole, T_{1m}^m , and electric quadrupole, T_{2m}^e , terms are of primary importance, since the electric dipole term vanishes by parity conservation. On the other hand, if the initial and final states have opposite parity, the electric dipole term is of importance.

It should be pointed out that the dipole approximation can be obtained directly by approximating $e^{i\vec{q}\cdot\vec{r}} \approx 1$ in Equation 15. In this approximation either the magnetic or electric dipole term contributes to the magnetic scattering amplitude. The next approximation $e^{i\vec{q}\cdot\vec{r}} \approx 1 + i\vec{q}\cdot\vec{r}$ includes an extra contribution from the electric (T_{2m}^e) or magnetic (T_{2m}^m) quadrupole term. For elastic scattering very near the forward direction the magnitude of the scattering vector is approximately equal to zero ($|\vec{q}| \approx 0$) and only the magnetic dipole term contributes to the scattering amplitude. Using Equations 30, 36 and A.9, it may be shown that in this limit the magnetic dipole term is proportional to the magnetization operator,

$$\lim_{|\vec{q}| \rightarrow 0} T_{1m}^m = \frac{1}{2\mu_0} \int d\vec{r} M_m(\vec{r}) . \quad (38)$$

Without an explicit expression for the microscopic current density, one can proceed no further than giving exact expressions for the multipole operators and the small q limit of these expressions.

Nonrelativistic Current Density

Nonrelativistically, the current density can be separated quite generally into magnetization and convection current densities $\vec{j}_m$ and $\vec{j}_c$,

respectively, with

$$\vec{j}(\vec{r}) = \vec{j}_c(\vec{r}) + \vec{j}_m(\vec{r}) \quad , \quad (39)$$

We shall use the point-charge-point-magnetic moment expressions for the atomic current density which are commonly used in the radiation problem.⁴²

These expressions neglect the effects of the internal structure of the particles in the system which is an excellent approximation in all low energy problems. Then the magnetization and convection currents are

$$\vec{j}_m(\vec{r}) = \sum_i g_i \frac{\hbar e_i}{2m_i} \nabla \times (\vec{s}_i \delta(\vec{r} - \vec{r}_i)) \quad , \quad (40)$$

and

$$\vec{j}_c(\vec{r}) = \sum_i \frac{e_i}{2} (\vec{v}_i \delta(\vec{r} - \vec{r}_i) + \delta(\vec{r} - \vec{r}_i) \vec{v}_i) \quad (41)$$

where $\vec{r}_i$, e_i and g_i are the charge, position and g factor of the i^{th} particle, respectively. The velocity operator of the i^{th} electron is determined by the momentum dependent terms in the atomic Hamiltonian,

$$\vec{v}_i = \frac{i}{\hbar} [H, \vec{r}_i] = \frac{\partial H}{\partial \vec{p}_i} \quad . \quad (42)$$

The momentum dependent terms in the atomic Hamiltonian can be written as

$$H = H_0 + H_1 + H_2 + \dots \quad , \quad (43)$$

where H_0 consists of the kinetic energy and the momentum independent terms in the atomic Hamiltonian, H_1 consists of the other one particle momentum dependent terms such as the spin orbit and mass correction terms, H_2 denotes the two particle momentum dependent terms, etc. Then the velocity operator can be written as

$$\vec{v}_i = \frac{\vec{p}_i}{m} + \sum_j \frac{\partial H_i}{\partial \vec{p}_i} \quad , \quad j = 1, 2 \dots \quad (44)$$

where $\vec{p}_i/m$ is the velocity operator for a free particle arising from the kinetic energy operator. The last terms in Equation 44 are corrections to the free particle velocity operator which are due to the fact that the atomic electrons are bound. These corrections are reflected in the multipole operators which may be written as

$$T_{km}^\pi = T_{km}^\pi(0) + \sum_j T_{km}^\pi(j) \quad (45)$$

where $\pi = e$ or m and the first term is due to the convection current associated with the kinetic energy operator and the magnetization current, while the other terms arise from the convection current associated with the one-particle, two-particle ... momentum dependent terms in the Hamiltonian.

The largest of the multipole operators are $T_{km}^e(0)$ and $T_{km}^m(0)$ for which analytical expressions have been derived in Appendix B,

$$T_{km}^{(e)}(0) = i^{k+1} \left(\frac{m}{e\hbar q} \right) \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \sum_i \left[\left\{ \frac{1(E_f - E_i)}{\hbar q} e_i Y_{km}(\hat{r}_i) \frac{d}{dr} (r_i j_k(qr_i)) + \right. \right. \quad (B.5)$$

$$\left. \left. \frac{q e_i}{2m_i} (j_k(qr_i) Y_{km}(\hat{r}_i) \vec{r}_i \cdot \vec{p}_i + \vec{p}_i \cdot \vec{r}_i j_k(qr_i) Y_{km}(\hat{r}_i)) \right\} - i \frac{g_i e_i \hbar q}{2m_i} \vec{s}_i \cdot \vec{\ell}_i (j_k(qr_i) Y_{km}(\hat{r}_i)) \right]$$

and

$$T_{km}^{(m)}(0) = i^k \left(\frac{m}{e\hbar q} \right) \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \sum_i \frac{e_i \hbar}{m_i} \left[i \nabla (j_k(qr_i) Y_{km}(\hat{r}_i)) \cdot \vec{\ell}_i \right. \quad (B.10)$$

$$\left. + \frac{g_i}{2} \vec{s}_i \cdot \nabla \times \vec{\ell}_i (j_k(qr_i) Y_{km}(\hat{r}_i)) \right].$$

In the expression for the electric multipole operator (Equation B.5), the term in curly brackets is due to the convection current, while the last term is due to the magnetization current. Similarly, in Equation B.10, the first term is due to the convection current, while the last term in the square brackets is due to the magnetization current. The multipole operators $T_{km}^e(j)$ and $T_{km}^m(j)$ which result from the corrections to the free particle velocity operator are substantially smaller than $T_{km}^e(0)$ and $T_{km}^m(0)$, respectively. Expressions for these operators are given in Appendix B.

This is as far as one can proceed without an expression for the atomic Hamiltonian. In Chapter IV, the matrix elements of these multipole operators will be evaluated and an expression for the magnetic scattering amplitude of an atom described by a nonrelativistic Hamiltonian will be developed.

Relativistic Formulation

To extend the formulation of magnetic scattering to a relativistic atom, we must examine the relativistic atomic Hamiltonian which can be written as

$$H = \sum_i H_D(i) + V, \quad (46)$$

where the sum is over the electrons of the atom and

$$H_D = c\vec{\alpha} \cdot \vec{p} + \beta mc^2 + \frac{Ze^2}{r}. \quad (47)$$

In this equation, H_D is the Dirac Hamiltonian for a single electron in the coulomb field of the nucleus, and V , which is usually approximated by the Breit interaction⁴³, describes the interaction between the electrons of the atom. For the Dirac matrices $\vec{\alpha}$ and β we will use the standard

representation

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (48)$$

where $\vec{\sigma}$ and 1 are the Pauli and unit matrices, respectively.

The interaction between the vector potential, $\vec{A}_n(\vec{r})$ created by the neutron and the current density of the atom can be obtained by using gauge invariance to replace $\vec{p}$ as it appears in the atomic Hamiltonian (Equation 46) by $\vec{p} - \frac{e}{c} \vec{A}_n(\vec{r})$. Providing the interaction, V , between the electrons is independent of their momenta (a condition satisfied by the Breit interaction), the interaction Hamiltonian which results from the application of gauge invariance to Equation 46 is

$$H_{int} = - \frac{1}{c} \int \vec{j}(\vec{r}) \cdot \vec{A}_n(\vec{r}) d\vec{r}, \quad (49)$$

where the relativistic current density

$$\vec{j}(\vec{r}) = \sum_i e \vec{\alpha}(i) \delta(\vec{r} - \vec{r}_i) \quad (50)$$

is expressed in terms of the relativistic electronic velocity, $c\vec{\alpha}$.

Except for the form in which the current density is written, the interaction Hamiltonian in Equation 49 is identical with that obtained in the nonrelativistic formulation (Equation 11). By using exactly the same manipulations as those used in the nonrelativistic formulation of the problem, the magnetic scattering amplitude can be expressed in terms of the relativistic multipole operators $T_{km}^{(e)}$ and $T_{km}^{(m)}$:

$$f(\vec{q}) = |\gamma| r_0 \vec{\sigma} \cdot (f | \sum_{k,m} \left(\frac{8\pi}{2k+1}\right)^{\frac{1}{2}} \{ \vec{X}_{km}^*(\hat{q}) T_{km}^{(e)} - i(\hat{q} \times \vec{X}_{km}^*(\hat{q})) T_{km}^{(m)} \} | i). \quad (51)$$

The relativistic electric and magnetic multipole operators defined by

$$T_{km}^{(e)} = \frac{1}{\sqrt{2}} \left(\frac{m}{e\hbar q} \right) \int \vec{A}_{km}^{(e)} \cdot \vec{j} d\vec{r}, \quad (52)$$

and

$$T_{km}^{(m)} = \frac{1}{\sqrt{2}} \left(\frac{m}{e\hbar q} \right) \int \vec{A}_{km}^{(m)} \cdot \vec{j} d\vec{r}, \quad (53)$$

are similar in form to their nonrelativistic counterparts (Equations 23 and 24). However, in the relativistic treatment the current density operator is determined by the Dirac matrices and thus the multipole operators are no longer simply irreducible tensors of rank k as in the non-relativistic formulation. Instead, they are 4×4 matrices whose nonzero elements are irreducible tensors of rank k .

As in the nonrelativistic formulation, the calculation of the magnetic scattering amplitude reduces to evaluating matrix elements of the multipole operators. The calculation of the matrix elements of the multipole operators can be conveniently performed by writing these operators in a slightly different form. Using Equation 50 we can rewrite the relativistic multipole operator as

$$T_{km}^{(m)} = -i^k \left(\frac{mc}{\hbar q} \right) (2\pi(2k+1))^{1/2} \sum_i j_k(qr_i) \vec{\alpha} \cdot \vec{X}_{km}. \quad (54)$$

Similarly, using Equations 34 and 50, the electric multipole operator can be written as

$$T_{km}^{(e)} = i^{k+1} \left(\frac{m}{\hbar q} \right) \left(\frac{2\pi(2k+1)}{k(k+1)} \right)^{1/2} \sum_i \left\{ -\frac{i\omega}{q} Y_{km}(\hat{r}_i) \frac{d}{dr_i} (r_i j_k(qr_i)) + \right. \\ \left. cq j_k(qr_i) Y_{km}(\hat{r}_i) \vec{r}_i \cdot \vec{\alpha}(i) \right\}. \quad (55)$$

The direct evaluation of the matrix elements of these operators can be quite involved, and the general information necessary for calculating them is presented in Chapter III. In Chapter V, this general theory for scattering by a relativistic atom has been applied to the rare earths.

CHAPTER III. REVIEW OF ATOMIC CALCULATIONS

In Chapter II, it was shown that for scattering from atoms described both by relativistic and nonrelativistic Hamiltonians, the calculation of the magnetic scattering amplitude could be reduced to evaluating matrix elements of magnetic and electric multipole operators. The atomic and nuclear physicists have developed many techniques which can be used to simplify the calculation of these matrix elements. Since these techniques are often unfamiliar to the solid state physicist, this chapter will be concerned with the exposition of these techniques.

The basic theorems and definitions of Racah algebra used throughout this work will be presented. Specifically, the $3-j$, $6-j$ and $9-j$ symbols will be defined and explicit expressions will be given for many of these symbols needed later in this work. Similarly, an irreducible tensor operator shall be defined and the operators used in this work shall be expressed as products of irreducible tensor operators. The Wigner-Eckart theorem shall be stated and the reduced matrix elements of operators used in this work given.

An introduction to atomic structure and the classification of atomic states will be given. The relativistic and nonrelativistic atomic Hamiltonians will be presented and the solutions of these Hamiltonians in the central field approximation will be discussed. Also, the classification of the atomic states will be presented along with the calculation of the matrix elements of the Racah tensors.

Racah Algebra

The eigenvalue problem for angular momentum can be written as

$$\begin{aligned} J_z |jm\rangle &= m|jm\rangle, \\ J^2 |jm\rangle &= j(j+1)|jm\rangle, \end{aligned} \quad (56)$$

where $|jm\rangle$ is a ket vector of the eigenbasis common to the angular momentum operators $\vec{J}$ and J_z (the z component of $\vec{J}$). The angular momentum quantum number j , must be a nonnegative integral or half integral number, and the only allowed values of the quantum number m are the $2j+1$ quantities $-j, -j+1, \dots, j-1, j$.

The coupling of eigenstates $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$ of two commuting angular momentum operators $\vec{J}_1$ and $\vec{J}_2$, respectively, to form eigenstates $|j_1 j_2 jm\rangle$ of the angular momentum operator $\vec{J} = \vec{J}_1 + \vec{J}_2$, is often performed using the Clebsch Gordon coefficient[†] $(j_1 m_1 j_2 m_2 | j_1 j_2 jm)$,

$$|j_1 j_2 jm\rangle = \sum_{m_1 m_2} (j_1 m_1 j_2 m_2 | j_1 j_2 jm) |j_1 m_1\rangle |j_2 m_2\rangle. \quad (57)$$

However in this work, we will primarily use the 3- j symbols which were introduced by Wigner⁴⁴ to provide a more symmetrized form of the Clebsch Gordon coefficient. The 3- j symbol is simply related to the Clebsch Gordon coefficient by

$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} = \frac{(-)^{j_1-j_2+m}}{\sqrt{2j+1}} (j_1 m_1 j_2 m_2 | j_1 j_2 jm), \quad (58)$$

[†]The notation and choice of phase is that of Condon and Shortley.¹²

where the quantity in the large parentheses is a 3-j symbol.

There are several properties common to all 3-j symbols. The 3-j symbol in Equation 58 is automatically equal to zero unless $m_1 + m_2 - m = 0$ and $|j_1 - j_2| \leq j \leq j_1 + j_2$ (this last condition is known as a triangular relation). Due to general symmetry properties, a 3-j symbol is equal to a different symbol or simply related to another one by a phase factor. A list of these symmetry properties relating different 3-j symbols is given in Table 1. Furthermore, orthogonality relations exist among the 3-j symbols since they are used to expand one orthonormal set in terms of another (see Equations 57 and 58). A list of these orthogonality relations is given in Table 1.

Numerical values for all 3-j symbols used in this work have been presented as square roots of rational numbers by Rotenberg et al.⁴⁵. Many explicit algebraic expressions for 3-j symbols have been given by Edmonds³⁶, de-Shalit and Talmi⁴⁶, and Rotenberg et al.⁴⁵. Some of the most useful of these algebraic expressions and some identities involving 3-j symbols have been summarized in Appendix C.

The 3-j symbol was shown to be the expansion coefficient between the coupled and uncoupled states of two angular momentum operators. If we consider the coupling of eigenstates of three commuting angular momentum operators, the 6-j symbol can be defined as an expansion coefficient connecting two differently coupled sets of states of these operators.[†] The 6-j symbol can be expressed quite generally in terms of the 3-j

[†]See for example Rotenberg et al.⁴⁵.

Table 1. Properties of the 3-j, 6-j and 9-j symbols

	3-j	6-j	9-j
Symbols	$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix}$	$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{Bmatrix}$	$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{Bmatrix}$
Triangular	$(0 - 0 - 0)$	$0 - 0 - 0$	$0 - 0 - 0$
Relations;	and $m_1 + m_2 + m = 0$	$\begin{array}{ccc} & 0 & \\ & / \quad \backslash & \\ 0 & & 0 \\ & 0 & \\ 0 - 0 & / & \backslash 0 - 0 \end{array}$	$\begin{array}{ccc} 0 & 0 & 0 \\ & & \\ 0 - 0 - 0 & 0 & 0 & 0 \\ & & \\ 0 - 0 - 0 & 0 & 0 & 0 \end{array}$
Symmetry	- invariant for even permutation of rows	- invariant for interchange of any two columns	- invariant for an even permutation of rows or columns
Properties ^b	- multiplied by $(-)^{j_1+j_2+j}$ for an odd permutation of rows	- invariant for interchange of upper and lower arguments in each of any two of the columns	- multiplied by $(-)^{j_1+j_2+j_3+j_4+j_{12}+j_{34}+j_{13}+j_{24}+j}$ for odd permutation of rows or columns
	- multiplied by $(-)^{j_1+j_2+j}$ for a change in sign of all elements in bottom row		- invariant for reflection of the symbol about either diagonal.

^a $0 - 0 - 0$ denotes a triangular condition must exist between circled elements, for the symbol to be nonzero, for example $\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix}$ implies $j_1 + j_2 \geq j$ $j_1 + j \geq j_2$ $j_2 + j \geq j_1$ for the symbol to be nonzero.

^b For the 3-j and 6-j symbols more symmetry properties have been given by Regge.⁴⁵

Table 1. (Continued)

	3-j	6-j	9-j
Orthogonality Relations	$\sum_{jm} (2j+1) \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j \\ m'_1 & m'_2 & m \end{pmatrix} = \delta(m_1, m'_1) \delta(m_2, m'_2)$	$\sum_{j_{23}} (2j_{23}+1) \times \left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{matrix} \right\} \times$	$\sum_{j_{13}j_{24}} (2j_{13}+1)(2j_{24}+1) \left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13}j_{24}j \end{matrix} \right\} \times$
	$\sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j' \\ m_1 & m_2 & m' \end{pmatrix} = \frac{\delta(j_3, j'_3) \delta(m_3, m'_3)}{(2j+1)}$	$\left\{ \begin{matrix} j_1 & j_2 & j'_{12} \\ j_3 & j & j_{23} \end{matrix} \right\} \times = \frac{\delta(j_{12}, j'_{12})}{(2j_{12}+1)}$	$\left\{ \begin{matrix} j_1 & j_2 & j'_{12} \\ j_3 & j_4 & j'_{34} \\ j_{13}j_{24}j \end{matrix} \right\} \times = \frac{\delta(j_{12}, j'_{12}) \delta(j_{34}, j'_{34})}{(2j_{12}+1)(2j_{34}+1)}$

symbols using the relation

$$\left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{matrix} \right\} = \sum_{\text{all } m} (-)^s \begin{pmatrix} j_1 & j_2 & j_{12} \\ m_1 & m_2 & m_{12} \end{pmatrix} \begin{pmatrix} j_1 & j & j_{23} \\ m_1 & m & -m_{23} \end{pmatrix} \begin{pmatrix} j_3 & j_2 & j_{23} \\ -m_3 & m_2 & m_{23} \end{pmatrix} \times$$

$$\begin{pmatrix} j_3 & j & j_{12} \\ m_3 & -m & m_{12} \end{pmatrix} \quad (59)$$

where the quantity in the curly brackets is a 6-j symbol and $s = j_3 + j + j_{23} + m_3 + m + m_{23}$.

As with the 3-j symbols, there are many general properties common to all 6-j symbols. A summary of the orthogonality relations, symmetry properties, and triangular relations for 6-j symbols is given in Table 1. Numerical expressions for all of the 6-j symbols used in this work have been presented as square roots of rational numbers by Rotenberg et al.⁴⁵, and algebraic expressions for specific 6-j symbols have been given by many authors.^{36,46-49} As was the case for the 3-j symbols, some of the most important algebraic expressions and identities for the 6-j symbols used in this work are listed in Appendix C.

If instead of considering the coupling of three angular momenta, the coupling of four angular momenta is considered, the 9-j symbol can be defined as the transformation coefficient between coupling schemes in which pairs of angular momenta are coupled together with the resultant angular momenta then coupled to the final value. Specifically, the 9-j symbol can be used to define the transformation from LS to jj coupled

states. If we consider angular momentum operators $\vec{L}_1, \vec{L}_2, \vec{S}_1, \vec{S}_2$ whose eigenstates are $|\ell_1 m_1\rangle, |\ell_2 m_2\rangle, |s_1 m_1^s\rangle$ and $|s_2 m_2^s\rangle$, respectively: in LS coupling eigenstates of $\vec{S} = \vec{S}_1 + \vec{S}_2$ and $\vec{L} = \vec{L}_1 + \vec{L}_2$ are formed and then combined to give eigenstates $|(s_1 s_2) s, (\ell_1 \ell_2) \ell, j m\rangle$ of the operator $\vec{J} = \vec{L} + \vec{S}$. In the jj coupling scheme, eigenstates of the operators

$$\vec{J}_1 = \vec{S}_1 + \vec{L}_1$$

and

$$\vec{J}_2 = \vec{S}_2 + \vec{L}_2$$

are formed and then combined to give eigenstates $|(s_1 \ell_1) j_1, (s_2 \ell_2) j_2, j m\rangle$ of the operator $\vec{J} = \vec{J}_1 + \vec{J}_2$. The transformation between the LS and jj coupled states is given by

$$|(s_1 \ell_1) j_1, (s_2 \ell_2) j_2, j m\rangle = \sum_{s \ell} [(2j_1+1)(2j_2+1)(2s+1)(2\ell+1)]^{\frac{1}{2}} \times \quad (60)$$

$$\left\{ \begin{matrix} s_1 & \ell_1 & j_1 \\ s_2 & \ell_2 & j_2 \\ s & \ell & j \end{matrix} \right\} |(s_1 s_2) s, (\ell_1 \ell_2) \ell, j m\rangle,$$

where the quantity in the curly brackets is a 9-j symbol. The 9-j symbol can be expressed quite generally in terms of 6-j symbols as

$$\left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{matrix} \right\} = \sum_J (-)^{2J} \left\{ \begin{matrix} j_1 & j_3 & j_{13} \\ j_{24} & j & J \end{matrix} \right\} \left\{ \begin{matrix} j_2 & j_4 & j_{24} \\ j_3 & J & j_{34} \end{matrix} \right\} \left\{ \begin{matrix} j_{12} & j_{34} & j \\ J & j_1 & j_2 \end{matrix} \right\}, \quad (61)$$

or in terms of 3-j symbols

$$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{Bmatrix} = \sum_{\text{all } m} \begin{pmatrix} j_1 & j_2 & j_{12} \\ m_1 & m_2 & m_{12} \end{pmatrix} \begin{pmatrix} j_3 & j_4 & j_{34} \\ m_3 & m_4 & m_{34} \end{pmatrix} \begin{pmatrix} j_{13} & j_{24} & j \\ m_{13} & m_{34} & m \end{pmatrix} \quad (62)$$

$$\begin{pmatrix} j_1 & j_3 & j_{13} \\ m_1 & m_3 & m_{13} \end{pmatrix} \begin{pmatrix} j_2 & j_4 & j_{24} \\ m_2 & m_4 & m_{24} \end{pmatrix} \begin{pmatrix} j_{12} & j_{34} & j \\ m_{12} & m_{34} & m \end{pmatrix}.$$

Triangular relations, symmetry properties, and orthogonality relations for the 9-j symbols are given in Table I. Many algebraic expressions for the 9-j symbols used in this work are given in Appendix C.

The angular momentum eigenstates which have been discussed enter atomic problems in a direct and physical way when the Hamiltonian of the atom is taken to be spherically symmetric. The corresponding set of operators entering such atomic problems are the irreducible tensor operators. An example of an irreducible tensor operator would be the spherical harmonics Y_{km} , which transform among themselves like the components of an irreducible tensor of rank k under a rotation of the coordinate system. This transformation property is implicit in Racah's⁵⁰ definition that an irreducible tensor operator T_{kq} is any operator with $2k+1$ components which satisfy the commutation relations

$$[J_z, T_{kq}] = qT_{kq},$$

$$[J_{\pm}, T_{kq}] = \sqrt{k(k+1) - q(q\pm 1)} T_{k, q\pm 1}, \quad (63)$$

where $J_{\pm} = J_x \pm iJ_y$ and J_x, J_y and J_z are the cartesian components of the angular momentum operator $\vec{J}$. Using this definition it may be shown that the electron spin operator $\vec{s}$ and the orbital angular momentum operator $\vec{\ell}$ form irreducible spherical tensor operators of rank 1 in the spaces spanned by their eigenstates (the spin and orbital spaces, respectively). It may also be shown that the spherical components of the position vector ($r_p = \vec{r} \cdot \vec{e}_p$) form irreducible spherical tensors of rank 1 in the orbital space.

Irreducible spherical tensor components T_{k_1, q_1} and T_{k_2, q_2} can be coupled to form another irreducible spherical tensor component, T_{kq} , by calculating the tensor product

$$T_{kq} \equiv [T_{k_1} \times T_{k_2}]_q^k = (-)^{k_2 - k_1 - q} \sum_{q_1 q_2} (2k+1)^{\frac{1}{2}} \begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{pmatrix} \times T_{k_1, q_1} T_{k_2, q_2} \quad (64)$$

An example of such a tensor product is the vector spherical harmonic which was defined in Appendix A;

$$\vec{Y}_{k, \kappa, l}^m = [Y_{\kappa} \times \vec{e}]_m^k.$$

Throughout this work we will use many tensor products of operators defined in the spin and orbital spaces associated with the electron angular momentum operators $\vec{s}$ and $\vec{\ell}$, respectively. The irreducible tensor products of these operators are defined in the space spanned by the eigenstates of the total angular momentum operator $\vec{J} = \vec{\ell} + \vec{s}$. Table 2

Table 2. Tensor products of operators

Operator ^a	Expression as a Tensor Product	Rank in the spin space	Rank in the orbital space	Rank in the space spanned by eigenvectors of $j+l+S$
$\vec{s} \cdot \vec{Y}_{k,\kappa,l}^m$	$(-)^{k+\kappa+1} [\vec{s} \times Y_k]_m^k$	1	κ	k
$\vec{s} \cdot \vec{\ell} (j_k Y_{km}) = \sqrt{k(k+1)} \times$				
$j_k \vec{s} \cdot \vec{Y}_{k,k,l}^m$	$= \sqrt{k(k+1)} [s \times j_k Y_k]_m^k$	1	k	k
$\nabla (j_k Y_{km}) \cdot \vec{\ell}$	$q [(\frac{k+1}{2k+1})^{\frac{1}{2}} [j_{k+1} Y_{k+1} \times \vec{\ell}]_m^k + (\frac{k}{2k+1})^{\frac{1}{2}} [j_{k-1} Y_{k-1} \times \vec{\ell}]_m^k]$	0	k	k

^aIn these expressions j_k is taken to be the spherical bessel function whose argument is $q \cdot r$, where r is the magnitude of the position vector.

Table 2. (Continued)

Operator ^a	Expression as a Tensor Product	Rank in the spin space	Rank in the orbital space	Rank in the space spanned by eigenvectors of $j+l+S$
$\vec{s} \cdot \nabla \times \{ \vec{\ell}(j_k Y_{km}) \}$	$i q \sqrt{k(k+1)} \left(-\left(\frac{k}{2k+1}\right)^{\frac{1}{2}} [\vec{s} \times j_{k+1} Y_{k+1}]_m^k + \left(\frac{k+1}{2k+1}\right)^{\frac{1}{2}} [\vec{s} \times j_{k-1} Y_{k-1}]_m^k \right)$	1	k+1 and k-1	k
$(\vec{s} \times \vec{r}) \cdot \vec{\ell}(j_k Y_{km})$	$i r \sqrt{k(k+1)} \left[\left(\frac{k}{2k+1}\right)^{\frac{1}{2}} [\vec{s} \times j_k Y_{k+1}]_m^k + \left(\frac{k+1}{2k+1}\right)^{\frac{1}{2}} [\vec{s} \times j_k Y_{k-1}]_m^k \right]$	1	k+1 and k-1	k
$\vec{s} \cdot \vec{r} j_k Y_{km}$	$ \vec{r} \left[-\left(\frac{k+1}{2k+1}\right)^{\frac{1}{2}} [\vec{s} \times j_k Y_{k+1}]_m^k + \left(\frac{k}{2k+1}\right)^{\frac{1}{2}} [s \times j_k Y_{k-1}]_m^k \right]$	1	k+1 and k-1	k

lists many of these operators and gives expressions for them as tensor products.

