INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Order Number 9514204

**Scattering operator for elastic and inelastic resonant x-ray
scattering**

Luo, Jin, Ph.D.

Rice University, 1994

U·M·I

**300 N. Zeeb Rd.
Ann Arbor, MI 48106**

RICE UNIVERSITY

**Scattering Operator for Elastic and Inelastic
Resonant X-Ray Scattering**

by

Jin Luo

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE:

A handwritten signature in black ink, reading "George T. Trammell", written over a horizontal line.

George T. Trammell
Professor of Physics

A handwritten signature in black ink, reading "James P. Hannon", written over a horizontal line.

James P. Hannon
Professor of Physics

A handwritten signature in black ink, reading "F. Curtis Michel", written over a horizontal line.

F. Curtis Michel
Professor of Space Physics

Houston, Texas

January, 1994

Scattering Operator for Elastic and Inelastic Resonant X-Ray Scattering

Jin Luo

Abstract

I have shown that in the fast collision approximation, the scattering operator for resonant x-ray scattering can be expressed in terms of simple spin-orbital moment operators $M^{(k)}(l, s)$ of the valence shell involved in the resonance. Using these operators, one not only can determine the thermal expectation values of the various spin-orbit multipole moments in the valence shell through the coherent elastic scattering and absorption, but also can obtain the moment-moment correlation functions [Van Hove scattering function $S(\mathbf{q}, \omega)$] among the various atoms of the scattering sample from the coherent elastic and inelastic scattering. We have applied the effective scattering operators to the x-ray magnetic scattering in $La_{2-x}Sr_xCuO_4$ high temperature superconductors, and obtained the relations between the scattering cross-section and the Van Hove scattering function, and the instantaneous correlation function of the spins in these materials. This theory is applicable to the analysis of a broad range of resonant x-ray elastic and inelastic scattering and absorption experiments involving rare earth, actinide and transition elements.

Acknowledgments

I would like to thank my advisors, George Trammell and Jim Hannon, for their stimulated discussions and great insights on the subject that they have provided to me , and for their easy-going nature to put up with me. I thank Professor Peter Nordlander for allowing me to use his group's computers. I thank Mike Hamrick for providing the computing result of the scattering amplitude of Cu^{2+} in $La_{2-x}Sr_xCuO_4$. My appreciation also goes to Chizuko Dutta, Eddy Timmermans, Xiaomin Hu and Murat Berk from whom I have received help and friendship. I am also very grateful to my parents for the continual support and encouragement that they have provided in my life. Finally, it is to my most supportive and loving husband, Bob, that I owe the most thanks. Thank God he helped me typing up this thesis with all the nasty formulas. I would like to dedicate this thesis to Bob and our daughter Laura.

Contents

Abstract	ii
Acknowledgments	iii
List of Tables	v
List of Illustrations	vi
1 Introduction	1
2 Scattering Operator F_{EL}	8
2.1 Scattering Operator in Spherical Tensor Form	8
2.2 Spherical Scattering Operators $F_q^{(k)}$'s and the Multipole Moments $M_q^{(k)}$'s.	11
2.3 $E1$ Scattering Operators F_{E1}	15
2.4 $E2$ Scattering Operators F_{E2}	20
2.5 Determination of the Scattering Tensors $F_q^{(k)}(\omega)_{EL}$	25
2.6 Sum Rules	28
2.7 Discussion.	32
3 Scattering Operator for Transitions to d Bands.	38
4 Inelastic Scattering in $La_{2-x}Sr_xCuO_4$ High-Temperature Superconductors	42
4.1 Introduction.	42
4.2 Effective Spin Scattering Operator.	44
4.3 Van Hove Scattering Function $S(Q, \omega)$	48

5 Conclusions.	51
A The Theory of Resonant X-Ray Magnetic Scattering	53
B Scattering Operator $S_{LM';LM}$	59
C Polarization Tensors $T_{q(E1)}^{(k)*}$ for $E1$ scattering.	67
D Polarization Tensors $T_{q(E2)}^{(k)*}$ for $E2$ Scattering.	70
E Spin-Orbital Coupled Tensor Operators $\overline{W}^{(\kappa,l)k}$.	75
F The Equivalence between $V^{(2n)}(1)$ and $C^{(2n)}(\hat{\mathbf{r}})$.	82
G Rotation Matrix Elements $D_{m,n}^{(j)}(\alpha, \beta, \gamma)$	83
H Scattering Operator $F_{q(EL)}^{(k)}$ in a SLJ-Coupled System.	86
I The Generalized Scattering Operator $\overline{S}_{LM';LM}$.	89
J Multipole Moments $\overline{M}^{(k)}$.	93
K Spin Scattering Operator.	99
Bibliography	103

Tables

2.1 Coefficients in Eq.(2.35). Here $6j(k) = \begin{Bmatrix} 1 & l_2 & l_1 \\ l_2 & 1 & k \end{Bmatrix}$, and

$$9j(l, k) = \begin{Bmatrix} l_1 & l_1 & 1 \\ l_2 & l_2 & l \\ 1 & 1 & k \end{Bmatrix}. \dots\dots\dots 17$$

2.2 Coefficients in Eqs.(2.36). Here $6j(k) = \begin{Bmatrix} 1 & l_2 & l_1 \\ l_2 & 1 & k \end{Bmatrix}$,

$$9j(l, k) = \begin{Bmatrix} l_1 & l_1 & 1 \\ l_2 & l_2 & l \\ 1 & 1 & k \end{Bmatrix}, a = \frac{(2l_1+1)}{(j_{\pm}+\frac{1}{2})}\alpha'(j_{\pm}), b = \sqrt{\frac{(2l_1+1)}{l_1(l_1+1)}}\beta', \text{ and}$$

$$c = \sqrt{\frac{(2l_1+1)}{l_1(l_1+1)}}\gamma'. \dots\dots\dots 18$$

2.3 Coefficients in Eq.(2.48). Here $6j(k) = \begin{Bmatrix} 2 & l_2 & l_1 \\ l_2 & 2 & k \end{Bmatrix}$,

$$9j(l, k) = \begin{Bmatrix} l_1 & l_1 & 1 \\ l_2 & l_2 & l \\ 2 & 2 & k \end{Bmatrix}, a = \frac{(2l_1+1)}{(j_{\pm}+\frac{1}{2})} \frac{\alpha(j_{\pm})}{(2l_2+1)}, b = \sqrt{\frac{(2l_1+1)}{l_1(l_1+1)}} \frac{\beta}{(2l_2+1)}, \text{ and}$$

$$c = \sqrt{\frac{(2l_1+1)}{l_1(l_1+1)}} \frac{\gamma}{(2l_2+1)}. \dots\dots\dots 20$$

2.4	Coefficients in Eqs.(2.52). Here $6j(k) = \begin{Bmatrix} 1 & l_2 & l_1 \\ l_2 & 1 & k \end{Bmatrix}$,	
	$9j(l, k) = \begin{Bmatrix} l_1 & l_1 & 1 \\ l_2 & l_2 & l \\ 1 & 1 & k \end{Bmatrix}$	22
B.1	$C_{l, M-\mu; \frac{1}{2}\mu}^{jM}$	. 59
B.2	Special formulas for 3j symbols.	61
G.1	Formulas for $d_{m,n}^j(\beta)$ for $j = 1$ and 2	84

Illustrations

- 1.1 The pure EL resonant transition scattering: (a) A core electron ($n_c l_1 j_1$) is excited to the valence shell ($n l_2$) by an incident photon ($\mathbf{k}_0, \mathbf{e}_0$), (b) subsequently a valence electron ($n l_2$) jumps back to the core hole emitting a photon ($\mathbf{k}_f, \mathbf{e}_f$). 3
- 1.2 The figure copied from the Holmium experiment[1]. “Top: The absorption measured through a 5- μm holmium film plotted as the incident x-ray energy is tuned through the L_{III} edge. Bottom: Integrated magnetic intensities of the σ -(solid circles) and π - (open circles) polarized components of the scattering at the $(0, 0, 4 + \tau)$, $(0, 0, 2 + \tau)$, and $(0, 0, 2 + 3\tau)$ reflections. The solid lines are drawn only to guide the eye. Insets, bottom: Corresponding degree of linear polarization plotted vs energy. The solid vertical line indicates the energy of the inflection point of the L_{III} absorption edge.” 5
- 1.3 The figure copied from the theoretical calculations of Holmium[2]. “Relative scattered intensities (theoretical) vs x-ray energy for the L_{III} edge in Ho: (a) $(004+\tau)$, (b) $(002 + 2\tau)$, (c) $(002+3\tau)$, and (d) $(002+4\tau)$. The solid lines give the $\sigma \leftrightarrow \sigma$ scattering, and the dashed lines give $\sigma \leftrightarrow \pi$.” 6

4.1	Resonant scattering from p -state to $d(x^2 - y^2)$ state, only $(\mathbf{e}_0)_\perp \ (\hat{\mathbf{k}}_0 \times \hat{\mathbf{z}})$ component and $(\mathbf{e}_f)_\perp \ (\hat{\mathbf{k}}_f \times \hat{\mathbf{z}})$ component are involved to excite the core electron. The component of $\mathbf{e}_0$ or $\mathbf{e}_f$ parallel to $\hat{\mathbf{z}}$ give zero contribution to the scattering.	46
-----	---	----

Chapter 1

Introduction

There has been a rapid increase in resonant x-ray magnetic scattering studies since the initial work by Gibbs, et al.[1, 2]. From magnetic structure determination to critical scattering, resonant x-ray magnetic scattering has become a powerful probe of magnetism complimentary to magnetic neutron scattering[3]. But important questions remain: how is resonant x-ray magnetic scattering related to the atomic spin and orbital moments, and what are the essential differences between neutron and resonant x-ray magnetic scattering? In this thesis I address these questions.

The neutron magnetic scattering operator f_n is proportional to the Fourier transform of the magnetic moment density, $f_n \propto \mu_n \cdot \{\hat{k} \times [\mathbf{L}(\kappa) + 2\mathbf{S}(\kappa)] \times \hat{k}\}$, and neutron scattering studies have been the chief means for magnetic structure and excitation spectra determination in magnetic materials[4]. Also the nonresonant x-ray magnetic scattering operator has the simple form, $f_m \propto \mathbf{L}(\kappa) \cdot \mathbf{A} + \mathbf{S}(\kappa) \cdot \mathbf{B}$, again linear in $\mathbf{L}(\kappa)$ and $\mathbf{S}(\kappa)$, which allows similar magnetic structure information to be obtained as from neutron scattering[5], although f_m is quite small, typically $\approx 0.01r_0$, in comparison to $f_n \approx r_0$ for neutron scattering.

Near absorption edges, very large resonant enhancements to magnetic sensitive x-ray scattering occur, with amplitudes ranging from $0.1r_0 - 100r_0$ [1, 2]. This strongly enhanced “magnetic” x-ray scattering is actually electric multipole resonance scattering with the magnetic sensitivity arising from the effects of exchange and spin-orbit correlation[2]. Although the origin of the magnetic sensitivity is well understood [2], it is not at all obvious that there is a simple relation of the scattering amplitude F_{EL}

to the atomic orbital and spin moments, as is the case for neutron and nonresonant x-ray magnetic scattering. The existence of such a relation is of great importance for interpreting resonant magnetic scattering measurements.

The resonant scattering process we are interested in can be described by the following picture: A core electron ($n_c l_1 j_1$) absorbing an incident photon ($\mathbf{k}_0, \mathbf{e}_0$) is excited to an unoccupied valence state and subsequently a valence electron ($n l_2$) jumps back to the core hole emitting a photon ($\mathbf{k}_f, \mathbf{e}_f$) (see Fig. 1.1). The resonant scattering amplitude for this process is proportional to (see Appendix A)

$$f_{Res} \propto \sum_I \frac{\langle \psi_f | \mathbf{p} \cdot \mathbf{A} | I \rangle \langle I | \mathbf{p} \cdot \mathbf{A} | \psi_0 \rangle}{E_I - E_0 - \hbar\omega - i\Gamma/2}, \quad (1.1)$$

where the summation is taken over the resonant excited states, and Γ is the width of the excited state $| I \rangle$.

If the spread Δ of the energies E_I is small compared to either the width Γ , or the frequency deviation $\Delta\omega = (E_I - E_0 - \hbar\omega)$ from resonance, the scattering amplitude can be simplified by replacing E_I by an average $\bar{E}_I$, and taking the energy denominator $[\bar{E}_I - E_0 - \hbar\omega - i\Gamma/2]^{-1}$ out of the summation, then using the closure relation, $\sum_I | I \rangle \langle I | = 1$, we have

$$f_{Res} \propto \frac{1}{E_I - E_0 - \hbar\omega - i\Gamma/2} \langle \psi_f | (\mathbf{p} \cdot \mathbf{A})(\mathbf{p} \cdot \mathbf{A}) | \psi_0 \rangle. \quad (1.2)$$

This is a familiar procedure in atomic physics[6]

In this approximation, we keep the leading term ($n = 0$) in the expansion $[E_I - E_0 - \hbar\omega - i\Gamma/2]^{-1} = [\bar{E}_I - E_0 - \hbar\omega - i\Gamma/2]^{-1} \sum_{n=0}^{\infty} [-\Delta_I / (\bar{E}_I - E_0 - \hbar\omega - i\Gamma/2)]^n$. Here $\Delta_I = (E_I - \bar{E}_I)$ is the deviation of E_I from the central energy $\bar{E}_I$ of the excited states. The next (linear) term will be a small correction if Δ_I is small compared to either Γ or $\Delta\omega$, or also if there is destructive interference between the $\pm\Delta_I$ contributions.

This is in fact a “fast collision” approximation: When the core electron is initially injected into an unoccupied valence state above, then generally it and the core hole

exert torques on each other and the other valence electrons, causing changes in the state of these electrons. The rate at which these changes take place, however, is determined by ΔE_I , and to a good approximation they can be neglected if $\Delta E_I \Delta t$ is small, where $\Delta t = |\Delta\omega - i\Gamma/2|^{-1}$ measures the collision duration.

Figure 1.1: The pure EL resonant transition scattering: (a) A core electron ($n_c l_1 j_1$) is excited to the valence shell ($n l_2$) by an incident photon (k_0, e_0), (b) subsequently a valence electron ($n l_2$) jumps back to the core hole emitting a photon (k_f, e_f).

Although the energy levels E_I become continuously distributed bands in crystals, the core hole impurity produced by the scattering light reduces the energy spread Δ of the excited states smaller than the normal band width W , due to the Coulomb attractions between the core hole and valence electrons. In addition, the width of the excited state Γ is larger than the intrinsic width Γ_i (which is the decay rate of an isolated excited atom),

$$\Gamma = \Gamma_i + \Gamma_b,$$

where the excited band width Γ_b is the tunneling rate of the excited electron crossing the potential barrier to the neighbor sites (which is also smaller than the normal band width W because of the core hole Coulomb attraction). Nevertheless, there are still a lot of cases where the energy splitting Δ is small compared to the width Γ , so that the splitting is not resolved, and the fast collision approximation can be applied.

For example, in the metallic holmium, the band widths $W(4f) \simeq 2eV$, and $W(5d) \gtrsim 5eV$ [7, 8]. The magnetic resonant scattering on holmium at the L_3 edge has shown that $\Gamma(L_3 \rightarrow 4f) \simeq 6eV$, and $\Gamma(L_3 \rightarrow 5d) \simeq 7.5eV$ [1] (see Fig.1.2. Notice that $\Gamma_i(L_3) \simeq 4.5eV$ [9]). In this case the fast collision approximation is equivalent to the atomic-like model, which has been used by Hannon et al.[2] and Hamrick[10] to calculate the resonant scattering amplitude of rare earth and actinide elements. Their results of holmium at L_3 edge resonant scattering, based on a virtual E_2 transition to the $4f$ -shell and an E_1 transition to the narrow $5d$ -band, give satisfactory agreement with the experimental results[1] (see Fig. 1.3).

However, for the M_4, M_5 transitions in the rare earths, $\Delta \gtrsim \Gamma$ and the multiplet structure can be resolved. The higher-order contributions can be included with multiplet calculations of the type performed by Thole, et al.[11], but these higher-order corrections will have a more complex operator form. The simplicity of the fast-collision approximation can be regained, by tuning off resonance so that $\Delta \ll |\Delta\omega|$.

Figure 1.2: The figure copied from the Holmium experiment[1]. "Top: The absorption measured through a 5- μm holmium film plotted as the incident x-ray energy is tuned through the L_{III} edge. Bottom: Integrated magnetic intensities of the σ -(solid circles) and π - (open circles) polarized components of the scattering at the $(0,0,4+\tau)$, $(0,0,2+\tau)$, and $(0,0,2+3\tau)$ reflections. The solid lines are drawn only to guide the eye. Insets, bottom: Corresponding degree of linear polarization plotted vs energy. The solid vertical line indicates the energy of the inflection point of the L_{III} absorption edge."

Figure 1.3: The figure copied from the theoretical calculations of Holmium[2]. “Relative scattered intensities (theoretical) vs x-ray energy for the L_{III} edge in Ho: (a) $(004+\tau)$, (b) $(002+2\tau)$, (c) $(002+3\tau)$, and (d) $(002+4\tau)$. The solid lines give the $\sigma \leftrightarrow \sigma$ scattering, and the dashed lines give $\sigma \leftrightarrow \pi$.”

Even off resonance, the M_4, M_5 scattering amplitudes will be appreciable because they are $\approx 10 - 100r_0$ at resonance.

In this thesis I show that for the important case of “quasielastic” scattering, if the fast collision approximation can be made, then indeed, the resonant scattering amplitude F_{EL} is simply related to the spin-orbital moment operators of the valence shell

$$F_{EL} \propto \sum_{k=0}^{2L} T_{EL}^{(k)}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0) \cdot M_{EL}^{(k)}(l, s). \quad (1.3)$$

Here the $M_{EL}^{(k)}(l, s)$ are k th rank spin-orbital moments of the valence shell involved in the resonance, and $T_{EL}^{(k)}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)$ are k th rank x-ray polarization tensors defined in Chapter 2.

Thus, for an $E1$ transition, F_{E1} contains up to quadrupole spin-orbital moments, and for an $E2$ transition up to hexadecapole moments. The odd-order moments are odd under time reversal T , while the even-order moments are even under T , and include the charge multipole moments, as well as spin-orbital multipole moments. Coherent resonant x-ray scattering then determines correlations between these moments, and gives important information, not obtainable from neutron and nonresonant x-ray magnetic scattering.

In Chapter 2, we derive scattering operators for the elastic and inelastic resonant x-ray scattering, and obtain the relations between the scattering operators F_{EL} and the multipole moment operator $M_{q(EL)}^{(k)}$ in the valence shell. Our z -component of the first-rank term $M_{0(E1)}^{(1)}$ gives the result of Thole et al.[12] and Carra et al.[13] obtained from the circular dichroism.

In Chapter 3 we will derive the generalized scattering operator for the transition to the d -band, where the spin exchange effects are concerned.

In Chapter 4 we will apply the scattering operator obtained in Chapter 2 to the inelastic scattering in $La_{2-x}Sr_xCuO_4$ high-temperature superconductors. The spin-spin correlation (Van Hove scattering function) will also be discussed.

Chapter 2

Scattering Operator F_{EL}

2.1 Scattering Operator in Spherical Tensor Form

The resonant scattering process we are interested in can be described by the following picture: A core electron ($n_c l_1 j_1$) absorbing an incident photon ($\mathbf{k}_0, \mathbf{e}_0$) is excited to an unoccupied valence orbital, and subsequently a valence electron ($n l_2$) jumps back to the core hole emitting a photon ($\mathbf{k}_f, \mathbf{e}_f$) (see Fig. 1.1). The resonant scattering amplitude for this process is proportional to (see Appendix A)

$$f_{Res} \propto \sum_I \frac{\langle \psi_f | \mathbf{p} \cdot \mathbf{A} | I \rangle \langle I | \mathbf{p} \cdot \mathbf{A} | \psi_0 \rangle}{E_I - E_0 - \hbar\omega - i\Gamma/2}. \quad (2.1)$$

Making the general multipole expansion, we can express the scattering amplitude in terms of electric multipole transitions, magnetic multipole transitions, and electric and magnetic mixed multipole transitions. However, in this thesis I only concentrate on electric multipole resonant scattering, the rest of them can be solved similarly.

The scattering amplitude for electric multipole resonant scattering is given by (see Appendix A)

$$f = 4\pi\lambda_0 \sum_{M',M} [\mathbf{e}_f^* \cdot \mathbf{Y}_{LM'}^{(e)}(\hat{\mathbf{k}}_f)] [\mathbf{Y}_{LM}^{(e)*}(\hat{\mathbf{k}}_0) \cdot \mathbf{e}_0] \langle \psi_f | F_{LM',LM}^{(e)}(\omega) | \psi_0 \rangle. \quad (2.2)$$

Here

$$\langle \psi_f | F_{LM',LM}^{(e)}(\omega) | \psi_0 \rangle = \sum_I \frac{1}{2\lambda_{IO}} \left[\frac{\langle \psi_f | J_{LM'}^{(e)\dagger} | I \rangle \langle I | J_{LM}^{(e)} | \psi_0 \rangle}{E_I - E_0 - \hbar\omega - i\Gamma/2} \right], \quad (2.3)$$

and the current operator is given by

$$J_{LM}^{(e)} = \sum \langle nl_2 m_2 m_s | \frac{-4\pi i^L k^L}{(2L+1)!!} \sqrt{\frac{L+1}{L}} Q_{LM} | n_c j_1 l_1 m_1 m_s \rangle \times C_{l_1 m_1, \frac{1}{2} m_s}^{j_1 m_j} \hat{a}_{m_2 m_s}^\dagger \hat{b}_{j_1 m_j}, \quad (2.4)$$

where $Q_{LM} = er^L Y_{LM}$ is the usual electric multipole-moment, $\hat{a}$ and $\hat{a}^\dagger$ are annihilation and creation operators for an (nl_2) electron in the valence shell, the operators $\hat{b}$ and $\hat{b}^\dagger$ for an $(n_c l_1 j_1)$ electron in the core shell. $|I\rangle = |(nl_2)^{+1} (n_c l_1 j_1)^{-1} \psi_0\rangle$ is the excited state with an electron excited to the partially-filled valence shell (nl_2) leaving a hole in the core shell $(n_c l_1 j_1)$. Γ is the width of the excited state. Here we restrict our attention to “quasi-elastic” scattering, where the final state $|\psi_f\rangle$ corresponds to the same configuration as the initial state $|\psi_0\rangle$, i.e. all core levels filled and the same number of valence shell electrons as initially, but not necessarily the same state, e.g. $|(nl_2)^\nu L, S, J, M\rangle \rightarrow |(nl_2)^\nu L', S', J', M'\rangle$ transitions may occur, where ν is the number of electrons in the (nl_2) valence shell.

The scattering operator F_{EL} can be defined from the scattering amplitude f in Eq.(2.2), that is $\langle \psi_f | F_{EL} | \psi_0 \rangle = f$. Insert the following identity

$$\sum_{M'_1, M_1} \sum_{k, q} \left(\frac{2k+1}{2L+1} \right) C_{LM'; kq}^{LM} C_{LM'_1; kq}^{LM_1} = \sum_{M'_1, M_1} \delta_{M, M_1} \delta_{M', M'_1} = 1, \quad (2.5)$$

into Eq.(2.2), the scattering operator F_{EL} is expressed in the spherical tensor form

$$F_{EL} = 4\pi\lambda_o \sum_{k, q} T_q^{(k)*}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_o, \hat{\mathbf{k}}_o)_{EL} F_q^{(k)}(\omega)_{EL}, \quad (2.6)$$

where $q = -k, \dots, k, k = 0, \dots, \min\{2L, 2l_2\}$. Usually $2L < 2l_2$, for the cases we are interested in. Therefore, $k = 0, \dots, 2L$, later on. The polarization tensors $T_q^{(k)*}$ and the spherical scattering-operators $F_q^{(k)}(\omega)_{EL}$ are defined as follows

$$T_q^{(k)*}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_o, \hat{\mathbf{k}}_o)_{EL} = \sqrt{\frac{2k+1}{2L+1}} \sum_{M', M} C_{LM'; kq}^{LM} [\mathbf{e}_f^* \cdot \mathbf{Y}_{LM'}^{(e)}(\hat{\mathbf{k}}_f)] [\mathbf{Y}_{LM}^{(e)*}(\hat{\mathbf{k}}_o) \cdot \mathbf{e}_o], \quad (2.7)$$

$$F_q^{(k)}(\omega)_{EL} = \sqrt{\frac{2k+1}{2L+1}} \sum_{M,M'} C_{LM';kq}^{LM} F_{LM';LM}^{(e)}(\omega). \quad (2.8)$$

The $\mathbf{e}, \hat{\mathbf{k}}$ dependence of the scattering for the $(n_c l_1 j_1) \rightarrow (n l_2)$ resonance is given by the spherical tensors $T_q^{(k)}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)_{EL}$, while the spherical tensor operators $F_q^{(k)}(\omega)$ involve various spin-orbital multipole-moment operators of the valence electrons (as discussed in the next section), and also have some dependence on the multiplet, exchange, and crystal-field splittings of the intermediate excited-states $| I >$. The scattering tensor $F_q^{(k)}(\omega)_{EL}$ can be selected out experimentally because of the different angular dependences.

2.2 Spherical Scattering Operators $F_q^{(k)}$'s and the Multipole Moments $M_q^{(k)}$'s.

A great simplification for the structure of the operator $F_q^{(k)}(\omega)$ occurs for the important cases where the fast collision approximation can be applied. Because either the width Γ , or the frequency deviation $\Delta\omega = (E_I - E_o - \hbar\omega)$ from resonance, is large compared to the energy splitting Δ of the excited-state configuration, the energy denominator $[E_I - E_o - \hbar\omega - i\Gamma/2]^{-1}$, can then be treated as a simple factor out of the summation for the $(n_c l_1 j_1) \rightarrow (n l_2)$ resonance. In this case the $F_q^{(k)}(\omega)$'s factor into a single scalar resonance factor R [Eq.(2.10) below] and multipole-moment operators $M_q^{(k)}$ which are simple single-particle operators summed over the valence electrons in the initial configuration.

In the fast collision approximation, we can express the $F_{LM';LM}^{(e)}(\omega)$ in the following form

$$F_{LM';LM}^{(e)}(\omega) = R(l_1 j_1; L; l_2) S_{LM';LM}(l_1 j_1; l_2), \quad (2.9)$$

where the dimensionless “reduced resonance scattering-amplitude” $R(l_1 j_1; L; l_2)$ contains the square of the radial matrix-elements corresponding to the $(n_c l_1 j_1) \rightarrow (n l_2)$ electric multipole-transition and the resonance denominator,

$$R(l_1 j_1; L; l_2) = K(l_1 L l_2) | \langle R_{n l_2}(r) | r^L | R_{n_c l_1 j_1}(r) \rangle |^2 / [E_I - E_o - \hbar\omega - i\Gamma/2]. \quad (2.10)$$

Here $K(l_1 L l_2) = (e^2/\lambda^{2L+1}) \{ (2l_1 + 1)(2L + 1)(L + 1) / [L(2l_2 + 1)] \} [C_{l_1 0; L 0}^{l_2 0} / (2L + 1)!!]^2$, and the scattering operator $S_{LM';LM}$ obeys,

$$\begin{aligned} \langle \psi_f | S_{LM';LM}(l_1 j_1; l_2) | \psi_0 \rangle = \sum_{all\ m, m'} \langle \psi_f | \hat{b}_{j_1 m'}^\dagger \hat{a}_{m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger \hat{b}_{j_1 m_j} | \psi_0 \rangle \\ [C_{l_1 m'_1; \frac{1}{2} m'_s}^{j_1 m'_j} C_{l_1 m_1; \frac{1}{2} m_s}^{j_1 m_j} C_{l_1 m'_1; LM'}^{l_2 m'_2} C_{l_1 m_1; LM}^{l_2 m_2}]. \end{aligned} \quad (2.11)$$

Since the core states are filled in the initial and final states, we have

$$\langle \psi_f | \hat{b}_{j_1 m_j}^\dagger \hat{a}_{m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger \hat{b}_{j_1 m_j} | \psi_0 \rangle = \delta_{m'_j m_j} \langle \psi_f | \hat{a}_{m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger | \psi_0 \rangle. \quad (2.12)$$

The operators $\hat{a}_{m_2 m_s}^\dagger \hat{a}_{m'_2 m'_s}$ can be expressed by the spin-orbital double-tensor operators $W_{\mu m}^{(\kappa, l)}$, which are given by Judd[6]. Similarly, we define other double-tensor operators for “hole” multipole moments

$$\overline{W}_{\mu m}^{(\kappa, l)} = \sqrt{\frac{(2\kappa + 1)(2l + 1)}{2(2l_2 + 1)}} \sum_{m_2 m_s m'_2 m'_s} (-\hat{a}_{m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger) C_{\frac{1}{2} m'_s; \kappa \mu}^{\frac{1}{2} m_s} C_{l_2 m'_2; l m}^{l_2 m_2}, \quad (2.13)$$

to express the operators $\hat{a}_{m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger$. The operators $\overline{W}_{\mu m}^{(\kappa, l)}$ and $W_{\mu m}^{(\kappa, l)}$ are the same except for $\kappa = 0, l = 0$,

$$\overline{W}^{(0,0)} = W^{(0,0)} - \sqrt{2(2l_2 + 1)} \quad \text{for } \kappa = l = 0, \quad (2.14)$$

$$\overline{W}_{\mu m}^{(\kappa, l)} = W_{\mu m}^{(\kappa, l)} \quad \text{for others.} \quad (2.15)$$

The operators $\overline{W}_{\mu m}^{(\kappa, l)} \propto \sum_{i \in l_2} [s_\mu^{(\kappa)} V_m^{(l)}(1)]_i$, where $V^{(l)}(l_i)$ is the l th rank symmetric tensor of l_i (see Appendix E), which is defined $V_m^{(n)}(1) = C_{1\mu; n-1, m-\mu}^{nm} l_\mu V_{m-\mu}^{(n-1)}(1)$, and $V^{(0)}(1) = 1$.