The advantage of expressing operators as spherical tensors can be clearly seen from the Wigner Eckart theorem

$$\langle j_1 m_1 | T_{kq} | j_2 m_2 \rangle = (-)^{j_1 - m_1} \begin{pmatrix} j_1 & k & j_2 \\ -m_1 & q & m_2 \end{pmatrix} \langle j_1 || T_k || j_2 \rangle, \quad (65)$$

where $\langle j_1 || T_k || j_2 \rangle$ is a reduced matrix element which is independent of any magnetic quantum numbers. Thus all dependence on the azimuthal component of angular momentum can be factored into the 3-j symbol. Also, the 3-j symbol in Equation 65 contains all the angular momentum selection rules for the matrix element. Several of the reduced angular matrix elements of operators used in this work are given below:

$$\langle \ell' || \vec{r} || \ell \rangle = [(2\ell+1)\ell(\ell+1)]^{\frac{1}{2}} \delta(\ell', \ell) \quad (66a)$$

$$\langle \frac{1}{2} || s || \frac{1}{2} \rangle = [\frac{1}{2} \cdot \frac{3}{2} \cdot 2]^{\frac{1}{2}} = \sqrt{\frac{3}{2}} \quad (66b)$$

$$\langle \ell || Y_k || \ell \rangle = (-)^{\ell} (2\ell+1) \left[\frac{2k+1}{4\pi} \right]^{\frac{1}{2}} \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}$$

$$\langle \ell || [Y_{k'} \times \vec{r}]^k || \ell \rangle = (2k+1)^{\frac{1}{2}} (-)^{k+\ell} \begin{pmatrix} k & 1 & k' \\ \ell & \ell & \ell \end{pmatrix} \begin{pmatrix} \ell & k' & \ell \\ 0 & 0 & 0 \end{pmatrix} \times \quad (66c)$$

$$(2\ell+1) \left[\frac{(2k'+1)(2\ell+1)(\ell+1)\ell}{4\pi} \right]^{\frac{1}{2}}$$

$$\langle \frac{1}{2} || 1 || \frac{1}{2} \rangle = \sqrt{2} \quad (66d)$$

Atomic Structure

In the expose of Racah algebra which has been presented, only eigenstates of angular momentum operators have been considered and no mention has been made of the wavefunction of a many electron atom. Before the wavefunction of a many electron atom can be discussed, some understanding of the atomic Hamiltonian and the central field approximation must be obtained.

The exact form of the relativistic Hamiltonian for a many electron atom is a problem that is far from solved. In Chapter II, we assumed that the relativistic atomic Hamiltonian could be written as a sum of one electron Dirac Hamiltonians and that the interaction between the electrons could be approximated by the Breit interaction (see Equations 46 and 47).

To order $(Z\alpha)^2$, the nonrelativistic limit of this Hamiltonian is³⁴

$$H_{nr} = H_C + H_P + H_{MC} + H_{DAR} + H_{SO} + H_{BP} \quad (67.a)$$

where the nonrelativistic contributions we will consider later are given by

$$H_C = \sum_i \left[\frac{\vec{p}_i^2}{2m} - e U(r_i) \right], \quad (67.b)$$

$$H_{MC} = -\sum_i \frac{\vec{p}_i^4}{8m^3 c^2}, \quad (67.c)$$

$$H_{SO} = \sum_i \xi(r_i) \vec{\ell}_i \cdot \vec{s}_i, \quad (67.d)$$

and the sums are over the electrons of the atom. In this equation, H_C is the central field Hamiltonian, H_P is a perturbing Hamiltonian which

includes the effects of a nonaveraged potential, H_{MC} is the mass correction term, H_{DAR} is the Darwin term, H_{SO} is the spin orbit term and

$$H_{BP} = H_{soo} + H_{oo} + H_{ss}$$

is the Breit-Pauli term which contains the spin-other-orbit (H_{soo}), orbit-orbit (H_{oo}), and spin-spin (H_{ss}) interactions. Also $U(r_i)$ is a spherically averaged potential, and $\xi(\vec{r}_i)$ is the spin-orbit coupling constant.

The solutions of the relativistic and nonrelativistic Hamiltonians (Equations 67 and 46, respectively) will be obtained in the central field approximation. The postulates of the central field approximation are the same for both relativistic and nonrelativistic calculations. Each electron is visualized as moving in the potential produced by all the other electrons of the atom. The potential is assumed to be spherically symmetric, which has the consequence that the wavefunction of a single electron can be factorized into a radial and angular part. This means that nonrelativistically the one electron wavefunction can be written as

$$|n \frac{1}{2} \ell m_s m_\ell \rangle = f_{n\ell}(r) Y_{\ell m_\ell}(\vec{r}) \chi_{m_s}^{\frac{1}{2}} \quad (68)$$

where $f_{n\ell}(r)$ is a radial electronic wavefunction, and $\chi_{m_s}^{\frac{1}{2}}$ is a Pauli spin matrix. Relativistically, the one electron states can be written as,

$$|n\ell jm_m\rangle = \begin{pmatrix} \frac{F_{n\ell j}(r)}{r} |n\ell jm_j\rangle \\ i \frac{G_{n\ell j}(r)}{r} |\bar{n}\ell jm_j\rangle \end{pmatrix}, \quad (69a)$$

where the radial wavefunctions F and G satisfy

$$\left(\frac{d}{dr} + \frac{\chi}{r}\right)G(r) = -\frac{1}{\hbar c}(-E + mc^2 + eU(r))F(r) \quad (69b)$$

$$\left(\frac{d}{dr} - \frac{\chi}{r}\right)F(r) = -\frac{1}{\hbar c}(E + mc^2 - eU(r))G(r)$$

and they are normalized by

$$\int_0^\infty (F^2(r) + G^2(r))dr = 1. \quad (69c)$$

In these equations, $U(\vec{r})$ is the average potential in which the electron moves, E is the energy, $\vec{\ell} = 2j - \vec{s}$, and the angular portion of the wavefunction can be written as

$$| \ell j m_j \rangle = \sum_{m_s m_\ell} \begin{pmatrix} \frac{1}{2} & \ell & j \\ m_s & m_\ell & -m_j \end{pmatrix} (-)^{\frac{1}{2} - \ell - m_j} \sqrt{2j+1} Y_{\ell m_\ell}(\hat{r}) \chi_{m_s}^{\frac{1}{2}} \quad (70)$$

where $\chi_{m_s}^{\frac{1}{2}}$ is a Pauli spin matrix. Finally, the last tenet of the central field approximation is that the electrons obey the Pauli exclusion principle so that no two electrons can have the same quantum numbers and their total wavefunction is antisymmetric with respect to the simultaneous permutation of the spin and spatial coordinates of any pair of electrons. To satisfy the Pauli exclusion principle, the many electron wavefunctions are constructed from the one electron solutions (Equations 68 and 69a) by constructing the Slater determinantal product states

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\alpha^1) & \phi_2(\alpha^1) & \dots & \phi_N(\alpha^1) \\ \phi_1(\alpha^2) & \phi_2(\alpha^2) & \dots & \phi_N(\alpha^2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\alpha^N) & \phi_2(\alpha^N) & \dots & \phi_N(\alpha^N) \end{vmatrix} \quad (71)$$

where ϕ are one electron wavefunctions (Equations 68 and 69a) and α^i represents the quantum numbers of the i^{th} electron.

It is well known that the many electron wavefunctions which are solutions of the atomic Hamiltonian in the central field approximation can be broken into configurations; a configuration being a group of electrons whose quantum numbers differ only in the magnetic quantum number m . Most atomic calculations are performed in the LS coupling scheme[†] in which the spin and orbital momentum of electrons in a configuration are separately coupled to give $\vec{L}$ and $\vec{S}$, respectively. These are in turn coupled to give a total angular momentum $\vec{J}$ and projection M . The atomic wavefunctions are then expanded in terms of the Russell-Saunders states which have quantum numbers S , L , J and M . These Russell-Saunders states can be written in terms of the one electron wavefunctions by constructing linear combinations of the Slater determinants.¹² However, if there are three or more electrons in the configuration, there may be more than one linear combination of Slater determinants which gives the quantum numbers L , S , J and M .⁵¹ Thus to uniquely label a state we must find additional quantum numbers.

Racah⁵⁰ has shown that a systematic classification of the Russell-Saunders states may be given using group theory. The way in which a particular state transforms under the operations of a group, can be labeled by the irreducible representations of the group. These irreducible representations then play the role of the additional quantum numbers

[†]See for example Wybourne.⁵¹

needed to uniquely specify the state. Using this scheme to classify the atomic states produces a great simplification in the evaluation of matrix elements.

Classification of States

In Racah's classification scheme the shell, rather than the configuration, is treated as the basic unit of atomic structure. Judd⁵² has recognized that the structure of the shell can be elucidated using second quantization, because the atomic creation and annihilation operators enable one to pass freely from configuration to configuration. Thus to understand the classification of the atomic states, an introduction to second quantization will be presented and groups will be formed from the atomic creation and annihilation operators. Throughout this section we will limit our discussion to the classification of LS states of the l^n configuration. A LS state $|\tau S L M_S M_L\rangle$ is related to a Russell-Saunders state $|\tau S L J M\rangle$ by the coupling transformation,

$$|\tau S L J M\rangle = (-)^{L-S-M} \sum_{m_1 m_2} (2J+1)^{\frac{1}{2}} \begin{pmatrix} S & L & J \\ M_S & M_L & M \end{pmatrix} |\tau S L M_S M_L\rangle \quad (72)$$

where τ represents the additional quantum numbers which we are seeking.

The basic idea of the second quantization method is to transfer to operators the properties that are ordinarily thought of as being characteristic of eigenfunctions. To do this we define the creation operator for the single particle nonrelativistic and relativistic states as

$$a^+(n\frac{1}{2}l m_s m_l) |0\rangle = |n\frac{1}{2}l m_s m_l\rangle \quad (73)$$

and

$$q^+(n\frac{1}{2}l j m) |0\rangle = |n\frac{1}{2}l j m\rangle$$

respectively, where $|0\rangle$ and $|0\rangle$ both denote the vacuum state. Taking the adjoints of both sides of these equations leads to a set of equations for the annihilation operators,

$$\langle 0 | a(n\frac{1}{2}l m_s m_l) = \langle n\frac{1}{2}l m_s m_l |$$

and

$$\langle 0 | q(n\frac{1}{2}l m_s m_l) = \langle n\frac{1}{2}l j m |$$

Anticommutation relations exist for the creation and annihilation operators. Since the many electron wavefunction (Equation 71) is written as a determinant which changes sign if two rows or columns are interchanged, the creation and annihilation operators must satisfy anticommutation relations,

$$[a^+(n\frac{1}{2}l m_s m_l), a^+(n'\frac{1}{2}l' m'_s m'_l)]_+ = 0 \quad (74)$$

$$[a(n\frac{1}{2}l m_s m_l), a(n'\frac{1}{2}l' m'_s m'_l)]_+ = 0$$

for the nonrelativistic case and

$$[q^+(n\frac{1}{2}l j m), q^+(n'\frac{1}{2}l' j' m')]_+ = 0$$

$$[q(n\frac{1}{2}l j m), q(n'\frac{1}{2}l' j' m')]_+ = 0$$

for the relativistic case. If the antisymmetric many electron

wavefunctions are to be normalized, we must require that

$$[a^+(n\frac{1}{2}l m_s m_l), a(n'\frac{1}{2}l' m'_s m'_l)]_+ = \delta(n, n') \delta(l, l') \delta(m_s, m'_s) (m_l m'_l) \quad (75)$$

and

$$[q^+(n\frac{1}{2}l j m), q(n'\frac{1}{2}l' j' m')]_+ = \delta(n, n') \delta(l, l') \delta(m_s, m'_s) (m_l m'_l) .$$

As expected there is a great deal of similarity in the structure of the anticommutation relations for both relativistic and nonrelativistic creation and annihilation operators. The structure of the algebra for relativistic and nonrelativistic creation and annihilation operators can be made identical by defining a relativistic one electron sl state by the equation

$$|n\frac{1}{2}l m_s m_l\rangle = \sum_{jm} \sqrt{2j+1} \quad (-)^{l-\frac{1}{2}-m} \begin{pmatrix} \frac{1}{2} & l & j \\ m_s & m_l & -m \end{pmatrix} |n\frac{1}{2}l j m\rangle \quad (76)$$

Such an expansion is equivalent to ignoring the small components of the states $|n\frac{1}{2}l j m\rangle$. Since it has the proper nonrelativistic limit for the expansion from the states $|sl j m\rangle$ to $|sl m_s m_l\rangle$, the definition can be justified as reasonable and meaningful in the nonrelativistic limit.

A relativistic creation operator $a^+(n\frac{1}{2}l m_s m_l)$ for the sl state given in Equation 76, can be correspondingly defined

$$a^+(n\frac{1}{2}l m_s m_l) = \sum_{jm} \sqrt{2j+1} \quad (-)^{l-\frac{1}{2}-m} \begin{pmatrix} \frac{1}{2} & l & j \\ m_s & m_l & -m \end{pmatrix} q^+(n\frac{1}{2}l j m). \quad (77)$$

Utilizing this definition, it may be shown that the relativistic creation operator $a^+(n\frac{1}{2}l m_s m_l)$ satisfies exactly the same commutation relations as

the nonrelativistic creation operator for sl states (Equation 73). Thus we can proceed to study the algebra formed by the creation operators for sl states without regard to whether they are relativistic or non-relativistic.

The basic tensoral properties of the creation and annihilation operators for sl states can be seen by investigating their commutation with the operators $\vec{L}$ and $\vec{S}$. One can easily show that

$$[L_z, a^+(n\frac{1}{2}l m_s m_l)] = m_l a^+(n\frac{1}{2}l m_s m_l)$$

$$[L_{\pm}, a^+(n\frac{1}{2}l m_s m_l)] = \sqrt{l(l+1) - m_l(m_l \pm 1)} a^+(n\frac{1}{2}l m_s m_{l \pm 1})$$

and

(78)

$$[S_z, a^+(n\frac{1}{2}l m_s m_l)] = m_s a^+(n\frac{1}{2}l m_s m_l)$$

(79)

$$[S_{\pm}, a^+(n\frac{1}{2}l m_s m_l)] = \sqrt{\frac{3}{4} - m_s(m_s \pm 1)} a^+(n\frac{1}{2}l m_{s \pm 1} m_l)$$

Comparing these equations with the commutation relations used to define a spherical tensor operator (Equations 63) it is seen that the $a^+(n\frac{1}{2}l m_s m_l)$ form the components of a spherical of rank l in the orbital space and the components of a spherical tensor of rank $\frac{1}{2}$ in the spin space. Since the creation operators $a^+(n\frac{1}{2}l m_s m_l)$ are components of spherical tensors in the spin and orbital spaces, they can be coupled using their tensoral properties,

$$[a^+(n\frac{1}{2}l), a(n\frac{1}{2}l)]_{m'm''}^{k'k''} = \sum_{\substack{m_s, m_l \\ m'_s, m'_l}} \begin{pmatrix} l & l & k'' \\ m_l & -m'_l & -m'' \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & k' \\ m_s & -m'_s & -m' \end{pmatrix} \quad (80)$$

$$\times [k', k'']^{\frac{1}{2}} (-)^{m''+m'+m'_s+m'_l+\frac{1}{2}+l} a^+(n\frac{1}{2}l m_s m_l) a(n\frac{1}{2}l m'_s m'_l),$$

where $[k', k'']$ stands for $(2k'+1)(2k''+1)$. The right hand side of this equation can be rewritten as

$$- \sum_{\substack{m_s m_l \\ m'_s m'_l}} a^+(n\frac{1}{2}l m_s m_l) [n\frac{1}{2}l m_s m_l | w_{m'm''}^{(k', k'')} | n\frac{1}{2}l m'_s m'_l] a(n\frac{1}{2}l m_s m_l) \quad (81)$$

where $[]$ stands for $\langle \rangle$ or $()$ and $w_{m'm''}^{(k', k'')}$ are the components of single particle Racah double tensors. The single particle Racah double tensors are defined by their reduced matrix elements as

$$[n\frac{1}{2}l || w^{(k', k'')} || n\frac{1}{2}l'] = [k', k'']^{\frac{1}{2}} \delta(l, l').$$

To understand the nature of these double tensors, we introduce unit tensors $t^{k'}$ and $v^{k''}$ which act in the spin and orbital spaces, respectively, of a single electron. The unit tensors are defined by their reduced matrix elements

$$(s || t^{k'} || s') = (2k'+1)^{\frac{1}{2}} \delta(s, s') \quad (82a)$$

$$(l || v^{k''} || l') = (2k''+1)^{\frac{1}{2}} \delta(l, l').$$

The $(2k'+1)(2k''+1)$ products

$$w_{m' m''}^{(k', k'')} = t_{m'}^{k'} v_{m''}^{k''} \quad (-k' \leq m' \leq k'; -k'' \leq m'' \leq k'') \quad (82b)$$

are the components of the double tensors defined in Equation 81. Thus, the double tensors $w^{(k', k'')}$ are tensors of rank k' and k'' in the spin and orbital spaces, respectively. Using the single particle operator $w_{m' m''}^{(k', k'')}$ defined by Equation 81, we can define one particle operators

$$W_{m' m''}^{(k', k'')} = \sum_i w_{m' m''}^{(k', k'')} \quad (i) \quad (82c)$$

where the sum is over the electrons of the ℓ^N configuration and the tensors $W^{(k', k'')}$ will be referred to as the Racah double tensors. The Racah double tensors play a central role in the theory of atomic structure. They are simply related to the generators of the groups used to classify the atomic states, and thus the matrix elements of the Racah double tensors are considerably simplified by symmetry properties.

Also, by virtue of Equation 81 the tensor product $[a^+(n \frac{1}{2} \ell), a(n \frac{1}{2} \ell)]_{m_k m_k}^{k k}$ can be considered to be the second quantized form of the Racah double tensors.

To ascertain which groups can be used to classify the atomic states, the structure of Lie algebras must be briefly reviewed. Lie⁵³ studied the properties of groups for which all elements could be generated from transformations which are infinitesimally different from the identity transformation. All operators in the group can then be expanded in the form

$$S_\alpha = 1 + \sum_\sigma \delta a^\sigma \chi_\sigma$$

where δa^σ are parameters and x_σ are the infinitesimal generators of the group. The generators satisfy the commutation relations

$$[x_\alpha, x_\beta] = \sum_\gamma c(\alpha, \beta, \gamma) x_\gamma \quad (83)$$

and the basic structure of the group is determined by the constants $c(\alpha, \beta, \gamma)$. The commutation relations in Equation 83 are much too general for determining groups which are useful in classifying the atomic states, so we will restrict our attention to groups for which the infinitesimal operators can be divided into two types $H_1, H_2, \dots, H_\ell$ and $E_\alpha, E_\beta, \dots, E_\gamma$, satisfying the commutation relations

$$\begin{aligned} [H_i, H_j] &= 0 \\ [H_i, E_\alpha] &= \alpha_i E_\alpha \\ [E_\alpha, E_\beta] &= c(\alpha, \beta, \alpha+\beta) E_{\alpha+\beta} \quad (\beta \neq -\alpha) \end{aligned} \quad (84)$$

and

$$[E_\alpha, E_{-\alpha}] = \sum_i \alpha_i H_i.$$

Cartan⁵⁴ has showed that with only five exceptions, the simple groups fall into four general classes: special unitary groups, rotation groups in an even number of dimensions, rotation groups in an odd number of dimensions, and symplectic groups. The numbers $(\alpha_1, \alpha_2, \dots, \alpha_\ell)$ form the components of a vector in an ℓ dimensional space which is called a root. Cartan⁵⁴, Van der Warden⁵⁵, and Racah⁵⁶ have catalogued the root figures of simple groups which can be used to identify groups formed from the creation and annihilation operators.

To identify the groups useful in the classification of $(n \ell^N)$ configurations, let us restrict our attention to the set of all creation and annihilation operators possessing identical values of n and ℓ . For a fixed value of n and ℓ there are $8\ell+4$ such operators, however they are not the generators of a group, because they are not closed with respect to commutation. If the $(4\ell+2)(8\ell+3)$ distinct nonzero commutations are added to the set of creation and annihilation operators, the group is closed with respect to commutation. The commutators $\frac{1}{2}[a^+(\alpha), a^+(\beta)]$, $\frac{1}{2}[a(\alpha), a(\beta)]$ and $\frac{1}{2}[a^+(\alpha), a(\beta)]$ (for $\alpha \neq \beta$), can be replaced by $a^+(\alpha)a^+(\beta)$, $a(\alpha)a(\beta)$ and $a^+(\alpha)a(\beta)$ owing to Equation 74, giving the set of operators:

$$\begin{aligned} &[a^+(\alpha), a(\alpha)], \quad a^+(\alpha)a(\beta) \quad (\alpha \neq \beta), \quad a^+(\alpha)a^+(\beta), \quad a(\alpha)a(\beta), \\ &a^+(\alpha) \text{ and } a(\alpha) \end{aligned} \quad (85)$$

where $\alpha = (n \frac{1}{2} \ell m_s m_\ell)$ and $\beta = (n \frac{1}{2} \ell' m'_s m'_\ell)$.

Judd⁵⁷ has shown that the group corresponding to this augmented set of operators can be found by first selecting the operators

$$H_\alpha = \frac{1}{2}[a^+(\alpha), a(\alpha)]$$

so that

$$\begin{aligned} [H_\alpha, a^+(\beta)] &= \delta(\alpha, \beta) a^+(\beta) \\ [H_\alpha, a(\beta)] &= -\delta(\alpha, \beta) a(\beta) \\ [H_\alpha, a^+(\beta)a^+(\gamma)] &= \{\delta(\alpha, \beta) + \delta(\alpha, \gamma)\} a^+(\beta)a^+(\gamma) \\ [H_\alpha, a(\beta)a(\gamma)] &= -\{\delta(\alpha, \beta) + \delta(\alpha, \gamma)\} a(\beta)a(\gamma) \\ [H_\alpha, a^+(\beta)a(\gamma)] &= \{\delta(\alpha, \beta) - \delta(\alpha, \gamma)\} a^+(\beta)a(\gamma) \end{aligned} \quad (86)$$

The root figure formed by these equations can be identified as belonging to the proper rotation group in $8l+5$ dimensions, $R(8l+5)$.

A subgroup of this group can easily be found by discarding the creation and annihilation operators $a^+(\alpha)$ and $a(\alpha)$ from the set in Equation 85. The remaining operators are closed with respect to commutation and the root figure of the group can again be found by identifying $H_\alpha = \frac{1}{2}[a^+(\alpha), a(\alpha)]$ and $E = (a^+(\alpha) a(\beta) (\alpha \neq \beta), a^+(\alpha) a^+(\beta) \text{ and } a(\alpha) a(\beta))$ as in Equations 85 and 86. The resulting subgroup can be identified as another proper rotation group, $R(8l+4)$. Since the operators $a^+(\alpha) a^+(\beta)$ and $a(\alpha)a(\beta)$ connect configurations differing in two electrons or none, the classification scheme is automatically broken up into sets of configurations $(nl)^N$ with N odd and even. No operator of $R(8l+4)$ can connect members of these two different sets, and it follows that by eliminating the operators $a^+(\alpha)a^+(\beta)$ and $a(\alpha)a(\beta)$ leaving only those of the type $\frac{1}{2}[a^+(\alpha), a(\beta)]$ and $a^+(\alpha)a(\beta) (\alpha \neq \beta)$, another subgroup can be found. This subgroup is $U(4l+2)$ and the commutation relations that the operators of the group satisfy can be written very concisely in terms of the tensor products $[a^+a]^{\kappa k}$ (see Equation 79). These tensor products of the creation and annihilation operators are the second quantized form of the Racah double tensor $W^{(\kappa, k)}$ and are thus the generators of the group $U(4l+2)$. The commutation relation obeyed by the Racah tensors is

$$[W_{\pi q}^{(\kappa k)}, W_{\pi' q'}^{(\kappa k)}] = \sum (-)^{1+\pi''+q''} \{(-)^S - 1\} [\kappa, \kappa', \kappa'', k, k', k'']^{\frac{1}{2}} W_{\pi'' q''}^{(\kappa'' k'')} \quad (87)$$

$$\left\{ \begin{matrix} \kappa & \kappa' & \kappa'' \\ s & s' & s'' \end{matrix} \right\} \left\{ \begin{matrix} k & k' & k'' \\ \ell & \ell' & \ell'' \end{matrix} \right\} \begin{pmatrix} \kappa & \kappa' & \kappa'' \\ \pi & \pi' & -\pi'' \end{pmatrix} \begin{pmatrix} k & k' & k'' \\ q & q' & -q'' \end{pmatrix}$$

where $S = \kappa + \kappa' + \kappa'' + k + k' + k''$ and the sum is performed over all double primed quantities. The group $U(4\ell+2)$ is not particularly useful in classifying the atomic states, however a subgroup $Sp(4\ell+2)$ generated by the Racah tensors $W^{(\kappa k)}$ with $\kappa+k$ odd is particularly useful. From the commutation relations in Equation 87, we can see that there is a natural separation between the subgroups of $U(4\ell+2)$ formed by $W^{(\kappa k)}$ with $\kappa+k$ odd and even.

Thus far we have shown that $U(4\ell+2)$ and $Sp(4\ell+2)$ are subgroups of $R(8\ell+4)$ which can be used to classify the atomic states. Another useful subgroup of $R(8\ell+4)$ is the group $R_Q(3)$, having the generators,

$$Q_+ = \left(\frac{[\ell]}{2} \right)^{\frac{1}{2}} [a^+(n\frac{1}{2}\ell) a^+(n\frac{1}{2}\ell)]^{oo},$$

$$Q_- = -\left(\frac{[\ell]}{2} \right)^{\frac{1}{2}} [a(n\frac{1}{2}\ell) a(n\frac{1}{2}\ell)]^{oo}, \quad (88)$$

$$Q_z = -\left(\frac{[\ell]}{8} \right)^{\frac{1}{2}} \{ [a^+(n\frac{1}{2}\ell) a(n\frac{1}{2}\ell)]^{oo} + [a(n\frac{1}{2}\ell) a^+(n\frac{1}{2}\ell)]^{oo} \}.$$

The vector $\vec{Q}$ formed by (Q_+, Q_-, Q_z) is called the quasispin. By direct calculation it may be shown that

$$[\vec{Q}, W^{(\kappa k)}] = 0 \quad (\kappa+k) = \text{odd},$$

and thus the direct product group $R_Q(3) \times Sp(4\ell+2)$ is a subgroup of

$R(8\ell+4)$.

We want to find subgroups of the direct product group which separate the spin and orbital spaces. To do this we follow Judd⁵⁸ and Armstrong⁵⁹ and find subgroups of $Sp(4\ell+2)$ by selecting two subsets of the Racah tensors; $W^{(1,0)}$ and $W^{(0,k)}$. The Racah tensor $W^{(1,0)}$ has rank 1 in the spin space and rank 0 in the orbital space. The Racah tensors $W^{(0,k)}$ have rank 0 in the spin space and rank k in the orbital space. It can be simply shown that

$$[W^{(1,0)}, W^{(0,k)}] = 0,$$

and that $W^{(1,0)}$ and $W^{(0,k)}$ are the generators of the groups $R_S(3)$ and $R(2\ell+1)$, respectively. Thus the direct product group $R_Q(3) \times R_S(3) \times R(2\ell+1)$ is a subgroup of which separates the spin and orbital spaces. It may also be shown that the group $R_L(3)$ generated by $W^{(0,1)}$ is a subgroup of $R(2\ell+1)$. Thus the complete decomposition of the shell to an individual term is described by

$$\begin{aligned} R(8\ell+5) &\supset R(8\ell+4) \supset R_Q(3) \times Sp(4\ell+2) \supset R_Q(3) \times R_S(3) \times R(2\ell+1) \\ &\supset R_Q(3) \times R_S(3) \times R_L(3). \end{aligned} \quad (89)$$

There are alternative ways in which this decomposition can be performed. For the case of f electrons an unexpected simplification in the chain of decomposition occurs. From the general commutation relation for the group $Sp(4\ell+2)$ (Equation 87 with $\kappa+k$ odd), we would expect the commutator of two components of $W^{(0,5)}$ to yield components of tensors $W^{(0,k')}$ for which $k' = 1, 3, 5$. However, the 6-j symbol

$$\begin{Bmatrix} 5 & 5 & 3 \\ 3 & 3 & 0 \end{Bmatrix} = 0 ,$$

and all terms for which $k'' = 3$ disappear. This allows a group to be formed from the operators $W^{(05)}$ and $W^{(01)}$. The group can be identified as the special group G_2 , and for f electrons we can use the more detailed decomposition $R(7) \supset G_2 \supset R_L(3)$.

To use the chain of decompositions given in Equation 89 to classify the atomic states, the concept of a representation and basis function must be introduced. A set of functions are said to form a basis for a group if any operator of the group acting on the functions produces another function (or sum of functions) from the set. A representation can be thought of as a group of matrices or linear transformations which correspond to the abstract group elements. To construct a representation, the action of a set of group generators on a set of basis states must be catalogued, and a label given to the representation. By treating the atomic states as a set of basis states for the decomposition given in Equation 89 we can label the atomic states according to the irreducible representations of the groups.