The scattering operator $S_{LM'; LM}$ can now be expressed in terms of $\overline{W}_{\mu m}^{(\kappa, l)}$, and, utilizing the theorems of Yutsis, Levinson and Vanagas[14] to evaluate the Clebsch-Gordon sums, we have (see Appendix B)

$$\begin{aligned} S_{LM'; LM}(l_1 j_\pm; l_2) &= \sum_l \left[-\frac{(j_\pm + \frac{1}{2})}{(2l_1 + 1)} c_l \overline{W}_m^{(0, l)} C_{LM'; l m}^{LM} \right. \\ &\quad \left. \pm \sum_{k=|l-1|, \neq l}^{l+1} d_{kl} \overline{W}_q^{(1, l)k} C_{LM'; k q}^{LM} \right], \end{aligned} \quad (2.16)$$

where $\overline{W}_q^{(1, l)k}$ is the spin-orbital coupled tensor operator,

$$\overline{W}_q^{(1, l)k} = \sum_{\mu, m} C_{1\mu; l m}^{k q} \overline{W}_{\mu, m}^{(1, l)} \quad (2.17)$$

and

$$c_l = (-1)^l \sqrt{\frac{2(2l+1)}{2L+1}} (2l_2+1) \begin{Bmatrix} L & l_2 & l_1 \\ l_2 & L & l \end{Bmatrix},$$

$$d_{kl} = \sqrt{\frac{l_1(l_1+1)2(2l+1)}{(2l_1+1)(2L+1)}} (2l_2+1) \sqrt{2k+1} \begin{Bmatrix} l_1 & l_1 & 1 \\ l_2 & l_2 & l \\ L & L & k \end{Bmatrix}. \quad (2.18)$$

Notice that $d_{kl} = 0$ unless $1 + l + k$ is even because two columns are identical in the $9j$ symbol in Eq.(2.18).

It is really interesting to look into the structure of the scattering operator $S_{LM';LM}$ in Eq.(2.16). $S_{LM';LM}$ consists of the purely orbital moments $\overline{W}_m^{(0,l)}$ and the spin-coupled orbital moments $\overline{W}_q^{(1,l)k}$. This fact may be understood as: In the resonant scattering described by Eq.(2.2) and (2.3), an $(n_c l_1 j_1)$ core electron is excited to an (nl_2) valence shell by absorbing a photon with $|LM\rangle$ angular momentum, and then an (nl_2) electron in the valence shell jumps back to the core hole, emitting a photon with $|LM'\rangle$ angular momentum. Notice that the transition current $J_{LM}^{(e)}$ in the scattering process is proportional to the usual charge multipole moment Q_{LM} ($er^L Y_{LM}$), which is a purely spatial (orbital) operator. But the electrons transferred out of and back into the core state $(n_c l_1 j_1 m_j)$ carry the spins. There are four independent operators. The operators $\hat{a}_{m_2 \downarrow} \hat{a}_{m_2 \uparrow}^\dagger$ and $\hat{a}_{m_2 \uparrow} \hat{a}_{m_2 \downarrow}^\dagger$ flip a spin from down to up and from up to down in the valence shell, and contribute to the spin-orbital double-tensor operators $\overline{W}_{1m}^{(1,l)}$ and $\overline{W}_{-1m}^{(1,l)}$ respectively. The other two operators are $\hat{a}_{m_2 \uparrow} \hat{a}_{m_2 \uparrow}^\dagger \pm \hat{a}_{m_2 \downarrow} \hat{a}_{m_2 \downarrow}^\dagger$. The operator with the plus sign describing the symmetrical scattering current contributes to the purely orbital moment operators $\overline{W}_m^{(0,l)}$. The one with the minus sign contributes to the spin-orbital double-tensor operators $\overline{W}_{0m}^{(1,l)}$.

The scattering operator $S_{LM';LM}$ in Eq.(2.16) can be written as

$$S_{LM';LM}(l_1 j_\pm; l_2) \equiv \sum_{k,q} M_q^{(k)}(l_1 j_\pm; L; l_2) C_{LM';kq}^{LM}, \quad (2.19)$$

where $M_q^{(k)}$ is a linear combination of the q -components of the various k th-rank moments in the valence shell,

$$M_q^{(k)}(l_1 j_\pm; L; l_2) = -\frac{(j_\pm + \frac{1}{2})}{2l_1 + 1} c_k \overline{W}_q^{(0,k)} \pm [d_{k,|k-1|} \overline{W}_q^{(1,k-1)k} + d_{k,(k+1)} \overline{W}_q^{(1,k+1)k}], \quad (2.20)$$

where c_k and $d_{k,l}$ ($l = |k-1|, l = k+1$) are given in Eq.(2.18).

From Eq.(2.8) and (2.9), the spherical tensor scattering operator $F_q^{(k)}(\omega)_{EL}$ is proportional to the multipole-moment operator $M_q^{(k)}(l_1 j_\pm; L; l_2)$ defined in Eq.(2.20),

$$F_q^{(k)}(\omega)_{EL} = R(l_1 j_\pm; L; l_2) \sqrt{\frac{2L+1}{2k+1}} M_q^{(k)}(l_1 j_\pm; L; l_2), \quad (2.21)$$

where R is the reduced amplitude given in Eq.(2.10).

The total scattering operator F_{EL} in Eq.(2.6) is then the product of $4\pi\lambda_o R$, and the sum of scalar products of the multipole moment operators $M^{(k)}(l_1 j_1; L; l_2)$ and the polarization tensors $T_{EL}^{(k)}$:

$$F_{EL} = 4\pi\lambda_o R(l_1 j_1; L; l_2) \sum_{k=0}^{2L} \sum_{q=-k}^k \sqrt{\frac{2L+1}{2k+1}} T_q^{(k)*}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)_{EL} M_q^{(k)}(l_1 j_1; L; l_2), \quad (2.22)$$

The above result is obtained from the fast collision approximation, which is suited for the cases where either the width Γ , or the frequency deviation $\Delta\omega$, is large compared to the energy splitting Δ of the excited states. In this approximation, the terms $(\Delta E_I \Delta t)^n$ ($n \geq 1$) are neglected, where ΔE_I is proportional to the changing rate of the electrons in the valence states, and $\Delta t = |\Delta\omega - i\Gamma/2|^{-1}$ is the scattering duration. Neglecting $\Delta E_I \Delta t$ terms means that the collision is so fast that the valence shell can be considered as “rigid” during the scattering processes.

2.3 E1 Scattering Operators F_{E1} .

We have derived the general formula which relates the scattering operator F_{EL} to spin-orbital coupled moments $M_q^{(k)}$ of the atoms in the fast collision approximation. In the following two sections, we are going to apply these results obtained in the previous section to show the scattering operators for $E1$ and $E2$ resonant scattering explicitly.

For the important case of $E1$ resonant scattering, the scattering operator F_{E1} is given from Eq.(2.6)

$$F_{E1} = 4\pi\lambda_0 \sum_{k,q} T_q^{(k)*}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)_{E1} F_q^{(k)}(\omega)_{E1}, \quad (2.23)$$

where $T_{q(E1)}^{(k)*}$ is given in Appendix C

$$T_{q(E1)}^{(k)*} = -\frac{3}{8\pi}(-1)^q V_{-q}^{(k)}(\mathbf{e}_f^* \otimes \mathbf{e}_0), \quad (2.24)$$

and

$$V_q^{(k)}(\mathbf{e}_f^* \otimes \mathbf{e}_0) = \sum_{\mu,\nu} C_{1\mu;1\nu}^{kq}(e_f^*)_{\mu}(e_0)_{\nu}. \quad (2.25)$$

That is

$$V^{(0)} = -\frac{1}{\sqrt{3}}(\mathbf{e}_f^* \cdot \mathbf{e}_0), \quad (2.26)$$

$$V^{(1)} = \frac{i}{\sqrt{2}}(\mathbf{e}_f^* \times \mathbf{e}_0), \quad (2.27)$$

$$V_{\pm 2}^{(2)} = (\mathbf{e}_f^*)_{\pm 1}(\mathbf{e}_0)_{\pm 1}, \quad (2.28)$$

$$V_{\pm 1}^{(2)} = \frac{1}{\sqrt{2}}[(\mathbf{e}_f^*)_{\pm 1}(\mathbf{e}_0)_0 + (\mathbf{e}_f^*)_0(\mathbf{e}_0)_{\pm 1}], \quad (2.29)$$

$$V_0^{(2)} = \frac{1}{\sqrt{6}}[3(\mathbf{e}_f^*)_0(\mathbf{e}_0)_0 - (\mathbf{e}_f^* \cdot \mathbf{e}_0)]. \quad (2.30)$$

$V_q^{(k)}$ are only dependent on the polarization vectors $\mathbf{e}_f$ and $\mathbf{e}_0$ of the scattering light, and independent of the wave vectors $\hat{\mathbf{k}}_f$ and $\hat{\mathbf{k}}_0$. The scattering operator F_{E1} then becomes

$$F_{E1} = -\frac{3}{2}\lambda_0 \sum_k \mathbf{V}^{(k)}(\mathbf{e}_f^* \otimes \mathbf{e}_0) \cdot \mathbf{F}^{(k)}(\omega)_{E1}, \quad (2.31)$$

with

$$\mathbf{V}^{(k)} \cdot \mathbf{F}^{(k)} = \sum_{q=-k}^k (-1)^q V_{-q}^{(k)} F_q^{(k)}. \quad (2.32)$$

In the fast collision approximation $F_q^{(k)}$ is proportional to the multipole moment $M_q^{(k)}$ in Eq.(2.21),

$$F_{E1} = -\frac{3}{2}\lambda_0 R(l_1 j_1; 1; l_2) \sum_{k=0}^2 \sqrt{\frac{3}{2k+1}} \mathbf{V}^{(k)}(\mathbf{e}_f^* \otimes \mathbf{e}_0) \cdot \mathbf{M}^{(k)}(l_1 j_1; 1; l_2). \quad (2.33)$$

Explicitly,

$$\begin{aligned} F_{E1}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0) &= \frac{3}{2}\lambda_0 R(l_1 j_1; 1; l_2) [(\mathbf{e}_f^* \cdot \mathbf{e}_0) M^{(0)}(l_1 j_1; 1; l_2) \\ &- \frac{i}{\sqrt{2}}(\mathbf{e}_f^* \times \mathbf{e}_0) \cdot \mathbf{M}^{(1)}(l_1 j_1; 1; l_2) - \sqrt{\frac{3}{5}} \mathbf{V}^{(2)}(\mathbf{e}_f^* \otimes \mathbf{e}_0) \cdot \mathbf{M}^{(2)}(l_1 j_1; 1; l_2)], \end{aligned} \quad (2.34)$$

where $M^{(k)}(l_1 j_1; 1; l_2)$ can be obtained from Eq.(2.20) as

$$\begin{aligned} M^{(0)}(l_1 j_{\pm}; 1; l_2) &= -\alpha_0(j_{\pm}) \overline{W}^{(0,0)} \pm \gamma_0 \overline{W}^{(1,1)0}, \\ M^{(1)}(l_1 j_{\pm}; 1; l_2) &= \alpha_1(j_{\pm}) \overline{W}^{(0,1)} \pm \beta_1 \overline{W}^{(1,0)} \pm \gamma_1 \overline{W}^{(1,2)1}, \\ M^{(2)}(l_1 j_{\pm}; 1; l_2) &= -\alpha_2(j_{\pm}) \overline{W}^{(0,2)} \pm \beta_2 \overline{W}^{(1,1)2} \pm \gamma_2 \overline{W}^{(1,3)2}. \end{aligned} \quad (2.35)$$

The coefficients α , β and γ are given in Table 2.1. From the definitions of $\overline{W}^{(\kappa, l)k}$,

Table 2.1: Coefficients in Eq.(2.35). Here $6j(k) = \begin{Bmatrix} 1 & l_2 & l_1 \\ l_2 & 1 & k \end{Bmatrix}$, and

$$9j(l, k) = \begin{Bmatrix} l_1 & l_1 & 1 \\ l_2 & l_2 & l \\ 1 & 1 & k \end{Bmatrix}.$$

k	0	1	2
$\frac{(2l_1+1)}{(j_{\pm}+\frac{1}{2})} \frac{\alpha(j_{\pm})}{(2l_2+1)}$	$\sqrt{\frac{2}{3}} 6j(0)$	$\sqrt{2} 6j(1)$	$\sqrt{\frac{10}{3}} 6j(2)$
$\sqrt{\frac{(2l_1+1)}{l_1(l_1+1)}} \frac{\beta}{(2l_2+1)}$	0	$\sqrt{2} 9j(0, 1)$	$\sqrt{10} 9j(1, 2)$
$\sqrt{\frac{(2l_1+1)}{l_1(l_1+1)}} \frac{\gamma}{(2l_2+1)}$	$\sqrt{2} 9j(1, 0)$	$\sqrt{10} 9j(2, 1)$	$\sqrt{\frac{70}{3}} 9j(3, 2)$

we can show that (see Appendix E)

$$\begin{aligned}
M^{(0)}(l_1 j_{\pm}; 1; l_2) &= \alpha'_0(j_{\pm}) N_h(l_2) \mp \gamma'_0 \left[\sum_{i \in l_2} \mathbf{s}_i \cdot \mathbf{l}_i \right], \\
M^{(1)}(l_1 j_{\pm}; 1; l_2) &= \alpha'_1(j_{\pm}) \mathbf{L}(l_2) \pm \beta'_1 \mathbf{S}(l_2) \pm \gamma'_1 \left[\sum_{i \in l_2} \left(\mathbf{s}_i - \frac{3\{\mathbf{s}_i \cdot \mathbf{l}_i, \mathbf{l}_i\}_+}{2l_2(l_2+1)} \right) \right], \\
M^{(2)}(l_1 j_{\pm}; 1; l_2) &= -\alpha'_2(j_{\pm}) \left[\sum_{i \in l_2} V^{(2)}(\mathbf{l}_i \otimes \mathbf{l}_i) \right] \pm \beta'_2 \left[\sum_{i \in l_2} V^{(2)}(\mathbf{s}_i \otimes \mathbf{l}_i) \right] \\
&\quad \pm \gamma'_2 \left[\sum_{i \in l_2} V^{(2)}(\mathbf{s}_i \otimes V^{(3)}(\mathbf{l}_i)) \right].
\end{aligned} \tag{2.36}$$

where

$$\begin{aligned}
V_{\pm 2}^{(2)}(1) &= l_{\pm 1}^2, \\
V_{\pm 1}^{(2)}(1) &= \frac{1}{\sqrt{2}} (l_{\pm 1} l_0 + l_0 l_{\pm 1}), \\
V_0^{(2)}(1) &= \frac{1}{\sqrt{6}} (3l_0^2 - 1^2).
\end{aligned} \tag{2.37}$$

$$V_{\pm 3}^{(3)}(1) = l_{\pm 1} l_{\pm 1} l_{\pm 1},$$

$$V_{\pm 2}^{(3)}(1) = \frac{1}{\sqrt{3}} [l_0 l_{\pm 1} l_{\pm 1} + l_{\pm 1} l_0 l_{\pm 1} + l_{\pm 1} l_{\pm 1} l_0],$$

Table 2.2: Coefficients in Eqs.(2.36). Here $6j(k) = \begin{Bmatrix} 1 & l_2 & l_1 \\ l_2 & 1 & k \end{Bmatrix}$, $9j(l, k) = \begin{Bmatrix} l_1 & l_1 & 1 \\ l_2 & l_2 & l \\ 1 & 1 & k \end{Bmatrix}$, $a = \frac{(2l_1+1)}{(j_{\pm}+\frac{1}{2})}\alpha'(j_{\pm})$, $b = \sqrt{\frac{(2l_1+1)}{l_1(l_1+1)}}\beta'$, and $c = \sqrt{\frac{(2l_1+1)}{l_1(l_1+1)}}\gamma'$.

k	0	1	2
a	$\sqrt{\frac{(2l_2+1)}{3}}6j(0)$	$\sqrt{\frac{3(2l_2+1)}{l_2(l_2+1)}}6j(1)$	$\sqrt{\frac{50(2l_2+1)}{l_2(l_2+1)(2l_2+3)(2l_2-1)}}6j(2)$
b	0	$2\sqrt{(2l_2+1)}9j(0, 1)$	$\sqrt{\frac{60(2l_2+1)}{l_2(l_2+1)}}9j(1, 2)$
c	$2\sqrt{\frac{(2l_2+1)}{l_2(l_2+1)}}9j(1, 0)$	$2\sqrt{\frac{10(2l_2+1)l_2(l_2+1)}{(2l_2+3)(2l_2-1)}}9j(2, 1)$	$\frac{280\sqrt{\frac{2}{3}}(2l_2+1)9j(3, 2)}{\prod_{n=-3}^3(2l_2+1+n)^{\frac{1}{2}}}$

$$\begin{aligned}
V_{\pm 1}^{(3)}(1) &= \frac{1}{\sqrt{15}}[2(l_{\pm 1}l_0l_0 + l_0l_{\pm 1}l_0 + l_0l_0l_{\pm 1}) + (l_{\mp 1}l_{\pm 1}l_{\pm 1} + l_{\pm 1}l_{\mp 1}l_{\pm 1} + l_{\pm 1}l_{\pm 1}l_{\mp 1})] \\
V_0^{(3)}(1) &= \frac{1}{\sqrt{10}}[l_0(5l_0^2 + 1 - 3l^2)],
\end{aligned} \tag{2.38}$$

and

$$V_q^{(k)}(\mathbf{s} \otimes V^{(l)}(1)) = \sum_{\mu, m} C_{1\mu; l m}^{k q} S_{\mu} V_m^{(l)}(1). \tag{2.39}$$

Here α' , β' and γ' are given in Table 2.2. The operator sums are over the $(nl_2)^{\nu}$ electrons in the valence shell.

As we see from the above Eq.(2.36), the operator $\overline{W}^{(0, l)}$ is a purely l th-rank orbital moment

$$\overline{W}^{(0, l)} \propto \sum_{i \in l_2} \underbrace{[l_i \otimes l_i \cdots \otimes l_i]^l}_{l \text{ factors}} \propto \sum_{i \in l_2} [V^{(l)}(\hat{l}_i)],$$

and the operators $\overline{W}^{(1, l)k}$ are k th-rank, spin-coupled orbital moments

$$\overline{W}^{(1, l)k} \propto \sum_{i \in l_2} \{ \mathbf{S}_i \otimes \underbrace{[l_i \otimes l_i \cdots \otimes l_i]^l}_{l \text{ factors}} \}^k \propto \sum_{i \in l_2} [\mathbf{S}_i^{(1)} \otimes V^{(l)}(\hat{l}_i)]^k.$$

Using the Wigner-Eckart theorem, the quadrupole-moment operator $V^{(2)}(1 \otimes 1)$ and the “magnetic dipole field” operator $\mathbf{s} - \frac{3\{\mathbf{s} \cdot \mathbf{l}, \mathbf{l}\}_+}{2l(l+1)}$ can also be represented as functions of the operator $\mathbf{r}$,

$$\frac{1}{l(l+1)} V_q^{(2)}(1 \otimes 1) = \eta \sqrt{\frac{2}{3}} C_q^{(2)}(\hat{\mathbf{r}}), \quad (2.40)$$

and

$$\mathbf{s} - \frac{3\{\mathbf{s} \cdot \mathbf{l}, \mathbf{l}\}_+}{2l(l+1)} = \eta(\mathbf{s} - 3(\mathbf{s} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}), \quad (2.41)$$

where $\eta = -\frac{(2l+3)(2l-1)}{2l(l+1)}$ (see Appendix F) and $C_q^{(2)}(\hat{\mathbf{r}})$ are defined

$$C_q^{(2)}(\hat{\mathbf{r}}) = \sqrt{\frac{4\pi}{5}} Y_q^{(2)}(\hat{\mathbf{r}}), \quad (2.42)$$

$$\begin{aligned} C_{\pm 2}^{(2)}(\hat{\mathbf{r}}) &= \sqrt{\frac{3}{8}} \sin^2 \theta e^{\pm 2i\phi}, \\ C_{\pm 1}^{(2)}(\hat{\mathbf{r}}) &= \mp \sqrt{\frac{3}{2}} \cos \theta \sin \theta e^{\pm i\phi}, \\ C_0^{(2)}(\hat{\mathbf{r}}) &= \frac{1}{2} (3 \cos^2 \theta - 1). \end{aligned} \quad (2.43)$$

It is worthwhile to mention that this kind of transform $V^{(l)}(\hat{\mathbf{l}}) \propto C^{(l)}(\hat{\mathbf{r}})$ will be meaningful only if l is even, because when l is odd, $\langle l_2 m'_2 | C^{(2n+1)}(\hat{\mathbf{r}}) | l_2 m_2 \rangle = 0$, but $\langle l_2 m'_2 | V^{(2n+1)}(\hat{\mathbf{l}}) | l_2 m_2 \rangle \neq 0$, for all possible m_2 and m'_2 . The highest rank of $M_{q(E1)}^{(k)}$ is 2, which is the maximum angular momentum transferred by $E1$ scattering.

2.4 E2 Scattering Operators F_{E2} .

Similarly for $E2$ resonant scattering, we have

$$F_{E2} = 4\pi\lambda_0 \sum_{k=0}^4 \sum_{q=-k}^k T_q^{(k)*}(\mathbf{e}_f^*, \hat{\mathbf{e}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)_{E2} F_q^{(k)}(\omega)_{E2}, \quad (2.44)$$

where $T_{q(E2)}^{(k)*}$ is given in Appendix D

$$T_{q(E2)}^{(k)*} = \frac{5}{4\pi} (-1)^q U_{-q}^{(k)}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0). \quad (2.45)$$

The polarization tensors $U_q^{(k)}$ (given by Appendix D) depend not only on the polarization vectors $\mathbf{e}_f$ and $\mathbf{e}_0$, but also on the wave vectors $\hat{\mathbf{k}}_f$ and $\hat{\mathbf{k}}_0$ of the scattering light. The scattering operator F_{E2}

$$F_{E2} = 5\lambda_0 \sum_k U^{(k)}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0) \cdot F^{(k)}(\omega)_{E2}, \quad (2.46)$$

can also be written as the sum of scalar products of the polarization tensors $U^{(k)}$ and the multipole moment operators $M_{(E2)}^{(k)}$ in the fast collision approximation [see

Table 2.3: Coefficients in Eq.(2.48). Here $6j(k) = \left\{ \begin{matrix} 2 & l_2 & l_1 \\ l_2 & 2 & k \end{matrix} \right\}$, $9j(l, k) = \left\{ \begin{matrix} l_1 & l_1 & 1 \\ l_2 & l_2 & l \\ 2 & 2 & k \end{matrix} \right\}$, $a = \frac{(2l_1+1)}{(j_{\pm}+\frac{1}{2})} \frac{\alpha(j_{\pm})}{(2l_2+1)}$, $b = \sqrt{\frac{(2l_1+1)}{l_1(l_1+1)}} \frac{\beta}{(2l_2+1)}$, and $c = \sqrt{\frac{(2l_1+1)}{l_1(l_1+1)}} \frac{\gamma}{(2l_2+1)}$.

k	0	1	2	3	4
a	$\sqrt{\frac{2}{5}} 6j(0)$	$\sqrt{\frac{6}{5}} 6j(1)$	$\sqrt{2} 6j(2)$	$\sqrt{\frac{14}{5}} 6j(3)$	$3\sqrt{\frac{2}{5}} 6j(4)$
b	0	$\sqrt{\frac{6}{5}} 9j(0, 1)$	$\sqrt{6} 9j(1, 2)$	$\sqrt{14} 9j(2, 3)$	$3\sqrt{\frac{14}{5}} 9j(3, 4)$
c	$\sqrt{\frac{6}{5}} 9j(1, 0)$	$\sqrt{6} 9j(2, 1)$	$\sqrt{14} 9j(3, 2)$	$3\sqrt{\frac{14}{5}} 9j(4, 3)$	$3\sqrt{\frac{22}{5}} 9j(5, 4)$

Eq.(2.21)],

$$F_{E2} = 5\lambda_0 R(l_1 j_{\pm}; 2; l_2) \sum_{k,q} (-1)^q \sqrt{\frac{5}{2k+1}} U_{-q}^{(k)}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0) \cdot M_q^{(k)}(l_1 j_{\pm}; 2; l_2). \quad (2.47)$$

Here $M_q^{(k)}(l_1 j_{\pm}; 2; l_2)$ can be obtained from Eq.(2.20), and are

$$\begin{aligned} M^{(0)}(l_1 j_{\pm}; 2; l_2) &= -\alpha_0(j_{\pm}) \overline{W}^{(0,0)} \pm \gamma_0 \overline{W}^{(1,1)0} \\ M^{(1)}(l_1 j_{\pm}; 2; l_2) &= \alpha_1(j_{\pm}) \overline{W}^{(0,1)} \pm \beta_1 \overline{W}^{(1,0)} \pm \gamma_1 \overline{W}^{(1,2)1} \\ M^{(2)}(l_1 j_{\pm}; 2; l_2) &= -\alpha_2(j_{\pm}) \overline{W}^{(0,2)} \pm \beta_2 \overline{W}^{(1,1)2} \pm \gamma_2 \overline{W}^{(1,3)2} \\ M^{(3)}(l_1 j_{\pm}; 2; l_2) &= \alpha_3(j_{\pm}) \overline{W}^{(0,3)} \pm \beta_3 \overline{W}^{(1,2)3} \pm \gamma_3 \overline{W}^{(1,4)3} \\ M^{(4)}(l_1 j_{\pm}; 2; l_2) &= -\alpha_4(j_{\pm}) \overline{W}^{(0,4)} \pm \beta_4 \overline{W}^{(1,3)4} \pm \gamma_4 \overline{W}^{(1,5)4}. \end{aligned} \quad (2.48)$$

The coefficients α , β and γ are given in Table 2.3. For $E2$ transitions $M^{(0)}$, $M^{(1)}$, and $M^{(2)}$ given by Eq.(2.48) are the same as they are in Eq.(2.35) for $E1$ scattering, except with different coefficients (α , β and γ), and in addition F_{E2} [in Eq.(2.48)] also includes $M^{(3)}$ (octupole) and $M^{(4)}$ (hexadecapole) moment operator contributions.

From the definition of $\overline{W}^{(\kappa,l)k}$, these multipole moments $M_{q(E2)}^{(k)}$ also can be expressed as (see Appendix E)

$$\begin{aligned} M^{(0)}(l_1 j_{\pm}; 2; l_2) &= \alpha'_0(j_{\pm}) N_h(l_2) \mp \gamma'_0 \left[\sum_{i \in l_2} \mathbf{s}_i \cdot \mathbf{l}_i \right], \\ M^{(1)}(l_1 j_{\pm}; 2; l_2) &= \alpha'_1(j_{\pm}) L(l_2) \pm \beta'_1 S(l_2) \pm \gamma'_1 \left[\sum_{i \in l_2} \left(\mathbf{s}_i - \frac{3\{\mathbf{s}_i \cdot \mathbf{l}_i\} \mathbf{l}_i}{2l_2(l_2+1)} \right) \right], \\ M^{(2)}(l_1 j_{\pm}; 2; l_2) &= -\alpha'_2(j_{\pm}) \left[\sum_{i \in l_2} V^{(2)}(\mathbf{l}_i) \right] \pm \beta'_2 \left[\sum_{i \in l_2} V^{(2)}(\mathbf{s}_i \otimes \mathbf{l}_i) \right] \\ &\quad \pm \gamma'_2 \left[\sum_{i \in l_2} V^{(2)}(\mathbf{s}_i \otimes V^{(3)}(\mathbf{l}_i)) \right], \\ M^{(3)}(l_1 j_{\pm}; 2; l_2) &= \alpha'_3(j_{\pm}) \left[\sum_{i \in l_2} V^{(3)}(\mathbf{l}_i) \right] \pm \beta'_3 \left[\sum_{i \in l_2} V^{(3)}(\mathbf{s}_i \otimes V^{(2)}(\mathbf{l}_i)) \right] \\ &\quad \pm \gamma'_3 \left[\sum_{i \in l_2} V^{(3)}(\mathbf{s}_i \otimes V^{(4)}(\mathbf{l}_i)) \right] \\ M^{(4)}(l_1 j_{\pm}; 2; l_2) &= -\alpha'_4(j_{\pm}) \left[\sum_{i \in l_2} V^{(4)}(\mathbf{l}_i) \right] \pm \beta'_4 \left[\sum_{i \in l_2} V^{(4)}(\mathbf{s}_i \otimes V^{(3)}(\mathbf{l}_i)) \right] \\ &\quad \pm \gamma'_4 \left[\sum_{i \in l_2} V^{(4)}(\mathbf{s}_i \otimes V^{(5)}(\mathbf{l}_i)) \right]. \end{aligned} \quad (2.49)$$

Table 2.4: Coefficients in Eqs.(2.52). Here $6j(k) = \begin{Bmatrix} 1 & l_2 & l_1 \\ l_2 & 1 & k \end{Bmatrix}$, $9j(l, k) = \begin{Bmatrix} l_1 & l_1 & 1 \\ l_2 & l_2 & l \\ 1 & 1 & k \end{Bmatrix}$.

k	$\frac{(2l_1+1)}{(j_{\pm}+\frac{1}{2})}\alpha'(j_{\pm})$	$\sqrt{\frac{(2l_1+1)}{l_1(l_1+1)}}\beta'$	$\sqrt{\frac{(2l_1+1)}{l_1(l_1+1)}}\gamma'$
0	$\sqrt{\frac{(2l_2+1)}{5}}6j(0)$	0	$\sqrt{\frac{12(2l_2+1)}{5l_2(l_2+1)}}9j(1, 0)$
1	$\frac{3}{\sqrt{5}}\sqrt{\frac{(2l_2+1)}{l_2(l_2+1)}}6j(1)$	$\sqrt{\frac{12(2l_2+1)}{5}}9j(0, 1)$	$\sqrt{\frac{24l_2(l_2+1)(2l_2+1)}{(2l_2+3)(2l_2-1)}}9j(2, 1)$
2	$\frac{2\sqrt{30}(2l_2+1)6j(2)}{\prod_{n=-2}^2(2l_2+1+n)^{\frac{1}{2}}}$	$\sqrt{\frac{36(2l_2+1)}{l_2(l_2+1)}}9j(1, 2)$	$\frac{56\sqrt{10}(2l_2+1)9j(3, 2)}{\prod_{n=-3}^3(2l_2+1+n)^{\frac{1}{2}}}$
3	$\frac{28\sqrt{2}(2l_2+1)6j(3)}{\prod_{n=-3}^3(2l_2+1+n)^{\frac{1}{2}}}$	$\frac{4\sqrt{210}(2l_2+1)9j(2, 3)}{\prod_{n=-2}^2(2l_2+1+n)^{\frac{1}{2}}}$	$\frac{504\sqrt{2}(2l_2+1)9j(4, 3)}{\prod_{n=-4}^4(2l_2+1+n)^{\frac{1}{2}}}$
4	$\frac{36\sqrt{14}(2l_2+1)6j(4)}{\prod_{n=-4}^4(2l_2+1+n)^{\frac{1}{2}}}$	$\frac{168\sqrt{2}(2l_2+1)9j(3, 4)}{\prod_{n=-3}^3(2l_2+1+n)^{\frac{1}{2}}}$	$\frac{1584\sqrt{14}(2l_2+1)9j(5, 4)}{\sqrt{5}\prod_{n=-5}^5(2l_2+1+n)^{\frac{1}{2}}}$

where $V^{(2)}(1)$ and $V^{(3)}(1)$ are given in the previous section, and $V^{(4)}(1)$ and $V^{(5)}(1)$ are defined in Appendix E. They are

$$\begin{aligned}
V_{\pm 4}^{(4)} &= l_{\pm 1}l_{\pm 1}l_{\pm 1}l_{\pm 1}, \\
V_{\pm 3}^{(4)} &= \frac{1}{2}\{l_0l_{\pm 1}l_{\pm 1}l_{\pm 1}\}_{sp}, \\
V_{\pm 2}^{(4)} &= \frac{1}{2\sqrt{7}}[\{l_{\pm 1}l_{\pm 1}l_{+1}l_{-1}\}_{sp} + 2\{l_{\pm 1}l_{\pm 1}l_0l_0\}_{sp}], \\
V_{\pm 1}^{(4)} &= \frac{1}{2\sqrt{7}}[\{l_{\pm 1}l_{+1}l_0l_{-1}\}_{sp} + 2\{l_{\pm 1}l_0l_0l_0\}_{sp}], \\
V_0^{(4)} &= \frac{1}{\sqrt{70}}[\{l_{+1}l_{+1}l_{-1}l_{-1}\}_{sp} + 2\{l_0l_0l_{+1}l_{-1}\}_{sp} + 4l_0^4]. \tag{2.50}
\end{aligned}$$

Also

$$V_{\pm 5}^{(5)} = l_{\pm 1}l_{\pm 1}l_{\pm 1}l_{\pm 1}l_{\pm 1},$$

$$\begin{aligned}
V_{\pm 4}^{(5)} &= \frac{1}{\sqrt{5}} \{l_0 l_{\pm 1} l_{\pm 1} l_{\pm 1} l_{\pm 1}\}_{sp}, \\
V_{\pm 3}^{(5)} &= \frac{1}{3\sqrt{5}} [2\{l_0 l_0 l_{\pm 1} l_{\pm 1} l_{\pm 1}\}_{sp} + \{l_{\pm 1} l_{\pm 1} l_{\pm 1} l_{+1} l_{-1}\}_{sp}], \\
V_{\pm 2}^{(5)} &= \frac{1}{2\sqrt{15}} [\{l_{\pm 1} l_{\pm 1} l_{+1} l_0 l_{-1}\}_{sp} + 2\{l_{\pm 1} l_{\pm 1} l_0 l_0 l_0\}_{sp}], \\
V_1^{(5)} &= \frac{1}{\sqrt{210}} [\{l_{\pm 1} l_{+1} l_{+1} l_{-1} l_{-1}\}_{sp} + 2\{l_{\pm 1} l_{+1} l_{-1} l_0 l_0\}_{sp} + 4\{l_{\pm 1} l_0 l_0 l_0 l_0\}_{sp}], \\
V_0^{(5)} &= \frac{1}{3\sqrt{14}} [\{l_{+1} l_{+1} l_{-1} l_{-1} l_0\}_{sp} + 2\{l_{+1} l_{-1} l_0 l_0 l_0\}_{sp} + 4l_0^5]. \tag{2.51}
\end{aligned}$$

Here sp is used to denote the symmetry permutation. For example, $\{l_0 l_{\pm 1} l_{\pm 1}\}_{sp} = l_0 l_{\pm 1} l_{\pm 1} + l_{\pm 1} l_0 l_{\pm 1} + l_{\pm 1} l_{\pm 1} l_0$. The coupled tensors $V^{(k)}(\mathbf{s} \otimes V^{(l)})$ are

$$V^{(k)}(\mathbf{s} \otimes V^{(l)}) = \sum_{m, \mu} C_{1\mu; lm}^{kq} s_\mu V_m^{(l)}. \tag{2.52}$$

and the α' , β' and γ' are given in Table 2.4.

Again, the operators $V^{(2)}(1)$ and $V^{(4)}(1)$ can be replaced by the operators $C^{(2)}(\hat{\mathbf{r}})$ and $C^{(4)}(\hat{\mathbf{r}})$ respectively. They are related as

$$\frac{V^{(2)}(1)}{C^{(2)}(\hat{\mathbf{r}})} = \frac{V^{(k)}(\mathbf{s} \otimes V^{(2)}(1))}{V^{(k)}(\mathbf{s} \otimes C^{(2)}(\hat{\mathbf{r}}))} = -\frac{(2l+3)(2l-1)}{\sqrt{6}}, \tag{2.53}$$

and

$$\frac{V^{(4)}(1)}{C^{(4)}(\hat{\mathbf{r}})} = \frac{V^{(k)}(\mathbf{s} \otimes V^{(4)}(1))}{V^{(k)}(\mathbf{s} \otimes C^{(4)}(\hat{\mathbf{r}}))} = \frac{\frac{1}{4\sqrt{70}} \prod_{n=-4}^4 (2l+1+n)^{\frac{1}{2}}}{\sqrt{2l+1} C_{l0,40}^{l0}}. \tag{2.54}$$

For the operators applied in the l -shell (see Appendix F). Here $C^{(2)}(\hat{\mathbf{r}})$ is given in the previous section, and $C^{(4)}(\hat{\mathbf{r}})$ are defined

$$\begin{aligned}
C_q^{(4)}(\hat{\mathbf{r}}) &= \sqrt{\frac{4\pi}{9}} Y_q^{(4)}(\theta, \phi), \\
C_{\pm 4}^{(4)}(\hat{\mathbf{r}}) &= \sqrt{\frac{35}{128}} \sin^4 \theta e^{\pm 4i\phi}, \\
C_{\pm 3}^{(4)}(\hat{\mathbf{r}}) &= \mp \sqrt{\frac{35}{16}} \sin^3 \theta \cos \theta e^{\pm 3i\phi}, \\
C_{\pm 2}^{(4)}(\hat{\mathbf{r}}) &= \sqrt{\frac{5}{32}} \sin^2 \theta (7 \cos^2 \theta - 1) e^{\pm 2i\phi},
\end{aligned} \tag{2.55}$$

$$\begin{aligned}
C_{\pm 1}^{(4)}(\hat{\mathbf{r}}) &= \mp \sqrt{\frac{5}{16}} \sin \theta (7 \cos^3 \theta - 3 \cos \theta) e^{\pm i \phi}, \\
C_0^{(4)}(\hat{\mathbf{r}}) &= \frac{1}{8} (35 \cos^4 \theta - 30 \cos^2 \theta + 3).
\end{aligned} \tag{2.56}$$

It is interesting to notice that the polarization tensors $T_{(EL)}^{(k)}$ in scattering operator F_{EL} are different for different EL transitions. For example, for $k = 0$, $T_{(E1)}^{(0)} \propto (\mathbf{e}_f^* \cdot \mathbf{e}_0)$ and $T_{(E2)}^{(0)} \propto [\frac{(\mathbf{e}_f^* \cdot \mathbf{e}_0)(\hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_0) + (\mathbf{e}_f^* \cdot \hat{\mathbf{k}}_0)(\mathbf{k}_f \cdot \mathbf{e}_0)}{2}]$, but the multipole moments $M_{(EL)}^{(k)}$ have the same structure (contain the same information), i.e $M^{(k)} = \alpha \overline{W}^{(0,k)} \pm \beta \overline{W}^{(1,k-1)k} \pm \gamma \overline{W}^{(1,k+1)k}$, except α , β and γ are different for different EL transitions.

2.5 Determination of the Scattering Tensors $F_q^{(k)}(\omega)_{EL}$.

In coherent scattering, the scattering amplitude is determined by the expectation value of the scattering operator

$$f_{EL} = \langle F_{EL} \rangle. \quad (2.57)$$

Also from the optical theorem, the absorption cross-section is proportional to the imaginary part of the coherent forward scattering amplitude

$$\sigma_{ab} = \frac{4\pi}{k} \text{Im}[\langle F_{EL} \rangle] \big|_{\mathbf{k}_f = \mathbf{k}_0}^{\mathbf{e}_f = \mathbf{e}_0}. \quad (2.58)$$

From the previous sections and Eq.(2.6),

$$\langle F_{EL} \rangle = 4\pi\lambda_o \sum_{k,q} (-1)^q T_{-q}^{(k)}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)_{EL} \langle F_q^{(k)}(\omega)_{EL} \rangle,$$

where

$$T_{q(E1)}^{(k)} = -\frac{3}{8\pi} V_q^{(k)}(\mathbf{e}_f^* \otimes \mathbf{e}_0)$$

for $E1$ scattering, and

$$T_{q(E2)}^{(k)} = \frac{5}{4\pi} U_q^{(k)}(\mathbf{e}_f^*, \hat{\mathbf{k}}; \mathbf{e}_0, \hat{\mathbf{k}})$$

for $E2$ scattering. Because of their different angular dependences the expectation values of scattering tensors $F_q^{(k)}(\omega)_{EL}$ can be determined experimentally.

As we have known from rotation group theory the transformation of $Y_m^{(l)}(\hat{\mathbf{n}})$ to $Y_m^{(l)}(\hat{\mathbf{n}}')$ can be described as the following[15]: If the rotated direction eigenket $|\hat{\mathbf{n}}'\rangle$ can be defined as

$$|\hat{\mathbf{n}}'\rangle = D(R) |\hat{\mathbf{n}}\rangle, \quad (2.59)$$

and

$$D(R^{-1}) |l, m\rangle = \sum_{m'} |l, m'\rangle D_{m', m}^{(l)}(R^{-1}), \quad (2.60)$$

then

$$Y_m^{(l)}(\hat{n}') = \sum_{m'} Y_{m'}^{(l)}(\hat{n}) D_{m',m}^{(l)}(R^{-1}). \quad (2.61)$$

Similarly, rotated operators $T_q^{(k)}$ become

$$D^\dagger(R) T_q^{(k)} D(R) = \sum_{q'=-k}^k D_{q'q}^{(k)}(R^{-1}) T_{q'}^{(k)}. \quad (2.62)$$

If the (X, Y, Z) -coordinate system is fixed in the laboratory frame, and the (x, y, z) -coordinate system is fixed on the sample, then rotating the sample by $R(\alpha, \beta, \gamma)$, where α, β , and γ are the Euler angles, we have

$$\begin{aligned} F_q^{(k)}(x, y, z) &= D^\dagger(R) F_q^{(k)}(X, Y, Z) D(R) = \sum_{q'=-k}^k D_{q'q}^{(k)}(R^{-1}) F_{q'}^{(k)}(X, Y, Z) \\ &= D_{qq'}^{(k)*}(R) F_{q'}^{(k)}(X, Y, Z), \end{aligned} \quad (2.63)$$

$$F_q^{(k)}(X, Y, Z) = D(R) F_q^{(k)}(x, y, z) D^\dagger(R) = \sum_{q'=-k}^k D_{q'q}^{(k)}(R) F_{q'}^{(k)}(x, y, z), \quad (2.64)$$

and the scattering operators are related with the rotation angles as

$$\langle F_{EL}(\alpha, \beta, \gamma) \rangle = 4\pi\lambda_o \sum_{k,q,q'} (-1)^q T_{-q}^{(k)}(X, Y, Z)_{EL} \langle F_{q'}^{(k)}(x, y, z)_{EL} \rangle D_{q'q}^{(k)}(\alpha, \beta, \gamma). \quad (2.65)$$

Here $\langle F_q^{(k)}(xyz)_{EL} \rangle$ are defined in the sample coordinate system, $T_q^{(k)}(X, Y, Z)_{EL}$ are defined in the laboratory frame (X, Y, Z) , and (α, β, γ) are the Euler angles of the rotated sample (x, y, z) to the laboratory system (X, Y, Z) .

In principle, there are a total of $N_{g(EL)}$ components $F_q^{(k)}$ in the EL transitions,

$$N_{g(EL)} = \sum_{k=0}^{2L} (2k+1) = (2L+1)^2,$$

$N_{g(E1)} = 9$, and $N_{g(E2)} = 25$. That means if we rotate the sample (α, β, γ) at $N_{g(EL)}$ different Bragg angles, it should be sufficient to determine all $\langle F_q^{(k)} \rangle_{EL}$ from Eq.(2.65).

The rotation matrix elements $D_{m,n}^{(l)}$ are reduced when m or $n = 0$,

$$D_{m,0}^{(l)}(\alpha, \beta, \gamma) = \sqrt{\frac{4\pi}{2l+1}} Y_m^{(l)}(\beta, \alpha)^*, \quad (2.66)$$

$$D_{0,m}^{(l)}(\alpha, \beta, \gamma) = \sqrt{\frac{4\pi}{2l+1}} Y_m^{(l)}(\beta, \gamma). \quad (2.67)$$

Eq.(2.65) can become simpler in some cases.

First, if the polarization tensors $T_q^{(k)}(X, Y, Z)_{EL} \neq 0$, only if $q = 0$, then Eq.(2.65) becomes

$$\begin{aligned} \langle F_{EL}(\alpha, \beta, \gamma) \rangle &= 4\pi\lambda_o \sum_k \sqrt{\frac{4\pi}{2k+1}} T_0^{(k)}(X, Y, Z)_{EL} \\ &\times \sum_q (-1)^q \langle F_q^{(k)}(x, y, z)_{EL} \rangle Y_{-q}^{(k)}(\beta, \alpha). \end{aligned} \quad (2.68)$$

Second, if $F_q^{(k)}(x, y, z)_{EL} = 0$, unless $q = 0$, in the samples, then

$$\begin{aligned} \langle F_{EL}(\alpha, \beta, \gamma) \rangle &= 4\pi\lambda_o \sum_k \sqrt{\frac{4\pi}{2k+1}} \langle F_0^{(k)}(x, y, z)_{EL} \rangle \\ &\times \sum_q (-1)^q T_q^{(k)}(X, Y, Z)_{EL} Y_{-q}^{(k)}(\beta, \gamma). \end{aligned} \quad (2.69)$$

In any other cases we have to use Eq.(2.65) to determine the spherical scattering tensors $\langle F_{q(EL)}^{(k)} \rangle$. The rotation matrix elements $D_{m,n}^{(j)}(\alpha, \beta, \gamma)$ in general are given in Appendix G.

Since the spherical scattering tensor $F_q^{(k)}$ is proportional to the multipole-moment $M_q^{(k)}$ [see Eq. (2.21)] in the fast collision approximation, and $M_q^{(k)}$ is a linear combination of various spin-orbital moments $W^{(\kappa,l)k}_q$, applying proper sum rules of $F_q^{(k)}$'s, we can determine expectation values of orbital moment $W^{(0,k)}_q$ and spin-orbital coupled moments $W^{(1,l)k}_q$'s separately. In the next section, we are going to discuss the sum rules of the scattering tensor $F_q^{(k)}$'s.

2.6 Sum Rules

We have shown in Section 2.2 that the scattering operator $F_{(EL)}^{(k)}$ in the fast collision approximation is a linear combination of the various spin-orbital coupled tensor operators $W^{(\kappa,l)k}$.

$$F_q^{(k)}(\omega)_{EL} = R(l_1 j_{\pm}; L; l_2) \sqrt{\frac{2L+1}{2k+1}} M_q^{(k)}(l_1 j_{\pm}; L; l_2), \quad (2.70)$$

where

$$R(l_1 j_1; L; l_2) = K(l_1 L l_2) |< R_{nl_2}(r) | r^L | R_{n_{cl_1 j_1}}(r) >|^2 / [E_I - E_0 - \hbar\omega - i\Gamma/2], \quad (2.71)$$

and

$$M_q^{(k)}(l_1 j_{\pm}; L; l_2) = -\frac{(j_{\pm} + \frac{1}{2})}{2l_1 + 1} c_k \overline{W}_q^{(0,k)} \pm [d_{k,|k-1|} \overline{W}_q^{(1,k-1)k} + d_{k,(k+1)} \overline{W}_q^{(1,k+1)k}]. \quad (2.72)$$

Since the excitation widths $\Gamma(j_+)$ and $\Gamma(j_-)$ are very close to each other (the difference is about less than 10% [9]), and

$$|< R_{nl_2}(r) | r^L | R_{n_{cl_1 j_+}}(r) >| \simeq |< R_{nl_2}(r) | r^L | R_{n_{cl_1 j_-}}(r) >|,$$

we can make the following approximation

$$R(l_1; L_2; l_2) = R(l_1 j_+; L; l_2)_{\omega} = R(l_1 j_-; L; l_2)_{\omega'},$$

where $\omega' = \omega + \Delta E$, and $\Delta E = (E_{j_+} - E_{j_-})$ is determined by the energy difference of the two absorption edges.

We notice that the tensors $W^{(1,l)k}$ appear in the $F^{(k)}$'s with opposite signs for the EL transitions at j_+ and j_- edges. This gives rise to important sum rules in that the sum of the $F^{(k)}$'s from j_+ and j_- resonances contains only the orbital moment ($\overline{W}^{(0,k)}$),

$$[F^{(k)}]_{\omega}^{j_+} + [F^{(k)}]_{\omega+\Delta E}^{j_-} = -R(l_1; L; l_2) \sqrt{\frac{2L+1}{2k+1}} c_k \overline{W}^{(0,k)}. \quad (2.73)$$

Here c_k is given in Eq.(2.18), and from Appendix E, we have

$$\overline{W}^{(0,0)} = \frac{-N_h(l_2)}{\sqrt{2(2l_2 + 1)}}. \quad (2.74)$$

$$W_q^{(0,1)} = \frac{\sqrt{\frac{3}{2}}}{\sqrt{l_2(l_2 + 1)(2l_2 + 1)}} L_q(l_2). \quad (2.75)$$

$$W_q^{(0,2)} = -\sqrt{\frac{5(2l_2 + 3)(2l_2 - 1)}{2(2l_2 + 1)l_2(l_2 + 1)}} \sum_{i \in l_2} \mathbf{C}_q^{(2)}(\hat{\mathbf{r}}_i), \quad (2.76)$$

$$W_q^{(0,3)} = 4\sqrt{35} \left[\prod_{n=-3}^3 (2l_2 + 1 + n)^{-\frac{1}{2}} \right] \sum_{i \in l_2} V_q^{(3)}(\mathbf{l}_i), \quad (2.77)$$

$$W_q^{(0,4)} = \frac{3}{\sqrt{2(2l_2 + 1)}} [C_{l_2 0; 40}^{l_2 0}]^{-1} \sum_{i \in l_2} \mathbf{C}_q^{(4)}(\hat{\mathbf{r}}_i). \quad (2.78)$$

The hole number $N_h(l_2)$, the orbital angular momentum $\mathbf{L}(l_2)$, and the charge multipole moments $\mathbf{C}^{(2)}(\hat{\mathbf{r}})$ and $\mathbf{C}^{(4)}(\hat{\mathbf{r}})$, etc. can be determined from $F^{(k)}$'s for $k = 0, 1, 2$ and 4 respectively. Here the higher rank moments contain the information of the anisotropy, and crystal field of scattering samples.

One also can obtain the spin-orbital coupled moments $(\overline{W}^{(1,l)k})$ from the “difference” of $F^{(k)}$'s (assuming that the j_+ and j_- resonances are well resolved),

$$[F^{(k)}]_{\omega}^{j_+} - \left(\frac{l_1 + 1}{l_1}\right) [F^{(k)}]_{\omega + \Delta E}^{j_-} = R(l_1; L; l_2) \sqrt{\frac{2L + 1}{2k + 1}} \left(\frac{2l_1 + 1}{l_1}\right) G^{(k)}, \quad (2.79)$$

where

$$G^{(k)} \equiv \left[\sum_{l=|k-1|, (\neq k)}^{k+1} d_{kl} \overline{W}^{(1,l)k} \right], \quad (2.80)$$

and d_{kl} is given by Eq.(2.18). From Appendix E, we have

$$G^{(0)} = -\frac{\sqrt{2}d_{11}}{\sqrt{(2l_2 + 1)l_2(l_2 + 1)}} \left[\sum_{i \in l_2} \mathbf{s}_i \cdot \mathbf{l}_i \right], \quad (2.81)$$

$$\begin{aligned}
G^{(1)} &= d_{10} \sqrt{\frac{2}{2l_2 + 1}} \mathbf{S}(l_2) \\
&\quad - d_{12} \sqrt{\frac{(2l_2 + 3)(2l_2 - 1)}{(2l_2 + 1)l_2(l_2 + 1)}} \left[\sum_{i \in l_2} (\mathbf{s}_i - 3(\mathbf{s}_i \cdot \hat{\mathbf{r}}_i) \hat{\mathbf{r}}_i) \right],
\end{aligned} \tag{2.82}$$

$$\begin{aligned}
G^{(2)} &= \frac{d_{21} \sqrt{6}}{\sqrt{(2l_2 + 1)l_2(l_2 + 1)}} \left[\sum_{i \in l_2} V^{(2)}(\mathbf{s}_i \otimes \mathbf{l}_i) \right] \\
&\quad + \frac{d_{23} 8 \sqrt{35}}{\prod_{n=-3}^3 (2l_2 + 1 + n)^{-\frac{1}{2}}} \sum_{i \in l_2} V^{(2)}[\mathbf{s}_i \otimes V^{(3)}(\mathbf{l}_i)],
\end{aligned} \tag{2.83}$$

and so on. The $k = 0$ term is determined only by the spin-orbital coupling $\sum_{i \in l_2} \mathbf{s}_i \cdot \mathbf{l}_i$, while the $k \geq 1$ terms include the two spin-coupled orbital moments for each term. For example, the $k = 1$ term depends on the spin $\mathbf{S}(l_2)$ and “magnetic dipole field operator” $\sum_{i \in l_2} (\mathbf{s}_i - 3(\mathbf{s}_i \cdot \hat{\mathbf{r}}_i) \hat{\mathbf{r}}_i)$.

Such sum rules in the context of circular dichroism were also pointed out by Thole and Carra et al.[12, 13].

From the above sum rules, we can separate out the orbital moments $\overline{W}^{(0,k)}$ from the spin-coupled moments $\overline{W}^{(1,k-1)k}$ and $\overline{W}^{(1,k+1)k}$. But these sum rules can not separate two spin-coupled moments $\overline{W}^{(1,k-1)k}$ and $\overline{W}^{(1,k+1)k}$ for $k \geq 1$ terms.

In principle, we can to separate the two contributions of $\overline{W}^{(1,l)k}$ ($l = k + 1$ and $k - 1$) experimentally. such as, in the cases where there are at least two different l_1 core shells ($l_1 \geq 1$, for example, $3p$ and $3d$ shells). The scattering from the two different l_1 -core shells to the same nl_2 valence shell will give two equations of Eq.(2.79)

$$[F^{(k)}]_{\omega}^{j+} - \frac{(l_1 + 1)}{l_1} [F^{(k)}]_{\omega + \Delta E}^{j-} = R(l_1; L; l_2) \sqrt{\frac{2L + 1}{2k + 1}} \left(\frac{2l_1 + 1}{l_1} \right) \left[\sum_{l=|k-1|, l \neq k}^{k+1} d_{kl} \overline{W}^{(1,l)k} \right], \tag{2.84}$$

$$[F^{(k)}]_{\omega'}^{j'_+} - \left(\frac{l'_1 + 1}{l'_1} \right) [F^{(k)}]_{\omega' + \Delta E'}^{j'_-} = R(l'_1; L'; l_2) \sqrt{\frac{2L' + 1}{2k + 1}} \left(\frac{2l'_1 + 1}{l'_1} \right) \left[\sum_{l=|k-1|, l \neq k}^{k+1} d'_{kl} \overline{W}^{(1,l)k} \right]. \tag{2.85}$$

From these two equations we can determine the two unknowns $\overline{W}^{(1,l)k}$ ($l = k + 1$ and $k - 1$).