The representations of the groups $R_S(3)$ and $R_L(3)$ can be described by the quantum numbers S and L , respectively. The atomic states transform according to representations of $R(2\ell+1)$ and $Sp(4\ell+2)$ which are standardly denoted by the symbol W and the integer v , respectively. The integer number v is called the seniority. The irreducible representation of the group $R_Q(3)$ is described by the single quantum

number, Q , called the quasispin of the state. It can be shown that the quasispin contains the same information as v and N because

$$Q = \frac{1}{2} (2\ell + 1 - v)$$

and the z projection of the quasispin is related to the number of electrons in the state, N , by

$$M_Q = -\frac{1}{2} (2\ell + 1 - N).$$

The groups $R(8\ell + 5)$ and $R(8\ell + 4)$ describe the shell and are of little use in labeling an individual term. For the special case of f electrons, the representation, U , of the group G_2 can be used to label the LS states.

In Table 3, this classification scheme has been applied to the LS states, $|\theta\rangle$, which are coupled to form the Russell-Saunders states $|\theta JM\rangle$ of the tripositive ions (see Equation 72). The LS states of ions with $N > 7$ were labeled using the rule that states of the configuration ℓ^N form bases of the same representation as those of $\ell^{4\ell+2-N}$ with one exception: M_Q must be changed to $-M_Q$. These same labels can of course be used to uniquely specify the Russell-Saunders states constructed from the LS states.

Matrix Elements of Racah Double Tensors

The Racah double tensors $W_{m' m''}^{(k', k'')}$, used to classify the LS states were shown to be a product of unit tensors having a rank k'' in the orbital space defined by the operator $\vec{L} = \sum_i \ell_i$, and a rank k' in the spin space defined by the operator $\vec{S} = \sum_i s_i$. In forming the Russell-Saunders states from the LS states, the spin and orbital spaces were coupled to form eigenstates of the operator $\vec{J} = \vec{L} + \vec{S}$. For calculations in the space

Table 3. Classification of the Hunds rule ground states of rare earth ions

Ion	Configuration	LS Ground State	v	Q	M_Q	W	U
Ce ³⁺	f ¹	² F	1	3	-3	(100)	(10)
Pr ³⁺	f ²	³ H	2	5/2	-5/2	(110)	(11)
Nd ³⁺	f ³	⁴ I	3	2	-2	(111)	(20)
Pm ³⁺	f ⁴	⁵ I	4	3/2	-3/2	(111)	(20)
Sm ³⁺	f ⁵	⁶ H	5	1	-1	(110)	(11)
Eu ³⁺	f ⁶	⁷ F	6	1/2	-1/2	(100)	(10)
Gd ³⁺	f ⁷	⁸ S	7	0	0	(000)	(00)
Tb ³⁺	f ⁸	⁷ F	6	1/2	1/2	(100)	(10)
Dy ³⁺	f ⁹	⁶ H	5	1	1	(110)	(11)
Ho ³⁺	f ¹⁰	⁵ I	4	3/2	3/2	(111)	(20)
Er ³⁺	f ¹¹	⁴ I	3	2	2	(111)	(20)
Tm ³⁺	f ¹²	³ H	2	5/2	5/2	(110)	(11)
Yb ³⁺	f ¹³	² F	1	3	3	(100)	(10)

spanned by the eigenstates of the operator $\vec{J} = \vec{L} + \vec{S}$, we will use the Racah tensors $w_m^{(k', k'') k}$, which are tensor products of the Racah double tensors $w_{m' m''}^{(k', k'')}$ defined in Equations 80-82. This tensor product can be constructed by using the single particle operators $t^{k'}$, $v^{k''}$ and $w_{m' m''}^{(k', k'')}$ (see Equations 81a, 81b, and 81c, respectively) to define an operator

$$w_m^{(k', k'') k} = [w_m^{(k', k'')}]^k = [t^{k'} \times v^{k''}]^k_m, \quad (90)$$

which can be related to a one-particle Racah tensor by

$$w_m^{(k', k'') k} = \sum_i w_m^{(k', k'') k} (i), \quad (91)$$

where the sum is over the electrons of the ℓ^N configuration. The Racah tensor defined in Equations 90 and 91 is a tensor having rank k' in the spin space, k'' in the orbital space and k rank in the space spanned by the eigenstates of the operator $\vec{J} = \vec{L} + \vec{S}$. It may be shown that the tensors $w_m^{(0,1)1}$ and $w_m^{(1,0)1}$ are proportional to the operators L and S of the atom

$$w_m^{(0,1)1} = \left[\frac{3}{2\ell(\ell+1)(2\ell+1)} \right]^{\frac{1}{2}} L_m,$$

$$w_m^{(1,0)1} = \left[\frac{2}{2\ell+1} \right]^{\frac{1}{2}} S_m.$$

The matrix elements of the Racah tensors $w_m^{(k', k'') k}$ between Russell-Saunders states $|0JM\rangle$, are related to the matrix elements of the Racah double tensors by the generalized Wigner Eckart theorem,

$$\begin{aligned}
 (\theta JM | w_m^{(\kappa', k')} | \theta' J' M') &= (-)^{J-M} \begin{pmatrix} J & k & J' \\ -M & m & M' \end{pmatrix} (\theta J || w^{(\kappa', k')} || \theta' J') \\
 &= (-)^{J-M} [J, k, J']^{\frac{1}{2}} \begin{pmatrix} J & k & J' \\ -M & m & M' \end{pmatrix} \begin{Bmatrix} S & S' & \kappa' \\ L & L' & k' \\ J & J' & k \end{Bmatrix} (\theta || w^{(\kappa', k')} || \theta'), \quad (92)
 \end{aligned}$$

where $|\theta\rangle$ is a LS state. Thus the evaluation of matrix elements of Racah tensors $w_m^{(\kappa', k')}$ between Russell-Saunders states can be reduced to the calculation of reduced matrix elements of Racah double tensors $w^{(\kappa', k')}$ between LS states.

It has been shown that the Racah double tensors are the generators of the groups $R_S(3)$, $R_L(3)$, $Sp(4l+2)$ and $R(2l+1)$, used to classify the LS states. Selection rules based on group properties will then exist for their matrix elements. To see how these selection rules arise we consider two states ψ_A and ψ_B which form a basis labeled by representations Γ_A and Γ_B , respectively, of some group G . For an operator, O_C , which transforms according to a representation Γ_C , the matrix element $\langle \psi_A | O_C | \psi_B \rangle$ will vanish unless the Kronecker product⁵⁸,

$$\Gamma_A \times \Gamma_B = \sum_S c(A, B, S) \Gamma_S, \quad (93)$$

contains Γ_C with a nonzero coefficient, $c(A, B, C)$.

The selection rules resulting from the application of this theorem to matrix elements of Racah double tensors between LS states, have been given in Table 4.

In Table 4, v , W , U (or v' , W' , U') denote the seniority, the

Table 4. Selection rules for the matrix element $\langle SLM_S M_L | W_{m m'}^{(\kappa, k')} | S' L' M'_S M'_L \rangle (\kappa = 0, 1; k' = \text{even})$

	R(3)	Sp(4l+2)	R(2l+1)	G ₂ (f-electrons)
$W_{m m'}^{(0, k)}$	$M_L = m' + M'_L$ $M_S = m + M'_S$ $ L-L' \leq k \leq L+L'$ $S' = S$	$v' = v$ if $k = \text{odd}$ } $v' = v, v \pm 2$ if $k = \text{even}$ }	$W' = W$ if $k = \text{odd}$ } $c(WW'W'') \neq 0$ if $k = \text{even}$ }	$W(X, 2), W(X, 4), W(X, 6) \quad c(UU' (20)) \neq 0$ $W(X, 1), W(X, 5) \quad c(UU' (11)) \neq 0$ $W(X, 3) \quad c(UU' (10)) \neq 0$
$W_{m m'}^{(1, k')}$	$M_S = m' + M'_L$ $M_S = m + M'_S$ $ L-L' \leq k' \leq L+L'$ $S' = S, S \pm 1$	$v' = v$	$c(WW'W'') \neq 0$	$W(0, 1), W(0, 5) \quad U' = U$

irreducible representation of $R(2\ell+1)$, and the irreducible representation of G_2 which characterize the LS state $|SLM_S M_L\rangle$ (or $|S'L'M_S M_L\rangle$) and, W'' and U'' are the irreducible representations according to which the Racah double tensors transform under the operations of $R(2\ell+1)$ and G_2 , respectively. The selection rules based on the groups $R_S(3)$ and $R_L(3)$ are the familiar angular momentum selection rules. The selection rules based on $Sp(4\ell+2)$ (seniority) are equivalent to the selection rules based on $R_Q(3)$ (quasispin). The selection rules based on the group $R(2\ell+1)$ (or G_2) require a knowledge of the coefficient $C(W, W', W'')$ (or $C(U, U', U'')$), which is the coefficient of the representation W'' (or U'') in the decomposition of the Kronecker product $W \times W'$ (or $U \times U'$). The form of the Kronecker product is given in Equation 93, and it is seen that if the coefficient $C(W, W', W'')$ (or $C(U, U', U'')$ for f electrons) vanishes, the matrix element will be identically equal to zero. For d and f electrons the coefficient $C(W, W', W'')$ (or $C(U, U', U'')$ for f electrons) has been given in Tables 5-7. To use these tables, it must be realized that the tensors $W^{(1, k')}$ and $W^{(0, k)}$, ($k = \text{even}$) transform like the representations (20) and (200) of the groups $R(5)$ and $R(7)$, respectively. By virtue of Equation 92, Tables 4-7 also determine the selection rules for matrix elements of the Racah tensors $W_m^{(\kappa', k')k}$ between Russell-Saunders states.

The selection rules given in Tables 4-7 only determine if a matrix element of a Racah double tensor can be nonzero. The nonvanishing matrix elements between LS states $|\theta\rangle$, can be calculated using the theorem,

Table 5. The coefficients $c(UU'(20))$, $c(UU'(11))$, $c(UU'(10))$

U/U'	(00)	(10)	(11)	(20)	(21)	(30)	(22)	(31)	(40)
(00)		(0,0,1)	(0,1,0)	(1,0,0)					
(10)	(0,0,1)	(1,1,1)	(1,0,1)	(1,1,1)	(1,1,0)	(1,0,0)			
(11)	(0,1,0)	(1,0,1)	(1,1,0)	(1,1,1)	(1,0,1)	(1,1,0)	(0,1,0)	(1,0,0)	
(20)	(1,0,0)	(1,1,1)	(1,1,1)	(2,1,1)	(2,1,1)	(1,1,1)	(1,0,0)	(1,1,0)	
(21)		(1,1,0)	(1,0,1)	(2,1,1)	(2,2,1)	(2,1,1)	(1,0,1)	(2,1,1)	(1,1,0)
(30)		(1,0,0)	(1,1,0)	(1,1,1)	(2,1,1)	(2,1,1)	(1,1,0)	(2,1,1)	(1,1,1)
(22)			(0,1,0)	(1,0,0)	(1,0,1)	(1,1,0)	(1,1,0)	(1,1,1)	(1,0,0)
(31)			(1,0,0)	(1,1,0)	(2,1,1)	(2,1,1)	(1,1,1)	(3,2,1)	(2,1,1)
(40)				(1,0,0)	(1,1,0)	(1,1,1)	(1,0,0)	(2,1,1)	(2,1,1)

Table 6. The coefficients $c(WW'(20))$

W/W'	(00)	(10)	(11)	(20)	(21)	(22)
(00)				1		
(10)		1			1	
(11)			1	1	1	
(20)	1		1	1		1
(21)		1	1		2	1
(22)				1	1	1

Table 7. The coefficients $c(W'(200))$

W/W'	(000)	(100)	(110)	(200)	(111)	(210)	(211)	(220)	(221)	(222)
(000)				1						
(100)		1				1				
(110)			1	1			1			
(200)	1		1	1				1		
(111)					1	1	1			
(210)		1			1	2			1	
(211)			1		1		2	1	1	
(220)				1			1	1		1
(221)						1	1		2	1
(222)								1	1	1

$$\langle \theta \| W^{(k', k'')} \| \theta' \rangle = N[S, S', L, L', k', k'']^{\frac{1}{2}} \sum_{\bar{\theta}} (\theta \| \bar{\theta}) (\theta' \| \bar{\theta}) (-)^{\bar{S} + \frac{1}{2} + S + k' + \bar{L} + L + k''} \times$$

$$\begin{Bmatrix} S & k' & S' \\ \frac{1}{2} & \bar{S} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & k'' & L' \\ \ell & \bar{L} & \ell \end{Bmatrix} \quad (94)$$

where $\bar{\theta} \equiv \overline{\alpha SL}$ defines a term of ℓ^{N-1} and $(\theta \| \bar{\theta})$ is a coefficient of fractional parentage. For most cases of practical interest, the reduced matrix elements of the Racah double tensors, $W^{(0, k)}$ and $W^{(1, k')}$ ($k' = \text{even}$) have been tabulated. For the p^N , d^N and f^N configurations with $N \leq 2\ell+1$, Nielson and Koster⁶⁰ have tabulated the reduced matrix elements of operators $V^{(1, 1)}$ and U^k , which are related to the reduced matrix elements of the Racah double tensors by,

$$\langle \theta \| W^{(1, k)} \| \theta' \rangle = \sqrt{2(2k+1)} \langle \theta \| V^{(1, k)} \| \theta' \rangle$$

and

$$\langle \theta \| W^{(0, k)} \| \theta' \rangle = \sqrt{\frac{(2k+1)(2S+1)}{2}} \langle \theta \| U^k \| \theta' \rangle.$$

The reduced matrix elements of operators U^k and $V^{(k, 1)}$, which are related to the Racah double tensors by

$$\langle \theta \| W^{(1, k)} \| \theta' \rangle = \sqrt{2(2k+1)} \langle \theta \| V^{(k, 1)} \| \theta' \rangle$$

and

$$\langle \theta \| W^{(0, k)} \| \theta' \rangle = \sqrt{\frac{2k+1}{2}} \langle \theta \| U^k \| \theta' \rangle,$$

have been tabulated by Karaziya et al.⁶¹ for the p^N , d^N , f^2 , f^3 and f^4 configurations.

These tabulations of the reduced matrix elements can be used

indirectly to obtain most of the reduced matrix elements needed in a calculation, by using an equation obtained by Judd⁶²:

$$\begin{aligned}
 & \langle \ell^n v_1 \gamma S_1 L \| W^{(1, k')} \| \ell^n v_1 \gamma' S_1' L' \rangle = (-)^{x+2\ell+1+(n'+v_2)/2} (2\ell+2-v_1)^{-\frac{1}{2}} \\
 & \times \begin{pmatrix} \frac{1}{2}(2\ell+1-v_2) & 1 & \frac{1}{2}(2\ell+1-v_2') \\ \frac{1}{2}(2\ell+1-n') & 0 & -\frac{1}{2}(2\ell+1-n') \end{pmatrix}^{-1} \\
 & \langle \ell^{n'} v_2 \gamma S_2 L \| W^{(0, k')} \| \ell^{n'} v_2' \gamma' S_2' L' \rangle,
 \end{aligned}$$

where

$$S_2 = \frac{1}{2}(2\ell+1-v_1),$$

$$v_2 = 2\ell+1-2S_1,$$

$$v_2' = 2\ell+1-2S_1'$$

(95)

and for d and f-electrons

$$x = v_1 + 1 + v_2 \delta(v_2, v_2')$$

In this equation v_1 , v_2 and v_2' are seniorities and n' can have any value for which the states $\langle \ell^{n'} v_2 \gamma S L \rangle$ and $|\ell^{n'} v_2' \gamma' S_2' L' \rangle$ exist. For d and f-electrons (if $v_2 = v_2'$), Equation 95 can be simplified to

$$\begin{aligned}
& \langle \ell^n v_1 \gamma SL \| W^{(1, k')} \| \ell^n v_1 \gamma SL \rangle \\
& = (-)^{v_1 + v_2} \left[\frac{(2\ell + 3 - v_2)(2\ell + 2 - v_2)(2\ell + 1 - v_2)}{(2\ell + 2 - v_1)(2\ell + 1 - n')} \right]^{\frac{1}{2}} \langle \ell^{n'} v_2 \gamma SL \| W^{(0, k)} \| \ell^{n'} v_2 \gamma S_2 L \rangle
\end{aligned} \tag{96}$$

Reduced matrix elements of the Racah double tensors for states in the second half of a shell ($n \geq 2\ell + 1$) can be obtained from those in the first half by using the relation,

$$\begin{aligned}
& \langle \ell^n v SL \| W^{(k', k')} \| \ell^n v' S' L' \rangle \\
& = (-)^{k' + k' + 1 + (v - v')/2} \langle \ell^{4\ell + 2 - n} v SL \| W^{(k', k')} \| \ell^{4\ell + 2 - n} v' S' L' \rangle.
\end{aligned} \tag{97}$$

Using the tables of Nielson and Koster⁶⁰, and Karaziya et al.⁶¹, and Equation 96, the reduced matrix elements of the Racah double tensors needed for the evaluation of the magnetic scattering amplitude of rare earth ions in their ground state, have been tabulated in Table 8. Only the reduced matrix elements for ions with $n \leq 7$ are given because Equation 97 can be used to obtain reduced matrix elements for ions with $14 - n$ electrons. By using Equation 92, this table can be used to obtain the reduced matrix elements of the Racah tensors, calculated between Russell-Saunders ground states of the tripositive rare earth ions.

In the next two chapters we will show that the magnetic scattering amplitude can be expressed in terms of the Racah tensors discussed in this chapter.

Table 8. Reduced matrix elements $\langle 0 \| W(\kappa', k') \| 0 \rangle$ for the ground state of rare earth ions

Ion State	$W(0,1)$	$W(0,3)$	$W(0,5)$	$W(1,0)$	$W(1,2)$	$W(1,4)$	$W(1,6)$
$\text{Ce}^{3+} f^1 2F$	$(3)^{\frac{1}{2}}$	$(7)^{\frac{1}{2}}$	$(11)^{\frac{1}{2}}$	$(3)^{\frac{1}{2}}$	$(15)^{\frac{1}{2}}$	$3(3)^{\frac{1}{2}}$	$(39)^{\frac{1}{2}}$
$\text{Pr}^{3+} f^2 3H$	$(\frac{3}{2}) (\frac{55}{7})^{\frac{1}{2}}$	0	$-(\frac{429}{14})^{\frac{1}{2}}$	$2(\frac{33}{7})^{\frac{1}{2}}$	$(\frac{715}{42})^{\frac{1}{2}}$	$-2(\frac{39}{7})^{\frac{1}{2}}$	$-(\frac{1105}{21})^{\frac{1}{2}}$
$\text{Nd}^{3+} f^3 4I$	$(39)^{\frac{1}{2}}$	$-2(\frac{91}{33})^{\frac{1}{2}}$	$(\frac{442}{33})^{\frac{1}{2}}$	$(\frac{390}{7})^{\frac{1}{2}}$	$(\frac{5}{3}) (\frac{13}{11})^{\frac{1}{2}}$	$-(\frac{2}{11}) (\frac{1105}{3})^{\frac{1}{2}}$	$(\frac{5}{33}) (\frac{41990}{7})^{\frac{1}{2}}$
$\text{Pm}^{3+} f^4 5I$	$(\frac{1}{2}) (195)^{\frac{1}{2}}$	$-(\frac{455}{33})^{\frac{1}{2}}$	$(\frac{1105}{66})^{\frac{1}{2}}$	$2(\frac{195}{7})^{\frac{1}{2}}$	$-(\frac{5}{2}) (\frac{13}{22})^{\frac{1}{2}}$	$(\frac{1}{11}) (\frac{3315}{2})^{\frac{1}{2}}$	$-(\frac{5}{22}) (\frac{20995}{7})^{\frac{1}{2}}$
$\text{Sm}^{3+} f^5 6H$	$3(\frac{55}{14})^{\frac{1}{2}}$	0	$-(\frac{429}{7})^{\frac{1}{2}}$	$(165)^{\frac{1}{2}}$	$-(\frac{143}{6})^{\frac{1}{2}}$	$2(\frac{39}{5})^{\frac{1}{2}}$	$(\frac{221}{3})^{\frac{1}{2}}$
$\text{Eu}^{3+} f^6 7F$	$(\frac{21}{2})^{\frac{1}{2}}$	$7(\frac{1}{2})^{\frac{1}{2}}$	$(\frac{77}{2})^{\frac{1}{2}}$	$2(42)^{\frac{1}{2}}$	$-(\frac{70}{3})^{\frac{1}{2}}$	$-(42)^{\frac{1}{2}}$	$-(\frac{182}{3})^{\frac{1}{2}}$
$\text{Gd}^{3+} f^7 8S$	0	0	0	6	0	0	0

CHAPTER IV. MAGNETIC SCATTERING BY A NONRELATIVISTIC ATOM

In this chapter, the general theory of magnetic scattering developed in Chapter II will be applied to scattering by an unfilled shell of electrons in an atom or ion described by a nonrelativistic Hamiltonian. The theory presented in this chapter will be limited to the case in which the unfilled shell is in the ℓ^n electronic configuration; however, Dr. Stassis and I³⁰ have generalized the formalism to the case of scattering by mixed configurations. The multipole operators will be calculated in the extreme nonrelativistic limit, in which the electronic kinetic energy is the only significant momentum dependent term in the atomic Hamiltonian. The contribution to the multipole operators from the relativistic momentum dependent corrections to the atomic Hamiltonian will only be discussed briefly. To take advantage of the classification scheme for atomic states which was outlined in Chapter III, the multipole operators will be expanded in terms of the Racah tensors. The calculation of matrix elements of multipole operators can then be separated into evaluating matrix elements of the Racah tensors $W^{(0,k)k}$ and $W^{(1,k')k}$ ($k' = \text{even}$), and evaluating radial matrix elements which are coefficients of the Racah tensors in the expansion of the multipole operators.

For the case of elastic scattering by an atom in a single Russell-Sandars state of the ℓ^n configuration, it will be shown that the magnetic scattering amplitude can be written in the conventional form $p(\vec{q}) \vec{q}_m \cdot \vec{\sigma}$. General expressions for the magnetic scattering amplitude

$p(\vec{q})$ will be presented along with expressions for the magnetic form factor. The formalism will be illustrated by applying it to the rare earths.

In Chapter II it was shown that the magnetic scattering amplitude could be expressed quite generally in terms of matrix elements of the multipole operators characterizing the scattering system. It was shown that the magnetic scattering amplitude could be written as

$$f(\vec{q}) = (|\gamma| r_0) \vec{\sigma} \cdot \left[\sum_{k,m} \left(\frac{8\pi}{2k+1} \right)^{\frac{1}{2}} \{ \vec{X}_{km}^*(\hat{q}) \langle f | T_{km}^{(e)} | i \rangle - i (\hat{q} \times \vec{X}_{km}^*(\hat{q})) \langle f | T_{km}^{(m)} | i \rangle \} \right] \quad (27)$$

and that the multipole operators could be written as

$$T_{km}^{(\pi)} = T_{km}^{(\pi)}(0) + \sum_j T_{km}^{(\pi)}(j) \quad , \quad j = 1, 2, \dots \quad (45)$$

where $\pi = e$ or m . The first term in Equation 45 is due to the magnetization current and the convection current associated with the kinetic energy.

An expression for this term was given in Equations B.5 and B.10,

$$\begin{aligned} T_{km}^{(e)}(0) = & i^{k+1} \left(\frac{m}{e\hbar q} \right) \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \sum_i \left[\left\{ \frac{i(E_f - E_i)}{\hbar q} e_i Y_{km}(\hat{r}_i) \frac{d}{dr} (r_i j_k(qr_i)) + \right. \right. \\ & \left. \left. \frac{qe_i}{2m_i} (j_k(qr_i) Y_{km}(\hat{r}_i) \vec{r}_i \cdot \vec{p}_i + \vec{p}_i \cdot \vec{r}_i j_k(qr_i) Y_{km}(\hat{r}_i)) \right\} \right. \\ & \left. - i \frac{g_i e_i \hbar q}{2m_i} \vec{s}_i \cdot \vec{\ell}_i (j_k(qr_i) Y_{km}(\hat{r}_i)) \right] \end{aligned} \quad (B.5)$$

and

$$\begin{aligned} T_{km}^{(m)}(0) = & i^k \left(\frac{m}{e\hbar q} \right) \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \sum_i \frac{e_i \hbar}{m_i} \left[i \nabla (j_k(qr_i) Y_{km}(\hat{r}_i)) \cdot \vec{\ell}_i + \frac{g_i}{2} \vec{s}_i \cdot \nabla \times \right. \\ & \left. \vec{\ell}_i (j_k(qr_i) Y_{km}(\hat{r}_i)) \right] \end{aligned} \quad (B.10)$$

The operators $T_{km}^{\pi}(j)$ in Equation 45 are associated with the convection current due to the momentum dependent terms in the atomic Hamiltonian other than the kinetic energy. Momentum dependent terms in the atomic Hamiltonian (see Equations 67) other than the kinetic energy are due to relativistic effects and will be referred to as relativistic corrections to the atomic Hamiltonian. In light atoms the relativistic corrections to the Hamiltonian produce contributions to the convection current and consequently the multipole operators which are negligible in comparison with that of the kinetic energy. However for the rare earths and other heavy atoms, the largest of the relativistic corrections to the atomic Hamiltonian (in particular the spin-orbit and velocity correction to the electronic mass) can produce a small contribution to the convection current and consequently the multipole operators. In a recent paper²⁹, Dr. Stassis and I have examined these relativistic corrections to the magnetic scattering amplitude and found that for heavy atoms like the rare earths, their contribution is of the order of a few parts per thousand the total magnetic scattering amplitude.

To obtain matrix elements of the multipole operators (Equations B.5, B.10, B.11 and B.12), the atomic states $|JM\rangle$ of the ℓ^n configuration are customarily expanded in terms of Russell-Saunders states $|\theta JM\rangle$,

$$|JM\rangle = \sum_{\theta} a(\theta) |\theta JM\rangle, \quad (98)$$

where $\theta = \alpha SL$ and α stands for any additional quantum numbers such as seniority, quasispin..., needed to specify the state. The magnetic scattering amplitude can then be written as

$$f(\vec{q}) = \sum_{\theta, \theta'} a^*(\theta) a(\theta') f_{\theta' J' M'}^{\theta J M}(\vec{q}), \quad (99)$$

where $f_{\theta' J' M'}^{\theta J M}(\vec{q})$ is the scattering amplitude for the transition $\theta' J' M' \rightarrow \theta J M$ and is given by

$$f_{\theta' J' M'}^{\theta J M}(\vec{q}) = |\gamma| r_0 \vec{\sigma} \cdot \langle \theta J M | \sum_{k, m} \left(\frac{8\pi}{2k+1} \right)^{\frac{1}{2}} \{ \vec{X}_{km}^*(\hat{q}) T_{km}^{(e)} - i(q \times \vec{X}_{km}^*(\hat{q})) T_{km}^{(m)} \} | \theta' J' M' \rangle. \quad (100)$$

If the $a(\theta)$'s are known, the calculation of the magnetic scattering amplitude reduces to the evaluation of the matrix elements $\langle \theta J M | T_{km}^{\pi} | \theta' J' M' \rangle$ ($\pi = e$ or m) of the multipole operators. Since only transitions within the ℓ^n configuration are being considered, the parity of the initial and final states is the same and parity conservation can be used to show that only matrix elements of even order electric and odd order magnetic multipoles need be considered. This limited number of matrix elements will be evaluated using techniques which utilize our present day knowledge of atomic structure. They could, of course, be evaluated using the techniques of Condon and Shortley¹² or by brutally using fractional parentage coefficients and Racah algebra.⁵⁰ However, these techniques do not take full advantage of the symmetries of the atomic states.

Extreme Nonrelativistic Limit

In the extreme nonrelativistic limit, all the relativistic corrections to the atomic Hamiltonian are negligible and the only momentum dependent term in atomic Hamiltonian is the electronic kinetic energy. In this limit, the multipole operators are determined solely by Equations B.5 and B.10, since the convection current (Equation 41) is entirely due to the electronic kinetic energy. Since these multipole operators are one particle operators and we are only considering atomic transitions within the ℓ^n configuration, one electron angular momentum conservation produces the requirement that their order of multipolarity must be less than or equal to $2\ell+1$. Combining this result with the selection rules obtained from parity conservation yields the requirement that the order of multipolarity must be such that $k=1,3\dots 2\ell+1$ (or $k=2,4\dots 2\ell$) for magnetic (electric) multipoles to be nonvanishing.