In an LSJ -coupling system, whenever the scattering is within a manifold of good J ($|(nl_2)^\nu SLJM \rightarrow (nl_2)^\nu SLJM' \rangle$), then (see Appendix H)

$$W^{(\kappa,l)k} = \frac{\langle (nl_2)^\nu SLJ || W^{(\kappa,l)k} || (nl_2)^\nu SLJ \rangle}{\langle (nl_2)^\nu SLJ || V^{(k)}(\mathbf{J}) || (nl_2)^\nu SLJ \rangle} V_q^{(k)}(\mathbf{J}), \quad (2.86)$$

where $V^{(k)}(\mathbf{J})$'s are obtained by replacing $\mathbf{l}$ by $\mathbf{J}$ in $V^{(k)}(\mathbf{l})$ (see Appendix E). The reduced matrix elements $\langle || W^{(\kappa,l)k} || \rangle$ are given in Appendix H. Therefore, the ratio of $W^{(1,k-1)k}$ to $W^{(1,k+1)k}$ can be calculated in this system.

In particular,

$$\mathbf{S} = \mathbf{J} \left[\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right] \quad (2.87)$$

and Carra et al.[13] have shown for a Hund's Rule ground state

$$\sum_{i \in l_2} [\mathbf{s}_i - 3(\mathbf{s}_i \cdot \hat{\mathbf{r}}_i) \hat{\mathbf{r}}_i] = \mathbf{J}(l_2 - \nu + \frac{1}{2})C(LSJ), \quad (2.88)$$

where the coefficient $C(LSJ)$ is given as

$$C(LSJ) = \frac{3(S-J)^2(S+J+1)^2 - L(L+1)[L(L+1) + 2S(S+1) + 2J(J+1)]}{2(2l_2+3)(2l_2-1)(2L-1)SJ(J+1)}, \quad (2.89)$$

for the electron number of the valence shell $\nu \leq (2l_2 + 1)$. For $\nu \geq (2l_2 + 1)$, ν is replaced by $(4l_2 + 2 - \nu)$ in Eq.(2.88). For $L = 0$, configurations $(\nu = 0, 2l_2 + 1, 4l_2 + 2)$, $\langle (\sum_{i \in l_2} [\mathbf{s}_i - 3(\mathbf{s}_i \cdot \hat{\mathbf{r}}_i) \hat{\mathbf{r}}_i])_z \rangle = 0$.

Applying the sum rules obtained in this section to analyze the expectation values of $\langle F_\omega^{(k)} \rangle$'s, the expectation values of various spin-orbital multipole moments will be determined.

2.7 Discussion.

In this chapter I have shown that in the fast collision approximation the scattering operator F_{EL} is a linear combination of the spin-orbit multipole-moment operators $M_q^{(k)}$ of the valence electrons, for which I have given the explicit expressions [see Eq. (2.36) and (2.49)].

From the definition of $\overline{W}^{(\kappa,l)}$ (or $W^{(\kappa,l)}$) in Eq.(2.13), we see that there is a one-to-one mapping between the operators $\overline{W}^{(\kappa,l)}$ and the one-particle density matrix operators $\hat{\rho}_{m_2 m_s; m'_2 m'_s} (= \hat{a}_{m_2 m_s}^\dagger \hat{a}_{m'_2 m'_s})$. This mapping implies that if we know all $\overline{W}^{(\kappa,l)}$ ($\kappa = 0$ and 1 , $l \leq 2l_2$) then we could obtain the density matrix $\hat{\rho}(l_2)$. However, from resonant scattering and absorption we can only obtain some of $\overline{W}^{(\kappa,l)}$ (as we showed in this chapter, they are $\overline{W}^{(0,k)}$ and $\overline{W}^{(1,l)k}$ for $k \leq 2L$, and usually $L < l_2$), nevertheless this is important information of the valence electron distributions.

Since core electrons only can be excited into unoccupied valence states according to the Pauli exclusion principle, and a full shell (occupied states + unoccupied states) is invariant under rotational transforms, we have

$$W_{\mu m}^{(\kappa,l)}(electron) + W_{\mu m}^{(\kappa,l)}(hole) = \sqrt{2(2l_2 + 1)}\delta_{\kappa,0}\delta_{l,0}, \quad (2.90)$$

$$\overline{W}_{\mu m}^{(\kappa,l)} = -W_{\mu m}^{(\kappa,l)}(hole) = W_{\mu m}^{(\kappa,l)}(electron) - \sqrt{2(2l_2 + 1)}\delta_{\kappa,0}\delta_{l,0}. \quad (2.91)$$

$\overline{W}^{(\kappa,l)}$'s are the spin-orbital double moment operators of holes (unoccupied states), which are related to the electron multipole moments $W^{(\kappa,l)}(electron)$'s. That is why the scattering operators $F_q^{(k)}$'s are related with electron multipole moments $M_q^{(k)}$ ($\propto \alpha \overline{W}_q^{(0,k)} \pm \beta \overline{W}^{(1,k-1)k} \pm \gamma \overline{W}^{(1,k+1)k}$) of the valence shell.

The spin-orbital interaction splits the $n_c l_1$ core shell into $n_c l_1 j_-$ and $n_c l_1 j_+$ two subshells, and the spin-up and spin-down electrons have different probabilities in

$|l_1 j_+ m_j\rangle$ and $|l_1 j_- m_j\rangle$ states, i.e. $P(m_s)^{j_1 m_j} \neq P(-m_s)^{j_1 m_j}$. Thus, the resonant scattering through virtual transitions of core electrons is able to detect the spins in occupied valence shell (nl_2) via the exclusion principle and it is thusly that the $W^{(1,l)k}$'s enter into the $M_q^{(k)}$'s, in addition to the pure orbital moments $W^{(0,k)}$'s. When we sum up the scattering amplitudes from both the absorption edges, the two subshells ($j_\pm$) are mixed together artificially, the probabilities of the spin-up and spin-down electrons in each " $n_c l_1 m_1$ " orbital are the same, then the spin-orbital effects have "vanished". That is why the summed resonant scattering operators from two absorption edges are only proportional to the orbital moments of the valence shell ($F_q^{(k)(j_+ + j_-)} \propto \overline{W}_q^{(0,k)}$).

Obviously, since there is no spin-orbital splitting in the s -shell, we can only obtain the purely orbital moments through the K -edge scattering. The scattering operators F_{EL} in Eq.(2.22) still hold except

$$M_q^{(k)}(l_1; L; l_2) = -c_k \overline{W}_q^{(0,k)}, \quad (2.92)$$

where c_k is given by Eq.(2.18).

Also due to the spin-orbital effects, the probabilities of the spin-up and spin-down electrons in each $|j_1 m_j\rangle$ state are reversed at different edges, i.e. $P(m_s)^{j_+ m_j} = P(-m_s)^{j_- m_j}$. Therefore, the various spin-coupled orbital moments $\overline{W}^{(1,l)k}$ appear in $M^{(k)}(j_\pm)$'s with opposite signs at j_+ and j_- edges. Taking the proper "difference" of the scattering from these two edges, the spin-coupled orbital moments are obtained,

$$\left(\frac{1}{2j_+ + 1} [F^{(k)}]^{j_+} - \frac{1}{2j_- + 1} [F^{(k)}]^{j_-} \right) \propto \left(\sum_{l=|k-1| \neq k}^{k+1} d_{kl} \overline{W}^{(1,l)k} \right).$$

The core shell spin-orbital splitting allows the resonant x-ray magnetic scattering to detect the spin coupled orbital moments $\overline{W}^{(1,l)k}$ in the valence shell, which is one of the most important differences when compared with neutron and nonresonant x-ray magnetic scattering.

In an SLJ -coupling system, for the scattering within a manifold of a good J ($|l_2^{\nu}SLJM\rangle \rightarrow |l_2^{\nu}SLJM'\rangle$), the spherical tensor scattering operator $F_q^{(k)}$ is proportional to the symmetric tensor $V_q^{(k)}(\mathbf{J})$ in the fast collision approximation (see Appendix H). The total scattering operator F_{EL} in Eq.(2.22) can be written out as

$$F_{EL} = 4\pi\lambda_0 R \sum_{k=0}^{2L} \sqrt{\frac{2L+1}{2k+1}} \frac{\langle l_2^{\nu}SLJM || M^{(k)} || l_2^{\nu}SLJ \rangle}{\langle J || V^{(k)}(\mathbf{J}) || J \rangle} \times T^{(k)}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)_{EL} \cdot V^{(k)}(\mathbf{J}), \quad (2.93)$$

where the reduced matrix elements of $\langle || M^{(k)} || \rangle$ and $\langle || V^{(k)}(\mathbf{J}) || \rangle$ are given in Appendix H and Appendix E respectively.

In coherent scattering, the scattering amplitude is determined by the expectation value of the scattering operator

$$f_{EL} = \langle F_{EL} \rangle. \quad (2.94)$$

Also from the optical theorem, the absorption cross-section is proportional to the imaginary part of the coherent forward scattering amplitude

$$\sigma_{ab} = \frac{4\pi}{k} \text{Im}[\langle F_{EL} \rangle] \Big|_{\mathbf{k}_f=\mathbf{e}_0}^{\mathbf{e}_f=\mathbf{e}_0}. \quad (2.95)$$

In the fast collision approximation, we can bring F_{EL} from Eq.(2.22) into Eq.(2.95) and obtain

$$\begin{aligned} \sigma_{ab} = & \left(\frac{4\pi}{k}\right)^2 \frac{K(l_1 L l_2) |\langle n l_2 | r^L | n_c l_1 j_1 \rangle|^2 \Gamma/2}{[(\Delta E - \hbar\omega)^2 + \Gamma^2/4]} \\ & \times \sum_{kq} \sqrt{\frac{2L+1}{2k+1}} T_q^{(k)*}(\mathbf{e}_0^* \hat{\mathbf{k}}_0; \mathbf{e}_0 \hat{\mathbf{k}}_0)_{(EL)} \langle M_{q(EL)}^{(k)} \rangle, \end{aligned} \quad (2.96)$$

where $T_q^{(k)*}(\mathbf{e}_0^* \hat{\mathbf{k}}_0; \mathbf{e}_0 \hat{\mathbf{k}}_0)_{EL}$, $M_{q(EL)}^{(k)}$ and $K(l_1 L l_2)$ are given by Eq.(2.8), Eq.(2.20) and Eq.(2.10) respectively.

The coherent scattering amplitudes and absorptions are determined by the thermal expectation values (or ensemble averages) of the spin-orbital moments $M_q^{(k)}$'s

of the valence shell in the fast-collision approximation. Applying the sum rules to $\langle M_{q(j\pm)}^{(k)} \rangle$'s, the expectation values of the various moments can be obtained. Such as, from the zeroth rank moment $\langle M_{(j\pm)}^{(0)} \rangle$, the total hole number $\langle N_h(l_2) \rangle$, and the spin-orbit coupling $\langle \sum_{i \in l_2} \mathbf{s}_i \cdot \mathbf{l}_i \rangle$ can be determined. From the first rank moment $\langle M_{(j\pm)}^{(1)} \rangle$, the orbital angular momentum $\langle \mathbf{L} \rangle$, spin $\langle \mathbf{S} \rangle$ and the "magnetic dipole field" $\langle \sum_{i \in l_2} (\mathbf{s}_i - 3(\mathbf{s}_i \cdot \hat{\mathbf{r}}_i)\hat{\mathbf{r}}_i) \rangle$ are obtained. The second rank moment $\langle M_{(j\pm)}^{(2)} \rangle$ will give the information on the quadrupole moment, and so on.

Coherent elastic resonant x-ray scattering has been used to investigate the magnetic spiral structure (such as in a holmium crystal by Gibbs et al.[1]). The scattering amplitudes of these EL scattering have been shown by Hannon et al.[2] to only contain the $q = 0$ components of $F_q^{(k)}$. The reason for this is very simple: In a coherent scattering (or absorption) processes, the final atomic state is the same as the initial atomic state, i.e. $| (nl_2)^\nu L, S, J, M \rangle \rightarrow | (nl_2)^\nu L, S, J, M \rangle$, or $| (nl_2)^\nu \alpha M \rangle \rightarrow | (nl_2)^\nu \alpha M \rangle$, for the cases where the spin exchange or local magnetic field effect is much stronger than the crystal field effect. The total angular momentum $\mathbf{J}$ and J_z are both almost good quantum numbers, or only J_z is an almost good quantum number. $\Delta J_z = 0$ for these systems in coherent scattering. Under this constraint only $F_0^{(k)}$'s contribute to the scattering amplitude. Any other $q (\neq 0)$ will cause the spin flip $\Delta J_z \neq 0$, which will give a different final state $|\psi_f\rangle$. Therefore, the scattering amplitudes (or absorptions) are functions of $\mathbf{e}_z$'s and $\hat{\mathbf{k}}_z$'s in $T_0^{(k)}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)_{EL}$, where $\hat{\mathbf{z}}$ is the local magnetic field direction. This gives the way to detect the magnetic crystal structure, as discussed in Hamrick's MA thesis[10]. This is also the reason to explain why the circular dichroism in $E1$ transition is a function of $\cos\theta$, where θ is the angle between the wave vector $\hat{\mathbf{k}}$ and the magnetic field direction $\hat{\mathbf{z}}$ in the sample [due to $(\hat{\mathbf{e}}^* \times \hat{\mathbf{e}})_z \propto \hat{k}_z = \cos\theta$].

In the inelastic or “quasi-elastic” resonant scattering, the final state is not necessarily the same as the initial state, e.g. $| (nl_2)^\nu L, S, J, M \rangle \rightarrow | (nl_2)^\nu L', S', J', M' \rangle$. In these cases, the scattering amplitudes would include all the q -components ($q = \Delta J_z = M - M'$) of $F_q^{(k)}$, as shown in Eq.(2.2) and (2.8). In fact, this also may occur in coherent scattering (or absorption) for the systems where the crystal field or any other bonding force can not be neglected compared to the local magnetic field. In these cases different M_J states are mixed in the energy states. $\langle F_q^{(k)} \rangle \neq 0$ for some of the q -components. It depends on the symmetry of the last partially filled states or the first immediately unoccupied states. For instance, in $E1$ scattering (or absorption) to a d band, if the last partially filled states are the $d_{x^2-y^2}$ nondegenerate orbital states, for which only $q = 0$ components $F_0^{(k)}$ contribute to the scattering amplitude. But if the last partially filled states have d_{xz} (or d_{yz}) symmetry, the scattering amplitude may include the non-zero contributions from all the q -components ($q = -k, \dots, k; k \leq 2$). In any event, the scattering operators obtained in this thesis are more general for all the cases of electric multipole scattering and absorption.

Applying the scattering operators to the inelastic coherent scattering, one can also obtain moment-moment correlations and dynamic excitation spectra. We will discuss this by an example in Chapter 4.

The scattering operators obtained in this chapter are in the fast collision approximation, which holds in the cases where either the width Γ , or the frequency deviation $\Delta\omega = (E_I - E_0 - \hbar\omega)$ from resonance, is large compared to the energy splitting Δ of the excited states. Explicitly, this approximation should be rather good for resonant scattering at the L_2, L_3 edges in the rare earths and actinides, as well as for the M_4, M_5 edges in the actinides, for which $\Delta \gtrsim \Gamma$ and the splitting is not resolved. For example, for the rare earth L_2, L_3 transitions to the $4f$ shell, the splitting $\Delta \gtrsim 2eV$ [7, 8], while $\Gamma > 4.5eV$ [9]. However, for the M_4, M_5 transitions in the rare

earths, $\Delta \gtrsim \Gamma$ and the multiplet structure can be resolved. The simplicity of the fast-collision approximation [Eqs.(2.22)] can be regained, by tuning off resonance so that $\Delta \ll |\Delta\omega|$. Even off resonance, the M_4, M_5 scattering amplitudes will be appreciable because they are $\approx 10 - 100r_0$ at resonance.

Some resonant magnetic effects do depend explicitly on the separation of E_I into spin-up and spin-down bands, and upon the m_s dependence of the current matrix elements. This is particularly true for transitions to d bands. The generalization of Eq.(2.22) and (2.36) to treat this important case is given in the next chapter.

Chapter 3

Scattering Operator for Transitions to d Bands.

As we have mentioned in the last chapter, some resonant magnetic effects depend explicitly on the separation of E_I into spin-up and spin-down bands, and upon the m_s dependence of the current matrix elements. This is not described by the scattering operator as given by chapter 2. In particular, this is the case for the first observed resonant magnetic scattering ($2p_{3/2}$ to $5d$ in Ho)[1]. In this chapter, we are going to derive the generalized scattering operator to treat this important case.

We now assume that there is an exchange splitting Δ between the spin-up and spin-down valence states,

$$\Delta E_{I0}^{\pm} = \Delta E_{I0} \mp \frac{\Delta}{2}, \quad (3.1)$$

and different radial matrix-elements to these states,

$$\langle r^L \rangle^{\pm} = \langle r^L \rangle (1 \pm \delta/2). \quad (3.2)$$

Then the scattering operator $F_{LM',LM}$ [see Eq.(2.9)] becomes (see Appendix I)

$$F_{LM',LM} = \frac{\bar{R}(l_1, j_1; L; l_2)}{1 - \Delta^2} \bar{S}_{LM',LM}, \quad (3.3)$$

where $\bar{R}$ is determined in Eq.(2.10) by the mean value of the radial matrix elements and the mean value of the energy ΔE_{I0} in the resonance denominator, and the scattering operator $\bar{S}_{LM',LM}$ is

$$\bar{S}_{LM',LM} = \sum_{l=0}^{2L} \left\{ -\frac{(j_{\pm} + \frac{1}{2})}{(2l_1 + 1)} c_l [(1 + \Delta\delta) \bar{W}_q^{(0,l)} + \epsilon \bar{W}_{0q}^{(1,l)}] C_{LM',lq}^{LM} \right.$$

$$\pm \sum_{k=|l-1|(\neq l)}^{l+1} d_{kl} [\bar{W}_q^{(1,l)k} + (\epsilon \bar{W}_q^{(0,l)} + \bar{\Delta} \delta \bar{W}_{0q}^{(1,l)}) C_{lq;10}^{kq}] C_{LM';kq}^{LM} \} . \quad (3.4)$$

The coefficients c_l and d_{kl} have been given in Eq.(2.18),

$$\bar{\Delta} = \frac{\Delta}{\Gamma(X-i)}, \quad (3.5)$$

$$X = [\Delta E_{I0} - \hbar\omega]/[\Gamma/2], \quad (3.6)$$

and

$$\epsilon = \delta + \bar{\Delta}. \quad (3.7)$$

Here $\delta \ll 1$, but $\bar{\Delta}$ is not necessarily small.

From the scattering operator $\bar{S}_{LM';LM}$ we can define the modified multipole moments $\bar{M}_q^{(k)}(l_1, j_{\pm}; L; l_2)$

$$\bar{S}_{LM';LM} \equiv \sum_{k,q} \bar{M}_q^{(k)}(l_1 j_{\pm}; L; l_2) C_{LM';kq}^{LM}. \quad (3.8)$$

That is

$$\begin{aligned} \bar{M}_q^{(k)}(l_1 j_{\pm}; L; l_2) &= -\frac{(j_{\pm} + \frac{1}{2})}{2l_1 + 1} c_k [(1 + \bar{\Delta} \delta) \bar{W}_q^{(0,k)} + \epsilon \bar{W}_{0q}^{(1,k)}] \\ &\pm \sum_{l=|k-1|(\neq k)}^{k+1} d_{kl} [\bar{W}_q^{(1,l)k} + (\epsilon \bar{W}_q^{(0,l)} + \bar{\Delta} \delta \bar{W}_{0q}^{(1,l)}) C_{lq;10}^{kq}] \end{aligned} \quad (3.9)$$

Then the spherical scattering operator $F_q^{(k)}(\omega)_{EL}$, defined in Eq.(2.8) becomes

$$F_q^{(k)}(\omega)_{EL} = \frac{\bar{R}(l_1 j_{\pm}; L; l_2)}{1 - \bar{\Delta}^2} \sqrt{\frac{2L+1}{2k+1}} \bar{M}_q^{(k)}(l_1 j_{\pm}; L; l_2), \quad (3.10)$$

The total scattering operator F_{EL} in Eq.(2.6) is still in the same form

$$F_{EL} = 4\pi \lambda_0 \sum_{k,q} T_q^{(k)*}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)_{EL} F_q^{(k)}(\omega)_{EL}. \quad (3.11)$$

Bringing Eq.(3.10) into Eq.(3.11), the generalized scattering operator F_{EL} is obtained

$$F_{EL} = 4\pi \lambda_0 \frac{\bar{R}(l_1 j_{\pm}; L; l_2)}{1 - \bar{\Delta}^2} \sum_{k=0}^{2L} \sum_{q=-k}^k \sqrt{\frac{2L+1}{2k+1}} T_{q(EL)}^{(k)*} \bar{M}_q^{(k)}(l_1 j_{\pm}; L; l_2). \quad (3.12)$$

For an $E1$ transition we have

$$F_{E1} = -\frac{3}{2}\lambda_0 \frac{\overline{R}(l_1 j_1; L; l_2)}{1 - \overline{\Delta}^2} \sum_{k=0}^2 \sqrt{\frac{3}{2k+1}} V^{(k)}(\mathbf{e}_f^* \otimes \mathbf{e}_0) \cdot \overline{M}^{(k)}(l_1 j_1; 1; l_2), \quad (3.13)$$

that is

$$\begin{aligned} F_{E1} = & \frac{3}{2}\lambda_0 \frac{\overline{R}(l_1 j_1; L; l_2)}{1 - \overline{\Delta}^2} [(\mathbf{e}_f^* \cdot \mathbf{e}_0) \overline{M}^{(0)}(l_1 j_1; 1; l_2) \\ & - \frac{i}{\sqrt{2}} (\mathbf{e}_f^* \times \mathbf{e}_0) \cdot \overline{M}^{(1)}(l_1 j_1; 1; l_2) - \sqrt{\frac{3}{5}} V^{(2)}(\mathbf{e}_f^* \otimes \mathbf{e}_0) \cdot \overline{M}^{(2)}(l_1 j_1; 1; l_2)]. \end{aligned} \quad (3.14)$$

Here (see Appendix J)

$$M^{(0)}(l_1 j_{\pm}; 1; l_2) = \alpha'_0(j_{\pm}) [(1 + \overline{\Delta}\delta) N_h(l_2) - 2\epsilon S_z]$$

$$\mp \gamma'_0 \left[\sum_{i \in l_2} (\mathbf{s}_i \cdot \mathbf{l}_i) + \frac{\epsilon}{2} L_z + \frac{\overline{\Delta}\delta}{2} L_z^{(s)} \right],$$

$$M^{(1)}(l_1 j_{\pm}; 1; l_2) = \alpha'_1(j_{\pm}) [(1 + \overline{\Delta}\delta) \mathbf{L} + \epsilon \mathbf{L}^{(s)}]$$

$$\pm \beta'_1 [\mathbf{S} - (\frac{\epsilon}{2} P_{hole} - \overline{\Delta}\delta S_z) \mathbf{z}]$$

$$\pm \gamma'_1 \sum_{i \in l_2} \left[\left(\mathbf{s} - \frac{3\{\mathbf{s} \cdot \mathbf{l}, \mathbf{l}\}_+}{2l_2(l_2+1)} \right)_i + \frac{\epsilon}{2} \left(\mathbf{z} - \frac{3\{l_z, \mathbf{l}\}_+}{2l_2(l_2+1)} \right)_i \right]$$

$$+ \frac{\overline{\Delta}\delta}{2} \left(\mathbf{z} - \frac{3\{l_z, \mathbf{l}\}_+}{2l_2(l_2+1)} \right)_i^{(s)}],$$

$$M^{(2)}(l_1 j_{\pm}; 1; l_2) = -\alpha'_2(j_{\pm}) \sum_{i \in l_2} [(1 + \overline{\Delta}\delta) V^{(2)}(\mathbf{l}_i \otimes \mathbf{l}_i) + \epsilon V^{(2)}(\mathbf{l}_i \otimes \mathbf{l}_i)^{(s)}]$$

$$\begin{aligned}
& \pm \beta'_2 \sum_{i \in l_2} [V^{(2)}(\mathbf{s}_i \otimes \mathbf{l}_i) + \frac{\epsilon}{2} V^{(2)}(\mathbf{z} \otimes \mathbf{l}_i) + \frac{\overline{\Delta}\delta}{2} V^{(2)}(\mathbf{z} \otimes \mathbf{l}_i)^{(s)}] \\
& \pm \gamma'_2 \sum_{i \in l_2} [V^{(2)}(\mathbf{s}_i \otimes V^{(3)}(\mathbf{l}_i)) + \frac{\epsilon}{2} V^{(2)}(\mathbf{z} \otimes V^{(3)}(\mathbf{l}_i)) \\
& + \frac{\overline{\Delta}\delta}{2} V^{(2)}(\mathbf{z} \otimes V^{(3)}(\mathbf{l}_i))^{(s)}], \tag{3.15}
\end{aligned}$$

where $\mathbf{z}$ is the unit vector of the local field direction, $O^{(s)} = O(\uparrow) - O(\downarrow)$, and the coefficients α' , β' and γ' are given in Table 2.2. This is the form of $E1$ scattering operator F_{E1} applicable to the $p \rightarrow d$ resonances in the transition elements, rare earths and actinides.

For the example of the $Ho\ 2p_{\frac{3}{2}} \rightarrow 5d$ resonance, we have found that the dominant contribution to the linear magnetic term $M_0^{(1)}$ comes from the difference δ between the spin-up and spin-down radial matrix-elements. Inclusion of this contribution, as given by Eq.(3.15), reverses the sign of $M_0^{(1)}$, and is necessary to obtain agreement with the experimental observations[10].

Chapter 4

Inelastic Scattering in $La_{2-x}Sr_xCuO_4$ High-Temperature Superconductors

4.1 Introduction.

The scattering operators obtained in previous chapters also can be applied to the inelastic coherent scattering, from which one can obtain moment-moment correlations and dynamic excitation spectra.

In this chapter, we are going to apply the scattering operators derived in chapter 2 to show how the Van Hove scattering function $S(Q, \omega)$ in $La_{2-x}Sr_xCuO_4$ high-temperature superconductors can be determined by resonant x-ray scattering.

As we know that in scattering processes, the maximum momentum transfer occurs at back scattering,

$$q_{max} = 2 |k_0| = 2\left(\frac{2\pi}{\lambda_0}\right), \quad (4.1)$$

which gives the spacial resolution

$$d = \frac{\lambda_0}{2}. \quad (4.2)$$

For the resonant energy $\Delta E_{IO} = 951.0 eV$ at the $Cu L_2$ edge[9], we have $\lambda_0 = 13\text{\AA}$ and $d = 6.5\text{\AA}$. This is comparable to the magnetic lattice period ($\sqrt{2}a = 5.4\text{\AA}$, $a = 3.8\text{\AA}$) in $La_{2-x}Sr_xCuO_4$. Since $q_{max} = 0.83 q_{BZ}$ ($q_{BZ} = \frac{2\pi}{\sqrt{2}a}$), a large fraction of the Brillouin zone can be explored.

The magnetic correlations and excitations in high-temperature superconducting $La_{2-x}Sr_xCuO_4$ [17] and lightly doped $La_{2-x}Sr_xCuO_4$ [18] have been studied by neu-

tron scattering, which indicates unusually broad magnetic excitation spectra, from several meV to higher than $100\ meV$. The use of resonant x-ray magnetic scattering for probing the high energy magnetic fluctuations would be a useful complement to the neutron scattering studies.

4.2 Effective Spin Scattering Operator.

The scattering operator for E1 resonant scattering has been given in Eq.(2.34) as

$$F(j_{\pm}) = \frac{3}{2}\lambda_0 R[(\mathbf{e}_f^* \cdot \mathbf{e}_0)M_{(j_{\pm})}^{(0)} - \frac{i}{\sqrt{2}}(\mathbf{e}_f^* \times \mathbf{e}_0) \cdot M_{(j_{\pm})}^{(1)} - \sqrt{\frac{3}{5}}V^{(2)}(\mathbf{e}_f^* \otimes \mathbf{e}_0) \cdot M_{(j_{\pm})}^{(2)}], \quad (4.3)$$

where $j_{\pm} = l_1 \pm \frac{1}{2}$, R is given by Eq.(2.10), and the $M_{(j_{\pm})}^{(k)}$'s are given in Eq.(2.36)

$$\begin{aligned} M^{(0)}(l_1 j_{\pm}; 1; l_2) &= \alpha'_0(j_{\pm})N_h(l_2) \mp \gamma'_0[\sum_{i \in l_2} \mathbf{s}_i \cdot \mathbf{l}_i], \\ M^{(1)}(l_1 j_{\pm}; 1; l_2) &= \alpha'_1(j_{\pm})\mathbf{L}(l_2) \pm \beta'_1\mathbf{S}(l_2) \pm \gamma'_1[\sum_{i \in l_2} (\mathbf{s}_i - \frac{3\{\mathbf{s}_i \cdot \mathbf{l}_i, \mathbf{l}_i\}_+}{2l_2(l_2+1)})], \\ M^{(2)}(l_1 j_{\pm}; 1; l_2) &= -\alpha'_2(j_{\pm})[\sum_{i \in l_2} V^{(2)}(\mathbf{l}_i \otimes \mathbf{l}_i)] \pm \beta'_2[\sum_{i \in l_2} V^{(2)}(\mathbf{s}_i \otimes \mathbf{l}_i)] \\ &\quad \pm \gamma'_2[\sum_{i \in l_2} V^{(2)}(\mathbf{s}_i \otimes V^{(3)}(\mathbf{l}_i))]. \end{aligned} \quad (4.4)$$

For an orbitally nondegenerate ground state, the only difference from one site to another is the spin. In this case, we can project out the orbital dependence of these operators, transfer the scattering operator into the “spin-scattering” operator, that is

$$F_S(j_{\pm}) = \frac{3}{2}\lambda_0 R[A(j_{\pm}) \mp \sum_{\mu=-1}^1 (-1)^{\mu} B_{-\mu} S_{\mu}]. \quad (4.5)$$

The parameters A and B_{μ} are determined by the orbital part of the ground state and the polarization of the scattering light. The spin operators S_{μ} are defined

$$S_{\mu} = \frac{\sqrt{3}}{2} \sum_{m'_s m_s} C_{\frac{1}{2}m'_s; 1\mu}^{\frac{1}{2}m_s} \hat{a}_{m_s}^+ \hat{a}_{m'_s}, \quad (4.6)$$

or $S_{\mu} = \frac{1}{2}\sigma_{\mu}$ in the matrix form, where σ_{μ} are the Pauli matrices.

In $La_{2-x}Sr_xCuO_4$, we assume that each Cu^{2+} has a single d hole of $x^2 - y^2$ symmetry, then, the ground state of a Cu^{2+} ion can be written as

$$|\Psi_{\sigma}\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{2\sigma} + \hat{a}_{-2\sigma}) |0\rangle, \quad (4.7)$$

where $|0\rangle$ is a full filled d shell, $|0\rangle = \prod_{m_2 m_s} \hat{a}_{m_2 m_s}^\dagger |Vacuum\rangle$. Let us evaluate the matrix elements of the scattering operator $F(j_\pm)$ in Eq.(4.3) for this orbitally nondegenerate ground state,

$$\langle \sigma' | F_s(j_\pm) | \sigma \rangle = \langle \Psi_{\sigma'} | F(j_\pm) | \Psi_\sigma \rangle, \quad (4.8)$$

where $|\sigma\rangle = \hat{a}_\sigma |\tilde{0}\rangle$, and $|\tilde{0}\rangle$ is a nondegenerate orbital filled with both spin-up and spin-down electrons, $|\tilde{0}\rangle = \hat{a}_\uparrow^\dagger \hat{a}_\downarrow^\dagger |Vacuum\rangle$. The “spin-scattering” operator is obtained (see Appendix K)

$$\begin{aligned} F_S(j_\pm) &= \frac{3}{2} \lambda_0 R \left\{ [(\mathbf{e}_f^* \cdot \mathbf{e}_0) \frac{\alpha_0(j_\pm)}{\sqrt{10}} - (3\mathbf{e}_{fz}^* \cdot \mathbf{e}_{0z} - \mathbf{e}_f^* \cdot \mathbf{e}_0) \frac{\alpha_2(j_\pm)}{\sqrt{70}}] \right. \\ &\quad \left. \mp \frac{i}{\sqrt{2}} (\mathbf{e}_f^* \times \mathbf{e}_0) \cdot [\sqrt{\frac{2}{5}} \beta_1 \mathbf{S} + \sqrt{\frac{2}{35}} \gamma_1 (\mathbf{S} - 3S_z \hat{\mathbf{z}})] \right\} \\ &= \frac{3}{2} \lambda R [A(j_\pm) \mp \sum_{\mu=-1}^1 (-1)^\mu B_{-\mu} S_\mu]. \end{aligned} \quad (4.9)$$

Here $\alpha_0(j_\pm)$, $\alpha_2(j_\pm)$, β_1 and γ_1 are given by Table 2.1, and

$$A = [(\mathbf{e}_f^* \cdot \mathbf{e}_0) \frac{\alpha_0(j_\pm)}{\sqrt{10}} - (3\mathbf{e}_{fz}^* \cdot \mathbf{e}_{0z} - \mathbf{e}_f^* \cdot \mathbf{e}_0) \frac{\alpha_2(j_\pm)}{\sqrt{70}}] \equiv A_{xy} + A_z, \quad (4.10)$$

in which

$$A_z = (\mathbf{e}_{fz}^* \cdot \mathbf{e}_{0z}) \left(\frac{\alpha_0(j_\pm)}{\sqrt{10}} - \frac{2\alpha_2(j_\pm)}{\sqrt{70}} \right), \quad (4.11)$$

and

$$A_{xy} = (\mathbf{e}_{fx}^* \cdot \mathbf{e}_{0x} + \mathbf{e}_{fy}^* \cdot \mathbf{e}_{0y}) \left[\frac{\alpha_0(j_\pm)}{\sqrt{10}} + \frac{\alpha_2(j_\pm)}{\sqrt{70}} \right]. \quad (4.12)$$

Also

$$\begin{aligned} B_\pm &= \frac{i}{\sqrt{2}} (\mathbf{e}_f^* \times \mathbf{e}_0)_{\pm 1} b_\pm, \\ B_0 &= \frac{i}{\sqrt{2}} (\mathbf{e}_f^* \times \mathbf{e}_0)_0 b_0, \end{aligned} \quad (4.13)$$

where

$$b_{\pm} = (\sqrt{\frac{2}{5}}\beta_1 + \sqrt{\frac{2}{35}}\gamma_1), \quad (4.14)$$

and

$$b_0 = (\sqrt{\frac{2}{5}}\beta_1 - 2\sqrt{\frac{2}{35}}\gamma_1). \quad (4.15)$$

From Table 2.1, if we let $l_1 = 1$ and $l_2 = 2$, we have $A_z = 0$, $A = A_{xy}$, and $b_{\pm} = 0$. Then the scattering operator has become

$$F_S(j_{\pm}) = \frac{3}{2}\lambda_0 R[A_{xy}(j_{\pm}) \mp B_0 S_z]. \quad (4.16)$$

Notice that if $\mathbf{e}_0$ or $\mathbf{e}_f$ is parallel to $\hat{\mathbf{z}}$ (perpendicular to CuO_2 planes), the scattering amplitude is zero (only the polarizations parallel to CuO_2 planes are able to excite an electron from p -state to $d(x^2 - y^2)$ state (see Fig.4.1).

Furthermore, only the projection $[(\mathbf{e}_f^* \times \mathbf{e}_0) \cdot \mathbf{z}]$ is involved in the spin term (second term) of the spin-scattering operator $F_S(j_{\pm})$ in Eq.(4.16), which is in the order of $120 \frac{r_0}{x-i} (\mathbf{e}_f^* \times \mathbf{e}_0) \cdot \hat{\mathbf{z}}$, where r_0 stands for the classical radius of the electron, ($r_0 = \frac{e^2}{mc^2} \simeq 2.82 \times 10^{-13} \text{cm}$), $x = 2(E_I - E_0 - \hbar\omega_0)/\Gamma$, and $\Gamma = 0.62 \text{eV}$ for the lifetime of the $2p_{1/2}$

Figure 4.1: Resonant scattering from p -state to $d(x^2 - y^2)$ state, only $(\mathbf{e}_0)_{\perp} \| (\hat{\mathbf{k}}_0 \times \hat{\mathbf{z}})$ component and $(\mathbf{e}_f)_{\perp} \| (\hat{\mathbf{k}}_f \times \hat{\mathbf{z}})$ component are involved to excite the core electron. The component of $\mathbf{e}_0$ or $\mathbf{e}_f$ parallel to $\hat{\mathbf{z}}$ give zero contribution to the scattering.

atomic hole state as given by Krause et al.[9]. The actual width Γ here should include a contribution from electron hopping in the oxide, which is given approximately by the band width as much as a few eV , reducing the predicted amplitude proportionally.

If the Cu d -hole were in the $d(3z^2 - r^2)$ orbital, the “spin-scattering” operator would be (see Appendix K)

$$F_S(j_{\pm}) = \frac{3}{2}\lambda_0 R \left\{ [(\mathbf{e}_f^* \cdot \mathbf{e}_0) \frac{\alpha_0(j_{\pm})}{\sqrt{10}} + (3\mathbf{e}_{fz}^* \cdot \mathbf{e}_{0z} - \mathbf{e}_f^* \cdot \mathbf{e}_0) \frac{\alpha_2(j_{\pm})}{\sqrt{70}}] \right. \\ \left. \mp \frac{i}{\sqrt{2}} (\mathbf{e}_f^* \times \mathbf{e}_0) \cdot [\sqrt{\frac{2}{5}}\beta_1 \mathbf{S} - \sqrt{\frac{2}{35}}\gamma_1 (\mathbf{S} - 3S_z \hat{\mathbf{z}})] \right\}, \quad (4.17)$$

which includes different parameters of A and B_{μ} , and it would be nonzero, in the case where $\mathbf{e}_f$ and $\mathbf{e}_0$ both are parallel to the $\hat{\mathbf{z}}$ direction. This provides a way to detect the localized hole configuration, and test the theory[19] which proposed that as the doping increases O p -holes, the symmetry $d(x^2 - y^2)$ of Cu holes is mixed with the symmetry $d(3z^2 - r^2)$, $|\Psi_{\sigma}\rangle = (\hat{a}_{(x^2-y^2),\sigma} + \delta\hat{a}_{(3z^2-r^2),\sigma}) |0\rangle$.

4.3 Van Hove Scattering Function $S(Q, \omega)$.

As we discussed in the last section, for an orbitally-nondegenerate ground-state, the scattering operator can be transferred into the “spin-scattering” operator given in Eq.(4.5).

$$F_S(j_{\pm}) = \frac{3}{2}\lambda_0 R[A(j_{\pm}) \mp \sum_{\mu} B_{\mu} S_{\mu}].$$

The scattering amplitude of a crystal becomes

$$\begin{aligned} f &= \langle \psi_f | \sum_{\mathbf{n}} F_S e^{-i\mathbf{q}\cdot\mathbf{n}} | \psi_0 \rangle = \langle \psi_f | F_S(\mathbf{q}) | \psi_0 \rangle \\ &= \frac{3}{2}\lambda_0 R[A(j_{\pm})\delta_{f,0} \sum_{\mathbf{n}} e^{-i\mathbf{q}\cdot\mathbf{n}} \mp \sum_{\mu} B_{\mu} \langle \psi_f | S_{\mu}(\mathbf{q}) | \psi_0 \rangle], \end{aligned} \quad (4.18)$$

where $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_0$, $\omega = \omega_0 - \omega_f$ and $S(\mathbf{q}) = \sum_i \mathbf{S}_i e^{-i\mathbf{q}\cdot\mathbf{r}_i}$. The cross section is given by

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE_f} &= \langle |F_S(q)|^2 \rangle \delta(\omega + E_0 - E_f) \\ &= \sum_{0,f} P_0 \langle \psi_0 | F_S^*(\mathbf{q}) | \psi_f \rangle \langle \psi_f | F_S(\mathbf{q}) | \psi_0 \rangle \delta(\omega + E_0 - E_f). \end{aligned} \quad (4.19)$$

It is convenient to separate the cross section into a Bragg part and a diffuse parts:

$$\begin{aligned} \left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{Bragg} &= \left| \frac{3}{2}\lambda_0 R \right|^2 \{ |A(j_{\pm})|^2 \sum_{\mathbf{n},\mathbf{m}} e^{i\mathbf{q}\cdot(\mathbf{n}-\mathbf{m})} \\ &\quad \mp \sum_{\mu} [A(j_{\pm})^* B_{\mu} \langle S_{\mu}(\mathbf{q}) \rangle + A(j_{\pm}) B_{\mu}^* \langle S_{\mu}(-\mathbf{q}) \rangle] \sum_{\mathbf{n}} e^{i\mathbf{q}\cdot\mathbf{n}} \\ &\quad + \sum_{\mu,\nu} B_{\mu} B_{\nu}^* \langle S_{\mu}(\mathbf{q}) \rangle \langle S_{\nu}(-\mathbf{q}) \rangle \} \delta(\omega) \\ &= \left| \frac{3}{2}\lambda_0 R \right|^2 \left\{ \frac{(2\pi)^2 N}{V_0} |A(j_{\pm})|^2 \sum_{\mathbf{G}} \delta(\mathbf{q} - \mathbf{G}) \right. \\ &\quad \left. \mp \sum_{\mu} [A(j_{\pm})^* B_{\mu} \langle S_{\mu}(\mathbf{q}) \rangle + A(j_{\pm}) B_{\mu}^* \langle S_{\mu}(-\mathbf{q}) \rangle] \right\} \end{aligned}$$

$$\begin{aligned}
& \times N \sum_{\mathbf{G}} \delta(\mathbf{q} - \mathbf{G}) \\
& + \sum_{\mu, \nu} B_{\mu} B_{\nu}^* < S_{\mu}(\mathbf{q}) > < S_{\nu}(-\mathbf{q}) > \} \delta(\omega),
\end{aligned} \tag{4.20}$$

and

$$\begin{aligned}
\left(\frac{d^2 \sigma}{d\Omega dE_f} \right)_{diffuse} &= \left| \frac{3}{2} \lambda_0 R \right|^2 \sum_{\mu, \nu} B_{\mu} B_{\nu}^* \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \\
&\times [< S_{\mu}(\mathbf{q}, t) S_{\nu}(-\mathbf{q}) > - < S_{\mu}(\mathbf{q}) > < S_{\nu}(-\mathbf{q}) >].
\end{aligned} \tag{4.21}$$

Here, we have used

$$\delta(\omega + E_0 - E_f) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i(\omega - E_f + E_0)t}, \tag{4.22}$$

and

$$\begin{aligned}
& < S_{\mu}(\mathbf{q}) S_{\nu}(-\mathbf{q}) > \delta(\omega + E_0 - E_f) \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{0, f} P_0 < \psi_0 | e^{iHt} S_{\mu}(\mathbf{q}) e^{-iHt} | \psi_f > < \psi_f | S_{\nu}(-\mathbf{q}) | \psi_0 > \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} < S_{\mu}(\mathbf{q}, t) S_{\nu}(-\mathbf{q}, 0) > .
\end{aligned} \tag{4.23}$$

Now we get back to the scattering on $La_{2-x}Sr_xCuO_4$ crystals. First, if the vanishing result is obtained in the Bragg scattering with polarization of $\mathbf{e}_f$ or $\mathbf{e}_0$ parallel to the $\hat{\mathbf{z}}$ direction, we can conclude that the localized Cu holes include only the $d(x^2 - y^2)$ symmetry in $La_{2-x}Sr_xCuO_4$. Then the effective scattering operator is given by Eq.(4.16). The diffuse cross section is related to the van Hove scattering function as

$$\left(\frac{d^2 \sigma}{d\Omega dE_f} \right)_{diffuse} = N \left| \frac{3}{2} \lambda_0 R B_0 \right|^2 S^{zz}(\mathbf{Q}, \omega), \tag{4.24}$$

where the Van Hove scattering function is defined

$$S^{zz}(\mathbf{Q}, \omega) = \frac{1}{2\pi N} \int_{-\infty}^{\infty} < S_z(-\mathbf{Q}, 0) S_z(\mathbf{Q}, t) > e^{i\omega t} dt. \tag{4.25}$$

We can obtain the instantaneous correlation function by integrating the energy

$$S^{zz}(\mathbf{Q}) = \int d\omega S^{zz}(\mathbf{Q}, \omega) \equiv \frac{1}{N} \langle S^z(-\mathbf{Q}, 0) S^z(\mathbf{Q}, 0) \rangle. \quad (4.26)$$

Usually the cutoff energy in this integral is taken as twice the incident scattering energy ($2\omega_0$). Since the incident energy of resonant x-ray energy is much larger than the magnetic characteristic energy scale of the spin system, one will not run into the cutoff problem. The cutoff energy in the integration can be taken to infinity. But we can only obtain the dynamic spectra for $|\mathbf{Q}| \leq q_{max}$ ($= 0.83 q_{BZ}$) because the resonant energy for this transition is not high enough to cover the whole Brillouin zone. Nevertheless, resonant magnetic scattering is able to cover far more broad energy range (ω) than neutron magnetic scattering can do. It is a useful complement to the neutron scattering.

Chapter 5

Conclusions.

In this thesis, I have shown that the scattering amplitude operator F_{EL} for resonant x-ray scattering can be expressed in terms of simple spin-orbital moment operators $M_{EL}^{(k)}(\mathbf{l}, \mathbf{s})$ of the valence shell involved in the resonance. This holds for the important case of quasi-elastic scattering in the fast collision approximation. The odd-order moments are odd under time reversal, while the even order moments include the charge multipole moments $\sum_{i \in l_2} Y_q^{(k)}(\hat{\mathbf{r}}_i)$, as well as spin-orbital moment contribution.

The expression of the scattering operators derived in this thesis can show how the magnetic sensitivity in pure electric-multipole resonant scattering is obtained from the spin-orbital effect and the Pauli exclusion principle. Since the spin-orbital interaction exists in both the core and valence shell, two electrons, one excited up to the valence shell ($nl_2m_2m_s$) from the core state ($n_cl_1j_1m_j$) and the other jumping back to the core hole ($n_cl_1j_1m_j$) from the valence-shell state ($nl_2m'_2m'_s$), can have different spins. As a result of this, the spherical tensor scattering operator $F_q^{(k)}$ consists of not only the purely orbital moments $\overline{W}_q^{(0,k)} (\propto \sum_{i \in l_2} V_q^{(k)}(\hat{\mathbf{l}}_i)$, such as $N_h(l_2)$, $\mathbf{L}$, etc.) but also the spin-coupled orbital moments $\overline{W}_q^{(1,l)k} (\propto \sum_{i \in l_2} [\mathbf{S}_i^{(1)} \otimes \mathbf{V}^{(l)}(\hat{\mathbf{l}}_i)]^k$, such as $\sum_{i \in l_2} \mathbf{s}_i \cdot \mathbf{l}_i$, $\mathbf{S}$, etc.) in the fast collision approximation.

The existence of a simple relation between the spin-orbital moments $M^{(k)}(\mathbf{l}, \mathbf{s})$ and the scattering operator F_{EL} is of great importance for the interpretation of resonant x-ray scattering experiments. Because of their different angular dependencies, the

various multipole-moment $M_q^{(k)}$ can be selected out experimentally. The spin coupled orbital moments $\overline{W}^{(1,l)k}_q$ are involved in the scattering operator, which is the difference between resonant magnetic scattering and both neutron and nonresonant x-ray magnetic scattering. In addition, from simple sum rules obtained here, the purely orbital moments $\overline{W}^{(0,k)}_q$ can be separated out from the spin-coupled orbital moments $\overline{W}^{(1,l)k}_q$ experimentally.

Applying these scattering operators to coherent elastic scattering and absorption, one can determine the thermal expectation values of the various spin-orbit multipole-moments in the valence shell, such as spin-orbital coupling $\sum_{i \in l_2} \mathbf{s}_i \cdot \mathbf{l}_i$, orbital angular momentum $\mathbf{L}$, spin $\mathbf{S}$ and “magnetic dipole field” $\sum_{i \in l_2} [\mathbf{s}_i - 3(\mathbf{s}_i \cdot \hat{\mathbf{r}}_i)\hat{\mathbf{r}}_i]$, etc..

Using these operators to analyze inelastic scattering, one can obtain the moment-moment correlations, $[S(\mathbf{Q}, \omega)]$ and the dynamic excitation spectra among the various atoms of the scattering sample. In particular, if the ground state of the atom is orbitally nondegenerate, the resonant x-ray scattering not only can determine the spin-spin correlation (Van Hove scattering function) but also can tell the orbital configuration of the localized spin, due to the scattering is sensitive to the orbital configuration.

The theory I have shown in this thesis is applicable to the analysis of a broad range of resonant x-ray elastic and inelastic scattering and absorption experiments involving rare earth, actinide and transition elements.

Complimentary to neutron magnetic scattering, the resonant x-ray magnetic scattering not only possesses the high- q resolution, large- ω coverage and tunable energy and polarization, but also is very sensitive to the orbital configuration of the localized spin. It has been employed from investigating the magnetic structure, phase behavior, and circular dichroism to critical scattering. It will have even broader uses in the future.

Appendix A

The Theory of Resonant X-Ray Magnetic Scattering

The general theory of the resonant x-ray magnetic scattering can be described as the following: For atoms in electromagnetic fields the nonrelativistic Hamiltonian (valid to order $(\frac{v}{c})^2$) is written as[20]

$$\begin{aligned}
 H = & \sum_j \frac{1}{2m} [\mathbf{p}_j - \frac{e}{c} \mathbf{A}(\mathbf{r}_j)]^2 - \sum_j \frac{Ze^2}{r_j} + \sum_{i < j} \frac{e^2}{r_{ij}} \\
 & - \frac{e\hbar}{2mc} \sum_j \boldsymbol{\sigma}_j \cdot \nabla \times \mathbf{A}(\mathbf{r}_j) - \frac{e\hbar}{4m^2c^2} \sum_j \boldsymbol{\sigma}_j \cdot \mathbf{E}(\mathbf{r}_j) \times [\mathbf{p}_j - \frac{e}{c} \mathbf{A}(\mathbf{r}_j)] \\
 & + \sum_{k\alpha} [\hat{a}_{k\alpha}^\dagger \hat{a}_{k\alpha} + \frac{1}{2}] \hbar \omega_k,
 \end{aligned} \tag{A.1}$$

which includes the electron kinetic energy (first term), the instantaneous Coulomb interactions (second and third terms), the Pauli interaction between spin and magnetic field (fourth term), the spin-orbital (or Thomas precession) interaction (fifth term), and the energy of the free electromagnetic radiation fields in the Coulomb gauge.

To a very good approximation ($\sqrt{\frac{k_f}{k_0}} \simeq 1$), the scattering amplitude for elastic and inelastic scattering[2, 21] to order $(\frac{\hbar\omega}{mc^2})^2$ is

$$\begin{aligned}
 f = & -r_0 < b | n(\mathbf{K}) | a > (\mathbf{e}_f^* \cdot \mathbf{e}_0) + i(\frac{\hbar\omega_0}{mc^2}) r_0 < b | \mathbf{S}(\mathbf{K}) | a > \cdot (\mathbf{e}_f^* \times \mathbf{e}_0) \\
 & + \sum_c \frac{< b | \mathbf{J}(-\mathbf{k}_f) \cdot \mathbf{e}_f^* | c > < c | \mathbf{J}(\mathbf{k}_0) \cdot \mathbf{e}_0 | a >}{E_c - E_a - \hbar\omega_0 - i\Gamma_c/2}
 \end{aligned}$$

$$+ \sum_c \frac{\langle b | \mathbf{J}(\mathbf{k}_0) \cdot \mathbf{e}_0 | c \rangle \langle c | \mathbf{J}(-\mathbf{k}_f) \cdot \mathbf{e}_f^* | a \rangle}{E_c - E_a + \hbar\omega_f}, \quad (\text{A.2})$$

where $\mathbf{K} = \mathbf{k}_0 - \mathbf{k}_f$ is the transferred momentum. The Fourier transforms of the electron charge density and spin density are defined

$$n(\mathbf{K}) = \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j}, \quad (\text{A.3})$$

$$\mathbf{s}(\mathbf{K}) = \sum_j \mathbf{s}_j e^{i\mathbf{K} \cdot \mathbf{r}_j}, \quad (\text{A.4})$$

and the current $\mathbf{J}(\mathbf{k}) \cdot \mathbf{e}$ is

$$\mathbf{J}(\mathbf{k}) \cdot \mathbf{e} = \left(\frac{e}{mc}\right) \sum_j \mathbf{e} \cdot [\mathbf{p}_j + i\hbar(\mathbf{s}_j \times \mathbf{k})] e^{i\mathbf{k} \cdot \mathbf{r}_j}. \quad (\text{A.5})$$

Following Hannon[21], and Blume and Gibbs[5] the elastic coherent scattering-amplitude f consists of the Thomson scattering f_0 , the nonresonant magnetic scattering f_m , and the modified anomalous dispersion f_a ,

$$f = f_0 + f_m + f_a. \quad (\text{A.6})$$

They are defined

$$f_0 = -r_0 \langle n(\kappa) \rangle (\mathbf{e}_f^* \cdot \mathbf{e}_0), \quad (\text{A.7})$$

$$f_m = i\left(\frac{\hbar\omega_0}{mc^2}\right)r_0\left[\frac{1}{2} \langle \mathbf{L}(\mathbf{K}) \rangle \cdot \mathbf{A}'' + \langle \mathbf{S}(\mathbf{K}) \rangle \cdot \mathbf{B}\right], \quad (\text{A.8})$$

$$f_a = 2\pi\lambda_o \sum_a P_a \sum_c \left(\frac{1}{\lambda_{ca}}\right) \left[\frac{\langle a | \mathbf{J}(-\mathbf{k}_f) \cdot \mathbf{e}_f^* | c \rangle \langle c | \mathbf{J}(\mathbf{k}_0) \cdot \mathbf{e}_0 | a \rangle}{E_c - E_a - \hbar\omega_0 - i\Gamma_c/2} \right. \\ \left. - \frac{\langle a | \mathbf{J}(\mathbf{k}_0) \cdot \mathbf{e}_0 | c \rangle \langle c | \mathbf{J}(-\mathbf{k}_f) \cdot \mathbf{e}_f^* | a \rangle}{E_c - E_a + \hbar\omega_0} \right]. \quad (\text{A.9})$$

where P_a is the probability of the state $|a\rangle$. The Fourier transform of the orbital angular momentum density $\mathbf{L}(\mathbf{K})$ is given by

$$\mathbf{L}(\mathbf{K}) = \frac{1}{2} \sum_j [f(\mathbf{K} \cdot \mathbf{r}_j) \mathbf{l}_j + \mathbf{l}_j f(\mathbf{K} \cdot \mathbf{r}_j)], \quad (\text{A.10})$$

where

$$f(x) = 2 \sum_{n=0}^{\infty} \frac{(ix)^n}{(n+2)n!}. \quad (\text{A.11})$$

The polarization vectors $\mathbf{A}''$ and $\mathbf{B}$ are

$$\mathbf{A}'' = \mathbf{A}' - (\mathbf{A}' \cdot \hat{\mathbf{K}})\hat{\mathbf{K}}, \quad (\text{A.12})$$

$$\mathbf{A}' = \left(\frac{K}{k_0}\right)^2 (\mathbf{e}_f^* \times \mathbf{e}_0) = -4 \sin^2 \theta (\mathbf{e}_f^* \times \mathbf{e}_0), \quad (\text{A.13})$$

and

$$\mathbf{B} = (\mathbf{e}_f^* \times \mathbf{e}_0) + (\hat{\mathbf{k}}_f \times \mathbf{e}_f^*)(\hat{\mathbf{k}}_f \cdot \mathbf{e}_0) - (\hat{\mathbf{k}}_0 \times \mathbf{e}_0)(\hat{\mathbf{k}}_0 \cdot \mathbf{e}_f^*) - (\hat{\mathbf{k}}_f \times \mathbf{e}_f^*) \times (\hat{\mathbf{k}}_0 \times \mathbf{e}_0) \quad (\text{A.14})$$

respectively.