In order to take full advantage of the symmetry properties of the Russell-Saunders states, the multipole operators must be expressed in terms of the Racah tensors (see Equations 90 and 91) which are simply related to the generators of the groups used to classify the LS states (see Chapter III). To express the multipole operators in terms of the Racah tensors, we must first express them as tensor products of the form

$$C_{km} = \sum_i c_{km}(i), \quad (101)$$

where the one-electron operators are tensor products

$$c_{km} = [a_{k_1} \times b_{k_2}]_m^k \quad (102)$$

with $a_{\kappa'}$, a tensor of rank κ' in the spin space and $b_{k'}$, a tensor of rank k' in the orbital space. The operators C_{km} can be expressed in terms of the Racah tensors by using Equation D.3 of Appendix D

$$C_{km} = [\kappa', k']^{-\frac{1}{2}} \left(\frac{1}{2} \| a_{\kappa'} \| \frac{1}{2} \right) (\alpha \ell \| b_{k'} \| \alpha' \ell) W_m^{(\kappa', k')} k \quad (D.3)$$

where $[\kappa', k']$ stands for $(2\kappa'+1)(2k'+1)$. Thus operators C_{km} can be factored into products of radial matrix elements and Racah tensors. The radial matrix element contains all the information about the radial electronic wavefunction and the matrix elements of the Racah tensors depend only upon the angular distribution of the atomic states. Thus by expressing the multipole operators as tensor products and applying Equation D.3, the multipole operators can be expressed in terms of the Racah tensors.

Using Table 2 of Chapter III, the magnetic multipole operator $T_{km}^m(0)$, can be written as a sum of tensor products

$$\begin{aligned} T_{km}^m(0) = & i^{k+1} \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \sum_i \left\{ \left(\frac{k+1}{2k+1} \right)^{\frac{1}{2}} [j_{k+1} Y_{k+1} \times \vec{r}_i]_m^k + \right. \\ & \left(\frac{k}{2k+1} \right)^{\frac{1}{2}} [j_{k-1} Y_{k-1} \times \vec{r}_i]_m^k + [k(k+1)]^{\frac{1}{2}} \left[- \left(\frac{k}{2k+1} \right)^{\frac{1}{2}} [j_{k+1} Y_{k+1} \times \vec{s}_i]_m^k + \right. \\ & \left. \left. \left(\frac{k+1}{2k+1} \right)^{\frac{1}{2}} [j_{k-1} Y_{k-1} \times \vec{s}_i]_m^k \right] \right\} \quad (103) \end{aligned}$$

Tensor products in the operator $T_{km}^m(0)$ which arise from the convection current associated with the electronic kinetic energy can be expanded into the Racah tensors $W^{(0,k)k}$, while tensor products arising from the

magnetization current can be expanded into Racah tensors $W^{(1,k')k}$ ($k'=k+1$). Similarly, the electric multipole operator, $T_{km}^e(0)$, can be written as

$$\begin{aligned}
 T_{km}^e(0) = & \left(\frac{m}{e\hbar q}\right) i^{k+1} \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \left[\sum_i \frac{ie_i(E_f - E_i)}{\hbar q} Y_{km}(\hat{r}_i) \frac{d}{dr}(r_i j_k(qr_i)) \right. \\
 & + \frac{qe_i}{2m_i} \left\{ j_k(qr_i) Y_{km}(\hat{r}_i) \vec{r}_i \cdot \vec{p}_i + \vec{p}_i \cdot \vec{r}_i j_k(qr_i) Y_{km}(\hat{r}_i) \right\} \\
 & \left. - i \frac{g_i e \hbar q}{2m_i} \vec{s}_i \cdot \vec{r}_i \left\{ j_k(qr_i) Y_{km}(\hat{r}_i) \right\} \right] \quad (104)
 \end{aligned}$$

where the terms in the large square brackets are tensors of rank k in the orbital space arising from the convection current and the last term is a tensor product arising from the magnetization current. The parts of the electric multipole operator $T_{km}^e(0)$ associated with the convection and magnetization currents can be expanded into the Racah tensors $W^{(0,k)k}$ and $W^{(1,k')k}$, respectively. Thus the magnetic and electric multipole operators have been expressed as tensor products of the form given in Equations 101 and 102.

Using Equation D.3 and calculating the appropriate one electron matrix elements, the multipole operators given in Equations 103 and 104 can be expanded into products of radial integrals and Racah tensors. To illustrate the type of calculations involved in this expansion, a detailed calculation will be presented for $T_{km}^m(0)$ -orbital, the portion

of the magnetic multipole arising from the convection current,

$$T_{km}^m(0)\text{-orbital} = \quad (105)$$

$$i^{k+1} \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \sum_i \left\{ \left(\frac{k+1}{2k+1} \right)^{\frac{1}{2}} [j_{k+1} Y_{k+1} \times \vec{r}_i]_m^k + \left(\frac{k}{2k+1} \right)^{\frac{1}{2}} [j_{k-1} Y_{k-1} \times \vec{r}_i]_m^k \right\}.$$

From the form in which the operator $T_{km}^m(0)\text{-orbital}$ is written, it is a simple matter to identify one electron operators C_{km} and use Equation D.3 to get

$$\begin{aligned} T_{km}^m(0)\text{-orbital} = & i^{k+1} \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \langle \frac{1}{2} || 1 || \frac{1}{2} \rangle W_m^{(0,k)k} \\ & \times \left[\left(\frac{k+1}{2k+1} \right)^{\frac{1}{2}} (2k+1)^{-\frac{1}{2}} \langle \ell || [j_{k+1} Y_{k+1} \times \vec{r}_i]_m^k || \ell \rangle \right. \\ & \left. + \left(\frac{k}{2k+1} \right)^{\frac{1}{2}} (2k+1)^{-\frac{1}{2}} \langle \ell || [j_{k-1} Y_{k-1} \times \vec{r}_i]_m^k || \ell \rangle \right]. \end{aligned} \quad (106)$$

Substituting for the reduced matrix elements of the operators acting in the orbital space, which have been tabulated in Equations 66, we find

$$\begin{aligned} T_{km}^m(0)\text{-orbital} = & i^{k+1} \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \langle \frac{1}{2} || 1 || \frac{1}{2} \rangle W_m^{(0,k)k} \times \\ & \left[\left(\frac{k+1}{2k+1} \right)^{\frac{1}{2}} (-)^{k+\ell} \begin{Bmatrix} k & 1 & k+1 \\ \ell & \ell & \ell \end{Bmatrix} \begin{pmatrix} \ell & k+1 & \ell \\ 0 & 0 & 0 \end{pmatrix} \bar{J}_{k+1} (2\ell+1) \times \right. \\ & \left. \left[\frac{(2k+3)(2\ell+1)\ell(\ell+1)}{4\pi} \right]^{\frac{1}{2}} + \left(\frac{k}{2k+1} \right)^{\frac{1}{2}} (-)^{k+\ell} \begin{Bmatrix} k & 1 & k-1 \\ \ell & \ell & \ell \end{Bmatrix} \begin{pmatrix} \ell & k-1 & \ell \\ 0 & 0 & 0 \end{pmatrix} \right. \\ & \left. \bar{J}_{k-1} (2\ell+1) \left[\frac{(2k-1)(2\ell+1)\ell(\ell+1)}{4\pi} \right] \right]. \end{aligned} \quad (107)$$

where

$$\bar{J}_k = \int_0^\infty r^2 f(r) f'(r) j_k(qr) dr \quad (108)$$

and $f(r)$ and $f'(r)$ denote one electron radial wavefunctions. By using the identities for 3-j and 6-j symbols given in Appendix C (in particular Equation C.5), this equation can be simplified

$$\begin{aligned} T_{km}^m(0)\text{-orbital} &= (-)^{k+l} (2l+1) \left[\frac{(2l+1)l(l+1)}{4\pi} \right]^{\frac{1}{2}} \times \\ & i^{k+1} \left[\frac{2\pi}{k(k+1)} \right]^{\frac{1}{2}} \langle \frac{1}{2} || 1 || \frac{1}{2} \rangle W_m^{(0,k)k} \times \\ & \left\{ \sqrt{(k+1)(2k+3)} \begin{Bmatrix} k & 1 & k+1 \\ l & l & l \end{Bmatrix} \begin{pmatrix} l & k+1 & l \\ 0 & 0 & 0 \end{pmatrix} (\bar{J}_{k+1} + \bar{J}_{k-1}) \right\}. \quad (109) \end{aligned}$$

This equation can be rewritten as

$$T_{km}^m(0)\text{-orbital} = i^{k+1} R_0 W^{(0,k)k}_m,$$

where we defined

$$\begin{aligned} R_0 &= (-)^{k+l} (2l+1) \frac{l(l+1)(2l+1)(2k+3)}{k}^{\frac{1}{2}} \begin{pmatrix} l & k+1 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} k+1 & 1 & k \\ l & l & l \end{Bmatrix} \times \\ & (\bar{J}_{k+1} + \bar{J}_{k-1}). \quad (110) \end{aligned}$$

Using Equations 103, 104 and D.3, along with the tables and identities given in Chapter III and Appendix C, similar expansions of the other multipole operators into products of radial integrals and Racah tensors can be obtained. The results of these calculations for the electric and

magnetic multipole operators are given below:

$$T_{km}^{(m)} = i^{k+1} [R_0(k) W_m^{(0,k)k} + \sum_{k'=k\pm 1} R_1(k', k) W_m^{(1,k')k}] ,$$

$$k = 1, 3, \dots, 2\ell + 1 \quad (111)$$

and

$$T_{km}^{(e)} = i^{k+1} [R_2(k) W_m^{(0,k)k} + R_1(k, k) W_m^{(1,k)k}] , \quad k = 2, 4, \dots, 2\ell .$$

$$(112)$$

where the radial integrals are given by

$$R_0(k) = (-)^{k+\ell} (2\ell+1) \left[\frac{\ell(\ell+1)(2\ell+1)(2k+3)}{k} \right]^{\frac{1}{2}} \begin{pmatrix} \ell & k+1 & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} k+1 & 1 & k \\ \ell & \ell & \ell \end{Bmatrix}$$

$$(\bar{J}_{k+1} + \bar{J}_{k-1}) , \quad (113)$$

$$R_1(k', k) = (-)^{\ell, k-k'-1} (2\ell+1) \left[\frac{(2k+1)(2k'+1)}{2} \right]^{\frac{1}{2}} \begin{pmatrix} k' & 1 & k \\ 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} \ell & k' & \ell \\ 0 & 0 & 0 \end{pmatrix} \bar{J}_{k'} ,$$

$$(114)$$

$$R_2(k) = \frac{(-)^{\ell}}{2i} (2\ell+1) \left[\frac{2k+1}{k(k+1)} \right]^{\frac{1}{2}} \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \bar{R}_2 , \quad (115)$$

and

$$\bar{R}_2 = \frac{-\hbar \omega}{\left(\frac{\hbar^2 q^2}{2m} \right)} \int_0^\infty r^2 f(r) f'(r) \frac{d(r j_k(qr))}{dr} dr$$

$$+ \int_0^\infty r^3 j_k(qr) \left(f \frac{df'}{dr} - f' \frac{df}{dr} \right) dr \quad (116)$$

The integrals $\bar{J}_k$ in these equations are defined by Equation 108 and can be evaluated using one electron radial wavefunctions obtained from some type of Hartree-Fock calculation. For elastic scattering ($f'(r) = f(r)$) these integrals are simply the Bessel transforms of the electronic radial density and have been calculated for all the transition metal⁶³ and rare earth atoms.⁶⁴ If the integrals $\bar{J}_k$ and $\bar{R}_2$ are known, the problem of evaluating the radial integrals reduces to calculating algebraic expressions containing 3-j and 6-j symbols. Evaluation of the 3-j and 6-j symbols in the radial integrals has been discussed in Chapter III and thus calculation of the radial integrals is a trivial problem. The only remaining difficulty in the evaluation of the multipole operators is the calculation of matrix elements of the Racah tensors $W^{(0,k)k}$ and $W^{(1,k')k}$ ($k' = \text{even}$). As was pointed out in Chapter III, the evaluation of matrix elements of the Racah tensors is simplified by selection rules based on the Groups $Sp(4l+2)$, $R(2l+1)$, $R(3)$, and G_2 (for f electrons), used in the classification of the Russell-Saunders states. It was also pointed out in Chapter III that matrix elements of the double Racah tensors in one configuration are related to those in another, so that the matrix elements of the Racah tensors can be obtained for all cases of practical interest from existing tabulations.^{60,61}

We have developed expressions for matrix elements of the multipole operators between Russell-Saunders states, which can be evaluated directly from tabulations compiled by atomic physicists. From these matrix elements the scattering amplitude $f_{\theta'J'M'}^{\theta JM}$ for the transition $\theta'J'M' \rightarrow \theta JM$ can be obtained from Equation 100, and the magnetic

scattering amplitude for an atom in a state $|JM\rangle$ of the ℓ^n electronic configuration can be obtained from Equation 99. If we consider elastic scattering by an atom in a single Russell-Saunders state of the ℓ^n configuration, the magnetic scattering amplitude can be written in a particularly simple form.

Elastic Scattering by an Atom in a Single Russell-Saunders State of the ℓ^n Configuration

For the case of elastic scattering by an atom in a single Russell-Saunders state $|0JM\rangle$, the electric multipole contribution to the magnetic scattering amplitude vanishes, leaving only the magnetic multipole contribution. Moreover, since the scattering is assumed to be elastic, only the $m=0$ components of the magnetic multipole operators contribute to the magnetic scattering amplitude. Thus the magnetic scattering amplitude can be written in the simple form

$$f(\vec{q}) = f_{0JM}^{\theta JM}(\vec{q}) = (|\gamma| r_0) \vec{\sigma} \cdot \langle 0JM | \sum_k -i \left(\frac{8\pi}{2k+1} \right)^{\frac{1}{2}} (\hat{q} \times \vec{X}_{k0}^*(\hat{q})) \times \tau_{k0}^m(0) | 0JM \rangle \quad k=1,3,\dots,2\ell+1. \quad (117)$$

This equation can be written in a more conventional form by using Equations A.13, A.7, A.4 and A.5 to write

$$\hat{q} \times \vec{X}_{k0}^*(\hat{q}) = \frac{i}{[k(k+1)]^{\frac{1}{2}}} \frac{dY_{k0}(\hat{q})}{d(\cos\theta)} \vec{q}_m, \quad (118)$$

where θ is the angle between the scattering vector $\hat{q}$ and the z axis of the laboratory coordinate system, which is of course taken as the axis

of quantization of the atom or ion. The vector $\vec{q}_m$ is commonly called the magnetic scattering vector and is determined by the component of the scattering vector perpendicular to the axis of quantization of the atom or ion,

$$\vec{q}_m = (\hat{q} \cdot \hat{\epsilon}_3) \hat{\epsilon}_3 - \hat{\epsilon}_3, \quad (119)$$

where $\hat{\epsilon}_3$ denotes a unit vector along the axis of quantization. Using this identity the magnetic scattering amplitude can be written in the conventional form[†]

$$f_{\theta JM}^{\theta JM}(\vec{q}) = p(\vec{q}) \vec{\sigma} \cdot \vec{q}_m,$$

where $p(\vec{q})$ is the quantity determined in an elastic scattering experiment and is sometimes referred to as the magnetic scattering amplitude. The magnetic scattering amplitude $p(\vec{q})$ is determined by the matrix elements of the multipole operators

$$p(\vec{q}) = (|\gamma| r_o) \sqrt{\frac{2}{k(k+1)}} P'_k(\cos \Theta) \langle \theta JM | T_{k0}^m | \theta JM \rangle, \quad (121)$$

where $P'_k(\cos \Theta)$ is the derivative of a Legendre polynomial.

The magnetic form factor is defined as $p(\vec{q})$ normalized to one in the forward direction ($|\vec{q}| \approx 0$). To normalize $p(\vec{q})$ to one in the forward direction, we must obtain an expression for $p(0)$. In Chapter II it was shown that for elastic scattering very near the forward direction only the magnetic dipole term was nonvanishing and that in this limit it was proportional to the magnetization operator (Equation 31). Since

[†]See for example Bacon.³

near the forward direction only the magnetic dipole term T_{10}^m contributes. In Equation 121, we find

$$p(0) = -\gamma r_0 \langle \theta JM | \frac{1}{2\mu_B} \int d\vec{r} \vec{M}(\vec{r}) \cdot \hat{\epsilon}_3 | \theta JM \rangle$$

where $\hat{\epsilon}_3$ is the axis of quantization of the atom. Using the fact that the atomic g factor is defined such that

$$g\mu_B M = -\langle \theta JM | \int d\vec{r} \vec{M}(\vec{r}) \cdot \hat{\epsilon}_3 | \theta JM \rangle, \quad (122)$$

the magnetic scattering amplitude in the forward direction $p(0)$ can be written in the particularly simple form

$$p(0) = \frac{\gamma r_0}{2} gM. \quad (123)$$

Providing we use the extreme nonrelativistic approximation to describe the atom, the g factor is equal to the well-known Landé factor

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (124)$$

If the effects of relativistic corrections such as the spin-orbit and mass correction terms are considered the atomic g factor will be slightly different from the Landé factor. Using the expression for $p(0)$ given in Equation 123, it is trivial to normalize the expression for $p(\vec{q})$ given in Equation 121 and obtain a form factor.

Since we are only considering scattering in the extreme non-relativistic limit, the g factor is equal to the well-known Landé factor and the form factor can be written as

$$\begin{aligned}
f_m(\vec{q}) &= -\frac{2}{gM} \langle \theta JM | \sum_k i^{k+1} \left[\frac{2}{k(k+1)} \right]^{\frac{1}{2}} P'_k(\cos\theta) \\
&\quad \times \{ R_0(k) W_0^{(0,k)} k + \sum_{k'=k\pm 1} R_1(k',k) W_0^{(1,k')} k \} | \theta JM \rangle \\
&= -\frac{2}{gM} \sum_k \left[\frac{2}{k(k+1)} \right]^{\frac{1}{2}} P'_k(\cos\theta) \langle \theta JM | T_{km}^{(m)} | \theta JM \rangle \\
&\quad k = 1, 3 \dots 2J+1
\end{aligned} \tag{125}$$

This formula gives the form factor of an atom in a single Russell-Saunders state. By setting $M=J$ in the formula, we obtain the form factor of an atom in its saturated state.

If a magnetic field, B , is applied to an atom in a single Russell-Saunders state, $|\theta JM\rangle$, the atomic state will be split into $2J+1$ levels whose probability of occupation P_M is proportional to $e^{-\beta M}$, where $\beta = g\mu_B B/kT$ and

$$P_M = \frac{e^{-\beta M}}{\sum_M e^{-\beta M}} \tag{126}$$

The form factor in this case can be accurately measured using polarized neutron techniques which sense the coherent magnetic scattering amplitude. The coherent magnetic scattering amplitude $\langle f_{\theta JM}^{\theta JM}(\vec{q}) \rangle$ is equal to the averaged magnetic scattering amplitude,

$$\langle f_{\theta JM}^{\theta JM}(\vec{q}) \rangle = \sum_M P_M f_{\theta JM}^{\theta JM}(\vec{q}), \tag{127}$$

In most cases of experimental interest, the condition, $\beta \ll 1$ (see Equation 125) is satisfied, and only the first two or three terms in the

expansion

$$e^{-\beta M} \approx 1 - \beta M + \frac{\beta^2 M^2}{2!} - \frac{\beta^3 M^3}{3!} + \dots \quad (128)$$

need be retained. The amplitude $f_{\theta JM}^{\theta JM}(\vec{q})$ depends only on M through the factor $(-)^{J-M} \begin{pmatrix} J & k & J \\ -M & 0 & M \end{pmatrix}$, which is a polynomial of degree k in M . Since only odd order multipoles contribute to the amplitudes $f_{\theta JM}^{\theta JM}(\vec{q})$, k must be odd and only odd powers of M in the expansion of $e^{-\beta M}$ (Equation 128) can contribute to the scattering amplitude. If we retain only the first three terms in the expansion of $e^{-\beta M}$, this means only the term $-\beta M$ can contribute to the scattering amplitude. In addition, only multipoles whose order of multipolarity, k , is less than or equal to the largest power of M retained in the expansion of $e^{-\beta M}$ will contribute to the magnetic scattering amplitude. Thus we find that in most cases of experimental interest only the magnetic dipole term ($k=1$) contributes significantly to the coherent magnetic scattering amplitude $\langle f_{\theta JM}^{\theta JM}(\vec{q}) \rangle$ so that

$$\langle f_{\theta JM}^{\theta JM}(\vec{q}) \rangle = \vec{u} \cdot \vec{q}_m \langle p(\vec{q}) \rangle, \quad (129)$$

and

$$\langle p(q) \rangle = (|\gamma| r_o) \frac{\chi_a(T) B}{g \mu_B J(J+1)(2J+1)^{1/2}} \langle \theta J || T_1^m || \theta J \rangle, \quad (130)$$

where $\chi_a(T)$ is the susceptibility and T_1^m is the magnetic dipole operator.

Very near the forward direction, the magnetic dipole term is

proportional to the magnetic moment (see Equation 38), and it may be shown that

$$\langle p(0) \rangle = \frac{\gamma r_0 \chi_a(T) B}{2\mu_B} \quad (131)$$

Using this relation to normalize $\langle p(q) \rangle$ to one in the forward direction, the induced moment form factor can be written as

$$f(q) = - \frac{1}{[J(J+1)(2J+1)]} \langle \theta J || T_1^m || \theta J \rangle \quad (132)$$

Elastic Scattering by Rare Earth Ions

Before we can use the theory of magnetic scattering developed in this chapter to analyze experimental results, the behavior of rare earth ions in solids must be briefly reviewed. The 4f and other electrons of the ion core which do not participate in the bonding in the solid are described as in an atomic model. Using this model to calculate the 4f wavefunctions in a solid is an excellent approximation because the 4f electrons are highly localized inside the closed 5s² and 5p⁶ shells which shield them from the neighboring ions. Usually the ion core is in the trivalent state with an electronic configuration consistent with a xenon structure of electrons (1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s² 4p⁶ 4d¹⁰ 5s² 5p⁶) and an unfilled 4f shell having a Hunds rule ground state. However, if the unfilled 4f shell of the trivalent ion is almost open (Ce,Pr), half filled (Sm,Eu,Tb), or closed (Tm,Yb), a 2⁺, 4⁺ or mixed valence state may have a lower ground state energy.

In this work we will only be considering elastic magnetic scattering by tripositive rare earth ions. Also, we will treat the ground state wavefunctions of the tripositive ions as pure Russell-Saunders states and not consider possible small admixtures of excited state wavefunctions. Thus, the magnetic form factor for tripositive rare earth ions can be calculated using results from our discussion of elastic scattering by an atom in a single Russell-Saunders state of the ℓ^n electronic configuration. Expressions which can be used to obtain the saturated and induced moment form factors of rare earth ions were given in Equations 125 and 132, respectively. To evaluate these, we must calculate the matrix elements of the multipole operators given in Equations 111 and 112. The multipole operators are determined by radial integrals (Equations 113-116) and Racah tensors.

Only the radial integrals $R_0(k)$ and $R_1(k',k)$ ($k' = \text{even}$), which are determined by Bessel transforms of the electronic radial density and 3-j and 6-j symbols, are needed for the evaluation of the multipole operators. By factoring out the Bessel transforms leaving $R_0(k)/(\bar{J}_{k+1} + \bar{J}_{k-1})$ and $R_1(k',k)/\bar{J}_{k'}$, we obtain quantities which depend only on the one electron orbital angular momentum quantum number and can be independently tabulated for all atoms within the ℓ^n electronic configuration. The quantities $R_0(k)/(\bar{J}_{k+1} + \bar{J}_{k-1})$ and $R_1(k',k)/\bar{J}_{k'}$, needed for the interpretation of elastic scattering experiments are given for d and f-electrons in Tables 9a and 9b. All the entries in the tables were obtained by using the references cited in Chapter III to evaluate the 3-j and 6-j symbols appearing in the radial integrals (Equations 113

Table 9a. Radial integrals for d-electrons:

k/k'	$\frac{R_1(k',k)}{\bar{j}_{k'}}$			$\frac{R_0(k)}{(\bar{j}_{k-1} + \bar{j}_{k+1})}$
	0	2	4	
1	$(5/2)^{\frac{1}{2}}$	$(5/14)^{\frac{1}{2}}$		$(5)^{\frac{1}{2}}$
2		$-5i/\sqrt{14}$		
3		$-(10/7)^{\frac{1}{2}}$	$-(15/14)^{\frac{1}{2}}$	$-(30)^{\frac{1}{2}}/7$
4			$3i(5/14)^{\frac{1}{2}}$	
5			$(15/7)^{\frac{1}{2}}$	0

Table 9b. Radial integrals for f-electrons

k/k'	$\frac{R_1(k',k)}{\bar{J}_{k'}}$				$\frac{R_0(k)}{(\bar{J}_{k-1} + \bar{J}_{k+1})}$
	0	2	4	6	
1	$(7/2)^{\frac{1}{2}}$	$(7/15)^{\frac{1}{2}}$			$(14)^{\frac{1}{2}}$
2		$-i(7/3)^{\frac{1}{2}}$			
3		$-(28/15)^{\frac{1}{2}}$	$-(21/22)^{\frac{1}{2}}$		$-(2)^{\frac{1}{2}}$
4			$3i(7/22)^{\frac{1}{2}}$		
5			$(21/11)^{\frac{1}{2}}$	$5(35/429)^{\frac{1}{2}}$	$(1/11)(70)^{\frac{1}{2}}$
6				$-5i(7/33)^{\frac{1}{2}}$	
7				$-10(14/429)^{\frac{1}{2}}$	0

and 114).

The calculation of the multipoles needed to obtain form factors for rare earth ions, is then reduced to the evaluation of matrix elements of the Racah tensors $W^{(0,k)k}$ and $W^{(1,k')k}$ ($k' = \text{even}$) between Russell-Saunders states. It was shown in Chapter III (see Equation 92) that using a generalized Wigner-Eckart theorem these matrix elements can be expressed in terms of reduced matrix elements of Racah double tensors. The reduced matrix elements of the Racah double tensors for the LS states comprising the Russell-Saunders ground states of rare earth ions with less than 8 electrons in the 4f shell were given in Table 8. The reduced matrix elements for ions with 8 or more electrons in the 4f shell have not been tabulated because they are identical with those of ions having $14-n$ electrons.

The matrix elements of the multipole operators can then be obtained in closed form in terms of Bessel transforms by using simple algebraic manipulations to combine the radial integrals with the matrix elements of the Racah tensors. Reduced matrix elements of the magnetic multipole operators for the ground states of rare earth ions have been tabulated in Table 10 as linear combinations of Bessel transforms $\bar{J}_k$. The induced moment form factor discussed in Equation 132 can be obtained directly from the first column of Table 10 by normalizing to 1 in the forward direction the reduced matrix element of the magnetic dipole operator $T_1^{(m)}$. Similarly if the state of the ion is known, Table 10 and Equation 125 can be used directly to obtain the form factor. For the important case of saturated rare earth ions, form factors for

experimental configurations having $\Theta = \pi/2$ are listed in Table 11. It should be noticed that the form factors for rare earth ions in their saturated states are expressed as linear combinations of the $\bar{J}_k$ with rational coefficients. The Bessel transforms $\bar{J}_k$ in terms of which the form factors of rare earth ions have been expressed, are determined by the 4f radial wavefunctions. Using Hartree-Fock calculations of the 4f radial wavefunctions, Blume *et al.*⁶⁴ evaluated the Bessel transforms for all tripositive rare earth ions. However, even early measurements of form factors of rare earth metals⁶⁵ showed that the experimentally determined form factor decreases with increasing scattering angle faster than would be predicted by calculations using the Bessel transforms obtained by Blume *et al.*⁶⁴ The resolution of this problem began when Moon *et al.*²³ performed accurate measurements on a system in which there was no orbital moment to complicate the interpretation of the data (Gd metal). They were able to show that the experimentally observed scattering amplitude for Gd metal could be separated in a logical manner into a local and diffuse part. The local part was determined by the 4f electron radial density, which was significantly expanded relative to calculations with non-relativistic Hartree-Fock wavefunctions. The diffuse part corresponded to the conduction electron polarization.