As we can see that from Eq.(A.8), the nonresonant magnetic scattering f_m is magnetically sensitive since it depends on the magnetic moments $\langle \mathbf{L}(\mathbf{K}) \rangle$ and $\langle \mathbf{S}(\mathbf{K}) \rangle$. But it is not obvious that the resonant scattering is also magnetically sensitive. However, Hannon et al[2] have explained the large increase in the intensity of the magnetic satellite Bragg peaks at L_2 and L_3 absorption edges, is due to electric multipole “x-ray Resonant exchange scattering”, XRES[2].

Near resonance the scattering amplitude f is dominated by the resonant term in the anomalous dispersion f_a , which is

$$f = 2\pi\lambda_o \sum_c \left(\frac{1}{\lambda_{ca}}\right) \frac{\langle b | \mathbf{J}(-\mathbf{k}_f) \cdot \mathbf{e}_f^* | c \rangle \langle c | \mathbf{J}(\mathbf{k}_0) \cdot \mathbf{e}_0 | a \rangle}{E_c - E_a - \hbar\omega_0 - i\Gamma_c/2}. \quad (\text{A.15})$$

The current component $\mathbf{J}(\mathbf{k}) \cdot \mathbf{e}$ given by Eq.(A.5) can be expanded in terms of multipole contributions as the standard treatments[22, 23]

$$\mathbf{J}(\mathbf{k}) \cdot \mathbf{e} = \sum_{q=e,m} \sum_{L,M} J_{LM}^{(q)} [\mathbf{Y}_{LM}^{(q)}(\hat{\mathbf{k}}) \cdot \mathbf{e}], \quad (\text{A.16})$$

where $q = e$, or m indicates an electric or magnetic multipole. The multipole moment operator $J_{LM}^{(q)}$ is given by

$$J_{LM}^{(q)} = -\frac{4\pi i^L k^L}{(2L+1)!!} \sqrt{\frac{L+1}{L}} Q_{LM}^{(q)}. \quad (\text{A.17})$$

For an electric 2^L -pole

$$Q_{LM}^{(e)} = E_{LM} + E_{LM}(s), \quad (\text{A.18})$$

where E_{LM} is the usual charge multipole of electrons

$$E_{LM} = \sum_j e r_j^L Y_{LM}(\hat{\mathbf{r}}_j), \quad (\text{A.19})$$

and $E_{LM}(s)$ is the spin-dependent electric multipole

$$E_{LM}(s) = \left(\frac{\hbar\omega}{mc^2}\right) \sum_j \{e l_j [r_j^L Y_{LM}(\hat{\mathbf{r}}_j)] \cdot \mathbf{s}_j / (L+1)\}. \quad (\text{A.20})$$

For a magnetic 2^L -pole

$$Q_{LM}^{(m)} \equiv M_{LM} = 2\mu_B \sum_j \{\nabla_j [r_j^L Y_{LM}(\hat{\mathbf{r}}_j)] \cdot [\frac{\mathbf{l}_j}{L+1} + \mathbf{s}_j]\}. \quad (\text{A.21})$$

In the most general case, the scattering amplitude in Eq.(A.15) is written as

$$f = 4\pi\lambda_o \sum_{q'L'M'} \sum_{qLM} [\mathbf{e}_f^* \cdot \mathbf{Y}_{L'M'}^{(q')}(\hat{\mathbf{k}}_f)] [\mathbf{Y}_{LM}^{(q)}(\hat{\mathbf{k}}_0) \cdot \mathbf{e}_0] < b | F_{L'M';LM}^{(q',q)} | a >, \quad (\text{A.22})$$

where

$$< b | F_{L'M';LM}^{(q',q)}(\omega) | a > = \sum_c \frac{1}{2\lambda_{ca}} \left[\frac{< b | J_{L'M'}^{(q')\dagger} | c > < c | J_{LM}^{(q)} | a >}{E_c - E_a - \hbar\omega - i\Gamma_c/2} \right]. \quad (\text{A.23})$$

For a pure electric multipole transition $q' = q = e$, and $L' = L$. Since the spin-dependent electric multipole $E_{LM}(s)$ in $J_{LM}^{(e)}$ is two orders smaller than the purely charge multipole E_{LM} , $E_{LM}(s)$ can be neglected in $J_{LM}^{(e)}$ in Eq.(A.18).

Hannon et al.[2, 21] have shown that for coherent elastic resonant scattering in the magnetically ordered crystal, because the crystal field effect is much smaller than the spin exchange or local magnetic field effect, the angular momentum z -component J_z is an almost good quantum number, and the final atomic state is equal to the initial atomic state, e.g. $| (nl_2)^\nu L, S, J, M_J > \rightarrow | (nl_2)^\nu L, S, J, M_J >$, or

$| (nl_2)^\nu \alpha M > \rightarrow | (nl_2)^\nu \alpha M >$, $\Delta J_z = 0$ in the scattering processes. This restricts $M' = M$ for $F_{LM';LM}^{(e)}(\omega)$ in Eq.(A.23). The scattering amplitude becomes

$$f = 4\pi\lambda_o \sum_M [\mathbf{e}_f^* \cdot \mathbf{Y}_{LM}^{(e)}(\hat{\mathbf{k}}_f)] [\mathbf{Y}_{LM}^{(e)*}(\hat{\mathbf{k}}_0) \cdot \mathbf{e}_0] < F_{LM}^{(e)} >, \quad (\text{A.24})$$

where

$$< F_{LM}^{(e)} > = < F_{LM;LM}^{(e,e)} > = \sum_{a,c} \frac{P_a}{2\lambda_{ca}} \left[\frac{< a | J_{LM}^{(e)\dagger} | c > < c | J_{LM}^{(e)} | a >}{E_c - E_a - \hbar\omega - i\Gamma_c/2} \right]. \quad (\text{A.25})$$

and

$$J_{LM}^{(e)} = -\frac{4\pi i^L k^L}{(2L+1)!!} \sqrt{\frac{L+1}{L}} \left[\sum_j e r_j^L Y_{LM}(\hat{\mathbf{r}}_j) \right]. \quad (\text{A.26})$$

From Eqs.(A.24-A.26), they have given the coherent resonant scattering amplitudes for $E1$ and $E2$ transitions,

$$\begin{aligned} f_{E1} = & \frac{3}{4}\lambda_o [(\mathbf{e}_f^* \cdot \mathbf{e}_0)(F_{11}^{(e)} + F_{1,-1}^{(e)}) - i(\mathbf{e}_f^* \times \mathbf{e}_0) \cdot \hat{\mathbf{z}}(F_{11}^{(e)} - F_{1,-1}^{(e)}) \\ & + (\mathbf{e}_f^* \cdot \hat{\mathbf{z}})(\mathbf{e}_0 \cdot \hat{\mathbf{z}})(2F_{10}^{(e)} - F_{11}^{(e)} - F_{1,-1}^{(e)})], \end{aligned} \quad (\text{A.27})$$

and

$$\begin{aligned} f_{E2} = & \frac{5}{4}\lambda_o \{ P_{E2}^{(0)} [F_{22}^{(e)} + F_{2,-2}^{(e)}] \\ & + P_{E2}^{(1)} \frac{1}{2} [F_{22}^{(e)} - F_{2,-2}^{(e)}] \\ & + P_{E2}^{(2)} [(F_{21}^{(e)} + F_{2,-1}^{(e)}) - (F_{22}^{(e)} + F_{2,-2}^{(e)})] \\ & + P_{E2}^{(3)} \frac{1}{2} [2(F_{21}^{(e)} - F_{2,-1}^{(e)}) - (F_{22}^{(e)} - F_{2,-2}^{(e)})] \\ & + P_{E2}^{(4)} [6F_{20}^{(e)} - 4(F_{21}^{(e)} + F_{2,-1}^{(e)}) + (F_{22}^{(e)} + F_{2,-2}^{(e)})] \}, \end{aligned} \quad (\text{A.28})$$

where

$$P_{E2}^{(0)} = (\hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_0)(\mathbf{e}_f^* \cdot \mathbf{e}_0) + (\hat{\mathbf{k}}_f \cdot \mathbf{e}_0)(\mathbf{e}_f^* \cdot \hat{\mathbf{k}}_0), \quad (\text{A.29})$$

$$\begin{aligned} P_{E2}^{(1)} = & -i(\hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_0)(\mathbf{e}_f^* \times \mathbf{e}_0)_z - i(\hat{\mathbf{k}}_f \cdot \mathbf{e}_0)(\mathbf{e}_f^* \times \hat{\mathbf{k}}_0)_z \\ & - i(\mathbf{e}_f^* \cdot \hat{\mathbf{k}}_0)(\hat{\mathbf{k}}_f \times \mathbf{e}_0)_z - i(\mathbf{e}_f^* \cdot \mathbf{e}_0)(\hat{\mathbf{k}}_f \times \hat{\mathbf{k}}_0)_z \end{aligned} \quad (\text{A.30})$$

$$\begin{aligned}
P_{E2}^{(2)} &= (\hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_0)(\mathbf{e}_{fz}^* \mathbf{e}_{0z}) + (\hat{\mathbf{k}}_f \cdot \mathbf{e}_0)(\mathbf{e}_{fz}^* \hat{\mathbf{k}}_{0z}) \\
&\quad + (\mathbf{e}_f^* \cdot \hat{\mathbf{k}}_0)(\hat{\mathbf{k}}_{fz} \mathbf{e}_{0z}) + (\mathbf{e}_f^* \cdot \mathbf{e}_0)(\hat{\mathbf{k}}_{fz} \hat{\mathbf{k}}_{0z})
\end{aligned} \tag{A.31}$$

$$\begin{aligned}
P_{E2}^{(3)} &= -i(\hat{\mathbf{k}}_{fz} \hat{\mathbf{k}}_{0z})(\mathbf{e}_f^* \times \mathbf{e}_0)_z - i(\hat{\mathbf{k}}_{fz} \mathbf{e}_{0z})(\mathbf{e}_f^* \times \hat{\mathbf{k}}_0)_z \\
&\quad - i(\mathbf{e}_{fz}^* \hat{\mathbf{k}}_{0z})(\hat{\mathbf{k}}_f \times \mathbf{e}_0)_z - i(\mathbf{e}_{fz}^* \mathbf{e}_{0z})(\hat{\mathbf{k}}_f \times \hat{\mathbf{k}}_0)_z
\end{aligned} \tag{A.32}$$

$$P_{E2}^{(4)} = \hat{\mathbf{k}}_{fz} \hat{\mathbf{k}}_{0z} \mathbf{e}_{fz}^* \mathbf{e}_{0z}. \tag{A.33}$$

Here $\hat{\mathbf{z}}$ is the unit vector of the local magnetic-field direction. They have shown that because the polarization function of the l th term is proportional to the l -factors of the z -components of the $(\mathbf{e}, \hat{\mathbf{k}})$ vectors, the l th term in the scattering amplitude will contribute to the magnetic satellite n th peaks ($n = l, l-2, \dots, -l$). Since $\hat{\mathbf{z}}$ is the local magnetic direction, the l th term is related to $\langle M^l \rangle$ in some way.

Appendix B

Scattering Operator $S_{LM';LM}$

From Eq.(2.11) and (2.12), the scattering operator $S_{LM';LM}(l_1 j_1; l_2)$ is defined

$$S_{LM';LM}(l_1 j_1; l_2) = \sum_{all\ m, m'} \hat{a}_{m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger [C_{l_1 m'_1; \frac{1}{2} m'_s}^{j_1 m_j} C_{l_1 m_1; \frac{1}{2} m_s}^{j_1 m_j}] C_{l_1 m'_1; LM'}^{l_2 m'_2} C_{l_1 m_1; LM}^{l_2 m_2}. \quad (B.1)$$

Explicitly,

$$\begin{aligned} S_{LM';LM}(l_1 j_1; l_2) &= \sum_{all\ m, m'} \hat{a}_{m'_2 m_s} \hat{a}_{m_2 m_s}^\dagger [C_{l_1 m_1; \frac{1}{2} m_s}^{j_1 m_j}]^2 C_{l_1 m_1; LM'}^{l_2 m'_2} C_{l_1 m_1; LM}^{l_2 m_2} \\ &+ \sum_{all\ m, m'} \hat{a}_{m'_2 \downarrow} \hat{a}_{m_2 \uparrow}^\dagger [C_{l_1, m_1+1; \frac{1}{2}, -\frac{1}{2}}^{j_1 m_j} C_{l_1 m_1; \frac{1}{2}, \frac{1}{2}}^{j_1 m_j}] C_{l_1, m_1+1; LM'}^{l_2 m'_2} C_{l_1 m_1; LM}^{l_2 m_2} \\ &+ \sum_{all\ m, m'} \hat{a}_{m'_2 \uparrow} \hat{a}_{m_2 \downarrow}^\dagger [C_{l_1, m_1-1; \frac{1}{2}, \frac{1}{2}}^{j_1 m_j} C_{l_1 m_1; \frac{1}{2}, -\frac{1}{2}}^{j_1 m_j}] C_{l_1, m_1-1; LM'}^{l_2 m'_2} C_{l_1 m_1; LM}^{l_2 m_2} \\ &= d_{LM';LM}(l_1 j_1; l_2) + n_{LM';LM}(l_1 j_1; l_2). \end{aligned} \quad (B.2)$$

Table B.1: $C_{l, M-\mu; \frac{1}{2} \mu}^{jM}$

$\mu \setminus j$	$l - \frac{1}{2}$	$l + \frac{1}{2}$
$\frac{1}{2}$	$-\sqrt{\frac{l-M+\frac{1}{2}}{2l+1}}$	$\sqrt{\frac{l+M+\frac{1}{2}}{2l+1}}$
$-\frac{1}{2}$	$\sqrt{\frac{l+M+\frac{1}{2}}{2l+1}}$	$\sqrt{\frac{l-M+\frac{1}{2}}{2l+1}}$

The first term, with $m'_s = m_s$, contributes to the diagonal term $d_{LM';LM}$, the second and the third term, with $m'_s = -m_s$, contribute to the nondiagonal term $n_{LM';LM}$.

For $j_1 = j_- (= l_1 - \frac{1}{2})$, from the table (B.1) and (B.2), we have

$$[C_{l_1, m_1; \frac{1}{2}, \frac{1}{2}}^{j_-, m_1 + \frac{1}{2}}]^2 = \frac{l_1 - m_1}{2l_1 + 1},$$

$$[C_{l_1, m_1; \frac{1}{2}, -\frac{1}{2}}^{j_-, m_1 - \frac{1}{2}}]^2 = \frac{l_1 + m_1}{2l_1 + 1},$$

and

$$m_1 = \sqrt{l_1(l_1 + 1)} C_{l_1, m_1; 10}^{l_1, m_1}.$$

Thus,

$$\begin{aligned} d_{LM';LM}(l_1 j_-; l_2) &= \sum [\hat{a}_{m'_2 \uparrow} \hat{a}_{m_2 \uparrow}^\dagger \frac{l_1 - m_1}{2l_1 + 1} + \hat{a}_{m'_2 \downarrow} \hat{a}_{m_2 \downarrow}^\dagger \frac{l_1 + m_1}{2l_1 + 1}] C_{l_1, m_1; LM'}^{l_2 m'_2} C_{l_1, m_1; LM}^{l_2 m_2} \\ &= \sum [\frac{l_1}{2l_1 + 1} (\hat{a}_{m'_2 \uparrow} \hat{a}_{m_2 \uparrow}^\dagger + \hat{a}_{m'_2 \downarrow} \hat{a}_{m_2 \downarrow}^\dagger) \\ &\quad - \frac{\sqrt{l_1(l_1 + 1)}}{2l_1 + 1} C_{l_1, m_1; 10}^{l_1, m_1} (\hat{a}_{m'_2 \uparrow} \hat{a}_{m_2 \uparrow}^\dagger - \hat{a}_{m'_2 \downarrow} \hat{a}_{m_2 \downarrow}^\dagger)] C_{l_1, m_1; LM'}^{l_2 m'_2} C_{l_1, m_1; LM}^{l_2 m_2}. \end{aligned} \quad (B.3)$$

Also, from

$$[C_{l_1, m_1 + 1; \frac{1}{2}, -\frac{1}{2}}^{j_-, m_1 + \frac{1}{2}} C_{l_1, m_1; \frac{1}{2}, \frac{1}{2}}^{j_-, m_1 + \frac{1}{2}}] = (-1) \sqrt{\frac{l_1 - m_1}{2l_1 + 1}} \sqrt{\frac{l_1 + m_1 + 1}{2l_1 + 1}} = \frac{\sqrt{2l_1(l_1 + 1)}}{2l_1 + 1} C_{l_1, m_1; 11}^{l_1, (m_1 + 1)},$$

and

$$[C_{l_1, m_1 - 1; \frac{1}{2}, \frac{1}{2}}^{j_-, m_1 - \frac{1}{2}} C_{l_1, m_1; \frac{1}{2}, -\frac{1}{2}}^{j_-, m_1 - \frac{1}{2}}] = (-1) \sqrt{\frac{l_1 + m_1}{2l_1 + 1}} \sqrt{\frac{l_1 - m_1 + 1}{2l_1 + 1}} = (-1) \frac{\sqrt{2l_1(l_1 + 1)}}{2l_1 + 1} C_{l_1, m_1; 1, -1}^{l_1, (m_1 - 1)},$$

Table B.2: Special formulas for 3j symbols.

$$\begin{aligned}
\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix} &= 0 \quad \text{if } j_1 + j_2 + j_3 \text{ is odd.} \\
\begin{pmatrix} j + \frac{1}{2} & j & \frac{1}{2} \\ m & -m - \frac{1}{2} & \frac{1}{2} \end{pmatrix} &= (-1)^{j-m-\frac{1}{2}} \sqrt{\frac{j-m+\frac{1}{2}}{(2j+2)(2j+1)}} \\
\begin{pmatrix} j+1 & j & 1 \\ m & -m-1 & 1 \end{pmatrix} &= (-1)^{j-m-1} \sqrt{\frac{(j-m)(j-m+1)}{(2j+3)(2j+2)(2j+1)}} \\
\begin{pmatrix} j+1 & j & 1 \\ m & -m & 0 \end{pmatrix} &= (-1)^{j-m-1} \sqrt{\frac{(j+m+1)(j-m+1)}{(2j+3)(j+1)(2j+1)}} \\
\begin{pmatrix} j & j & 1 \\ m & -m-1 & 1 \end{pmatrix} &= (-1)^{j-m} \sqrt{\frac{(j-m)(j+m+1)}{(j+1)(2j+1)(2j)}} \\
\begin{pmatrix} j & j & 1 \\ m & -m & 0 \end{pmatrix} &= (-1)^{j-m} \frac{m}{\sqrt{(2j+1)(j+1)j}} \\
\begin{pmatrix} j & j & 0 \\ m & -m & 0 \end{pmatrix} &= (-1)^{j-m} \frac{1}{\sqrt{2j+1}} \\
\begin{pmatrix} j & j & 2 \\ m & -m & 0 \end{pmatrix} &= (-1)^{j-m} \frac{3m^2-j(j+1)}{\sqrt{(2j+3)(j+1)(2j+1)j(2j-1)}}
\end{aligned}$$

$$\text{Note : } C_{j_1 m_1; j_2 m_2}^{j m} = (-1)^{j_2-j_1-m} \sqrt{2j+1} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix}$$

we have

$$\begin{aligned}
n_{LM'; LM}(l_1 j_-; l_2) &= \frac{\sqrt{2l_1(l_1+1)}}{2l_1+1} \sum [\hat{a}_{m_2' \downarrow} \hat{a}_{m_2 \uparrow}^{*} C_{l_1 m_1; 11}^{l_1(m_1+1)} C_{l_1(m_1+1); LM'}^{l_2 m_2'} C_{l_1 m_1; LM}^{l_2 m_2} \\
&\quad - \hat{a}_{m_2' \uparrow} \hat{a}_{m_2 \downarrow}^{*} C_{l_1 m_1; 1, -1}^{l_1(m_1-1)} C_{l_1(m_1-1); LM'}^{l_2 m_2'} C_{l_1 m_1; LM}^{l_2 m_2}].
\end{aligned} \tag{B.4}$$

According to the definition of the spin-orbit double-tensors $\overline{W}_{\mu m}^{(\kappa, l)}$ in Eq.(2.13), we can express the operators $\hat{a}_{m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger$ in terms of $\overline{W}_{\mu m}^{(\kappa, l)}$,

$$\hat{a}_{m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger = - \sum_{\kappa, \mu, l, m} \sqrt{\frac{(2\kappa + 1)(2l + 1)}{2(2l_2 + 1)}} C_{\frac{1}{2}m'_s; \kappa \mu}^{\frac{1}{2}m_s} C_{l_2 m'_2; l m}^{l_2 m_2} \overline{W}_{\mu m}^{(\kappa, l)}. \quad (\text{B.5})$$

Therefore, the operators $\hat{a}_{m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger$ in Eq.(B.3) and (B.4) can be expressed as follows

$$\hat{a}_{m'_2 \uparrow} \hat{a}_{m_2 \uparrow}^\dagger + \hat{a}_{m'_2 \downarrow} \hat{a}_{m_2 \downarrow}^\dagger = - \sum_{l=0}^{2l_2} \sqrt{\frac{2(2l + 1)}{2l_2 + 1}} \overline{W}_m^{(0, l)} C_{l_2 m'_2; l m}^{l_2 m_2}, \quad (\text{B.6})$$

$$\hat{a}_{m'_2 \uparrow} \hat{a}_{m_2 \downarrow}^\dagger - \hat{a}_{m'_2 \downarrow} \hat{a}_{m_2 \uparrow}^\dagger = - \sum_{l=0}^{2l_2} \sqrt{\frac{2(2l + 1)}{2l_2 + 1}} \overline{W}_{0, m}^{(1, l)} C_{l_2 m'_2; l m}^{l_2 m_2}, \quad (\text{B.7})$$

$$\hat{a}_{m'_2 \downarrow} \hat{a}_{m_2 \uparrow}^\dagger = \sum_{l=0}^{2l_2} \sqrt{\frac{2l + 1}{2l_2 + 1}} \overline{W}_{1, m}^{(1, l)} C_{l_2 m'_2; l m}^{l_2 m_2}, \quad (\text{B.8})$$

$$\hat{a}_{m'_2 \uparrow} \hat{a}_{m_2 \downarrow}^\dagger = - \sum_{l=0}^{2l_2} \sqrt{\frac{2l + 1}{2l_2 + 1}} \overline{W}_{-1, m}^{(1, l)} C_{l_2 m'_2; l m}^{l_2 m_2}. \quad (\text{B.9})$$

Proof (B.6):

$$\begin{aligned} \hat{a}_{m'_2 \uparrow} \hat{a}_{m_2 \uparrow}^\dagger + \hat{a}_{m'_2 \downarrow} \hat{a}_{m_2 \downarrow}^\dagger &= \sum_{m_s} C_{\frac{1}{2}m'_s; 00}^{\frac{1}{2}m_s} \hat{a}_{m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger \\ &= \sum_{m'_s, m_s} C_{\frac{1}{2}m'_s; 00}^{\frac{1}{2}m_s} \left[\sum_{\kappa, \mu, l, m} - \sqrt{\frac{(2\kappa + 1)(2l + 1)}{2(2l_2 + 1)}} \right. \\ &\quad \left. \times C_{\frac{1}{2}m'_s; \kappa \mu}^{\frac{1}{2}m_s} C_{l_2 m'_2; l m}^{l_2 m_2} \overline{W}_{\mu m}^{(\kappa, l)} \right] \\ &= - \sum_{l=0}^{2l_2} \sqrt{\frac{2(2l + 1)}{(2l_2 + 1)}} \overline{W}_m^{(0, l)} C_{l_2 m'_2; l m}^{l_2 m_2} \end{aligned}$$

Here we have used $C_{\frac{1}{2}m'_s; 00}^{\frac{1}{2}m_s} = \delta_{m_s, m'_s}$, and

$$\sum_{m'_s, m_s} C_{\frac{1}{2}m'_s; s \pi}^{\frac{1}{2}m_s} C_{\frac{1}{2}m'_s; \kappa \mu}^{\frac{1}{2}m_s} = \frac{2}{(2\kappa + 1)} \delta(\kappa, s) \delta(\mu, \pi).$$

Proof (B.7):

$$\begin{aligned}
\hat{a}_{m'_2\uparrow}\hat{a}_{m_2\uparrow}^\dagger - \hat{a}_{m'_2\downarrow}\hat{a}_{m_2\downarrow}^\dagger &= \sqrt{3} \sum_{m_s, m'_s} C_{\frac{1}{2}m'_s;10}^{\frac{1}{2}m_s} \hat{a}_{m'_2m'_s} \hat{a}_{m_2m_s}^\dagger \\
&= \sqrt{3} \sum_{m'_s, m_s} C_{\frac{1}{2}m_s;10}^{\frac{1}{2}m_s} \left[\sum_{\kappa, \mu, l, m} -\sqrt{\frac{(2\kappa+1)(2l+1)}{2(2l_2+1)}} \right. \\
&\quad \left. \times C_{\frac{1}{2}m'_s; \kappa\mu}^{\frac{1}{2}m_s} C_{l_2m'_2; lm}^{l_2m_2} \overline{W}_{\mu m}^{(\kappa, l)} \right] \\
&= \sum_{l=0}^{2l_2} -\sqrt{\frac{2(2l+1)}{(2l_2+1)}} \overline{W}_{0 m}^{(1, l)} C_{l_2m'_2; lm}^{l_2m_2}.
\end{aligned}$$

Here $C_{\frac{1}{2}m_s;10}^{\frac{1}{2}m_s} = \frac{2}{\sqrt{3}}m_s$.

Proof (B.8):

$$\begin{aligned}
\hat{a}_{m'_2\downarrow}\hat{a}_{m_2\uparrow}^\dagger &= \left(-\sqrt{\frac{3}{2}}\right) \sum_{m_s, m'_s} C_{\frac{1}{2}m'_s;11}^{\frac{1}{2}m_s} \hat{a}_{m'_2m'_s} \hat{a}_{m_2m_s}^\dagger \\
&= \left(-\sqrt{\frac{3}{2}}\right) \sum_{m'_s, m_s} C_{\frac{1}{2}m'_s;11}^{\frac{1}{2}m_s} \left[\sum_{\kappa, \mu, l, m} -\sqrt{\frac{(2\kappa+1)(2l+1)}{2(2l_2+1)}} C_{\frac{1}{2}m'_s; \kappa\mu}^{\frac{1}{2}m_s} C_{l_2m'_2; lm}^{l_2m_2} \overline{W}_{\mu m}^{(\kappa, l)} \right] \\
&= \left(-\sqrt{\frac{3}{2}}\right) \sum_{l=0}^{2l_2} \left(-\frac{2}{3}\right) \sqrt{\frac{3(2l+1)}{2(2l_2+1)}} \overline{W}_{1 m}^{(1, l)} C_{l_2m'_2; lm}^{l_2m_2} \\
&= \sum_{l=0}^{2l_2} \sqrt{\frac{2l+1}{2l_2+1}} \overline{W}_{1 m}^{(1, l)} C_{l_2m'_2; lm}^{l_2m_2}.
\end{aligned}$$

Here $C_{\frac{1}{2}-\frac{1}{2};11}^{\frac{1}{2}\frac{1}{2}} = -\sqrt{\frac{2}{3}}$, $C_{\frac{1}{2}m'_s;11}^{\frac{1}{2}m_s} = 0$ (others).

Proof (B.9):

$$\begin{aligned}
\hat{a}_{m'_2\downarrow}\hat{a}_{m_2\uparrow}^\dagger &= \sqrt{\frac{3}{2}} \sum_{m_s, m'_s} C_{\frac{1}{2}m'_s;1,-1}^{\frac{1}{2}m_s} \hat{a}_{m'_2m'_s} \hat{a}_{m_2m_s}^\dagger \\
&= \sqrt{\frac{3}{2}} \sum_{m'_s, m_s} C_{\frac{1}{2}m'_s;1,-1}^{\frac{1}{2}m_s} \left[\sum_{\kappa, \mu, l, m} -\sqrt{\frac{(2\kappa+1)(2l+1)}{2(2l_2+1)}} C_{\frac{1}{2}m'_s; \kappa\mu}^{\frac{1}{2}m_s} C_{l_2m'_2; lm}^{l_2m_2} \overline{W}_{\mu m}^{(\kappa, l)} \right]
\end{aligned}$$

$$\begin{aligned}
&= \sqrt{\frac{3}{2}} \sum_{l=0}^{2l_2} \left(-\frac{2}{3}\right) \sqrt{\frac{3(2l+1)}{2(2l_2+1)}} \bar{W}_{-1\ m}^{(1,l)} C_{l_2 m_2'; l m}^{l_2 m_2} \\
&= - \sum_{l=0}^{2l_2} \sqrt{\frac{2l+1}{2l_2+1}} \bar{W}_{-1\ m}^{(1,l)} C_{l_2 m_2'; l m}^{l_2 m_2}
\end{aligned}$$

Here $C_{\frac{1}{2}\frac{1}{2};1-1}^{\frac{1}{2}-\frac{1}{2}} = \sqrt{\frac{2}{3}}$, $C_{\frac{1}{2}m';1-1}^{\frac{1}{2}m_s} = 0$ (others).

Bringing Eq.(B.6-B.9) into Eq.(B.3) and (B.4), then we can write the scattering operator $S_{LM';LM}(l_1 j_-; l_2)$ as

$$S_{LM';LM}(l_1 j_-; l_2) = \sum_{l=0}^{2L} [-a_l^{(-)} A_{LM}(l) \bar{W}_m^{(0,l)} + b_l B_{LM}^{(\mu)}(l) \bar{W}_{\mu\ m}^{(1,l)}] \quad (\text{B.10})$$

where

$$a_l^{(-)} = \frac{(j_- + \frac{1}{2})}{(2l_1 + 1)} \sqrt{\frac{2(2l+1)}{(2l_2 + 1)}}, \quad b_l = \sqrt{\frac{2(2l+1)}{(2l_2 + 1)}} \frac{\sqrt{l_1(l_1 + 1)}}{(2l_1 + 1)}, \quad (\text{B.11})$$

$$A_{LM}(l)_m = \sum C_{l_2 m_2'; l m}^{l_2 m_2} C_{l_1 m_1; LM'}^{l_2 m_2'} C_{l_1 m_1; LM}^{l_2 m_2} \quad (\text{B.12})$$

$$B_{LM}^{(\mu)}(l)_m = \sum C_{l_1 m_1; 1\mu}^{l_1 m_1'} C_{l_2 m_2'; l m}^{l_2 m_2} C_{l_1 m_1'; LM'}^{l_2 m_2'} C_{l_1 m_1; LM}^{l_2 m_2}. \quad (\text{B.13})$$

Applying the theorems of Yutsis, Levinson and Vanagas[14], the following identities hold

$$\begin{aligned}
&\sum_{n_1, n_2, n_3} (-1)^{l_1 - n_1 + l_2 - n_2 + l_3 - n_3} \begin{pmatrix} l_1 & j_1 & l_2 \\ n_1 & m_1 & -n_2 \end{pmatrix} \begin{pmatrix} l_2 & j_2 & l_3 \\ n_2 & m_2 & -n_3 \end{pmatrix} \begin{pmatrix} l_3 & j_3 & l_1 \\ n_3 & m_3 & -n_1 \end{pmatrix} \\
&= (-1)^{j_1 + j_2 + j_3} \begin{Bmatrix} j_1 & j_2 & j_3 \\ l_3 & l_1 & l_2 \end{Bmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \quad (\text{B.14})
\end{aligned}$$

and,

$$\sum_{n_1, n_2, n_3, n_4} (-1)^{l_1 - n_1 + l_2 - n_2 + l_3 - n_3 + l_4 - n_4} \begin{pmatrix} l_1 & j_1 & l_2 \\ -n_1 & m_1 & n_2 \end{pmatrix} \begin{pmatrix} l_2 & j_2 & l_3 \\ -n_2 & m_2 & n_3 \end{pmatrix}$$

$$\begin{aligned}
& \times \begin{pmatrix} l_3 & j_3 & l_4 \\ -n_3 & m_3 & n_4 \end{pmatrix} \begin{pmatrix} l_4 & j_4 & l_1 \\ -n_4 & m_4 & n_1 \end{pmatrix} \\
& = \sum_{k,q} (2k+1) (-1)^{k-q} (-1)^{j_3+j_4-l_2-l_4-k} \begin{Bmatrix} l_4 & l_3 & j_3 \\ l_1 & l_2 & j_1 \\ j_4 & j_2 & k \end{Bmatrix} \\
& \times \begin{pmatrix} j_1 & j_3 & k \\ m_1 & m_3 & q \end{pmatrix} \begin{pmatrix} k & j_4 & j_2 \\ -q & m_4 & m_2 \end{pmatrix}. \tag{B.15}
\end{aligned}$$

Utilizing these identities to evaluate the Clebsch-Gordon sums,

$$A_{LM}(l)_m = (-1)^l \frac{(2l_2+1)^{3/2}}{\sqrt{2L+1}} \begin{Bmatrix} L & l_2 & l_1 \\ l_2 & L & l \end{Bmatrix} C_{LM';lm}^{LM} \tag{B.16}$$

$$B_{LM}^{(\mu)}(l)_m = -\sqrt{\frac{(2l_1+1)}{2L+1}} (2l_2+1)^{3/2} \sum_{k=|l-1|, \neq l}^{l+1} \sqrt{2k+1} \begin{Bmatrix} l_1 & l_1 & 1 \\ l_2 & l_2 & l \\ L & L & k \end{Bmatrix} C_{1\mu;lm}^{kq} C_{LM';kq}^{LM}. \tag{B.17}$$

Similarly, we can also show the scattering operator $S_{LM';LM}(l_1 j_+; l_2)$ at the j_+ ($= l_1 + \frac{1}{2}$) edge. The scattering operators $S_{LM';LM}(l_1 j_{\pm}; l_2)$ at both edges are expressed in terms of $\bar{W}_{\mu m}^{(\kappa, l)}$ as

$$S_{LM';LM}(l_1 j_{\pm}; l_2) = \sum_{l=0}^{2L} [-a_l^{\pm} A_{LM}(l)_m \bar{W}_m^{(0,l)} \mp b_l \sum_{\mu=-1}^1 B_{LM}^{(\mu)}(l)_m \bar{W}_{\mu m}^{(1,l)}], \tag{B.18}$$

where

$$a_l^{\pm} = \frac{(j_{\pm} + \frac{1}{2})}{(2l_1+1)} \sqrt{\frac{2(2l+1)}{(2l_2+1)}}, \tag{B.19}$$

b_l , $A_{LM}(l)_m$, and $B_{LM}^{(\mu)}(l)_m$ are given in Eq.(B.11), (B.16) and (B.17) respectively.

The scattering operator $S_{LM';LM}$ then becomes

$$\begin{aligned}
S_{LM';LM}(l_1 j_{\pm}; l_2) &= \sum_l [-\frac{(j_{\pm} + \frac{1}{2})}{(2l_1+1)} c_l \bar{W}_m^{(0,l)} C_{LM';lm}^{LM} \\
&\quad \pm \sum_{k=|l-1|, \neq l}^{l+1} d_{kl} \bar{W}_q^{(1,l)k} C_{LM';kq}^{LM}], \tag{B.20}
\end{aligned}$$

where $\overline{W}^{(1,l)k}_q$ is the spin-orbit coupled tensor operator,

$$\overline{W}^{(1,l)k}_q = \sum_{\mu,m} C_{1\mu;l m}^{kq} \overline{W}^{(1,l)}_{\mu,m}, \quad (\text{B.21})$$

and

$$\begin{aligned} c_l &= (-1)^l \sqrt{\frac{2(2l+1)}{2L+1}} (2l_2+1) \begin{Bmatrix} L & l_2 & l_1 \\ l_2 & L & l \end{Bmatrix}, \\ d_{kl} &= \sqrt{\frac{l_1(l_1+1)2(2l+1)}{(2l_1+1)(2L+1)}} (2l_2+1) \sqrt{2k+1} \begin{Bmatrix} l_1 & l_1 & 1 \\ l_2 & l_2 & l \\ L & L & k \end{Bmatrix}. \end{aligned} \quad (\text{B.22})$$

Notice that $d_{kl} = 0$ unless $1+l+k$ is even because two columns are identical in the $9j$ symbol.

Appendix C

Polarization Tensors $T_q^{(k)*}$ for $E1$ scattering.

The polarization tensors $T_q^{(k)*}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)_{EL}$ are defined in Eq.(2.7)

$$T_q^{(k)*}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)_{EL} = \sqrt{\frac{2k+1}{2L+1}} \sum_{M', M} C_{LM'; kq}^{LM} [\mathbf{e}_f^* \cdot \mathbf{Y}_{LM'}^{(e)}(\hat{\mathbf{k}}_f)] [\mathbf{Y}_{LM}^{(e)*}(\hat{\mathbf{k}}_0) \cdot \mathbf{e}_0], \quad (\text{C.1})$$

where

$$\mathbf{e} \cdot \mathbf{Y}_{LM}^{(e)}(\hat{\mathbf{k}}) = \sqrt{\frac{4\pi(2L+1)}{3(L+1)}} \sum_{\mu=-1}^1 C_{1\mu; L-1, M-\mu}^{LM} Y_{1\mu}(\hat{\mathbf{e}}) Y_{L-1, M-\mu}(\hat{\mathbf{k}}). \quad (\text{C.2})$$

For $E1$ scattering,

$$\mathbf{e} \cdot \mathbf{Y}_{1M}^{(e)}(\hat{\mathbf{k}}) = \frac{1}{\sqrt{2}} Y_{1M}(\mathbf{e}) = \sqrt{\frac{3}{8\pi}} e_{1M}, \quad (\text{C.3})$$

$$\mathbf{e} \cdot \mathbf{Y}_{1M}^{(e)*}(\hat{\mathbf{k}}) = \frac{1}{\sqrt{2}} Y_{1M}^*(\mathbf{e}) = \sqrt{\frac{3}{8\pi}} (-1)^M e_{1-M}. \quad (\text{C.4})$$

Here we have used

$$Y_{LM}^*(\mathbf{e}) = (-1)^M Y_{L-M}(\mathbf{e}). \quad (\text{C.5})$$

Therefore

$$\begin{aligned} T_q^{(k)*}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)_{E1} &= \sqrt{\frac{2k+1}{3}} \sum_{M', M} C_{1M'; kq}^{1M} [\mathbf{e}_f^* \cdot \mathbf{Y}_{1M'}^{(e)}(\hat{\mathbf{k}}_f)] [\mathbf{Y}_{1M}^{(e)*}(\hat{\mathbf{k}}_0) \cdot \mathbf{e}_0] \\ &= \sqrt{\frac{2k+1}{3}} \sum_{M', M} C_{1M'; kq}^{1M} \frac{3}{8\pi} [(e_f^*)_{1M'} (e_0)_{1-M} (-1)^M] \\ &= \frac{3}{8\pi} \sqrt{2k+1} \sum_{M', M} (-1)^{k-1-M} \begin{pmatrix} 1 & k & 1 \\ M' & q & -M \end{pmatrix} \end{aligned}$$

$$\begin{aligned}
& \times (e_f^*)_{1M'}(e_0)_{1-M}(-1)^M \\
& = -\frac{3}{8\pi} \sum_{M',M} \sqrt{2k+1} \begin{pmatrix} 1 & 1 & k \\ M' & -M & q \end{pmatrix} \\
& \quad \times (e_f^*)_{1M'}(e_0)_{1-M} \\
& = -\frac{3}{8\pi} \sum_{M',M} C_{1M';1-M}^{k-q}(e_f^*)_{1M'}(e_0)_{1-M}(-1)^q \\
& = -\frac{3}{8\pi} (-1)^q V_{-q}^{(k)}(\mathbf{e}_f^* \otimes \mathbf{e}_0). \tag{C.6}
\end{aligned}$$

Here

$$V_q^{(k)}(\mathbf{e}_f^* \otimes \mathbf{e}_0) = \sum_{M',M} C_{1M';1M}^{kq}(\mathbf{e}_f^*)_{1M'}(\mathbf{e}_0)_{1M}. \tag{C.7}$$

We have proved

$$T_q^{(k)*}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)_{E1} = -\frac{3}{8\pi} (-1)^q V_{-q}^{(k)}(\mathbf{e}_f^* \otimes \mathbf{e}_0). \tag{C.8}$$

From the definition of $V_q^{(k)}(\mathbf{e}_f^* \otimes \mathbf{e}_0)$ in Eq.(C.7) we can write them out explicitly.

For $k = 0$,

$$V^{(0)} = -\frac{1}{\sqrt{3}}(\mathbf{e}_f^* \cdot \mathbf{e}_0). \tag{C.9}$$

For $k = 1$,

$$\begin{aligned}
V_{+1}^{(1)} &= \frac{1}{\sqrt{2}}[(e_f^*)_{+1}(e_0)_0 - (e_f^*)_0(e_0)_{+1}] \\
&= \frac{1}{2}[(e_{fz}^* e_{0x} - e_{fx}^* e_{0z}) + i(e_{fz}^* e_{0y} - e_{fy}^* e_{0z})], \tag{C.10}
\end{aligned}$$

$$\begin{aligned}
V_0^{(1)} &= \frac{1}{\sqrt{2}}[(e_f^*)_{+1}(e_0)_{-1} - (e_f^*)_{-1}(e_0)_{+1}] \\
&= \frac{i}{\sqrt{2}}(e_{fx}^* e_{0y} - e_{fy}^* e_{0x}),
\end{aligned}$$

$$\begin{aligned}
V_{-1}^{(1)} &= \frac{1}{\sqrt{2}}[(e_f^*)_0(e_0)_{-1} - (e_f^*)_{-1}(e_0)_0] \\
&= \frac{1}{2}[(e_{fz}^*e_{0x} - e_{fx}^*e_{0z}) - i(e_{fz}^*e_{0y} - e_{fy}^*e_{0z})].
\end{aligned} \tag{C.11}$$

For $k = 2$,

$$\begin{aligned}
V_{\pm 2}^{(2)} &= (e_f^*)_{\pm 1}(e_0)_{\pm 1} = \frac{1}{2}[(e_{fx}^*e_{0x} - e_{fy}^*e_{0y}) \pm i(e_{fx}^*e_{0y} + e_{fy}^*e_{0x})], \\
V_{\pm 1}^{(2)} &= \frac{1}{\sqrt{2}}[(e_f^*)_{\pm 1}(e_0)_0 + (e_f^*)_0(e_0)_{\pm 1}] \\
&= \mp \frac{1}{2}[(e_{fx}^*e_{0z} + e_{fz}^*e_{0x}) \pm i(e_{fy}^*e_{0z} + e_{fz}^*e_{0y})], \\
V_0^{(2)} &= \frac{1}{\sqrt{6}}[3(e_f^*)_0(e_0)_0 - (\mathbf{e}_f^* \cdot \mathbf{e}_0)] = \frac{1}{\sqrt{6}}[2e_{fz}^*e_{0z} - e_{fx}^*e_{0x} - e_{fy}^*e_{0y}]. \tag{C.12}
\end{aligned}$$

Here

$$\begin{aligned}
e_{\pm 1} &= \mp \frac{1}{\sqrt{2}}(e_x \pm ie_y), \\
e_0 &= e_z.
\end{aligned} \tag{C.13}$$

The Cartesian forms of these polarization tensors are

$$V^{(0)} = -\frac{1}{\sqrt{3}}(\mathbf{e}_f^* \cdot \mathbf{e}_0) \tag{C.14}$$

$$V^{(1)} = \frac{i}{\sqrt{2}}(\mathbf{e}_f^* \times \mathbf{e}_0) \tag{C.15}$$

$$V_{ij}^{(2)} = \frac{(e_{fi}^*e_{0j} + e_{fj}^*e_{0i})}{2} - \frac{1}{3}(\mathbf{e}_f^* \cdot \mathbf{e}_0)\delta_{ij}. \tag{C.16}$$

Appendix D

Polarization Tensors $T_{q(E2)}^{(k)*}$ for $E2$ Scattering.

For $E2$ scattering, the polarization tensors $T_{q(E2)}^{(k)*}$ can be obtained from Eq.(C.1) and (C.2),

$$T_q^{(k)*}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_0, \hat{\mathbf{k}}_0)_{E2} = \sqrt{\frac{2k+1}{5}} \sum_{M', M} C_{LM'; kq}^{LM} [\mathbf{e}_f^* \cdot Y_{2M'}^{(e)}(\hat{\mathbf{k}}_f)] [Y_{2M}^{(e)*}(\hat{\mathbf{k}}_0) \cdot \mathbf{e}_0]. \quad (\text{D.1})$$

Since

$$\mathbf{e} \cdot Y_{2M}^{(e)}(\hat{\mathbf{k}}) = \sqrt{\frac{4\pi \cdot 5}{3 \cdot 3}} \sum_{\mu=-1}^1 C_{1\mu; 1, M-\mu}^{2M} Y_{1\mu}(\mathbf{e}) Y_{1, M-\mu}(\hat{\mathbf{k}}) = \sqrt{\frac{5}{4\pi}} V_M^{(2)}(\mathbf{e} \otimes \hat{\mathbf{k}}), \quad (\text{D.2})$$

due to $Y_{1M}(\hat{\mathbf{x}}) = \sqrt{\frac{3}{4\pi}} \hat{\mathbf{x}}_{1M}$, and from

$$Y_{2M}^{(e)*}(\hat{\mathbf{k}}) \cdot \mathbf{e} = (-1)^M \sqrt{\frac{5}{4\pi}} V_{-M}^{(2)}(\mathbf{e} \otimes \hat{\mathbf{k}}), \quad (\text{D.3})$$

due to

$$\mathbf{Y}_{jM}^{(e)} = \mathbf{Y}_{j, j-1, M}, \quad (\text{D.4})$$

$$\mathbf{Y}_{jM}^* = \mathbf{Y}_{j, l, -M} (-1)^{j+l+1+M}, \quad (\text{D.5})$$

and

$$\mathbf{Y}_{LM}^{(e)} = (-1)^M \mathbf{Y}_{L, -M}^{(e)}, \quad (\text{D.6})$$

we have

$$\begin{aligned} T_{q(E2)}^{(k)*} &= \frac{5}{4\pi} \sqrt{\frac{2k+1}{5}} \sum_{M', M} C_{2M'; kq}^{2M} V_{M'}^{(2)}(\mathbf{e}_f^* \otimes \hat{\mathbf{k}}_f) V_{-M}^{(2)}(\mathbf{e}_0 \otimes \hat{\mathbf{k}}_0) (-1)^M \\ &= \frac{5}{4\pi} (-1)^q U_{-q}^{(k)} [V^{(2)}(\mathbf{e}_f^* \otimes \hat{\mathbf{k}}_f) \otimes V^{(2)}(\mathbf{e}_0 \otimes \hat{\mathbf{k}}_0)]. \end{aligned} \quad (\text{D.7})$$

Here $C_{2M';kq}^{2M} = (-1)^{M-q} \sqrt{\frac{5}{2k+1}} C_{2M';2,-M}^{k,-q}$ has been used.

$$V_q^{(2)}(\mathbf{a} \otimes \mathbf{b}) = \begin{cases} a_{\pm 1} b_{\pm 1} & (q = \pm 2), \\ \frac{1}{\sqrt{2}}[a_{\pm 1} b_0 + a_0 b_{\pm 1}] & (q = \pm 1), \\ \frac{1}{\sqrt{6}}[3a_0 b_0 - \mathbf{a} \cdot \mathbf{b}] & (q = 0). \end{cases} \quad (\text{D.8})$$

and

$$U_q^{(k)}[V_{(f)}^{(2)} \otimes V_{(0)}^{(2)}] = \sum_{M',M} C_{2M';2M}^{kq} V_{M'}^{(2)}(f) V_M^{(2)}(0). \quad (\text{D.9})$$

Since

$$V_{\pm 2}^{(2)} V_{\mp 2}^{(2)} = \frac{1}{4} [P_{E2}^{(0)} \pm \frac{1}{2} P_{E2}^{(1)} - P_{E2}^{(2)} \mp \frac{1}{2} P_{E2}^{(3)} + P_{E2}^{(4)}], \quad (\text{D.10})$$

$$V_{\pm 1}^{(2)} V_{\mp 1}^{(2)} = \frac{-1}{4} [P_{E2}^{(2)} \pm P_{E2}^{(3)} - 4P_{E2}^{(4)}], \quad (\text{D.11})$$

$$V_0^{(2)} V_0^{(2)} = \frac{1}{4} [6P_{E2}^{(4)}]. \quad (\text{D.12})$$

where $P_{E2}^{(k)}$ ($k = 0, \dots, 4$) are given in Appendix A, then $U_0^{(k)}$ are obtained easily:

$$U_0^{(0)} = \frac{1}{2\sqrt{5}} P_{E2}^{(0)} = \frac{1}{2\sqrt{5}} [(\mathbf{e}_f^* \cdot \mathbf{e}_0)(\hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_0) + (\mathbf{e}_f^* \cdot \hat{\mathbf{k}}_0)(\hat{\mathbf{k}}_f \cdot \mathbf{e}_0)], \quad (\text{D.13})$$

$$\begin{aligned} U_0^{(1)} &= \frac{1}{2\sqrt{10}} P_{E2}^{(1)} = \frac{-i}{2\sqrt{10}} [(\mathbf{e}_f^* \times \mathbf{e}_0)_z (\hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_0) + (\mathbf{e}_f^* \times \hat{\mathbf{k}}_0)_z (\hat{\mathbf{k}}_f \cdot \mathbf{e}_0) \\ &\quad + (\hat{\mathbf{k}}_f \times \mathbf{e}_0)_z (\mathbf{e}_f^* \cdot \hat{\mathbf{k}}_0) + (\hat{\mathbf{k}}_f \times \hat{\mathbf{k}}_0)_z (\mathbf{e}_f^* \cdot \mathbf{e}_0)], \end{aligned} \quad (\text{D.14})$$

$$\begin{aligned} U_0^{(2)} &= \frac{1}{2\sqrt{14}} [2P_{E2}^{(0)} - 3P_{E2}^{(2)}] \\ &= -\frac{1}{2\sqrt{14}} [(3e_{fz}^* e_{0z} - \mathbf{e}_f^* \cdot \mathbf{e}_0)(\hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_0) + (3e_{fz}^* \hat{k}_{0z} - \mathbf{e}_f^* \cdot \hat{\mathbf{k}}_0)(\hat{\mathbf{k}}_f \cdot \mathbf{e}_0) \\ &\quad + (3\hat{k}_{fz} e_{0z} - \hat{\mathbf{k}}_f \cdot \mathbf{e}_0)(\mathbf{e}_f^* \cdot \hat{\mathbf{k}}_0) + (3\hat{k}_{fz} \hat{k}_{0z} - \hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_0)(\mathbf{e}_f^* \cdot \mathbf{e}_0)], \end{aligned} \quad (\text{D.15})$$

$$U_0^{(3)} = \frac{1}{2\sqrt{40}}[P_{E2}^{(1)} - 5P_{E2}^{(3)}], \quad (\text{D.16})$$

$$U_0^{(4)} = \frac{1}{2\sqrt{70}}[P_{E2}^{(0)} - 5P_{E2}^{(2)} + 35P_{E2}^{(4)}]. \quad (\text{D.17})$$

$$(\text{D.18})$$

From the above we can easily obtain

$$\begin{aligned} U_q^{(1)} &= \frac{1}{2\sqrt{10}}P_q^{(1)} = \frac{-i}{2\sqrt{10}}[(\mathbf{e}_f^* \times \mathbf{e}_0)_q(\hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_0) + (\mathbf{e}_f^* \times \hat{\mathbf{k}}_0)_q(\hat{\mathbf{k}}_f \cdot \mathbf{e}_0) \\ &\quad + (\hat{\mathbf{k}}_f \times \mathbf{e}_0)_q(\mathbf{e}_f^* \cdot \hat{\mathbf{k}}_0) + (\hat{\mathbf{k}}_f \times \hat{\mathbf{k}}_0)_q(\mathbf{e}_f^* \cdot \mathbf{e}_0)], \end{aligned} \quad (\text{D.19})$$

$$\begin{aligned} U_q^{(2)} &= -\frac{1}{2}\sqrt{\frac{3}{7}}[V_q^{(2)}(\mathbf{e}_f^* \otimes \mathbf{e}_0)(\hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_0) + V_q^{(2)}(\mathbf{e}_f^* \otimes \hat{\mathbf{k}}_0)(\hat{\mathbf{k}}_f \cdot \mathbf{e}_0) \\ &\quad + V_q^{(2)}(\hat{\mathbf{k}}_f \otimes \mathbf{e}_0)(\mathbf{e}_f^* \cdot \hat{\mathbf{k}}_0) + V_q^{(2)}(\hat{\mathbf{k}}_f \otimes \hat{\mathbf{k}}_0)(\mathbf{e}_f^* \cdot \mathbf{e}_0)]. \end{aligned} \quad (\text{D.20})$$

Reorganizing the results from

$$U_q^{(3)} = \sum C_{2\mu;2\nu}^{3q} V_\mu^{(2)}(\mathbf{e}_f^* \otimes \hat{\mathbf{k}}_f) V_\nu^{(2)}(\mathbf{e}_0 \otimes \hat{\mathbf{k}}_0), \quad (\text{D.21})$$

we have

$$\begin{aligned} U_{\pm 3}^{(3)} &= \frac{i}{4}[V_{\pm 2}^{(2)}(\mathbf{e}_f^* \otimes \mathbf{e}_0)(\hat{\mathbf{k}}_f \times \hat{\mathbf{k}}_0)_{\pm 1} + V_{\pm 2}^{(2)}(\mathbf{e}_f^* \otimes \hat{\mathbf{k}}_0)(\hat{\mathbf{k}}_f \times \mathbf{e}_0)_{\pm 1} \\ &\quad + V_{\pm 2}^{(2)}(\hat{\mathbf{k}}_f \otimes \mathbf{e}_0)(\mathbf{e}_f^* \times \hat{\mathbf{k}}_0)_{\pm 1} + V_{\pm 2}^{(2)}(\hat{\mathbf{k}}_f \otimes \hat{\mathbf{k}}_0)(\mathbf{e}_f^* \times \mathbf{e}_0)_{\pm 1}], \end{aligned} \quad (\text{D.22})$$

$$\begin{aligned} U_{\pm 2}^{(3)} &= \frac{i}{4}\sqrt{\frac{3}{2}}[V_{\pm 1}^{(2)}(\mathbf{e}_f^* \otimes \mathbf{e}_0)(\hat{\mathbf{k}}_f \times \hat{\mathbf{k}}_0)_{\pm 1} + V_{\pm 1}^{(2)}(\mathbf{e}_f^* \otimes \hat{\mathbf{k}}_0)(\hat{\mathbf{k}}_f \times \mathbf{e}_0)_{\pm 1} \\ &\quad + V_{\pm 1}^{(2)}(\hat{\mathbf{k}}_f \otimes \mathbf{e}_0)(\mathbf{e}_f^* \times \hat{\mathbf{k}}_0)_{\pm 1} + V_{\pm 1}^{(2)}(\hat{\mathbf{k}}_f \otimes \hat{\mathbf{k}}_0)(\mathbf{e}_f^* \times \mathbf{e}_0)_{\pm 1}], \end{aligned} \quad (\text{D.23})$$

$$\begin{aligned}
U_{\pm 1}^{(3)} &= \frac{i}{4} \sqrt{\frac{3}{10}} [\sqrt{3} V_0^{(2)} (\mathbf{e}_f^* \otimes \mathbf{e}_0) (\hat{\mathbf{k}}_f \times \hat{\mathbf{k}}_0)_{\pm 1} + \sqrt{3} V_0^{(2)} (\mathbf{e}_f^* \otimes \hat{\mathbf{k}}_0) (\hat{\mathbf{k}}_f \times \mathbf{e}_0)_{\pm 1} \\
&\quad + \sqrt{3} V_0^{(2)} (\hat{\mathbf{k}}_f \otimes \mathbf{e}_0) (\mathbf{e}_f^* \times \hat{\mathbf{k}}_0)_{\pm 1} + \sqrt{3} V_0^{(2)} (\hat{\mathbf{k}}_f \otimes \hat{\mathbf{k}}_0) (\mathbf{e}_f^* \times \mathbf{e}_0)_{\pm 1} \\
&\quad + V_{\pm 1}^{(2)} (\mathbf{e}_f^* \otimes \mathbf{e}_0) (\hat{\mathbf{k}}_f \times \hat{\mathbf{k}}_0)_z + V_{\pm 1}^{(2)} (\mathbf{e}_f^* \otimes \hat{\mathbf{k}}_0) (\hat{\mathbf{k}}_f \times \mathbf{e}_0)_z \\
&\quad + V_{\pm 1}^{(2)} (\hat{\mathbf{k}}_f \otimes \mathbf{e}_0) (\mathbf{e}_f^* \times \hat{\mathbf{k}}_0)_z + V_{\pm 1}^{(2)} (\hat{\mathbf{k}}_f \otimes \hat{\mathbf{k}}_0) (\mathbf{e}_f^* \times \mathbf{e}_0)_z], \\
U_0^{(3)} &= \frac{i}{4\sqrt{10}} [(\mathbf{e}_f^* \times \mathbf{e}_0)_z (5k_{fz}k_{0z} - \hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_0) + (\mathbf{e}_f^* \times \hat{\mathbf{k}}_0)_z (5k_{fz}e_{0z} - \hat{\mathbf{k}}_f \cdot \mathbf{e}_0) \\
&\quad + (\hat{\mathbf{k}}_f \times \mathbf{e}_0)_z (5e_{fz}k_{0z} - \mathbf{e}_f^* \cdot \hat{\mathbf{k}}_0) + (\hat{\mathbf{k}}_f \times \hat{\mathbf{k}}_0)_z (5e_{fz}e_{0z} - \mathbf{e}_f^* \cdot \mathbf{e}_0)]. \quad (\text{D.24})
\end{aligned}$$