Davis and Cooke⁶⁶ analyzed the local part of the form factor and suggested that this discrepancy was due to the fact that the 4f wavefunctions are only accurately obtainable from a relativistic treatment. Freeman and Desclaux⁶⁷ then proposed that the Bessel transforms $\bar{J}_k$

Table 10. Reduced matrix elements $\langle \theta J || \pi_{km}^{(m)}(0) || \theta J \rangle$ for the ground state of rare earth ions

Ion	$\langle \theta J \pi_1^{(m)}(0) \theta J \rangle$	$\langle \theta J \pi_3^{(m)}(0) \theta J \rangle$	$\langle \theta J \pi_5^{(m)}(0) \theta J \rangle$	$\langle \theta J \pi_7^{(m)}(0) \theta J \rangle$
Ce ³⁺ ² F _{5/2}	$-3(\frac{15}{14})^{\frac{1}{2}} (\bar{j}_0 + \frac{8}{5} \bar{j}_2)$	$-3(\frac{6}{35})^{\frac{1}{2}} (\bar{j}_2 + \frac{10}{3} \bar{j}_4)$	$-(\frac{15}{77})^{\frac{1}{2}} (\bar{j}_4 + 12 \bar{j}_6)$	0
Pr ³⁺ ³ H ₄	$-12(\frac{1}{5})^{\frac{1}{2}} (\bar{j}_0 + \frac{74}{45} \bar{j}_2)$	$\frac{26}{5}(\frac{7}{165})^{\frac{1}{2}} (\bar{j}_2 + \frac{15}{11} \bar{j}_4)$	$\frac{2}{11}(\frac{195}{11})^{\frac{1}{2}} (\bar{j}_4 + \frac{248}{39} \bar{j}_6)$	$-\frac{34}{33}(\frac{70}{143})^{\frac{1}{2}} \bar{j}_6$
Nd ³⁺ ⁴ I _{9/2}	$-6(\frac{10}{11})^{\frac{1}{2}} (\bar{j}_0 + \frac{119}{66} \bar{j}_2)$	$\frac{35}{11}(\frac{70}{143})^{\frac{1}{2}} (\bar{j}_2 + \frac{40}{33} \bar{j}_4)$	$-\frac{5950}{363}(\frac{1}{143})^{\frac{1}{2}} (\bar{j}_4 + \frac{1698}{455} \bar{j}_6)$	$\frac{950}{1573}(\frac{595}{143})^{\frac{1}{2}} \bar{j}_6$
Pm ³⁺ ⁵ I ₄	$-9(\frac{1}{5})^{\frac{1}{2}} (\bar{j}_0 + \frac{224}{99} \bar{j}_2)$	$\frac{21}{11}(\frac{21}{55})^{\frac{1}{2}} (\bar{j}_2 + \frac{64}{99} \bar{j}_4)$	$-\frac{238}{363}(\frac{15}{143})^{\frac{1}{2}} (\bar{j}_4 - \frac{1152}{91} \bar{j}_6)$	$-\frac{1615}{1573}(\frac{70}{143})^{\frac{1}{2}} \bar{j}_6$
Sm ³⁺ ⁶ H _{5/2}	$-\frac{1}{2}(\frac{30}{7})^{\frac{1}{2}} (\bar{j}_0 + \frac{244}{45} \bar{j}_2)$	$-\frac{13}{3}(\frac{2}{105})^{\frac{1}{2}} (\bar{j}_2 + \frac{15}{11} \bar{j}_4)$	$\frac{39}{77}(\frac{35}{33})^{\frac{1}{2}} (\bar{j}_4 - \frac{92}{117} \bar{j}_6)$	0
Gd ³⁺ ⁸ S _{7/2}	$-3(14)^{\frac{1}{2}} \bar{j}_0$	0	0	0
Tb ³⁺ ⁷ F ₆	$-\frac{3}{2}(\frac{273}{2})^{\frac{1}{2}} (\bar{j}_0 + \frac{10}{27} \bar{j}_2)$	$-\frac{14}{11}(\frac{182}{33})^{\frac{1}{2}} \bar{j}_4$	$\frac{1}{11}(\frac{7735}{33})^{\frac{1}{2}} (\bar{j}_4 - \frac{9}{13} \bar{j}_6)$	$\frac{5}{33}(\frac{22610}{429})^{\frac{1}{2}} \bar{j}_6$
Dy ³⁺ ⁶ H _{15/2}	$-4(\frac{85}{3})^{\frac{1}{2}} (\bar{j}_0 + \frac{8}{15} \bar{j}_2)$	$2(\frac{646}{455})^{\frac{1}{2}} (\bar{j}_2 + \frac{4}{11} \bar{j}_4)$	$-\frac{2}{11}(\frac{1615}{143})^{\frac{1}{2}} (\bar{j}_4 - \frac{64}{13} \bar{j}_6)$	$-\frac{20}{429}(\frac{260015}{39})^{\frac{1}{2}} \bar{j}_6$
Ho ³⁺ ⁵ I ₈	$-\frac{15}{2}(\frac{17}{2})^{\frac{1}{2}} (\bar{j}_0 + \frac{46}{75} \bar{j}_2)$	$\frac{1}{10}(\frac{2261}{2})^{\frac{1}{2}} (\bar{j}_2 + \frac{10}{11} \bar{j}_4)$	$-\frac{5}{4}(\frac{1615}{286})^{\frac{1}{2}} (\bar{j}_4 + \frac{76}{65} \bar{j}_6)$	$\frac{5}{143}(\frac{520030}{13})^{\frac{1}{2}} \bar{j}_6$

Table 10. (Continued)

Ion	$\begin{matrix} (m) \\ \langle \theta J \pi_1(0) \theta J \rangle \end{matrix}$	$\begin{matrix} (m) \\ \langle \theta J \pi_3(0) \theta J \rangle \end{matrix}$	$\begin{matrix} (m) \\ \langle \theta J \pi_5(0) \theta J \rangle \end{matrix}$	$\begin{matrix} (m) \\ \langle \theta J \pi_7(0) \theta J \rangle \end{matrix}$
$\text{Er}^{3+} 4f_{15/2}$	$-6\left(\frac{51}{5}\right)^{\frac{1}{2}}(\bar{j}_0 + \frac{88}{135}\bar{j}_2)$	$\frac{6}{5}\left(\frac{646}{455}\right)^{\frac{1}{2}}(\bar{j}_2 + \frac{40}{33}\bar{j}_4)$	$\frac{2}{11}\left(\frac{1615}{143}\right)^{\frac{1}{2}}(\bar{j}_4 + \frac{24}{13}\bar{j}_6)$	$-\frac{40}{429}\left(\frac{260015}{39}\right)^{\frac{1}{2}}\bar{j}_6$
$\text{Tm}^{3+} 3H_6$	$-\frac{7}{2}\left(\frac{91}{6}\right)^{\frac{1}{2}}(\bar{j}_0 + \frac{2}{3}\bar{j}_2)$	$-\left(\frac{182}{33}\right)^{\frac{1}{2}}(\bar{j}_2 + \frac{4}{11}\bar{j}_4)$	$-\frac{7}{22}\left(\frac{7735}{33}\right)^{\frac{1}{2}}(\bar{j}_4 + \frac{2}{13}\bar{j}_6)$	$\frac{25}{33}\left(\frac{22610}{429}\right)^{\frac{1}{2}}\bar{j}_6$
$\text{Yb}^{3+} 2F_{7/2}$	$-\frac{24}{7}\left(\frac{7}{2}\right)^{\frac{1}{2}}(\bar{j}_0 + \frac{2}{3}\bar{j}_2)$	$-\frac{4}{7}(77)^{\frac{1}{2}}(\bar{j}_2 + \frac{4}{11}\bar{j}_4)$	$-\frac{8}{7}\left(\frac{455}{22}\right)^{\frac{1}{2}}(\bar{j}_4 + \frac{2}{13}\bar{j}_6)$	$-10\left(\frac{70}{143}\right)^{\frac{1}{2}}\bar{j}_6$

could be calculated using relativistic Dirac Fock wavefunctions if the $\bar{J}_k$ (Equation 108) were replaced by the relativistic generalization

$$\bar{J}_k = \frac{\ell+1}{(2\ell+1)} \int (F_+^2 + G_+^2) j_k(qr) dr + \frac{\ell}{2\ell+1} \times \int (F_-^2 + G_-^2) j_k(qr) dr, \quad (133)$$

where $F_{\pm} = F_{n\ell j = \ell \pm \frac{1}{2}}$ and $G_{\pm} = G_{n\ell j = \ell \pm \frac{1}{2}}$ are one electron radial wavefunctions (see Equations 69). In the Dirac Fock calculations, the 4f radial density was found to be expanded relative to the Hartree Fock results, due to a relativistic contraction of the inner shells which changes the potential in which the 4f electrons move. Using the relativistic generalization given in Equation 133, agreement has been obtained with the local part of the form factor in Gd^{23} and Er^{24} metals, and in a truly ionic compound $Tb(OH)_3$.²⁵

Although the relativistic generalization for the Bessel transforms (Equation 133) reproduces experimental results, it is somewhat inconsistent to evaluate with relativistic wavefunctions an expression for the 4f form factor which was originally derived by assuming that the ion could be described by a nonrelativistic Hamiltonian. In fact the 4f-electron form factors calculated using the relativistic generalization for the Bessel transforms defined in Equation 133, differ by a few parts per thousand from form factors calculated using the relativistic formalism which will be discussed in Chapter V. These small differences can be of some importance in experiments designed to measure the form factor of the conduction electrons. Specifically, conduction electron

form factors have been obtained for Er²⁴ and Gd²⁹ metals by subtracting the scattering amplitude of the localized 4f electrons from the experimentally determined scattering amplitude. Since the conduction electron contribution to the total magnetic scattering amplitude is only a few percent at small scattering angles, changes of the order of a few parts per thousand in the localized 4f form factor can be of importance in the quantitative analysis of the conduction electron form factor.

In the next chapter we will compare the results of calculations using a relativistic formalism with those performed using the relativistic generalizations of the Bessel transforms (Equation 133) to evaluate nonrelativistic expressions for the scattering amplitude. The results of this comparison have been summarized in Tables 13a, 13b, 13c, 14a, 14b and 14c of Chapter V.

Table 11. Saturated rare earth form factors

Ion Form Factor for Saturated Rare Earths with $\Theta = \frac{\pi}{2}$

$\text{Ce}^{3+} f^1 2F_{5/2}$	$\bar{J}_0 + \frac{3}{2} \bar{J}_2 - \frac{29}{88} \bar{J}_4 + \frac{1}{22} \bar{J}_6$
$\text{Pr}^{3+} f^2 3H_4$	$\bar{J}_0 + \frac{1357}{792} \bar{J}_2 + \frac{157}{1936} \bar{J}_4 - \frac{11675}{139392} \bar{J}_6$
$\text{Nd}^{3+} f^3 4I_{9/2}$	$\bar{J}_0 + \frac{1113}{572} \bar{J}_2 + \frac{7525}{37752} \bar{J}_4 + \frac{10295}{100672} \bar{J}_6$
$\text{Pm}^{3+} f^4 5I_4$	$\bar{J}_0 + \frac{10297}{4356} \bar{J}_2 + \frac{14581}{207636} \bar{J}_4 - \frac{7550975}{129564864} \bar{J}_6$
$\text{Sm}^{3+} f^5 6H_{5/2}$	$\bar{J}_0 + \frac{95}{18} \bar{J}_2 - \frac{611}{2904} \bar{J}_4 - \frac{23}{2178} \bar{J}_6$
$\text{Gd}^{3+} f^7 8S_{7/2}$	$\bar{J}_0$
$\text{Tb}^{3+} f^8 7F_6$	$\bar{J}_0 + \frac{10}{27} \bar{J}_2 - \frac{1}{12} \bar{J}_4 + \frac{5}{432} \bar{J}_6$
$\text{Dy}^{3+} f^9 6H_{15/2}$	$\bar{J}_0 + \frac{7}{12} \bar{J}_2 + \frac{21}{880} \bar{J}_4 - \frac{43}{1056} \bar{J}_6$
$\text{Ho}^{3+} f^{10} 5I_8$	$\bar{J}_0 + \frac{41}{60} \bar{J}_2 + \frac{81}{880} \bar{J}_4 + \frac{31}{528} \bar{J}_6$
$\text{Er}^{3+} f^{11} 4I_{15/2}$	$\bar{J}_0 + \frac{37}{54} \bar{J}_2 + \frac{3}{88} \bar{J}_4 - \frac{95}{2376} \bar{J}_6$

Table 11. (Continued)

Ion	Form Factor for Saturated Rare Earths with $\Theta = \frac{\pi}{2}$
$\text{Tm}^{3+} f^{12} {}^3\text{H}_6$	$\bar{J}_0 + \frac{25}{42} \bar{J}_2 - \frac{51}{616} \bar{J}_4 + \frac{5}{528} \bar{J}_6$
$\text{Yb}^{3+} f^{13} {}^2\text{F}_{7/2}$	$\bar{J}_0 + \frac{5}{12} \bar{J}_2 - \frac{3}{88} \bar{J}_4 + \frac{5}{2112} \bar{J}_6$

CHAPTER V. MAGNETIC SCATTERING BY A RELATIVISTIC ATOM

In this chapter the relativistic formulation of magnetic scattering which was presented in Chapter II will be evaluated for an atom in the ℓ^n electronic configuration. Dr. Stassis and I²⁹ have obtained expressions which can be used to evaluate the scattering amplitude of an atom which is not in the ℓ^n configuration; however, these calculations will not be discussed in this work. To evaluate the matrix elements of the relativistic multipole operators (see Equations 52 and 53), we will use the effective operator approach. In this approach, an effective multipole operator is defined such that a relativistic result is obtained by taking matrix elements of this effective operator between nonrelativistic states of the atom. It will be shown that from the effective multipole operators, we can define an effective magnetic scattering amplitude which can be expressed in terms of relativistic radial integrals and the Racah tensors. For an atom in a single Russell-Saunders state of the ℓ^n configuration, the effective magnetic scattering amplitude has a particularly simple form. Using the expressions developed in this chapter for the effective magnetic scattering amplitude, scattering by rare earth ions will be considered.

In Chapter II it was shown that the calculation of the magnetic scattering amplitude of a relativistic atom can be reduced to the evaluation of matrix elements of the relativistic multipole operators. The direct evaluation of these matrix elements can be quite involved for two reasons. First, relativistic calculations are usually performed in

the j-j coupling scheme, however the atomic states (especially those of rare earth ions) are much nearer to the LS limit. Thus an expansion of the atomic wavefunction in terms of LS coupled Russell-Saunders states only contains a few terms, while the corresponding expansion in j-j coupling often contains a great many terms. Second, it has been traditional in atomic physics to use a nonrelativistic description of states and operators. To circumvent these problems, we will again draw on work performed by atomic physicists, and use the effective operator approach first introduced by Sandars and Beck⁶⁸ in the study of hyperfine structure.

The basic idea of the effective operator approach is to define an effective operator such that the matrix element of the effective operator taken between nonrelativistic states of the atom is identical to the matrix element of the actual operator taken between relativistic atomic states. To do this, Sandars and Beck⁶⁸ introduced the concept of an LS coupled relativistic state $|\tau SLJM^R\rangle$, which is constructed by requiring that in the nonrelativistic limit it become equal to the corresponding nonrelativistic LS coupled state $|\tau SLJM\rangle$. In the central field approximation this can be done according to the following recipe:

- 1) Take a nonrelativistic Russell-Saunders state $|\tau SLJM\rangle$ and expand it into single particle wavefunctions of the form (see Equation 70)

$$|n\frac{1}{2}l m_s m_l\rangle = f(r) Y_{lm_l}(\hat{r}) \chi_{m_s}^{\frac{1}{2}}$$

- 2) Replace the nonrelativistic states $|n\frac{1}{2}l m_s m_l\rangle$ with their

relativistic equivalents defined in Equation 76 of Chapter III:

$$|n\frac{1}{2}l m_s m_l\rangle = \sum_{jm} [j]^{\frac{1}{2}} (-)^{l-\frac{1}{2}-m} \begin{pmatrix} \frac{1}{2} & l & j \\ m_s & m_l & -m \end{pmatrix} |n\frac{1}{2}lj m\rangle .$$

The resulting states $|\tau SLJM^R\rangle$ will be called LS coupled relativistic states, and in Chapter III it was shown that they can be classified with the same groups used to classify the nonrelativistic LS states.

With this definition of an LS coupled relativistic state, the problem of calculating matrix elements of a relativistic operator O , can be reduced to calculating matrix elements between nonrelativistic states by defining an effective operator O_e such that

$$(\tau SLJM^R | O | \tau' S' L' J' M')^R = \langle \tau SLJM | O_e | \tau' S' L' J' M' \rangle . \quad (134)$$

Thus the calculation of relativistic atomic matrix elements can be reduced to evaluating matrix elements of effective operators between nonrelativistic Russell-Saunders states. Reviews of the effective operator approach have been given by Armstrong⁵⁹ and Armstrong and Feneville.³⁴

To apply the effective operator approach to the evaluation of matrix elements of the multipole operators, it must be recognized that the relativistic multipole operators are one electron operators of the type,

$$B_{km} = \sum_i b_{km}(i) . \quad (135)$$

It is logical to expand the nonrelativistic effective operator corresponding to B_{km} into Racah tensors which are the generators of the groups used in the classification of the nonrelativistic states (see Chapter III),

$$B_{km}^{\text{effective}} = \sum_{\kappa', k'} A_{\kappa', k'}^k W_m^{(\kappa', k')} k \quad (136)$$

Then by substituting Equations 135 and 136 into Equation 134, we can show that the coefficients $A_{\kappa', k'}^k$ can be calculated from the one electron matrix elements

$$(n \frac{1}{2} \ell m_s m_\ell | b_{km} | n \frac{1}{2} \ell m_s m_\ell) = \langle n \frac{1}{2} \ell m_s m_\ell | \sum_{\kappa', k'} A_{\kappa', k'}^k W_m^{(\kappa', k')} k | n \frac{1}{2} \ell m_s m_\ell \rangle \quad (137)$$

Using the identifies and definitions presented in Chapter III, the matrix elements on both sides of this equation may be simplified and the coefficient $A_{\kappa', k'}^k$ can be shown to be determined by the reduced matrix element of the operator b_k ,

$$A_{\kappa', k'}^k = \sum_{j, j'} [j, j', \kappa', k']^{\frac{1}{2}} [k]^{-\frac{1}{2}} \left\{ \begin{matrix} \frac{1}{2} & \frac{1}{2} & \kappa' \\ \ell & \ell & k' \\ j & j' & k \end{matrix} \right\} \int r^2 dr (n \ell j || b_k || n \ell j'). \quad (138)$$

In this equation, the matrix element in the integrand is reduced only with respect to angular variables. Since each row and column of the 9-j symbol in Equation 138 must satisfy triangular conditions (see Table I), it is easily shown that the only possible nonvanishing coefficients are A_{0k}^k and $A_{1, k'}^k$ ($k'=k, k \pm 1$). Therefore, the effective multipole operators can be written as linear combinations of the tensors $W^{(0, k)k}$ and $W^{(1, k')k}$ ($k'=k, k \pm 1$). Thus, by using Equations 136 and 138 we can define an effective multipole operator and calculate matrix elements using non-relativistic atomic states.

The evaluation of matrix elements of the relativistic multipole operators using the effective operator approach can be conveniently performed by writing these operators in a form different from that given in Equations 54 and 55. By using Equations A.8, A.10 and A.14 the relativistic electric and magnetic multipole operators can be written as

$$T_{km}^{(e)} = i^{k+1} \left(\frac{m}{\hbar q} \right) \left(\frac{2\pi(2k+1)}{k(k+1)} \right)^{\frac{1}{2}} \sum_i \left[-\frac{i\omega}{q} Y_{km}(\hat{r}_i) \frac{d}{dr_i} (r_i j_k(qr_i)) + \frac{cqr_i j_k(qr_i)}{(2k+1)^{\frac{1}{2}}} \times \left\{ -(k+1)^{\frac{1}{2}} [\vec{\alpha}(i) \times Y_{k+1}(\hat{r}_i)]_m^k + (k)^{\frac{1}{2}} [\vec{\alpha}(i) \times Y_{k-1}(\hat{r}_i)]_m^k \right\} \right], \quad (139)$$

and

$$T_{km}^{(m)} = -i^k \left(\frac{mc}{\hbar q} \right) (2\pi(2k+1))^{\frac{1}{2}} \sum_i j_k(qr_i) [\vec{\alpha}(i) \times Y_k(\hat{r}_i)]_m^k. \quad (140)$$

The relativistic multipole operators are now expressed as tensor products and can be readily substituted into Equations 135, 136 and 138 to obtain effective multipole operators,

$$T_{km}^{(m)} = i^{k+1} \left[R^{(m)}(0, k, k) W_m^{(0, k)k} + \sum_{k'=k, k\pm 1} R^{(m)}(1, k', k) W_m^{(1, k')k} \right] \quad (141)$$

$k=1, 3, \dots, 2\ell+1; k' \leq 2\ell$

$$T_{km}^{(e)} = i^{k+1} \left[R^{(e)}(0, k, k) W_m^{(0, k)k} + \sum_{k'=k, k\pm 1} R^{(e)}(1, k', k) W_m^{(1, k')k} \right] \quad (142)$$

$k=2, 4, \dots, 2\ell; k' \leq 2\ell$

In these equations for the effective electric and magnetic multipole operators, the radial integrals $R(\kappa', k', k)$ correspond to the coefficients $A_{\kappa', k'}^k$ in Equation 136, and are given by

$$R^{(m)}(\kappa', k', k) = i \left(\frac{mc}{\hbar q} \right) \sqrt{2\pi} [\kappa', k']^{\frac{1}{2}} \int r^2 dr j_k(qr) \times$$

$$\sum_{j, j'} [j, j']^{\frac{1}{2}} \left\{ \begin{matrix} \frac{1}{2} & \frac{1}{2} & \kappa' \\ \ell & \ell & k' \\ j & j' & k \end{matrix} \right\} (n\ell j \| [\vec{\alpha} \times \mathbf{Y}_k]^k \| n\ell j')$$
(143)

and

$$R^{(e)}(\kappa', k', k) = \left(\frac{m}{\hbar q} \right) \left(\frac{2\pi}{k(k+1)} \right)^{\frac{1}{2}} [\kappa', k']^{\frac{1}{2}} \int r^2 dr \sum_{j, j'} [j, j']^{\frac{1}{2}} \left\{ \begin{matrix} \frac{1}{2} & \frac{1}{2} & \kappa' \\ \ell & \ell & k' \\ j & j' & k \end{matrix} \right\} \times$$

$$\left[-\frac{i\omega}{q} \frac{d}{dr} (r j_k(qr)) (n\ell j \| \mathbf{Y}_k \| n\ell j') + \frac{cq}{(2k+1)^{\frac{1}{2}}} r j_k(qr) \{ -(k+1)^{\frac{1}{2}} \times \right.$$

$$\left. (n\ell j \| [\vec{\alpha} \times \mathbf{Y}_{k+1}]^k \| n\ell j') + (k)^{\frac{1}{2}} (n\ell j \| [\vec{\alpha} \times \mathbf{Y}_{k-1}]^k \| n\ell j') \right\}].$$
(144)

The relativistic reduced matrix elements which appear in the radial integrals $R^\pi(\kappa', k', k)$ ($\pi=e$ or m), can be written as products of relativistic radial wavefunctions and nonrelativistic angular matrix elements:

$$(n\ell j \| [\vec{\alpha} \times \mathbf{Y}_{k'}]^k \| n\ell j') = i \frac{FG'}{r^2} \langle n\ell j \| [\vec{\sigma} \times \mathbf{Y}_{k'}]^k \| n\ell j' \rangle - \frac{iGG'}{r^2}$$

$$\langle n\ell j \| [\vec{\sigma} \times \mathbf{Y}_{k'}]^k \| n\ell j' \rangle$$
(145)

and

$$(n\ell j \| \mathbf{Y}_k \| n\ell j') = \frac{FF'}{r^2} \langle n\ell j \| \mathbf{Y}_k \| n\ell j' \rangle + \frac{GG'}{r^2} \langle n\ell j \| \mathbf{Y}_k \| n\ell j' \rangle,$$
(146)

where $\bar{\ell} = 2j - \ell$. Using the tabulation of reduced matrix elements of nonrelativistic operators given in Equations 66 and basic theorems of Racah algebra, Equations 145 and 146 can be rewritten as,

$$(n\ell j \| [\vec{\alpha} \times Y_{k''}]^k \| n \ell j') = (-)^{\ell} \left(\frac{3}{2\pi}\right)^{\frac{1}{2}} \frac{i}{r^2} [j, k, j', k'']^{\frac{1}{2}} \times$$

$$[[\ell, \bar{\ell}]^{\frac{1}{2}} \begin{pmatrix} \ell & k'' & \bar{\ell} \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} \frac{1}{2} & \ell & j \\ \frac{1}{2} & \bar{\ell} & j' \\ 1 & k'' & k \end{matrix} \right\} FG' + [\ell, \bar{\ell}]^{\frac{1}{2}} \begin{pmatrix} \bar{\ell} & k'' & \ell \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} \frac{1}{2} & \bar{\ell} & j \\ \frac{1}{2} & \ell & j' \\ 1 & k'' & k \end{matrix} \right\} GF'] \quad (147)$$

and

$$(n\ell j \| Y_k \| n \ell j') = (-)^{\ell} \frac{(2k+1)}{r^2 \sqrt{2\pi}} [j, j']^{\frac{1}{2}} [\ell, \ell]^{\frac{1}{2}} \left\{ \begin{matrix} \frac{1}{2} & \ell & j \\ \frac{1}{2} & \ell & j' \\ 0 & k & k \end{matrix} \right\} \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix} FF' -$$

$$[\bar{\ell}, \bar{\ell}]^{\frac{1}{2}} \left\{ \begin{matrix} \frac{1}{2} & \bar{\ell} & j \\ \frac{1}{2} & \bar{\ell} & j' \\ 0 & k & k \end{matrix} \right\} \begin{pmatrix} \bar{\ell} & k & \bar{\ell} \\ 0 & 0 & 0 \end{pmatrix} GG' \} \quad (148)$$

The relativistic radial integrals can then be obtained by substituting the expressions for the relativistic reduced matrix elements given in Equations 147 and 148 into Equations 143 and 144. The sum over the reduced matrix elements in Equations 143 and 144 can be performed with the aid of the tabulation of 9-j symbols given in Appendix C, and after some tedious algebraic manipulations, the relativistic radial integrals can be written as,

$$R^{(m)}(\kappa', k, k) = (-)^{k+\ell} (2\ell+1) \left[\frac{\ell(\ell+1)(2\ell+1)(2k+3)}{k} \right]^{\frac{1}{2}}$$

$$\begin{pmatrix} \ell & k+1 & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} k+1 & 1 & k \\ \ell & \ell & \ell \end{Bmatrix} j^{(m)}(\kappa', k, k) \quad (149)$$

$$R^{(\pi)}(1, k', k) = (-)^{\ell} i^{k-k'-1} (2\ell+1) \left[\frac{(2k+1)(2k'+1)}{2} \right]^{\frac{1}{2}}$$

$$\begin{pmatrix} k' & 1 & k \\ 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} \ell & k' & \ell \\ 0 & 0 & 0 \end{pmatrix} j^{(\pi)}(1, k', k)$$

$$k' = \underline{k+1} \text{ if } \pi = m; k' = k \text{ if } \pi = e \quad (150)$$

$$R^{(e)}(\kappa', k', k) = (-)^{k+\ell} \frac{i(2\ell+1)}{k(k+1)} [\ell(\ell+1)(2\ell+1)(2k+1)(2k'+1)]^{\frac{1}{2}}$$

$$\begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} k' & 1 & k \\ \ell & \ell & \ell \end{Bmatrix} j^{(e)}(\kappa', k', k) \quad (151)$$

$$k' = k, k \pm 1.$$

The integrals $j^{(\pi)}(\kappa', k', k)$ ($\pi = e$ or m) are given by:

$$j^{(m)}(0, k, k) = \frac{2mc}{\hbar(2\ell+1)^2} \int r (j_{k+1} + j_{k-1}) [(\ell+1)(F_+ G'_+ + G_+ F'_+) - \ell(F_- G'_- + G_- F'_-)]$$

$$- \frac{1}{2}(F_+ G'_- + G_+ F'_- + F_- G'_+ + G_- F'_+)] \quad (152.9)$$

$$j^{(m)}(1, k, k) = \frac{1}{\sqrt{k(k+1)}} \frac{mc}{\hbar(2\ell+1)} \int r (j_{k+1} + j_{k-1}) [(G_+ F_-' - F_- G_+') - (G_- F_+' - F_+ G_-')] dr \quad (152.b)$$

$$j^{(m)}(1, k+1, k) = \frac{2mc}{\hbar(2\ell+1)^2} \int \frac{r(j_{k+1} + j_{k-1})}{k(2k+1)} [-(\ell+1)(k+1)(2\ell-k)(F_{++}' + G_{++}') - \ell(k+1)(2\ell+k+2)(F_{--}' + G_{--}') + \frac{1}{2}(2\ell-k)(2\ell+k+2)(G_{+-}' + F_{+-}' + F_{-+}' + G_{-+}')] dr \quad (152.c)$$

$$j^{(m)}(1, k-1, k) = \frac{2mc}{\hbar(2\ell+1)^2} \int \frac{r(j_{k+1} + j_{k-1})}{(k+1)(2k+1)} [k(\ell+1)(2\ell+k+1)(F_{++}' + G_{++}') + k\ell(2\ell-k+1)(F_{--}' + G_{--}') + \frac{1}{2}(2\ell+k+1)(2\ell-k+1)(G_{+-}' + F_{+-}' + F_{-+}' + G_{-+}')] dr \quad (152.d)$$

$$j^{(e)}(1, k, k) = \frac{mc}{\hbar(2\ell+1)} \int r j_k [G_{+-}' + F_{-+}' - (F_{++}' + G_{++}')] dr \quad (152.e)$$

$$j^{(e)}(0, k, k) = \frac{\hbar\omega}{(\frac{\hbar^2 q^2}{2m})} \frac{1}{2(2\ell+1)^2} \int \frac{d}{dr} (r j_k) [(2\ell+k+2)(2\ell-k+1)(F_{++}' + G_{++}') + (2\ell+k+1)(2\ell-k)(F_{--}' + G_{--}') + k(k+1)(F_{+-}' + G_{+-}' + F_{-+}' + G_{-+}')] dr - \frac{mc}{\hbar(2\ell+1)^2} \int r j_k [(2\ell+k+2)(2\ell-k+1)(F_{++}' - G_{++}') + (2\ell+k+1)(2\ell-k)(F_{--}' - G_{--}') + k(k+1)(F_{+-}' - G_{+-}' + F_{-+}' - G_{-+}')] dr \quad (152.f)$$

$$j^{(e)}(1, k+1, k) = (k(k+1))^{\frac{1}{2}} \frac{mc}{\hbar(2\ell+1)^2} \int r j_k [(2\ell-k+1)(F_{++}' - G_{++}') - (2\ell+k+1)(F_{--}' - G_{--}') + k(F_{+-}' - G_{+-}' + F_{-+}' - G_{-+}')] dr \quad (152.g)$$

and

$$j^{(e)}(1, k-1, k) = (k(k+1))^{\frac{1}{2}} \frac{mc}{\hbar(2\ell+1)^2} \int r j_k [(2\ell+k+2)(F_{++}' - G_{++}') - (2\ell-k)(F_{--}' - G_{--}') - (k+1)(F_{+-}' - G_{+-}' + F_{-+}' - G_{-+}')] dr, \quad (152.h)$$

where $F_{\pm} = F_{n\ell j=\ell+\frac{1}{2}}$ and $G_{\pm} = G_{n\ell j=\ell+\frac{1}{2}}$ are one electron radial wavefunctions obtained from some type of Hartree-Fock-Dirac calculation.

Thus in Equations 141, 142 and 152 the relativistic multipole operators have been expressed as effective operators which are products of relativistic radial integrals and Racah tensors. It is clear from our discussion that the magnetic scattering amplitude can be formally written as

$$f(\vec{q}) = |\gamma| r_0 \vec{\sigma} \cdot \sum_{k,m} \left(\frac{8\pi}{2k+1} \right)^{\frac{1}{2}} \{ \vec{x}_{km}^*(\vec{q}) T_{km}^{(e)} - i(\vec{q} \times \vec{x}_{km}^*(\vec{q})) T_{km}^{(m)} \},$$

where $T_{km}^{(m)}$ and $T_{km}^{(e)}$ are effective multipole operators. To calculate matrix elements of these effective multipole operators, we only need to evaluate radial integrals and the matrix elements of Racah tensors between Russell-Saunders states. The calculation of the matrix elements of the Racah tensors has been discussed in Chapter III, and the radial integrals can be obtained if the one electron radial wavefunctions are known. It should be pointed out that with the exception of the tensor $w^{(1,k')}_k$ ($k' = \text{odd}$), the

same Racah tensors appear in the effective multipole operators as in the expansion of the nonrelativistic multipole operators (Equations 111-116). A detailed comparison of the effective multipole operators and the nonrelativistic multipole operators can be made by taking the nonrelativistic limit of the integrals $j^\pi(\kappa', k', k)$ ($\pi = e$ or m).

Nonrelativistic Limit

The integrals $j^\pi(\kappa', k', k)$ are expressed in terms of the radial wavefunctions F and G which can be formally expanded in a series of powers of $1/c$ where c is the velocity of light.[†] Keeping only the lowest order terms in the expansion, the nonrelativistic limit of F and G can be shown to be

$$F_{nlj} = R_{nl} \quad (153a)$$

$$G_{nlj} = -\frac{1}{2} \frac{\hbar}{mc} \left(\frac{d}{dr} - \frac{\chi_l}{r} \right) R_{nl}, \quad (153b)$$

where R_{nl} is the nonrelativistic radial wavefunction which is, of course, independent of j . This limit is often called the Pauli limit and the wavefunction is normalized to (but not including) order $1/c^2$. Then using Equations 153 and 152, the nonrelativistic limit of the integrals $j(\kappa', k', k)$, accurate to (but not including) order $(1/c^2)$, can be shown to be

[†]See, for example, Akhiezer and Berestetskii.⁶⁹

$$j^{(m)}(1, k, k) = j^{(e)}(1, k \pm 1, k) = 0 \quad (154a)$$

$$j^{(m)}(0, k, k) = \bar{j}_{k+1} + \bar{j}_{k-1} \quad (154b)$$

$$j^{(e)}(0, k, k) = \bar{R}_2 \quad (154c)$$

$$j^{(e)}(1, k, k) = \bar{j}_k \quad (154d)$$

where

$$\bar{j}_k = \int_0^\infty RR' j_k(qr) dr \quad (154e)$$

and

$$\bar{R}_2 = \frac{\hbar\omega}{2} \frac{q}{2m} \int_0^\infty RR' \frac{d(rj_k)}{dr} dr + \int_0^\infty rj_k \left(R \frac{dR'}{dr} - R' \frac{dR}{dr} \right) dr. \quad (154f)$$

Using these equations it is seen that the nonrelativistic limit to (but not including) order $1/c^2$ of the effective multipole operators is identical to the extreme nonrelativistic limit of the multipole operators discussed in Chapter IV. In the nonrelativistic limit it was assumed that the only momentum dependent term in the atomic Hamiltonian was the electronic kinetic energy. Other terms in the nonrelativistic atomic Hamiltonian (Equations 67) are relativistic corrections of the order of $1/c^2$ and their contribution to the multipole operators must be obtained from a nonrelativistic limit of the integrals $j^\pi(\kappa', k', k)$ consistent to (and including) order $1/c^2$.

Because relativistic effects such as spin-orbit coupling and relativistic mass correction are implicitly included in Dirac's equation,

their contribution to the multipole operators is included in Equations 141, 142 and 152. In fact, it may be shown that because spin-orbit coupling is implicitly included in Dirac's equation, the relativistic expression of the magnetic scattering amplitude contains angular matrix elements $W^{(1,k')k}$ where k' is an odd integer whereas these tensors are absent in the nonrelativistic scattering amplitude calculated including the momentum dependent spin orbit term in the atomic Hamiltonian.²⁹

Thus, using the effective operator approach, the calculation of the magnetic scattering amplitude has been reduced to evaluating relativistic radial integrals and matrix elements of the Racah tensors taken between nonrelativistic Russell-Saunders states. Relativistic effects such as the modification of the nonrelativistic current density due to relativistic corrections to the atomic Hamiltonian are implicitly included in the formalism. In the extreme nonrelativistic limit, where the electronic kinetic energy is the only important momentum dependent term in the atomic Hamiltonian, the relativistic multipole operators as well as the scattering amplitude become identical to those of the nonrelativistic formulation.

Elastic Scattering by an Atom in a Single Russell-Saunders State

In the nonrelativistic formulation discussed in Chapter IV, it was shown that the calculation of the magnetic scattering amplitude can be considerably simplified in the case of elastic scattering by an atom whose state is a single Russell-Saunders state. An equivalent simplification is expected when the problem is treated with the relativistic formalism which has been developed.

Using exactly the same arguments made in the nonrelativistic case, it may be shown that only the $m=0$ components of the effective multipole operators contribute to the scattering amplitude. The scattering amplitude can then be written in the conventional form $p(\vec{q}) \vec{q}_m \cdot \vec{\sigma}$ where $\vec{q}_m$ is the magnetic scattering vector and $p(\vec{q})$ is given by

$$p(\vec{q}) = |\gamma| r_0 \sum_k \left(\frac{2}{k(k+1)} \right)^{\frac{1}{2}} P'_k(\cos \Theta) \langle \theta JM | T_{k0}^{(m)} | \theta JM \rangle, \quad (155)$$

$$k=1, 3 \dots 2\ell+1$$

with $\theta = \alpha SL$, $P'_k(\cos \Theta)$, the derivative of a Legendre polynomial and Θ the angle between the axis of quantization of the atom and the scattering vector. The expression for $p(\vec{q})$ given in Equation 155, is identical to that obtained in the extreme nonrelativistic case (Equation 121), with the exception of the fact that $T_{k0}^{(m)}$ is now an effective magnetic multipole operator. Comparing the expressions for the effective multipole operator (Equations 141, 142, and 152) and the multipole operator obtained in the extreme nonrelativistic limit, Equations 111 through 116, it can be seen that for elastic scattering, the magnetic scattering amplitude can be obtained from the nonrelativistic expressions by simply replacing the nonrelativistic radial integrals R by their relativistic counterparts.

This prescription for obtaining the magnetic scattering amplitude of a relativistic atom is somewhat different from the prescription proposed by Freeman and Desclaux⁶⁷ which was discussed in Chapter IV. For elastic scattering, the relativistic radial integrals and non-relativistic radial integrals differ only in the integrals $j^\pi(\kappa', k', k)$

($\pi = e$ or m) and $\bar{J}_k$. Since the integrals $j^\pi(k', k)$ ($\pi = e$ or m) differ from the relativistic generalization of the $\bar{J}_k$ given in Equation 133, the resulting radial integrals cannot be the same. Thus we expect differences to exist between calculations of the magnetic scattering amplitude using the relativistic generalization proposed by Freeman and Desclaux⁶⁷ and calculations using the relativistic formalism presented in this chapter. The magnitude of these differences will be discussed when the relativistic formalism is applied to elastic scattering by rare earth ions.

In Chapter IV, it was shown that in the forward direction the magnetic scattering amplitude is proportional to the azimuthal component of the magnetic moment. For an atom in a single LS state, the azimuthal component of the magnetic moment can be written as $g\mu_B M$, where g is the atomic g factor which appears in the linear Zeeman term. Thus the magnetic scattering amplitude in the forward direction can be written as

$$p(0) = \frac{\gamma r_0}{2} gM.$$

In the extreme nonrelativistic case discussed in Chapter IV, g is determined by the simple Landé formula, however now g is determined from

$$gM = \lim_{|q| \rightarrow 0} \langle \theta JM | T_{k0}^m | \theta JM \rangle \quad (156)$$

where T_{k0}^m is an effective magnetic multipole operator. This g factor differs slightly from the Landé value because of relativistic corrections. These relativistic corrections have been examined by Perl and Hughes⁷⁰ and Abragam and Van Vleck⁷¹ using the nonrelativistic limit of Dirac's

equations. They found that the physical origin of the relativistic corrections was twofold. First, there is a mass correction effect resulting from the fact that the mass m of the electron must be replaced by $m(1 - \frac{v^2}{c^2})^{\frac{1}{2}}$. The mass correction to the g factor was first considered by Breit⁷² and Margenau.⁷³ Second, there is a spin-orbit coupling effect, which adds an extra moment due to the Larmor precession of the electrons.

Elastic Scattering by Rare Earth Ions

It was shown in Chapter IV that the $4f$ wavefunctions of rare earth ions in solids can usually be approximated with those of free tripositive ions. The ground state of the free tripositive ion is for all practical purposes a pure Russell-Saunders state. Thus in examining the form factors of rare earth ions we can use the results of our discussion of elastic scattering by atoms in a single Russell-Saunders state of the ℓ^n configuration. For this special case it was shown that the magnetic scattering amplitude can be obtained from the nonrelativistic expressions by simply replacing the nonrelativistic radial integrals (Equations 113 and 114) by their relativistic counterparts, $R(\kappa', k', k)$ (Equations 149-151). An inspection of these radial integrals shows that the nonrelativistic radial integrals can be obtained from their relativistic counterparts by replacing the integrals $j^m(\kappa', k', k)$ by their nonrelativistic limits (Equations 152), which are linear combinations of the Bessel transforms $\bar{J}_k$. Thus differences between relativistic and nonrelativistic scattering amplitudes result directly from the way the integrals

$j^m(\kappa', k', k)$ and $\bar{J}_k$ are evaluated.

The integrals $\bar{J}_k$ and $j^{(m)}(\kappa', k', k)$ (Equations 108 and 152, respectively) should properly be evaluated using wavefunctions obtained from Hartree-Fock and Dirac-Fock calculations, respectively. However, it was pointed out in Chapter IV that the 4f electrons cannot be adequately described with Hartree-Fock wavefunctions and thus a relativistic generalization of the integrals $\bar{J}_k$ was proposed by Freeman and Desclaux.⁶⁷ This relativistic generalization is given in Equation 133 and it has been commonly used to calculate the magnetic scattering amplitude of rare earth ions. It has also been pointed out that this relativistic generalization of the integrals $\bar{J}_k$ does not correspond with the integrals $j^m(\kappa', k', k)$.

To assess the differences between scattering amplitudes evaluated using the integrals $j^m(\kappa', k', k)$ and the relativistic generalizations of the Bessel transforms $\bar{J}_k$, relativistic Dirac-Fock calculations of the wavefunctions of tripositive Gd and Er ions have been performed. A multiconfigurational Dirac-Fock program written by J. P. Desclaux⁷⁴ was used to perform these calculations. In the program the wavefunctions are calculated using a variational technique to minimize

$$E = \sum_{VU} W_V W_U \langle \phi^V | H - H_B | \phi^U \rangle / \sum_V W_V^2, \quad (156)$$

where $H - H_B$ is the relativistic atomic Hamiltonian (Equations 46 and 47) with the Breit interaction removed. The numbers W_V in Equation 156 are the weights of the different configurations in the expansion

$$\psi = \sum_{v=1}^{\text{Number of configurations}} w_v \phi^v$$

where ψ is the total wavefunction of the atom and ϕ^v is an eigenfunction of the total angular momentum which can be expressed as an antisymmetric product of the one electron wavefunctions given in Equation 69. By appropriately picking the coefficients w_v , a particular LS state within the ℓ^n configuration can be constructed. However, it is convenient to use the same radial wavefunction for all LS states of the ℓ^n configuration, since differences between the radial wavefunctions of such states are usually quite small. Such an average wavefunction was obtained for Er and Gd ions by using the mixed configuration approximation which has been discussed by Mayers⁷⁵, Desclaux et al.⁷⁶ and Lindgren and Rosen.⁷⁷ In the mixed configuration approximation the weights w_v in Equation 156 are picked so that the wavefunction is obtained from the minimization of an average LS state energy. The prescription for obtaining the average energy of the LS states is to choose the weights w_v in Equation 156 to be equal to the square root of the sum of the degeneracies of all possible j-j states that can be formed from a given configuration. A list of the weights used for the calculation of the Gd and Er wavefunctions is given in Tables 12a and 12b, respectively.

Other details about the Dirac-Fock program have been documented by Desclaux.⁷⁴ Using the mixed configuration approximation which has been discussed, the Dirac-Fock program was run to obtain the 4f-wavefunctions of tripositive Er and Gd ions. The 4f wavefunctions obtained from the

Table 12a. Degeneracy of j-j configurations corresponding to f^7 (Gd^{3+})

Number of electrons in $j = l + \frac{1}{2}$ state	7	6	5	4	3	2	1
Number of electrons in $j = l - \frac{1}{2}$ state	0	1	2	3	4	5	0
Degeneracy of all possible j-j coupled states	8	168	840	1400	840	168	8

Table 12b. Degeneracy of j-j configurations corresponding to f^{11} (Er^{3+})

Number of electrons in $j = l + \frac{1}{2}$ state	5	6	7	8
Number of electrons in $j = l - \frac{1}{2}$ state	6	5	4	3
Degeneracy of all possible j-j coupled states	56	168	120	20

program were then used to evaluate the integral $j^m(\kappa', k', k)$ and the relativistic generalization of the Bessel transform $\bar{j}_k$ defined in Equation 133. From the integrals $j^m(\kappa', k', k)$, reduced matrix elements of the relativistic multipole operator $T_k^{(m)}$ were evaluated and from the relativistic generalizations of the Bessel transforms (see Equation 133), the reduced matrix elements of the nonrelativistic multipole operator $T_k^{(m)}(0)$ were evaluated. The results of this calculation for the Gd^{3+} ion are listed in Table 13a and results for the Er^{3+} ion are given in Tables 13b and 13c. Only reduced matrix elements of magnetic dipole operators have been tabulated for the Gd^{3+} ion because its ground state is $^8S_{7/2}$ and angular momentum conservation requires all other magnetic multipole moments to be identically equal to zero. However for Er^{3+} all reduced matrix elements of magnetic multipole operators whose order of multipolarity is less than or equal to 7 are nonvanishing and have been tabulated. From an inspection of tables 13a, 13b and 13c it is seen that there are small differences between reduced matrix elements of the relativistic and nonrelativistic multipole operators. These differences are, of course, reflected in the form factor obtained using the relativistic and nonrelativistic formulations of magnetic scattering. In Chapter IV it was pointed out that even changes of the order of a few parts per thousand in the 4f electron form factor can be of importance in the quantitative analysis of the conduction electron form factor of rare earth metals. This is due to the fact that the conduction electron contribution to the observed scattering amplitude is only a few percent at small scattering angles. Since a nonrelativistic scattering

Table 13a. Reduced matrix elements of multipole operators for Gd^{3+} ^a

$\sin(\theta)/\lambda$	$(\theta J T_1^m \theta J)^b$	$\langle \theta J T_1^m(0) \theta J \rangle^c$	Difference
0.0	-11.2165	-11.2250	0.0085
0.1000	-10.5259	-10.5394	0.0135
0.2000	- 8.7816	- 8.8067	0.0251
0.3000	- 6.6507	- 6.6868	0.0361
0.4000	- 4.6591	- 4.7018	0.0427
0.5000	- 3.0456	- 3.0899	0.0442
0.6000	- 1.8486	- 1.8907	0.0421
0.7000	- 1.0147	- 1.0524	0.0378
0.8000	- 0.4638	- 0.4963	0.0325
0.9000	- 0.1192	- 0.1464	0.0272
1.0000	0.0821	0.0600	0.0222
1.1000	0.1881	0.1703	0.0178
1.2000	0.2332	0.2190	0.0142

^aAll reduced matrix elements were evaluated using 4f wavefunctions obtained from mixed configuration Dirac-Fock calculations.

^bThe operator T_k^m is the effective multipole operator in Equation 141.

^cThe operator $T_k^m(0)$ is the nonrelativistic multipole operator given in Equation 111. The integrals $\bar{j}_k$ which are needed for the evaluation of matrix elements of this operator were calculated using the relativistic generalization given in Equation 133.

Table 13b. Reduced matrix elements of multipole operators for Er^{3+} ^a

$\sin(\theta)/\lambda$	Order of Multipolarity = 1			Order of Multipolarity = 3		
	$(\theta J \ T_1^m \ \theta J)^b$	$\langle \theta J \ T_1^m \ \theta J \rangle^c$	Difference	$(\theta J \ T_3^m \ \theta J)^c$	$\langle \theta J \ T_3^m(0) \ \theta J \rangle^c$	Difference
0.0	-19.1397	-19.1625	0.0228	0.0	0.0	0.0
0.1000	-18.4142	-18.4440	0.0298	0.0291	0.0288	0.0003
0.2000	-16.4957	-16.5410	0.0453	0.1034	0.1026	0.0008
0.3000	-13.9500	-14.0093	0.0593	0.1949	0.1941	0.0009
0.4000	-11.3008	-11.3674	0.0666	0.2790	0.2785	0.0004
0.5000	- 8.8705	- 8.9375	0.0669	0.3422	0.3424	-0.0003
0.6000	- 6.7995	- 6.8619	0.0624	0.3811	0.3820	-0.0009
0.7000	- 5.1120	- 5.1703	0.0552	0.3979	0.3993	-0.0015
0.8000	- 3.7878	- 3.8349	0.0471	0.3969	0.3987	-0.0018
0.9000	- 2.7657	- 2.8048	0.0390	0.3828	0.3849	-0.0020
1.0000	- 1.9925	- 2.0241	0.0316	0.3601	0.3622	-0.0021
1.1000	- 1.4157	- 1.4408	0.0251	0.3323	0.3343	-0.0020
1.2000	- 0.9907	- 1.0104	0.0198	0.3019	0.3038	-0.0019

^aAll reduced matrix elements were evaluated using 4f wavefunctions obtained from mixed configuration Dirac-Fock calculations.

^bThe operator T_k^m is the effective multipole operator in Equation 141.

^cThe operator T_k^m is the nonrelativistic multipole operator given in Equation 111. The integrals $\bar{j}_k$ which are needed for the evaluation of matrix elements of this operator were calculated using the relativistic generalization given in Equation 133.

Table 13c. Reduced matrix elements of multipole operators for Er^{3+} ^a

$\sin(\theta)/\lambda$	Order of Multipolarity = 5			Order of Multipolarity = 7		
	$\langle \theta J T_5^m \theta J \rangle^b$	$\langle \theta J T_5^m \theta J \rangle^c$	Difference	$\langle \theta J T_7^m \theta J \rangle^b$	$\langle \theta J T_7^m(0) \theta J \rangle^c$	Difference
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1000	-0.0002	-0.0002	0.0000	-0.0000	-0.0000	-0.0000
0.2000	-0.0021	-0.0021	0.0000	-0.0010	-0.0010	-0.0000
0.3000	-0.0083	-0.0083	0.0000	-0.0082	-0.0079	-0.0002
0.4000	-0.0197	-0.0199	0.0002	-0.0283	-0.0275	-0.0008
0.5000	-0.0349	-0.0353	0.0004	-0.0642	-0.0627	-0.0015
0.6000	-0.0519	-0.0524	0.0005	-0.1129	-0.1108	-0.0022
0.7000	-0.0624	-0.0691	0.0006	-0.1687	-0.1662	-0.0025
0.8000	-0.0832	-0.0839	0.0007	-0.2259	-0.2232	-0.0027
0.9000	-0.0953	-0.0959	0.0006	-0.2796	-0.2771	-0.0025
1.0000	-0.1043	-0.1049	0.0006	-0.3267	-0.3244	-0.0023
1.1000	-0.1104	-0.1109	0.0005	-0.3653	-0.3633	-0.0020
1.2000	-0.1137	-0.1140	0.0003	-0.3945	-0.3929	-0.0017

^aAll reduced matrix elements were evaluated using 4f wavefunctions obtained from mixed configuration Dirac-Fock calculations.

^bThe operator T_k^m is the effective multipole operator in Equation 141.

^cThe operator T_k^m is the nonrelativistic multipole operator given in Equation 111. The integrals $\bar{J}_k$ which are needed for the evaluation of matrix elements of this operator were calculated using the relativistic generalization given in Equation 133.

amplitude evaluated with the relativistic generalizations of the integrals $\bar{J}_k$ has been used in the past to analyze the measured form factors of Er and Gd metals, we can assess the importance of the differences shown in Tables 13a, 13b and 13c by reanalyzing this data.

Stassis et al.²⁴ measured the induced moment form factor of Er metal. The experiment was performed by Bragg scattering a monochromatic neutron beam from a crystal subjected to a field of 22kOe applied perpendicular to the scattering plane. The ratio of the coherent diffracted intensities of neutrons with spin orientations parallel and antiparallel to the applied field was measured. This quantity is called the polarization ratio and from it, the ratio of the coherent paramagnetic scattering amplitude $p(\theta)$ to the nuclear scattering amplitude b was extracted. The nuclear scattering amplitude b does not depend on the scattering angle and thus the angular dependence of the ratio $p(\theta)/b$ is equal to the form factor for the metal. The conduction electrons are much more spatially extended than the 4f-electrons and thus contribute to the measured form factor only at small values of $\sin \theta/\lambda$.

Thus the conduction electron contribution to the scattering can be obtained by subtracting from p/b a theoretical form factor for the 4f electrons which has been fit to the data at large values of $\sin \theta/\lambda$ where the contribution from the conduction electron polarization is expected to be negligibly small. Using this idea, Stassis et al.²⁴ separated the conduction electron contribution to p/b by fitting all data having $\sin \theta/\lambda > .35$ with an induced moment form factor which was evaluated with the relativistic generalizations of the Bessel transforms (see Equation 133). This is the

form factor which would be obtained by normalizing to one in the forward direction the reduced matrix element $\langle \theta J \| T_1^m(0) \| \theta J \rangle$ given in Table 13b. As we have seen such an analysis is inconsistent because a non-relativistic expression (Equations 111 through 116) was used to obtain the scattering amplitude and form factor for an atom described by a relativistic Dirac Hamiltonian. In order to be consistent, an expression for the scattering amplitude and form factor (Equations 149 through 152) derived from the relativistic Dirac Hamiltonian describing the atom must be used. Thus instead of using the reduced matrix elements $\langle \theta J \| T_1^m(0) \| \theta J \rangle$ (which were evaluated with relativistic radial wavefunctions by using Equation 133), the reduced matrix elements $(\theta J \| T_1^m \| \theta J)$ given in Table 13b should be used to obtain the induced moment form factor of the Er^{3+} ion.

In Tables 14a and 14b a reanalysis of this experiment is presented using the form factor obtained from the reduced matrix elements $(\theta J \| T_1^m \| \theta J)$ given in Table 13b. The ratios of p/b obtained by Stassis *et al.*²⁴ are also presented along with a fit consistent with the original analysis of the data. Results for the cases in which the magnetic field was applied parallel and perpendicular to the crystallographic c -axis have been separately tabulated because the magnetic susceptibility in these two cases is different. The differences between the fit and measured values of p/b for the high angle reflections are attributed to uncertainties involved in the experiment and the calculation. For the low angle reflections these differences are primarily a measure of the conduction electron form factor.

Table 14a. Induced moment form factor of erbium metal^a (H||c)

H	K	L	$\sin \theta/\lambda$	p/b^a measured	Fit using $\langle \theta J T_1^m(0) \theta J \rangle^b$	(Difference from p/b) $\times 10^4$	Fit using $\langle \theta J T_1^m \theta J \rangle^c$	(Difference from p/b) $\times 10^4$
0	0	0	0.0	0.05861	0.06320	54.	0.06363	50.
1	0	0	0.163	0.05919	0.05722	20.	0.05755	16.
1	1	0	0.283	0.04817	0.04769	5.	0.04788	3.
2	0	0	0.326	0.04428	0.04392	4.	0.04407	2.
2	1	0	0.432	0.03478	0.03482	0.	0.03487	-1.
3	0	0	0.489	0.02981	0.03031	-5.	0.03033	-5.
2	2	0	0.565	0.02564	0.02488	8.	0.02487	8.
3	1	0	0.588	0.02387	0.02339	5.	0.02336	5.
4	0	0	0.652	0.01912	0.01958	-5.	0.01954	-4.
3	2	0	0.711	0.01623	0.01651	-3.	0.01646	-2.

^aMeasurements performed by Stassis et al.²⁴ using the polarized neutron technique. Data was taken at 300°K by inducing a moment with a field of 22 kOe applied parallel to the crystallographic c axis. The value of p/b for $\sin \theta/\lambda = 0.0$ was obtained from susceptibility measurements.

^bThis is a least squares fit to the data with $\sin \theta/\lambda > .35$ using the induced moment form factor given in Equation 132. The form factor was evaluated using reduced matrix elements of the nonrelativistic multipole operator $T_1^m(0)$ given in Table 13b. This is the form factor used in the original analysis of the data.

^cThis is a least squares fit to the data with $\sin \theta/\lambda > .35$ using the induced moment form factor. The form factor was evaluated using reduced matrix elements of the relativistic multipole operator T_1^m given in Table 13b. It is more consistent to use this form factor in analyzing the data.

Table 14b. Induced moment form factor of erbium metal^a (H1c)

H	K	L	$\sin \theta/\lambda$	p/b^a measured	Fit using $\langle \theta J T_1^m(0) \theta J \rangle^b$	(Difference from p/b) $\times$ 10^4	Fit using $(\theta J T_1^m \theta J)^c$	(Difference from p/b) $\times$ 10^4
0	0	0	0.0	0.06085	0.05626	46.	0.05659	43.
0	0	2	0.179	0.05086	0.04994	9.	0.05018	7.
1	0	1	0.186	0.05049	0.04949	10.	0.04972	8.
1	0	2	0.241	0.04735	0.04564	17.	0.04581	15.
1	1	0	0.283	0.04416	0.04245	17.	0.04258	16.
1	0	3	0.313	0.04003	0.04011	-1.	0.04022	-2.
1	1	2	0.334	0.03891	0.03847	4.	0.03856	4.
2	0	1	0.338	0.03897	0.03815	8.	0.03824	7.
0	0	4	0.357	0.03705	0.03667	4.	0.03675	3.
2	0	2	0.372	0.03566	0.03551	2.	0.03557	1.
2	0	3	0.422	0.03176	0.03173	0.	0.03176	0.
1	1	4	0.455	0.02968	0.02933	3.	0.02935	3.
1	0	5	0.475	0.02723	0.02793	-7.	0.02793	-7.
0	0	6	0.536	0.02422	0.02391	3.	0.02389	3.
2	2	0	0.565	0.02247	0.02215	3.	0.02212	3.
2	2	2	0.593	0.02019	0.02053	-3.	0.02050	-3.
1	1	6	0.606	0.01996	0.01982	1.	0.01977	2.
1	0	7	0.646	0.01726	0.01772	-5.	0.01767	-4.
2	2	4	0.668	0.01643	0.01665	-2.	0.01660	-2.
2	0	7	0.704	0.01482	0.01500	-2.	0.01495	-1.
0	0	8	0.714	0.01414	0.01457	-4.	0.01451	-4.

^aMeasurements performed by Stassis et al.²⁴ using the polarized neutron technique. Data was taken at 300°K by inducing a moment with a field of 22 kOe applied perpendicular to the crystallographic c axis. The value of p/b for $\sin \theta/\lambda = 0.0$ was obtained from susceptibility measurements.

^bThis is a least squares fit to the data with $\sin \theta/\lambda > .35$ using the induced moment form factor given in Equation 132. The form factor was evaluated using reduced matrix elements of the non-relativistic multipole operator $T_1^m(0)$ given in Table 13b. This is the form factor used in the original analysis of the data.

^cThis is a least squares fit to the data with $\sin \theta/\lambda > .35$ using the induced moment form factor. The form factor was evaluated using reduced matrix elements of the relativistic multipole operator T_1^m given in Table 13b. It is more consistent to use this form factor to analyze the data.

It is seen that in the original analysis of the data the magnitude of the conduction electron polarization (this is determined by $p(0)/b$) was systematically overestimated by approximately ten percent. Moreover there are differences in the shape of the resultant conduction electron form factor. However these differences are sufficiently small so that the qualitative conclusions made by Stassis et al.²⁴ about the nature of the conduction electron polarization remain essentially unchanged.

Similarly the reduced matrix elements $\langle \theta J \| T_1^m \| \theta J \rangle$ which are tabulated in Table 13a for the tripositive gadolinium ion have been used to reanalyze the experiment performed by Moon et al.²³ In this experiment both polarized and unpolarized neutrons were used to obtain the form factor of gadolinium metal in a nearly saturated state. In reanalyzing this experiment, comparison has been made with the product of the magnetic moment μ and the form factor f , which was tabulated by Moon et al.²³ To make the comparison saturated state form factors obtained from the two sets of reduced matrix elements given in Table 13a ($\langle \theta J \| T_1^m(0) \| \theta J \rangle$ and $\langle \theta J \| T_1^m \| \theta J \rangle$) were fit to the 64 measured reflections having $\sin \theta/\lambda > .35$. Since the conduction electron polarization only appreciably affects the first few reflections the results of the fits have only been tabulated in Table 14c out to a value of $\sin \theta/\lambda < .43$. The difference between the fits and the product μf for reflections with $\sin \theta/\lambda > .25$ gives some indication of the uncertainties involved in the experiment and calculation. Again it is seen that an analysis using the reduced matrix elements $\langle \theta J \| T_1^m(0) \| \theta J \rangle$ overestimates the magnitude of the conduction electron polarization compared to a more

Table 14c. Saturated state form factor of gadolinium metal^a

h	k	l	$\sin \theta/\lambda$	μf^b Measured	Fit using $\langle \theta J T_1^m(0) \theta J \rangle^c$	(Difference from μf) $\times 10^2$	Fit using $(\theta J T_1^m \theta J)^d$	(Difference from μf) $\times 10^2$
0	0	0	0.0	6.92	6.36	56.	6.45	47.
0	1	0	0.1592	5.854	5.441	41.	5.507	35.
0	0	2	0.1725	5.437	5.300	14.	5.364	7.
0	1	1	0.1811	5.193	5.206	-1.	5.267	-7.
0	1	2	0.2348	4.544	4.580	-4.	4.629	-8.
1	1	0	0.2758	4.069	4.083	-1.	4.122	-5.
0	1	3	0.3038	3.757	3.745	1.	3.778	-2.
0	2	0	0.3185	3.699	3.570	13.	3.600	10.
0	2	1	0.3299	3.475	3.437	4.	3.467	1.
0	0	4	0.3450	3.336	3.263	7.	3.287	5.
0	2	2	0.3622	3.156	3.070	9.	3.090	7.
0	1	4	0.3800	2.824	2.876	-5.	2.893	-7.
0	2	3	0.4103	2.559	2.560	-1.	2.572	-1.
2	1	0	0.4213	2.399	2.451	-5.	2.461	-6.

^aResults of neutron diffraction experiments performed on single-crystal specimens of ¹⁶⁰Gd by Moon et al.²³ using both polarized and unpolarized neutrons. Data were obtained in the ferromagnetic state at 96 K for all hko reflections out to $\sin \theta/\lambda < 1.275$ and nearly all (0k1) peaks to $\sin \theta/\lambda < 1.04$.

^bThe quantity tabulated is the moment times the form factor. The product μf was obtained from the p/b ratios with the experimentally determined value for the nuclear scattering amplitude for ¹⁶⁰Gd. The value of p/b for $\sin \theta/\lambda = 0.0$ was obtained from susceptibility measurements.

^cThis is a least squares fit to all the data with $\sin \theta/\lambda > .35$ using the saturated state form factor given in Equation 125. The results are only presented for $\sin \theta/\lambda < .43$, and the form factor was evaluated from reduced matrix elements of the nonrelativistic multipole operator $T_k^m(0)$, given in Table 13a.

^dThis is a least squares fit to all the data with $\sin \theta/\lambda < .35$ using the reduced matrix elements of the relativistic multipole operator T_1^m given in Table 13a. Only results for $\sin \theta/\lambda < .43$ are shown. It is more consistent to use this form factor in analyzing the data.

consistent analysis using the $(\theta J \| T_1^m \| \theta J)$. However again, this over-estimation does not affect any qualitative conclusion made about the nature of the conduction electron magnetization density.

Thus we see that there are some small but significant differences between rare earth form factors evaluated using the relativistic theory of magnetic scattering which has been presented in this chapter, and those obtained from relativistic extensions or generalizations of the nonrelativistic theory presented in Chapter IV.

Discussions and Conclusions

The aim of this work has been to formulate an accurate theory of magnetic scattering that could be used to interpret experiments which measure the form factor of rare earth ions in solids. To do this, the similarity between the problem of magnetic scattering and the radiation problem in spectroscopy has been exploited. Using this analogy, it has been shown that the magnetic scattering amplitude of an atom described by either a relativistic or nonrelativistic Hamiltonian can be expressed in terms of matrix elements of magnetic and electric multipole operators. These matrix elements have been evaluated for atoms in the ℓ^n electronic configuration by applying techniques well known in modern spectroscopy.

In the nonrelativistic case, the magnetic and electric multipole operators were expanded in terms of Racah tensors, which are the generators of the groups used to classify the atomic states. This reduces the calculation of the magnetic scattering amplitude to the evaluation of radial integrals and matrix elements of the Racah tensors. The

nonvanishing matrix elements of the Racah tensors can be obtained for all cases of practical interest from tabulations compiled by atomic physicists. The radial integrals can be evaluated from one electron radial wavefunctions obtained from some type of Hartree-Fock calculation. However, since the 4f-wavefunctions of rare earth ions are only accurately obtainable from relativistic Dirac-Fock calculations, a relativistic generalization of these radial integrals (see Equation 133) has been commonly used to interpret elastic scattering experiments.

For the case in which the atom is described by a relativistic Hamiltonian, the matrix elements of the relativistic magnetic and electric multipole operators have been obtained using the effective operator approach, which was first introduced by Sandars and Beck⁶⁸ in the study of hyperfine interactions. By writing the relativistic electric and magnetic multipole operators in effective operator form, a relativistic result has been obtained by taking matrix elements of these effective operators between nonrelativistic states of the atom. The electric and magnetic multipole operators, written in effective operator form, have been expressed in terms of Racah tensors and relativistic radial integrals. The relativistic radial integrals can be calculated from Dirac-Fock radial wavefunctions, and the matrix elements of the Racah tensors are easily obtainable using the well-known techniques of atomic spectroscopy which have been discussed.

In applying this formulation of magnetic scattering to experiments performed on the rare earth metals, it was necessary to approximate the 4f electron wavefunctions in the solid with those of the tripositive

ion. In doing this, effects such as the screening of the nuclear charge by the conduction electrons, interband mixing and core polarization have been neglected. Harmon and Freeman²⁶ have theoretically examined these effects for Gd metal and found that, in fact, they are quite small. This conclusion is supported by the fact that excellent agreement has been obtained between the localized part of the form factors for Er and Gd metals and theoretical fits using this atomic model.

The ground state of a rare earth tripositive ion is nearly a single Russell-Saunders state and for elastic scattering from such a state it was shown that the magnetic scattering amplitude can always be written in the conventional form $p(\vec{q}) \vec{q}_m \cdot \vec{\sigma}$. General expressions for the amplitude $p(\vec{q})$ were obtained and the form factor was defined as the angular part of $p(\vec{q})$ normalized to one in the forward direction. The evaluation of the coherent magnetic scattering amplitude of an atom in a magnetic field was also discussed.

These expressions were used to compare calculations of the 4f electron form factor using the relativistic and nonrelativistic formulations of magnetic scattering. To do this, Dirac-Fock radial wavefunctions were calculated for Gd^{3+} and Er^{3+} ions using the mixed configuration approximation. In this approximation, all states of a given term are assumed to have the same radial wavefunction. The uncertainties introduced in the calculated form factor by making this approximation have been assessed by Freeman and Desclaux⁶⁷ and found to be quite small. Using this approximation the form factors obtained by Moon et al.²³ and Stassis et al.²⁴ for Er and Gd metals were reanalyzed. It was shown that

the form factor which was originally used to analyze these experiments overestimates the conduction electron polarization by approximately ten percent compared to an analysis using the relativistic treatment of magnetic scattering presented in this chapter. These differences do not change any qualitative conclusions which have been drawn from these experiments about the conduction electron polarization; however, they are of importance in a quantitative analysis of the conduction electron form factor.

It should be pointed out that even changes as small as a few parts per thousand in the 4f-electron form factor can produce appreciable changes in the conduction electron form factor. This is due to the fact that the conduction electron form factor was obtained by subtracting from the measurements, the dominant contribution of the 4f²-electrons. Although, all of the approximations used to obtain the relativistic 4f form factor are excellent, this subtraction procedure introduces uncertainties into the measured conduction electron form factor. To circumvent these problems, Dr. Stassis has recently performed measurements on Lu metal which has a closed shell of 4f electrons. Preliminary measurements indicate that the conduction electron distribution in Lu is quite similar to that of Er metal.

Finally, it should be noted that the nonrelativistic formulation of magnetic scattering presented in Chapter II is totally general and can be used to investigate magnetic scattering from systems other than atoms. Moreover, some novel predictions are contained in this general formulation of magnetic scattering. If the initial and final states of the scattering system have opposite parities, the electric dipole term may produce the

dominant contribution to the inelastic scattering cross section. Thus far such a contribution to the inelastic magnetic scattering cross section has not been experimentally reported, primarily because the energy of present day neutron beams is so low that only transitions between states of the same parities can occur. However, with the advent of higher energy neutron beams, such transitions may be observable.

APPENDIX A

In this appendix the basic properties of the vector spherical harmonics will be summarized. The vector spherical harmonic $\vec{Y}_{k,L,l}^m(\hat{r})$ is defined by

$$\vec{Y}_{k,l,l}^m(\hat{r}) = \sum_{M,q} Y_{lM}(\hat{r}) \vec{e}_q(lM1q|km), \quad (A.1)$$

where $(lM1q|km)$ is a Clebsch Gordon coefficient, $\vec{e}_q$ is a spherical unit vector and $Y_{lM}(\hat{r})$ is a spherical harmonic. From the definition of the vector spherical harmonics, it is seen that they are formed by coupling the spherical harmonics with the components of the spherical unit vectors (Equation 17). The vector spherical harmonics are often used in the multipole expansion of the electromagnetic field, and have been used throughout this work. In some cases in this work, the notation for the vector spherical harmonics adopted by Blatt and Weisskopf³⁹ has been used. The correlation between the notation for the vector spherical harmonic in Equation (A.1) and that of Blatt and Weisskopf is,

$$\vec{V}_{lm} = \vec{Y}_{l,l+1,l}^m, \quad \vec{X}_{lm} = \vec{Y}_{l,l,l}^m, \quad \vec{W}_{lm} = \vec{Y}_{l,l-1,l}^m. \quad (A.2)$$

The vector spherical harmonics can be expressed as analytical functions in a spherical polar coordinate system (r, θ, ϕ) associated with the unit vector system $(\hat{r}_1, \hat{\theta}_1, \hat{\phi}_1)$:

$$\begin{aligned} \vec{Y}_{\ell, \ell+1, 1}^m = & \hat{r}_1 \left\{ - \left(\frac{\ell+1}{2\ell+1} \right)^{\frac{1}{2}} Y_{\ell m} \right\} + \hat{\theta}_1 \left\{ \frac{1}{[(\ell+1)(2\ell+1)]^{\frac{1}{2}}} \frac{\partial Y_{\ell m}}{\partial \theta} \right\} \\ & + \hat{\phi}_1 \left\{ \frac{i m Y_{\ell m}}{[(\ell+1)(2\ell+1)]^{\frac{1}{2}} \sin \theta} \right\} \end{aligned} \quad (A.3)$$

$$\vec{Y}_{\ell, \ell, 1}^m = \hat{\theta}_1 \left\{ \frac{-m Y_{\ell m}}{[\ell(\ell+1)]^{\frac{1}{2}} \sin \theta} \right\} + \hat{\phi}_1 \left\{ \frac{-i}{[\ell(\ell+1)]^{\frac{1}{2}}} \frac{\partial Y_{\ell m}}{\partial \theta} \right\} \quad (A.4)$$

$$\begin{aligned} \vec{Y}_{\ell, \ell-1, 1}^m = & \hat{r}_1 \left\{ \left(\frac{\ell}{2\ell+1} \right)^{\frac{1}{2}} Y_{\ell m} \right\} + \hat{\theta}_1 \left\{ \frac{1}{[\ell(2\ell+1)]^{\frac{1}{2}}} \frac{\partial Y_{\ell m}}{\partial \theta} \right\} \\ & + \hat{\phi}_1 \left\{ \frac{i m Y_{\ell m}}{[\ell(2\ell+1)]^{\frac{1}{2}} \sin \theta} \right\} \end{aligned} \quad (A.5)$$

where the unit vectors $(\hat{r}_1, \hat{\theta}_1, \hat{\phi}_1)$ can be expressed in terms of unit vectors $(\hat{i}, \hat{j}, \hat{k})$ of a fixed right-handed Euclidian coordinate system by

$$\begin{aligned} \hat{r}_1 &= \hat{i} \sin \theta \cos \phi + \hat{j} \sin \theta \sin \phi + \hat{k} \cos \theta \\ \hat{\theta}_1 &= \hat{i} \cos \theta \cos \phi + \hat{j} \cos \theta \sin \phi - \hat{k} \sin \theta \\ \hat{\phi}_1 &= -\hat{i} \sin \phi + \hat{j} \cos \phi. \end{aligned} \quad (A.6)$$

The connection between the vector spherical harmonics of indices $+m$ and $-m$ are the following:

$$\vec{Y}_{\ell, \ell \pm 1, 1}^m(\hat{r}) = (-)^m \vec{Y}_{\ell, \ell \pm 1, 1}^{-m*}(\hat{r})$$

$$\vec{Y}_{\ell, \ell, 1}^m(\hat{r}) = (-)^{m+1} \vec{Y}_{\ell, \ell, 1}^{-m*}(\hat{r}) . \quad (\text{A.7})$$

The vector spherical harmonic can be generated from the scalar spherical harmonics by use of the identity

$$\vec{\ell} Y_{\ell m}(\hat{r}) = \sqrt{\ell(\ell+1)} \vec{Y}_{\ell, \ell, 1}^m(\hat{r}) , \quad (\text{A.8})$$

where $\vec{\ell}$ is the orbital angular momentum operator.

The gradient of a spherical Bessel function $j_k(qr)$ times a spherical harmonic and the product of a radial unit vector and a spherical harmonic can be written in terms of vector spherical harmonics:

$$\left(\frac{k+1}{2k+1}\right)^{\frac{1}{2}} j_{k-1} \vec{Y}_{k, k-1, 1}^m - \left(\frac{k}{2k+1}\right)^{\frac{1}{2}} j_{k+1} \vec{Y}_{k, k+1, 1}^m = \frac{1}{iq} \nabla \times (j_k \vec{X}_{km}) \quad (\text{A.9})$$

$$Y_{km} \vec{r} = \frac{r}{(2k+1)^{\frac{1}{2}}} \{ -(k+1)^{\frac{1}{2}} \vec{Y}_{k, k+1, 1}^m + (k)^{\frac{1}{2}} \vec{Y}_{k, k-1, 1}^m \} , \quad (\text{A.10})$$

In the derivation of the multipole expansion of the magnetic scattering amplitude, Equations 16-27, use was made of the identities

$$\hat{q} \times \vec{Y}_{k, k+1, 1}^m(\hat{q}) = i \left(\frac{k}{2k+1}\right)^{\frac{1}{2}} \vec{X}_{km}(\hat{q}) , \quad (\text{A.11})$$

$$\hat{q} \times \vec{Y}_{k, k-1, 1}^m(\hat{q}) = i \left(\frac{k+1}{2k+1}\right)^{\frac{1}{2}} \vec{X}_{km}(\hat{q}) , \quad (\text{A.12})$$

$$\hat{q} \times \vec{x}_{km} = \frac{i}{\sqrt{2k+1}} (\sqrt{k} \vec{Y}_{k,k+1,1}^m + \sqrt{k+1} \vec{Y}_{k,k-1,1}^m) \quad (A.13)$$

Also throughout this work use has been made of the fact that the dot product of any vector $\vec{\alpha}$ with a vector spherical harmonic can be written as a tensor product,

$$\vec{\alpha} \cdot \vec{Y}_{k,\lambda,l}^m = (-)^{k+\lambda+1} [\vec{\alpha} \times Y_{\lambda,m}^k] \quad (A.14)$$

A detailed list of other important identities has been given by Hill.⁷⁸

APPENDIX B

In this appendix, expressions for the multipole moment operators $T_{km}^m(0)$, $T_{km}^e(0)$, $T_{km}^e(j)$ and $T_{km}^m(j)$ ($j = 1, 2, \dots$) will be derived.

An expression for $T_{km}^e(0)$ can be obtained by substituting Equations 40 and 41 with $\vec{v}_i = \vec{p}_i/m$ into Equation (35) to get

$$\begin{aligned}
 T_{km}^{(e)}(0) = & i^{k+1} \left(\frac{m}{e\hbar q} \right) \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \sum_i \left\{ \left[\frac{i(E_f - E_i)}{\hbar q} e_i Y_{km}(\hat{r}_i) \frac{d}{dr} (r_i j_k(qr_i)) \right. \right. \\
 & + \left. \left. \frac{q e_i}{2m_i} \left(j_k(qr_i) Y_{km}(\hat{r}_i) \vec{r}_i \cdot \vec{p}_i + \vec{p}_i \cdot \vec{r}_i j_k(qr_i) Y_{km}(\hat{r}_i) \right) \right\} \\
 & + \frac{g_i \hbar e_i q}{2m_i} \int d\vec{r} j_k(qr) Y_{km}(\hat{r}) \vec{r} \cdot \nabla \times \left[\vec{s}_i \delta(\vec{r} - \vec{r}_i) \right] \}. \quad (B.1)
 \end{aligned}$$

The term in the curly brackets is due to the convection current, while the last term in the square brackets results from the magnetization current and can be simplified by writing

$$\begin{aligned}
 & \int d\vec{r} j_k(qr) Y_{km}(\hat{r}) \vec{r} \cdot \nabla \times \left[\vec{s}_i \delta(\vec{r} - \vec{r}_i) \right] \\
 & = \int d\vec{r} j_k(qr) Y_{km}(\hat{r}) \vec{r} \cdot \nabla \delta(\vec{r} - \vec{r}_i) \times \vec{s}_i \\
 & = \int d\vec{r} j_k(qr) Y_{km}(\hat{r}) \vec{r} \cdot [\hat{i} \delta'(y - y_i) \delta(x - x_i) \delta(z - z_i) s_{iz} \\
 & \quad - \hat{j} \delta'(z - z_i) \delta(x - x_i) \delta(y - y_i) s_{iy} + \hat{j} \dots], \quad (B.2)
 \end{aligned}$$

where $\hat{i}$, $\hat{j}$, and $\hat{k}$ are cartesian unit vectors and $\delta'(\)$ is the derivative of a delta function. By realizing that,

$$\begin{aligned} x_i s_{iz} \int j_k Y_{km} \delta'(y-y_i) dy &= -x_i s_{iz} \left[\frac{d(j_k Y_{km})}{dy} \right]_{y=y_i} \\ -x_i s_{iy} \int j_k Y_{km} \delta'(z-z_i) dz &= x_i s_{iy} \left[\frac{d(j_k Y_{km})}{dz} \right]_{z=z_i} \end{aligned} \quad (B.3)$$

Equation (B.2) can be simplified to

$$\begin{aligned} \int d\vec{r} j_k(qr) Y_{km}(\hat{r}) \vec{r} \cdot \nabla \times (\vec{s}_i \delta(\vec{r} - \vec{r}_i)) \\ = [-x_i s_{iz} \frac{d(j_k Y_{km})}{dy_i} + x_i s_{iy} \frac{d(j_k Y_{km})}{dz_i} + \dots] \\ = \vec{r}_i \cdot (\vec{s}_i \times \nabla(j_k Y_{km})) = -\vec{s}_i \cdot \vec{r}_i \times \nabla(j_k Y_{km}) = -i \vec{s}_i \cdot \vec{e}_i (j_k Y_{km}) \end{aligned} \quad (B.4)$$

Substituting this equation back into the expression for $T_{km}^e(0)$ we find,

$$\begin{aligned} T_{km}^{(e)}(0) &= i^{k+1} \left(\frac{m}{e \hbar q} \right) \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \sum_i \left[\left\{ \frac{i(E_f - E_i)}{\hbar q} e_i Y_{km}(\hat{r}_i) \frac{d}{dr} (r_i j_k(qr_i)) \right. \right. \\ &\quad \left. \left. + \frac{q e_i}{2m_i} \left(j_k(qr_i) Y_{km}(\hat{r}_i) \vec{r}_i \cdot \vec{p}_i + \vec{p}_i \cdot \vec{r}_i j_k(qr_i) Y_{km}(\hat{r}_i) \right) \right\} \right. \\ &\quad \left. - i \frac{g_i e_i \hbar q}{2m_i} \vec{s}_i \cdot \vec{e}_i (j_k(qr_i) Y_{km}(\hat{r}_i)) \right] \end{aligned} \quad (B.5)$$

This is the most compact expression that can be obtained for $T_{km}^e(0)$.

An expression for $T_{km}^m(0)$ can be obtained by substituting Equations 40 and 41 (with $\vec{v}_i = \vec{p}_i/m$) into Equation (29) to get

$$\begin{aligned}
 T_{km}^m(0) &= -2 \left(\frac{m}{e\hbar q} \right) c i^{k-1} \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \frac{1}{2c} \int d\vec{r} \vec{r} \times \vec{j}(\vec{r}) \cdot \nabla \left(j_k(qr_i) Y_{km}(\hat{r}_i) \right) \\
 &= \left(\frac{m}{e\hbar q} \right) i^{k-1} \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \int d\vec{r} i \vec{j}(r) \cdot \vec{\mathcal{L}}_i \left(j_k(qr_i) Y_{km}(\hat{r}_i) \right) \\
 &= \left(\frac{m}{e\hbar q} \right) i^{k-1} \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \left\{ \sum_i \frac{e_i i}{2m_i} \left[\vec{p}_i \vec{\mathcal{L}}_i \left(j_k(qr_i) Y_{km}(\hat{r}_i) \right) \right. \right. \\
 &\quad \left. \left. + \vec{\mathcal{L}}_i \left(j_k(qr_i) Y_{km}(\hat{r}_i) \right) \cdot \vec{p}_i \right] + \frac{e_i i \hbar g_i}{2m_i} \int d\vec{r} \vec{\mathcal{L}}_i \left(j_k(qr_i) Y_{km}(\hat{r}_i) \right) \right. \\
 &\quad \left. \cdot [\nabla \times (\vec{s}_i \delta(\vec{r} - \vec{r}_i))] \right\}. \tag{B.6}
 \end{aligned}$$

The last term in the curly brackets in Equation (B.6) is due to the spin magnetization current and can be simplified by writing

$$\begin{aligned}
 \int d\vec{r} \vec{\mathcal{L}}_i(j_k Y_{km}) \cdot [\nabla \times (\vec{s}_i \delta(\vec{r} - \vec{r}_i))] &= \int d\vec{r} \vec{\mathcal{L}}_i(j_k Y_{km}) \cdot [\nabla \delta(\vec{r} - \vec{r}_i) \times \vec{s}_i] \\
 &= \int dx dy dz \{ [\vec{\mathcal{L}}_i(j_k Y_{km})]_{\hat{x}} [\delta'(y-y_i) \delta(x-x_i) \delta(z-z_i) s_{iz} \\
 &\quad - s_{iy} \delta'(z-z_i) \delta(x-x_i) \delta(y-y_i)] \\
 &\quad + \dots \}
 \end{aligned}$$

$$\begin{aligned}
&= \int [\vec{\mathcal{E}}(j_k Y_{km})]_{\hat{x}} \delta'(y-y_i) s_{iz} dy - \int [\vec{\mathcal{E}}(j_k Y_{km})]_{\hat{x}} \delta'(z-z_i) s_{iy} dz + \dots, \\
&= -s_{iz} \frac{d}{dy} \left([\vec{\mathcal{E}}(j_k Y_{km})_{x=x_i}]_{\hat{x}} \right)_{y=y_i} \\
&\quad z=z_i \\
&+ s_{iy} \frac{d}{dz} \left([\vec{\mathcal{E}}(j_k Y_{km})_{x=x_i}]_{\hat{x}} \right)_{z=z_i} + \dots, \\
&\quad y=y_i \\
&= -s_{iz} \frac{\partial}{\partial y_i} [\vec{\mathcal{E}}_i(j_k(qr_i)Y_{km}(\hat{r}_i))]_{\hat{x}} \\
&+ s_{iy} \frac{d}{dz} [\vec{\mathcal{E}}_i(j_k(qr_i)Y_{km}(\hat{r}_i))]_{\hat{x}} + \dots, \\
&= (\vec{s} \times \nabla) \cdot \vec{\mathcal{E}}_i(j_k(qr_i)Y_{km}(\hat{r}_i)) = \vec{s}_i \cdot \nabla \times \vec{\mathcal{E}}_i(j_k(qr_i)Y_{km}(\hat{r}_i)). \quad (B.7)
\end{aligned}$$

Substituting the final expression from above back into $T_{km}^m(0)$ we find,

$$\begin{aligned}
T_{km}^{(m)}(0) &= i^k \left(\frac{m}{e\hbar q} \right) \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \sum_i \frac{e_i \hbar}{2m_i} [-i\nabla \cdot \vec{\mathcal{E}}_i(j_k(qr_i)Y_{km}(\hat{r}_i))] \\
&\quad - i\vec{\mathcal{E}}_i(j_k(qr_i)Y_{km}(\hat{r}_i)) \cdot \nabla + g_i \vec{s}_i \cdot \nabla \times \vec{\mathcal{E}}_i(j_k(qr_i)Y_{km}(\hat{r}_i))]. \quad (B.8)
\end{aligned}$$

This expression can be further simplified by writing

$$\begin{aligned}
\nabla \cdot \vec{\mathcal{E}}_i(j_k(qr_i)Y_{km}(\hat{r}_i)) &= \vec{\mathcal{E}}_i(j_k(qr_i)Y_{km}(\hat{r}_i)) \cdot \nabla \\
&= -\nabla(j_k(qr_i)Y_{km}(\hat{r}_i)) \cdot \vec{\mathcal{E}}_i. \quad (B.9)
\end{aligned}$$

Thus $T_{km}^m(0)$ can be written in the compact form,

$$T_{km}^{(m)}(0) = i^k \left(\frac{m}{e\hbar q} \right) \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \sum_i \frac{e_i \cdot \vec{r}_i}{m_i} \left[i \nabla \left(j_k(qr_i) Y_{km}(\hat{r}_i) \right) \cdot \vec{\epsilon}_i \right. \\ \left. + \frac{g_i}{2} \vec{s}_i \cdot \nabla \times \vec{\epsilon}_i \left(j_k(qr_i) Y_{km}(\hat{r}_i) \right) \right] . \quad (B.10)$$

The algebraic manipulations necessary to derive compact expressions for $T_{km}^e(j)$ and $T_{km}^m(j)$ are trivial and shall not be reproduced here. By simple calculation one can show that

$$T_{km}^{(e)}(j) = i^{k+1} \left(\frac{m}{e\hbar q} \right) \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \sum_i \frac{q e_i}{2} \left[j_k(qr_i) Y_{km}(\hat{r}_i) \vec{r}_i \right. \\ \left. \cdot \frac{\partial H_j}{\partial \vec{p}_i} + \frac{\partial H_j}{\partial \vec{p}_i} \cdot \vec{r}_i j_k(qr_i) Y_{km}(\hat{r}_i) \right] , \quad (B.11)$$

and that

$$T_{km}^m(j) = i^k \left(\frac{m}{e\hbar q} \right) \left[\frac{2\pi(2k+1)}{k(k+1)} \right]^{\frac{1}{2}} \sum_i \frac{e_i}{2} \left[\vec{\epsilon}_i \left(j_k(qr_i) Y_{km}(\hat{r}_i) \right) \right. \\ \left. \cdot \frac{\partial H_j}{\partial \vec{p}_i} + \frac{\partial H_j}{\partial \vec{p}_i} \cdot \vec{\epsilon}_i \left(j_k(qr_i) Y_{km}(\hat{r}_i) \right) \right] . \quad (B.12)$$

APPENDIX C

Some of the most useful identities and algebraic expressions for the 3-j, 6-j, and 9-j symbols used in this work will be given in this appendix.

3-j Symbols

In many of the computations in this work the symbol

$$\begin{pmatrix} j_1 & j_2 & j \\ 0 & 0 & 0 \end{pmatrix}$$

is encountered. This symbol is zero if $j_1 + j_2 + j$ is odd, so the j 's may be permuted without regard to change of sign of the symbol. The algebraic expression for this symbol is

$$\begin{aligned} \begin{pmatrix} j_1 & j_2 & j \\ 0 & 0 & 0 \end{pmatrix} &= (-)^{\frac{1}{2}J} \left[\frac{(J-2j_1)!(J-2j_2)!(J-j)!}{(J+1)!} \right]^{\frac{1}{2}} \\ &\times \frac{(\frac{1}{2}J)!}{(\frac{1}{2}J-j_1)!(\frac{1}{2}J-j_2)!(\frac{1}{2}J-j)!} \end{aligned} \quad (c.1)$$

Using this expression, one may show that:

$$\begin{pmatrix} \ell & k+1 & \ell+1 \\ 0 & 0 & 0 \end{pmatrix} = - \left[\frac{(2\ell+k+2)(k+1)}{(k+2)(2\ell+k+3)} \right]^{\frac{1}{2}} \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} \ell & k & \ell+1 \\ 0 & 0 & 0 \end{pmatrix} = - \left[\frac{k(2\ell+k+1)}{(k+1)(2\ell+k+2)} \right]^{\frac{1}{2}} \begin{pmatrix} \ell & \ell & k-1 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\begin{aligned}
\begin{pmatrix} \ell & k & \ell+1 \\ 0 & 0 & 0 \end{pmatrix} &= \left[\frac{(2\ell-k)(k+1)}{k(2\ell-k+1)} \right]^{\frac{1}{2}} \begin{pmatrix} \ell & k+1 & \ell \\ 0 & 0 & 0 \end{pmatrix} \\
\begin{pmatrix} \ell & k-1 & \ell+1 \\ 0 & 0 & 0 \end{pmatrix} &= \left[\frac{(2\ell-k+1)k}{(k-1)(2\ell-k+2)} \right]^{\frac{1}{2}} \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \\
\begin{pmatrix} \ell & k+1 & \ell-1 \\ 0 & 0 & 0 \end{pmatrix} &= \left[\frac{(k+1)(2\ell-k)}{(k+2)(2\ell-k-1)} \right]^{\frac{1}{2}} \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \\
\begin{pmatrix} \ell & k & \ell-1 \\ 0 & 0 & 0 \end{pmatrix} &= \left[\frac{k(2\ell-k+1)}{(k+1)(2\ell-k)} \right]^{\frac{1}{2}} \begin{pmatrix} \ell & \ell & k-1 \\ 0 & 0 & 0 \end{pmatrix} \\
\begin{pmatrix} \ell & k & \ell-1 \\ 0 & 0 & 0 \end{pmatrix} &= - \left[\frac{(k+1)(2\ell+k+2)}{k(2\ell+k+1)} \right]^{\frac{1}{2}} \begin{pmatrix} \ell & k+1 & \ell \\ 0 & 0 & 0 \end{pmatrix} \\
\begin{pmatrix} \ell & k-1 & \ell-1 \\ 0 & 0 & 0 \end{pmatrix} &= - \left[\frac{k(2\ell+k+1)}{(k-1)(2\ell+k)} \right]^{\frac{1}{2}} \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \\
\begin{pmatrix} \ell & k+1 & \ell \\ 0 & 0 & 0 \end{pmatrix} &= - \left[\frac{(2\ell+k+1)(2\ell-k+1)}{(2\ell-k)(2\ell+k+2)} \right]^{\frac{1}{2}} \frac{k}{k+1} \begin{pmatrix} \ell & k-1 & \ell \\ 0 & 0 & 0 \end{pmatrix}. \quad (C.2)
\end{aligned}$$

Some algebraic expressions for other 3-j symbols commonly encountered in this work are given below:

$$\begin{aligned}
\begin{pmatrix} k & 1 & k+1 \\ 1 & -1 & 0 \end{pmatrix} &= (-)^{k+1} \left[\frac{k}{2(2k+3)(2k+1)} \right]^{\frac{1}{2}} \\
\begin{pmatrix} k & 1 & k-1 \\ 1 & -1 & 0 \end{pmatrix} &= (-)^{k-1} \left[\frac{(k+1)}{2(2k-1)(2k+1)} \right]^{\frac{1}{2}}
\end{aligned}$$

$$\begin{pmatrix} k & 1 & k \\ 1 & -1 & 0 \end{pmatrix} = \frac{(-)^{k+1}}{\sqrt{2(2k+1)}} \quad (C.3)$$

6-j Symbols

Many of the 6-j symbols that were evaluated in this work were needed for the calculation of a 9-j symbol. These 6-j symbols shall not be presented here and only identities for the 6-j symbols used in the actual evaluation of the reduced matrix elements of the multipole operators will be given:

$$\begin{aligned} \begin{pmatrix} k & 1 & k+1 \\ \ell & \ell & \ell \end{pmatrix} &= (-)^{2\ell+k+1} \left[\frac{(2\ell+k+2)(k+1)(2\ell-k)}{4\ell(\ell+1)(2\ell+1)(2k+1)(2k+3)} \right]^{\frac{1}{2}} \\ \begin{pmatrix} k & 1 & k-1 \\ \ell & \ell & \ell \end{pmatrix} &= (-)^{2\ell+k} \left[\frac{(2\ell+k+1)k(2\ell-k+1)}{4\ell(\ell+1)(2\ell+1)(2k-1)(2k+1)} \right]^{\frac{1}{2}} \end{aligned} \quad (C.4)$$

An important identity involving 3-j and 6-j symbols is:

$$\sqrt{(k+1)(2k+3)} \begin{pmatrix} k & 1 & k+1 \\ \ell & \ell & \ell \end{pmatrix} \begin{pmatrix} \ell & k+1 & \ell \\ 0 & 0 & 0 \end{pmatrix} = \sqrt{k(2k-1)} \begin{pmatrix} k & 1 & k-1 \\ \ell & \ell & \ell \end{pmatrix} \begin{pmatrix} \ell & k-1 & \ell \\ 0 & 0 & 0 \end{pmatrix} \quad (C.5)$$

9-j Symbols

In the calculation magnetic scattering by a relativistic atom, the general 9-j symbol

$$\begin{pmatrix} j_2 & j_2 & k \\ \ell & \ell' & k' \\ j & j' & k \end{pmatrix} \quad (C.6a)$$

occurs frequently. Using the triangular relations listed in Table I, it is easily seen that k' can only take the values 0 or 1 and that if $k' = 0$, then necessarily $k' = k$, whereas if $k' = 1$, then $k' = k, k \pm 1$. For $k' = 1$ and $k' = k \pm 1, k$, this symbol can be most easily evaluated using an identity given by Edmonds,³⁶

$$\begin{aligned} \left\{ \begin{array}{ccc} \frac{1}{2} & \frac{1}{2} & 1 \\ l & l & k' \\ j & j' & k \end{array} \right\} &= \frac{(-)^{j+j'+k+k'}}{3 \left\{ \begin{array}{ccc} k & k' & 1 \\ \frac{1}{2} & \frac{1}{2} & \mu \end{array} \right\}} [(-)^{2\mu} \left\{ \begin{array}{ccc} j & j' & k \\ \frac{1}{2} & \mu & l \end{array} \right\} \left\{ \begin{array}{ccc} l & l & k' \\ \frac{1}{2} & \mu & j \end{array} \right\} \\ &+ \frac{(-)^{l+j'-\mu-1}}{2(2k+1)} \left\{ \begin{array}{ccc} k & l & l \\ \frac{1}{2} & j & j' \end{array} \right\} \delta_{k'k}] . \end{aligned} \quad (C.6b)$$

where μ is given the value $(k + k')/2$ if $k \neq k'$ or $k + \frac{1}{2}$ if $k' = k$.

For the case in which $k' = k$, the 9-j symbol in Equation (C.5) can be reduced to the 6-j symbol,

$$\left\{ \begin{array}{ccc} l & l' & k \\ j' & j & \frac{1}{2} \end{array} \right\}.$$

by using the relation

$$\begin{aligned} \left\{ \begin{array}{ccc} \frac{1}{2} & \frac{1}{2} & 1 \\ l & l' & k \\ j & j' & k \end{array} \right\} &= \left\{ \begin{array}{ccc} -\frac{1}{2} & \frac{1}{2} & 1 \\ l & l' & k \\ j & j' & k \end{array} \right\} = (-)^{l'j+k+\frac{1}{2}} \frac{2(2k+1)}{3k(k+1)} \frac{1}{2} \left\{ \begin{array}{ccc} l & l' & k \\ j & j' & \frac{1}{2} \end{array} \right\} \\ &\times [\{l(l+1) - l'(l'+1)\} - \{j(j+1) - j'(j'+1)\}]. \end{aligned} \quad (C.7)$$

If in the 9-j symbol of interest, Equation (C.6a), $k' = 0$, the symbol may be simplified using

$$\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ \ell & \ell' & k \\ j & j' & k \end{Bmatrix} = \frac{(-)^{\ell'+j+k+\frac{1}{2}}}{[2(2k+1)]^{\frac{1}{2}}} \begin{Bmatrix} j' & \ell' & \frac{1}{2} \\ \ell & j & k \end{Bmatrix} \quad (\text{C.8})$$

Using these identities, the table of 9-j symbols given below was obtained.

$$\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \ell & \ell & k+1 \\ \ell+\frac{1}{2} & \ell+\frac{1}{2} & k \end{Bmatrix} = -\frac{1}{4(\ell+1)(2\ell+1)} \left[\frac{2(k+1)(2\ell-k)(2\ell-k+1)}{3(2k+1)(2k+3)} \right]^{\frac{1}{2}} \quad (\text{C.9})$$

$$\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \ell & \ell & k+1 \\ \ell+\frac{1}{2} & \ell-\frac{1}{2} & k \end{Bmatrix} = -\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \ell & \ell & k+1 \\ \ell-\frac{1}{2} & \ell+\frac{1}{2} & k \end{Bmatrix} \\ = \frac{1}{4(2\ell+1)} \left[\frac{2k(2\ell-k)(2\ell+k+2)}{3(2k+1)(2k+3)\ell(\ell+1)} \right]^{\frac{1}{2}} \quad (\text{C.10})$$

$$\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \ell & \ell & k+1 \\ \ell-\frac{1}{2} & \ell-\frac{1}{2} & k \end{Bmatrix} = \frac{1}{4\ell(2\ell+1)} \left[\frac{2(k+1)(2\ell+k+1)(2\ell+k+2)}{3(2k+1)(2k+3)} \right]^{\frac{1}{2}} \quad (\text{C.11})$$

$$\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \ell & \ell & k \\ \ell+\frac{1}{2} & \ell+\frac{1}{2} & k \end{Bmatrix} = 0 \quad (\text{C.12})$$

$$\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \ell & \ell & k \\ \ell+\frac{1}{2} & \ell-\frac{1}{2} & k \end{Bmatrix} = \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \ell & \ell & k \\ \ell-\frac{1}{2} & \ell+\frac{1}{2} & k \end{Bmatrix} = \frac{1}{2\sqrt{6(2k+1)(\ell+1)\ell}} \quad (\text{C.13})$$

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \ell & \ell & k \\ \ell - \frac{1}{2} & \ell - \frac{1}{2} & k \end{pmatrix} = 0 \quad (\text{C.14})$$

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \ell & \ell & k-1 \\ \ell + \frac{1}{2} & \ell + \frac{1}{2} & k \end{pmatrix} = \frac{1}{12(\ell+1)(2\ell+1)} \left[\frac{6k(2\ell+k+1)(2\ell+k+2)}{(2k-1)(2k+1)} \right]^{\frac{1}{2}} \quad (\text{C.15})$$

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \ell & \ell & k-1 \\ \ell + \frac{1}{2} & \ell - \frac{1}{2} & k \end{pmatrix} = - \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \ell & \ell & k-1 \\ \ell - \frac{1}{2} & \ell + \frac{1}{2} & k \end{pmatrix} \\ = \frac{1}{12(2\ell+1)} \left[\frac{6(2\ell-k+1)(2\ell+k+1)(k+1)}{(2k-1)(2k+1)\ell(\ell+1)} \right]^{\frac{1}{2}} \quad (\text{C.16})$$

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \ell & \ell & k-1 \\ \ell - \frac{1}{2} & \ell - \frac{1}{2} & k \end{pmatrix} = - \frac{1}{12\ell(2\ell+1)} \left[\frac{6k(2\ell-k)(2\ell-k+1)}{(2k-1)(2k+1)} \right]^{\frac{1}{2}} \quad (\text{C.17})$$

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ \ell & \ell & k \\ \ell + \frac{1}{2} & \ell + \frac{1}{2} & k \end{pmatrix} = \frac{1}{2(\ell+1)(2\ell+1)} \left[\frac{(2\ell+k+2)(2\ell-k+1)}{2(2k+1)} \right]^{\frac{1}{2}} \quad (\text{C.18})$$

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ \ell & \ell & k \\ \ell - \frac{1}{2} & \ell + \frac{1}{2} & k \end{pmatrix} = \frac{1}{2(2\ell+1)} \left[\frac{k(k+1)}{2(2k+1)\ell(\ell+1)} \right]^{\frac{1}{2}} \quad (\text{C.19})$$

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ \ell & \ell & k \\ \ell - \frac{1}{2} & \ell - \frac{1}{2} & k \end{pmatrix} = \frac{1}{2\ell(2\ell+1)} \left[\frac{(2\ell+k+1)(2\ell-k)}{2(2k+1)} \right]^{\frac{1}{2}} \quad (\text{C.20})$$

It should be noted that the 9-j symbols in Equations (C.12) and (C.14) were identically equal to zero because, of the general identity:

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_1 & j_2 & j_3 \\ k_1 & k_2 & k_3 \end{Bmatrix} = 0 \quad \text{if } k_1 + k_2 + k_3 \text{ is odd.}$$

APPENDIX D

Any atomic operator can be expressed in terms of the Racah tensors. For a one particle operator

$$C_{km} = \sum_i c_{km}(i)$$

one can write

$$C_{km} = \sum_{K,K'} A(K,K',k) W_m^{(K,K')k}, \quad (D.1)$$

where the coefficients A are determined by requiring that

$$\langle \frac{1}{2} \alpha \ell j \| C_K \| \frac{1}{2} \alpha' \ell j' \rangle = \sum_{K,K'} A(K,K',k) [j, j', K, K', k]^{\frac{1}{2}} \left\{ \begin{matrix} \frac{1}{2} & \ell & j \\ \frac{1}{2} & \ell & j' \\ K & K' & k \end{matrix} \right\}.$$

Multiplying both sides of this equation by the 9-j symbol which appears on the right hand side of this equation, summing over j, j', and using the 9-j orthogonality relation one obtains

$$A(K,K',k) = \sum_{j,j'} [j, j', K, K']^{\frac{1}{2}} [k]^{-\frac{1}{2}} \left\{ \begin{matrix} \frac{1}{2} & \frac{1}{2} & K \\ \ell & \ell & K' \\ j & j' & k \end{matrix} \right\} \langle \frac{1}{2} \alpha \ell j \| C_K \| \frac{1}{2} \alpha' \ell j' \rangle. \quad (D.2)$$

If

$$c_k = [a_k, x b_k] k$$

then

$$(\frac{1}{2}\alpha \ell j \| c_k \| \frac{1}{2}\alpha' \ell j') = [j, j', k]^{\frac{1}{2}} \begin{Bmatrix} \frac{1}{2} & \ell & j \\ \frac{1}{2} & \ell & j' \\ k' & k' & k \end{Bmatrix} (\frac{1}{2} \| a_{k'} \| \frac{1}{2}) (\alpha \ell \| b_{k'} \| \alpha' \ell) .$$

Substituting this relation into (D.2) and using the 9-j orthogonality one finds

$$A(K, K', k) = \delta(K, K') \delta(K', k') [k', k']^{-\frac{1}{2}} (\frac{1}{2} \| a_{k'} \| \frac{1}{2}) (\alpha \ell \| b_{k'} \| \alpha' \ell) .$$

Substituting this relation into (D.1) one finally obtains

$$c_{km} = [k', k']^{-\frac{1}{2}} (\frac{1}{2} \| a_{k'} \| \frac{1}{2}) (\alpha \ell \| b_{k'} \| \alpha' \ell) w_m^{(k', k') k} . \quad (D.3)$$

BIBLIOGRAPHY

1. E. Fermi and H. Zinn, Phys. Rev. 70, 103 (1946).
2. I. I. Gurevich and L. V. Tarasov, Low Energy Neutron Physics (North-Holland Pub., New York, 1968).
3. G. E. Bacon, Neutron Diffraction (Oxford U.P., London, 1962).
4. P. A. Englestaff (Ed.), Thermal Neutron Scattering (Academic Press, London, 1965).
5. F. Bloch, Phys. Rev. 50, 259 (1936).
6. J. Schwinger, Phys. Rev. 51, 544 (1937).
7. O. Halpern and M. H. Johnson, Phys. Rev. 55, 898 (1939).
8. G. T. Trammell, Phys. Rev. 92, 1387 (1953).
9. S. Odier and D. Saint-James, J. Phys. Chem. Solids, 17, 117 (1960).
10. J. Schwinger, Phys. Rev. 73, 407 (1948).
11. L. L. Foldy, Rev. Mod. Phys. 30, 471 (1958).
12. E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra (Cambridge U.P., London, 1935).
13. D. F. Johnston, Proc. Phys. Soc. Land. 88, 37 (1966).
14. D. F. Johnston and D. E. Rimmer, J. Phys. C2, 1151 (1969).
15. S. W. Lovesey and D. E. Rimmer, Rep. Prog. Phys. 32, 333 (1969).
16. E. Balcar and S. W. Lovesey, Phys. Lett. A 31, 67 (1970).
17. E. Balcar, Proc. Int. Magnetism Conf. Moscow, Vol. 2 (Moscow: Nanka), 250 (1973).
18. S. W. Lovesey, J. Phys. C2, 470 (1969).
19. E. Balcar, S. W. Lovesey and F. A. Wedgewood, J. Phys. C3, 1292 (1970).
20. A. Mahendra and D. C. Khan, J. Phys. C4, 3307 (1971).

21. W. Marshall and S. W. Lovesey, Theory of Thermal Neutron Scattering (Oxford U.P., London, 1970).
22. G. H. Lander and T. O. Brun, J. Chem. Phys. 53, 1387 (1970).
23. R. M. Moon, W. C. Koehler, J. W. Cable and H. R. Child, Phys. Rev. B5, 997 (1972).
24. C. Stassis, G. R. Kline, A. J. Freeman and J. P. Desclaux, Phys. Rev. B13, 3916 (1976).
25. G. H. Lander, T. O. Brun, J. P. Desclaux and A. J. Freeman, Phys. Rev. B8, 3237 (1973).
26. B. N. Harmon and A. J. Freeman, Phys. Rev. B10, 1979 (1974).
27. H. Davis and J. Cooke, AIP Conf. Proc. 5, 1441 (1972).
28. A. J. Freeman and J. P. Desclaux, Int. J. Magnetism 3, 311 (1972).
29. C. Stassis and H. W. Deckman, Phys. Rev. 12, 1885 (1975).
30. C. Stassis and H. W. Deckman, J. Phys. C9, 2241 (1976).
31. C. Stassis and H. W. Deckman, "21st Annual Conference on Magnetism and Magnetic Materials," Magnetism and Magnetic Materials. (A.I.P., New York, 1976).
32. C. Stassis and H. W. Deckman, Phys. Rev. 13, 4943 (1976).
33. L. I. Schiff, Quantum Mechanics (McGraw Hill, New York, 1968).
34. L. Armstrong, Jr. and S. Feneville, Advances in Atomic and Molecular Physics, Vol. 10, (Academic Press, New York, 1974).
35. G. Drake, Phys. Rev. A3, 908 (1974).
36. A. R. Edmonds, Angular Momentum in Quantum Mechanics (Princeton U.P. U.P., Princeton, 1960).
37. W. Franz, Z. Physik 127, 363 (1950).
38. H. C. Corben and J. S. Schwinger, Phys. Rev. 58, 953 (1940).
39. J. M. Blatt and V. F. Weisskopf, Theoretical Nuclear Physics, (Wiley, New York, 1952).
40. M. E. Rose, Multipole Fields, (Wiley, New York, 1955).

41. M. E. Rose and D. M. Brink, Review of Mod. Phys. 39, 305 (1967).
42. A. de-Shalit and H. Feshbach, Theoretical Nuclear Physics Volume Nuclear Structure (Wiley, New York, 1974).
43. G. Breit, Phys. Rev. 34, 553 (1929).
44. E. P. Wigner, On the Matrices which Reduce the Kronecker Products of Representations of Simply Reducible Groups, (unpublished).
45. M. Rotenberg, R. Bivins, N. Metropolis, J. Wooten, Jr., The 3-j and 6-j Symbols, (Technology Press, Cambridge, 1959).
46. A. de-Shalit and I. Talmi, Nuclear Shell Theory, (Academic Press, New York, 1963).
47. D. M. Brink and G. R. Satchler, Angular Momentum (Clarendon Press, Oxford, 1968).
48. B. Shore and D. Menzel, Principles of Atomic Spectra (Wiley, New York, 1968).
49. E. El Baz and B. Castel, Graphical Methods of Spin Algebras (Marcel Dekker, New York, 1972).
50. C. L. Bedenharn and H. Van Dorn, Quantum Theory of Angular Momentum (Academic Press, New York, 1965).
51. B. G. Wybourne, Spectroscopic Properties of Rare Earths (Wiley, New York, 1965).
52. R. R. Judd, Operator Techniques in Atomic Spectroscopy (McGraw-Hill, New York, 1963).
53. S. Lie, Vorlesugen über kontinuierliche Gruppen, G. Scheffers, Ed. (Teubner Verlagsgesellschaft, Leipzig, 1893).
54. E. Cartan, Sur la Structure des Groupes de Transformations Finis et Continus (thesis, Paris, 1894).
55. B. L. Van der Warden, Math. Z. 37, 446 (1933).
56. G. Racah, Group Theory and Spectroscopy, in Springer Tracts in Modern Physics 37, 28 (1965).
57. B. R. Judd, Operator Techniques in Atomic Spectroscopy (McGraw-Hill, New York, 1963).

58. B. R. Judd, "Group Theory in Atomic Spectroscopy," in Group Theory and its Applications, E. M. Loeb, Ed. (Academic Press, New York, 1968).
59. L. Armstrong, Jr., Theory of the Hyperfine Structure of Free Atoms, (John Wiley, New York, 1971).
60. Nielson and Koster, Spectroscopic Coefficients for the p^n , d^n , and f^n Configurations, (M.I.T. Press, Cambridge, 1963).
61. R. I. Karaziya, Ya I. Vizbaraite, Z. B. Rudzikas and A. P. Jucys, Tolitsy dlya rascheta matrichnykh zlementov operatorov atomnykh velichin, Acad. Nouk. Lit. SSR, Int. Fiz. Mat., Moscow, 1967.
62. B. R. Judd, J. Math. Phys. 3, 557 (1962).
63. A. J. Freeman and R. E. Watson, Acta Cryst. 14, 27 (1961) and 14, 231 (1961).
64. M. Blume, A. J. Freeman, and R. E. Watson, J. Chem. Phys. 37, 1245 (1962).
65. W. C. Koehler, in Magnetic Properties of Rare Earth Metals, R. J. Elliot, Ed. (Plenum Press, New York, 1972).
66. H. Davis and J. Cooke, AIP Conference Proceedings 5, 1441 (1972).
67. A. J. Freeman and J. P. Desclaux, Int. J. Magnetism 3, 311 (1972).
68. P. G. H. Sandars and J. Beck, Proc. Roy. Soc., Ser. A 289, 97 (1965).
69. A. I. Akhiezer and V. B. Berestetskii, Quantum Electrodynamics (John Wiley, New York, 1965).
70. W. Perl and V. Hughs, Phys. Rev. 91, 842 (1953).
71. A. Abragam and J. H. Van Vleck, Phys. Rev. 92, 1448 (1953).
72. G. Breit, Nature 122, 649 (1928).
73. W. Margenau, Phys. Rev. 57, 383 (1948).
74. J. P. Desclaux, Computer Phys. Commun. 1, 151 (1969).
75. D. F. Mayers, J. de Phys. 315, C4-221 (1970).

76. J. P. Desclaux, C. M. Moser and G. Verhaegen, J. Phys. B4, 296 (1971).
77. I. Lindgren and A. Rosen, Case Studies in Atomic Physics 4, 97 (1974).
78. E. L. Hill, Am. J. Phys. 22, 211 (1954).

ACKNOWLEDGMENTS

The author would like to thank his advisor, Professor C. Stassis for the guidance, encouragement, and collaboration he provided during this study. The author would also like to thank Dr. B. N. Harmon for the assistance he provided in the computations reported in this work.

Finally the author would like to thank his wife and daughter for the understanding and encouragement they provided during his graduate studies.