From

$$U_q^{(4)} = \sum_{\mu, \nu} C_{2\mu; 2\nu}^{4q} V_\mu^{(2)} (\mathbf{e}_f^* \otimes \hat{\mathbf{k}}_f) V_\nu^{(2)} (\mathbf{e}_0 \otimes \hat{\mathbf{k}}_0) \quad (\text{D.25})$$

we have

$$U_{\pm 4}^{(4)} = (\mathbf{e}_f^*)_{\pm 1} (\hat{\mathbf{k}}_f)_{\pm 1} (\mathbf{e}_0)_{\pm 1} (\hat{\mathbf{k}}_0)_{\pm 1}, \quad (\text{D.26})$$

$$\begin{aligned}
U_{\pm 3}^{(4)} &= \frac{1}{2} [(\mathbf{e}_f^*)_{\pm 1} (\hat{\mathbf{k}}_f)_{\pm 1} (\mathbf{e}_0)_{\pm 1} (\hat{\mathbf{k}}_0)_z + (\mathbf{e}_f^*)_{\pm 1} (\hat{\mathbf{k}}_f)_{\pm 1} (\mathbf{e}_0)_z (\hat{\mathbf{k}}_0)_{\pm 1} \\
&\quad + (\mathbf{e}_f^*)_{\pm 1} (\hat{\mathbf{k}}_f)_z (\mathbf{e}_0)_{\pm 1} (\hat{\mathbf{k}}_0)_{\pm 1} + (\mathbf{e}_f^*)_z (\hat{\mathbf{k}}_f)_{\pm 1} (\mathbf{e}_0)_{\pm 1} (\hat{\mathbf{k}}_0)_{\pm 1}] \quad (\text{D.27})
\end{aligned}$$

$$\begin{aligned}
U_{\pm 2}^{(4)} &= \frac{1}{2\sqrt{7}} [3(\mathbf{e}_f^*)_{\pm 1} (\hat{\mathbf{k}}_f)_{\pm 1} (\mathbf{e}_0)_z (\hat{\mathbf{k}}_0)_z + 3(\mathbf{e}_f^*)_z (\hat{\mathbf{k}}_f)_z (\mathbf{e}_0)_{\pm 1} (\hat{\mathbf{k}}_0)_{\pm 1} \\
&\quad + 2(\mathbf{e}_f^*)_{\pm 1} (\hat{\mathbf{e}}_0)_{\pm 1} (\hat{\mathbf{k}}_f)_z (\hat{\mathbf{k}}_0)_z + 2(\mathbf{e}_f^*)_{\pm 1} (\hat{\mathbf{k}}_0)_{\pm 1} (\hat{\mathbf{k}}_f)_z (\hat{\mathbf{e}}_0)_z \\
&\quad + 2(\hat{\mathbf{k}}_f)_{\pm 1} (\hat{\mathbf{e}}_0)_{\pm 1} (\mathbf{e}_f^*)_z (\hat{\mathbf{k}}_0)_z + 2(\hat{\mathbf{k}}_f)_{\pm 1} (\hat{\mathbf{k}}_0)_{\pm 1} (\mathbf{e}_f^*)_z (\hat{\mathbf{e}}_0)_z], \quad (\text{D.28})
\end{aligned}$$

$$\begin{aligned}
U_{\pm 1}^{(4)} &= \frac{1}{2\sqrt{7}} [(\mathbf{e}_f^*)_{\pm 1} (\hat{\mathbf{k}}_f)_{\pm 1} [(\mathbf{e}_0)_{\mp 1} (\hat{\mathbf{k}}_0)_z + (\mathbf{e}_0)_z (\hat{\mathbf{k}}_0)_{\mp 1}] \\
&\quad + (\mathbf{e}_0)_{\pm 1} (\hat{\mathbf{k}}_0)_{\pm 1} [(\mathbf{e}_f^*)_{\mp 1} (\hat{\mathbf{k}}_f)_z + (\mathbf{e}_f^*)_z (\hat{\mathbf{k}}_f)_{\mp 1}] \\
&\quad + 3(\mathbf{e}_f^*)_{\pm 1} (\hat{\mathbf{k}}_f)_z (\mathbf{e}_0)_z (\hat{\mathbf{k}}_0)_z + 3(\mathbf{e}_f^*)_z (\hat{\mathbf{k}}_f)_{\pm 1} (\mathbf{e}_0)_z (\hat{\mathbf{k}}_0)_z \\
&\quad + 3(\mathbf{e}_f^*)_z (\hat{\mathbf{k}}_f)_z (\mathbf{e}_0)_{\pm 1} (\hat{\mathbf{k}}_0)_z + 3(\mathbf{e}_f^*)_z (\hat{\mathbf{k}}_f)_z (\mathbf{e}_0)_z (\hat{\mathbf{k}}_0)_{\pm 1}], \quad (\text{D.29})
\end{aligned}$$

$$\begin{aligned}
U_{\pm 0}^{(4)} = & \frac{1}{2\sqrt{70}} \{ [(\hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_0)(\mathbf{e}_f^* \cdot \mathbf{e}_0) + (\hat{\mathbf{k}}_f \cdot \mathbf{e}_0)(\mathbf{e}_f^* \cdot \hat{\mathbf{k}}_0)] \\
& - 5[(\hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_0)(\mathbf{e}_{fz}^* \mathbf{e}_{0z}) + (\hat{\mathbf{k}}_f \cdot \mathbf{e}_0)(\mathbf{e}_{fz}^* \hat{\mathbf{k}}_{0z}) \\
& + (\mathbf{e}_f^* \cdot \hat{\mathbf{k}}_0)(\hat{\mathbf{k}}_{fz} \mathbf{e}_{0z}) + (\mathbf{e}_f^* \cdot \mathbf{e}_0)(\hat{\mathbf{k}}_{fz} \hat{\mathbf{k}}_{0z})] \\
& + 35 \hat{\mathbf{k}}_{fz} \hat{\mathbf{k}}_{0z} \mathbf{e}_{fz}^* \mathbf{e}_{0z} \}.
\end{aligned} \tag{D.30}$$

Appendix E

Spin-Orbital Coupled Tensor Operators $\overline{W}^{(\kappa,l)k}$.

The spin-orbital double tensor operators $W^{(\kappa,l)}$ are defined by Judd[6].

$$W_{\mu m}^{(\kappa,l)} = \sqrt{\frac{(2\kappa+1)(2l+1)}{2(2l_2+1)}} \sum_{m_2 m_s m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger \hat{a}_{m'_2 m'_s} C_{\frac{1}{2} m'_s; \kappa \mu}^{\frac{1}{2} m_s} C_{l_2 m'_2; l m}^{l_2 m_2}, \quad (\text{E.1})$$

and the spin-orbital coupled tensors $W^{(\kappa,l)k}$ are

$$W^{(\kappa,l)k}_q = \sum_{\mu, m} C_{\kappa \mu; l m}^{k q} W_{\mu m}^{(\kappa,l)}. \quad (\text{E.2})$$

Replacing operators $\hat{a}_{m_2 m_s}^\dagger \hat{a}_{m'_2 m'_s}$ by $(-\hat{a}_{m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger)$, we defined the operators $\overline{W}_{\mu m}^{(\kappa,l)}$ and $\overline{W}^{(\kappa,l)k}_q$ in Eq.(2.13) and (2.17). The hole-density operators $\hat{a}_{m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger$ can be expressed by them. From the anticommutation relations of these operators

$$\{\hat{a}_{m_2 m_s}^\dagger, \hat{a}_{m'_2 m'_s}\} = \delta_{m_2, m'_2} \delta_{m_s, m'_s}, \quad (\text{E.3})$$

we can prove that

$$\overline{W}_{\mu m}^{(\kappa,l)} = W_{\mu m}^{(\kappa,l)}, \quad (\text{E.4})$$

Except, for $\kappa = l = 0$,

$$\overline{W}^{(0,0)} = W^{(0,0)} - \sqrt{2(2l_2+1)}. \quad (\text{E.5})$$

The particle and hole number operators are given by $W^{(0,0)}$ and $\overline{W}^{(0,0)}$ respectively,

$$\begin{aligned} W^{(0,0)} &= \frac{1}{\sqrt{2(2l_2+1)}} \sum_{m_2 m_s} \hat{a}_{m_2 m_s}^\dagger \hat{a}_{m_2 m_s} C_{\frac{1}{2} m_s; 00}^{\frac{1}{2} m_s} C_{l_2 m_2; 00}^{l_2 m_2} \\ &= \frac{1}{\sqrt{2(2l_2+1)}} \sum_{m_2 m_s} \hat{a}_{m_2 m_s}^\dagger \hat{a}_{m_2 m_s} = \frac{N(l_2)}{\sqrt{2(2l_2+1)}}, \end{aligned} \quad (\text{E.6})$$

and

$$\overline{W}^{(0,0)} = W^{(0,0)} - \sqrt{2(2l_2 + 1)} = \frac{N(l_2) - 2(2l_2 + 1)}{\sqrt{2(2l_2 + 1)}} = \frac{-N_h(l_2)}{\sqrt{2(2l_2 + 1)}}. \quad (\text{E.7})$$

For $\kappa = 0$ and $l \neq 0$, the orbital multipole moments $W^{(0,l)}(\propto \sum_{i \in l_2} Y^{(l)}(\hat{\mathbf{l}}_i))$ are expressed by

$$\begin{aligned} W^{(0,l)}_q &= \sqrt{\frac{2l+1}{2(2l_2+1)}} \sum_{m_2 m'_2 m_s} \hat{a}_{m_2 m_s}^\dagger \hat{a}_{m'_2 m_s} C_{l_2 m'_2}^{l_2 m_2; l q}, \\ &= \sqrt{\frac{2l+1}{2}} \sum_{m_2 m'_2 m_s} \hat{a}_{m_2 m_s}^\dagger \hat{a}_{m'_2 m_s} \frac{\langle l_2 m_2 | V_q^{(l)}(1) | l_2 m'_2 \rangle}{\langle l_2 | V^{(l)}(1) | l_2 \rangle}, \\ &= \sqrt{\frac{2l+1}{2}} \sum_{i \in l_2} \mathbf{u}_q^{(l)}(i) \end{aligned} \quad (\text{E.8})$$

where $\mathbf{u}^{(l)}$ are the symmetric unit tensors with the unit reduced matrix elements, $\langle l_2 || \mathbf{u}^{(l)} || l_2 \rangle = 1$. Therefore, we have

$$W^{(0,l)}_q = \sqrt{\frac{2l+1}{2}} [\langle l_2 || V^{(l)}(1) || l_2 \rangle]^{-1} \sum_{i \in l_2} V_q^{(l)}(\mathbf{l}_i). \quad (\text{E.9})$$

Here the symmetric tensors $V^{(k)}(1)$ are defined:

$$V_q^{(1)}(1) = l_q \quad (q = 0, \pm 1), \quad (\text{E.10})$$

$$\begin{aligned} V_{\pm 2}^{(2)}(1) &= l_{\pm 1}^2, \\ V_{\pm 1}^{(2)}(1) &= \frac{1}{\sqrt{2}}(l_{\pm 1} l_0 + l_0 l_{\pm 1}), \\ V_0^{(2)}(1) &= \frac{1}{\sqrt{6}}(3l_0^2 - l^2). \end{aligned} \quad (\text{E.11})$$

$$\begin{aligned} V_{\pm 3}^{(3)}(1) &= l_{\pm 1} l_{\pm 1} l_{\pm 1}, \\ V_{\pm 2}^{(3)}(1) &= \frac{1}{\sqrt{3}}[l_0 l_{\pm 1} l_{\pm 1} + l_{\pm 1} l_0 l_{\pm 1} + l_{\pm 1} l_{\pm 1} l_0], \\ V_{\pm 1}^{(3)}(1) &= \frac{1}{\sqrt{15}}[2(l_{\pm 1} l_0 l_0 + l_0 l_{\pm 1} l_0 + l_0 l_0 l_{\pm 1}) + (l_{\mp 1} l_{\pm 1} l_{\pm 1} + l_{\pm 1} l_{\mp 1} l_{\pm 1} + l_{\pm 1} l_{\pm 1} l_{\mp 1})], \\ V_0^{(3)}(1) &= \frac{1}{\sqrt{10}}[l_0(5l_0^2 + 1 - 3l^2)]. \end{aligned} \quad (\text{E.12})$$

If we use “ sp ” to denote the symmetry permutation, then $V_q^{(3)}(1)$ can be expressed as the following

$$\begin{aligned}
V_{\pm 3}^{(3)}(1) &= l_{\pm 1} l_{\pm 1} l_{\pm 1}, \\
V_{\pm 2}^{(3)}(1) &= \frac{1}{\sqrt{3}} \{l_0 l_{\pm 1} l_{\pm 1}\}_{sp}, \\
V_{\pm 1}^{(3)}(1) &= \frac{1}{\sqrt{15}} [2\{(l_{\pm 1} l_0 l_0)\}_{sp} + \{l_{+1} l_{-1} l_{\pm 1}\}_{sp}] \\
V_0^{(3)}(1) &= \frac{1}{\sqrt{10}} [l_0(5l_0^2 + 1 - 3l^2)].
\end{aligned} \tag{E.13}$$

and

$$\begin{aligned}
V_{\pm 4}^{(4)} &= l_{\pm 1} l_{\pm 1} l_{\pm 1} l_{\pm 1}, \\
V_{\pm 3}^{(4)} &= \frac{1}{2} \{l_0 l_{\pm 1} l_{\pm 1} l_{\pm 1}\}_{sp}, \\
V_{\pm 2}^{(4)} &= \frac{1}{2\sqrt{7}} [\{l_{\pm 1} l_{\pm 1} l_{+1} l_{-1}\}_{sp} + 2\{l_{\pm 1} l_{\pm 1} l_0 l_0\}_{sp}], \\
V_{\pm 1}^{(4)} &= \frac{1}{2\sqrt{7}} [\{l_{\pm 1} l_{+1} l_0 l_{-1}\}_{sp} + 2\{l_{\pm 1} l_0 l_0 l_0\}_{sp}], \\
V_0^{(4)} &= \frac{1}{\sqrt{70}} [\{l_{+1} l_{+1} l_{-1} l_{-1}\}_{sp} + 2\{l_0 l_0 l_{+1} l_{-1}\}_{sp} + 4l_0^4].
\end{aligned} \tag{E.14}$$

Also

$$\begin{aligned}
V_{\pm 5}^{(5)} &= l_{\pm 1} l_{\pm 1} l_{\pm 1} l_{\pm 1} l_{\pm 1}, \\
V_{\pm 4}^{(5)} &= \frac{1}{\sqrt{5}} \{l_0 l_{\pm 1} l_{\pm 1} l_{\pm 1} l_{\pm 1}\}_{sp}, \\
V_{\pm 3}^{(5)} &= \frac{1}{3\sqrt{5}} [2\{l_0 l_0 l_{\pm 1} l_{\pm 1} l_{\pm 1}\}_{sp} + \{l_{\pm 1} l_{\pm 1} l_{\pm 1} l_{+1} l_{-1}\}_{sp}], \\
V_{\pm 2}^{(5)} &= \frac{1}{2\sqrt{15}} [\{l_{\pm 1} l_{\pm 1} l_{+1} l_0 l_{-1}\}_{sp} + 2\{l_{\pm 1} l_{\pm 1} l_0 l_0 l_0\}_{sp}], \\
V_{\pm 1}^{(5)} &= \frac{1}{\sqrt{210}} [\{l_{\pm 1} l_{+1} l_{+1} l_{-1} l_{-1}\}_{sp} + 2\{l_{\pm 1} l_{+1} l_{-1} l_0 l_0\}_{sp} + 4\{l_{\pm 1} l_0 l_0 l_0 l_0\}_{sp}], \\
V_0^{(5)} &= \frac{1}{3\sqrt{14}} [\{l_{+1} l_{+1} l_{-1} l_{-1} l_0\}_{sp} + 2\{l_{+1} l_{-1} l_0 l_0 l_0\}_{sp} + 4l_0^5].
\end{aligned} \tag{E.15}$$

In the above l_q are defined,

$$l_{\pm 1} = \mp \frac{1}{\sqrt{2}} (l_x \pm i l_y),$$

$$l_0 = l_z \quad (\text{E.16})$$

and

$$l^2 = \sum_q (-1)^q l_q l_{-q} = l_x^2 + l_y^2 + l_z^2. \quad (\text{E.17})$$

The reduced matrix elements for various rank moments are

$$\begin{aligned} \langle l_2 \parallel V^{(1)}(l) \parallel l_2 \rangle &= \frac{1}{2} \prod_{n=-1}^1 [2l_2 + 1 + n]^{\frac{1}{2}}, \\ \langle l_2 \parallel V^{(2)}(l) \parallel l_2 \rangle &= \frac{1}{2\sqrt{6}} \prod_{n=-2}^2 [2l_2 + 1 + n]^{\frac{1}{2}}, \\ \langle l_2 \parallel V^{(3)}(l) \parallel l_2 \rangle &= \frac{1}{4\sqrt{10}} \prod_{n=-3}^3 [2l_2 + 1 + n]^{\frac{1}{2}}, \\ \langle l_2 \parallel V^{(4)}(l) \parallel l_2 \rangle &= \frac{1}{4\sqrt{70}} \prod_{n=-4}^4 [2l_2 + 1 + n]^{\frac{1}{2}}, \\ \langle l_2 \parallel V^{(5)}(l) \parallel l_2 \rangle &= \frac{1}{24\sqrt{14}} \prod_{n=-5}^5 [2l_2 + 1 + n]^{\frac{1}{2}}. \end{aligned} \quad (\text{E.18})$$

Bring the above results into Eq. (E.9), we have

$$W_q^{(0,1)} = \frac{\sqrt{\frac{3}{2}}}{\sqrt{l_2(l_2+1)(2l_2+1)}} L_q(l_2). \quad (\text{E.19})$$

$$W_q^{(0,2)} = 2\sqrt{15} \left[\prod_{n=-2}^2 (2l_2 + 1 + n)^{-\frac{1}{2}} \right] \sum_{i \in l_2} V_q^{(2)}(l_i), \quad (\text{E.20})$$

$$W_q^{(0,3)} = 4\sqrt{35} \left[\prod_{n=-3}^3 (2l_2 + 1 + n)^{-\frac{1}{2}} \right] \sum_{i \in l_2} V_q^{(3)}(l_i), \quad (\text{E.21})$$

$$W_q^{(0,4)} = 12\sqrt{35} \left[\prod_{n=-4}^4 (2l_2 + 1 + n)^{-\frac{1}{2}} \right] \sum_{i \in l_2} V_q^{(4)}(l_i), \quad (\text{E.22})$$

For $l = \text{even}$, we also can express $W_q^{(0,l)}$ in terms of $C_q^{(l)}(\hat{\mathbf{r}})$, that is

$$W_q^{(0,l)} = \sqrt{\frac{2l+1}{2}} [\langle l_2 \parallel C^{(l)}(\hat{\mathbf{r}}) \parallel l_2 \rangle]^{-1} \sum_{i \in l_2} C_q^{(l)}(\hat{\mathbf{r}}_i), \quad (\text{E.23})$$

where

$$\mathbf{C}_q^{(l)}(\hat{\mathbf{r}}) = \sqrt{\frac{4\pi}{2l+1}} Y_q^{(l)}(\theta, \phi), \quad (\text{E.24})$$

and

$$\langle l_2 \parallel \mathbf{C}^{(l)} \parallel l_2 \rangle = (-1)^l \sqrt{2l_2+1} C_{l_2 0; l 0}^{l_2 0}. \quad (\text{E.25})$$

Especially,

$$\langle l_2 \parallel \mathbf{C}^{(2)}(\hat{\mathbf{r}}) \parallel l_2 \rangle = -\sqrt{\frac{(2l_2+1)l_2(l_2+1)}{(2l_2+3)(2l_2-1)}}, \quad (\text{E.26})$$

and

$$\langle l_2 \parallel \mathbf{C}^{(4)}(\hat{\mathbf{r}}) \parallel l_2 \rangle = \sqrt{2l_2+1} C_{l_2 0; 4 0}^{l_2 0}. \quad (\text{E.27})$$

Therefore, $W^{(0,2)}$ and $W^{(0,4)}$ are also written out as

$$W_q^{(0,2)} = -\sqrt{\frac{5(2l_2+3)(2l_2-1)}{2(2l_2+1)l_2(l_2+1)}} \sum_{i \in l_2} \mathbf{C}_q^{(2)}(\hat{\mathbf{r}}_i), \quad (\text{E.28})$$

and

$$W_q^{(0,4)} = \frac{3}{\sqrt{2(2l_2+1)}} [C_{l_2 0; 4 0}^{l_2 0}]^{-1} \sum_{i \in l_2} \mathbf{C}_q^{(4)}(\hat{\mathbf{r}}_i). \quad (\text{E.29})$$

Here

$$\mathbf{C}_q^{(2)}(\hat{\mathbf{r}}) = \sqrt{\frac{4\pi}{5}} Y_q^{(2)}(\theta, \phi), \quad (\text{E.30})$$

$$\begin{aligned} \mathbf{C}_{\pm 2}^{(2)}(\hat{\mathbf{r}}) &= \sqrt{\frac{3}{8}} \sin^2 \theta e^{\pm 2i\phi}, \\ \mathbf{C}_{\pm 1}^{(2)}(\hat{\mathbf{r}}) &= \mp \sqrt{\frac{3}{2}} \cos \theta \sin \theta e^{\pm i\phi}, \\ \mathbf{C}_0^{(2)}(\hat{\mathbf{r}}) &= \frac{1}{2} (3 \cos^2 \theta - 1). \end{aligned} \quad (\text{E.31})$$

and

$$\mathbf{C}_q^{(4)}(\hat{\mathbf{r}}) = \sqrt{\frac{4\pi}{9}} Y_q^{(4)}(\theta, \phi), \quad (\text{E.32})$$

$$\begin{aligned}
C_{\pm 4}^{(4)}(\hat{\mathbf{r}}) &= \sqrt{\frac{35}{128}} \sin^4 \theta e^{\pm 4i\phi}, \\
C_{\pm 3}^{(4)}(\hat{\mathbf{r}}) &= \mp \sqrt{\frac{35}{16}} \sin^3 \theta \cos \theta e^{\pm 3i\phi}, \\
C_{\pm 2}^{(4)}(\hat{\mathbf{r}}) &= \sqrt{\frac{5}{32}} \sin^2 \theta (7 \cos^2 \theta - 1) e^{\pm 2i\phi}, \\
C_{\pm 1}^{(4)}(\hat{\mathbf{r}}) &= \mp \sqrt{\frac{5}{16}} \sin \theta (7 \cos^3 \theta - 3 \cos \theta) e^{\pm i\phi}, \\
C_0^{(4)}(\hat{\mathbf{r}}) &= \frac{1}{8} (35 \cos^4 \theta - 30 \cos^2 \theta + 3).
\end{aligned} \tag{E.33}$$

For $\kappa = 1$, spin coupled orbital moments $W_q^{(1,l)k} (\propto \sum_{i \in l_2} [\mathbf{s}_i \otimes V^{(l)}(\mathbf{l}_i)]_q^{(k)})$ are defined from the double tensor moments $W_m^{(1,l)}$. According to Eq.(E.1) and Eq.(E.2), we have

$$W_{\mu m}^{(1,l)} = \sqrt{2(2l_2 + 1)} \sum_{i \in l_2} \mathbf{s}_\mu(i) \mathbf{u}_m^{(l)}(i), \tag{E.34}$$

and

$$W_q^{(1,l)k} = \sqrt{2(2l_2 + 1)} \sum_{i \in l_2} V_q^{(k)} [\mathbf{s}_i \otimes \mathbf{u}_i^{(l)}]. \tag{E.35}$$

We can express them as

$$W_q^{(1,l)k} = \sqrt{2(2l_2 + 1)} [< l_2 \parallel V^{(l)}(\mathbf{l}) \parallel l_2 >]^{-1} \sum_{i \in l_2} V_q^{(k)} [\mathbf{s}_i \otimes V^{(l)}(\mathbf{l}_i)], \tag{E.36}$$

where

$$V_q^{(k)} [\mathbf{s} \otimes V^{(l)}(\mathbf{l})] = \sum_{\mu, m} C_{1\mu; l m}^{k q} \mathbf{s}_\mu V_m^{(l)}(\mathbf{l}). \tag{E.37}$$

In particular,

$$W^{(1,0)} = \sqrt{\frac{2}{2l_2 + 1}} \mathbf{S}(l_2), \tag{E.38}$$

$$W^{(1,1)0} = -\frac{\sqrt{2}}{\sqrt{(2l_2 + 1)l_2(l_2 + 1)}} \left[\sum_{i \in l_2} \mathbf{s}_i \cdot \mathbf{l}_i \right], \tag{E.39}$$

$$W^{(1,1)2} = \frac{\sqrt{6}}{\sqrt{(2l_2 + 1)l_2(l_2 + 1)}} \left[\sum_{i \in l_2} V^{(2)}(\mathbf{s}_i \otimes \mathbf{l}_i) \right], \tag{E.40}$$

$$W^{(1,2)1} = \sqrt{\frac{4l_2(l_2 + 1)}{(2l_2 + 1)(2l_2 + 3)(2l_2 - 1)}} \left[\sum_{i \in l_2} \left(\mathbf{s}_i - \frac{3\{\mathbf{s}_i \cdot \mathbf{l}_i, \mathbf{l}_i\}_+}{2l_2(l_2 + 1)} \right) \right], \tag{E.41}$$

or

$$W^{(1,2)1} = -\sqrt{\frac{(2l_2+3)(2l_2-1)}{(2l_2+1)l_2(l_2+1)}} \left[\sum_{i \in l_2} (\mathbf{s}_i - 3(\mathbf{s}_i \cdot \hat{\mathbf{r}}_i) \hat{\mathbf{r}}_i) \right]. \quad (\text{E.42})$$

$$W^{(1,2)3} = 4\sqrt{15} \left[\prod_{n=-2}^2 (2l_2+1+n)^{-\frac{1}{2}} \right] \sum_{i \in l_2} V^{(3)}[\mathbf{s}_i \otimes V^{(2)}(\mathbf{l}_i)], \quad (\text{E.43})$$

or

$$W^{(1,2)3} = -\sqrt{\frac{10(2l_2+3)(2l_2-1)}{(2l_2+1)l_2(l_2+1)}} V^{(3)}[\mathbf{s}_i \otimes \mathbf{C}^{(2)}(\hat{\mathbf{r}}_i)], \quad (\text{E.44})$$

$$W^{(1,3)2} = 8\sqrt{35} \left[\prod_{n=-3}^3 (2l_2+1+n)^{-\frac{1}{2}} \right] \sum_{i \in l_2} V^{(2)}[\mathbf{s}_i \otimes V^{(3)}(\mathbf{l}_i)], \quad (\text{E.45})$$

$$W^{(1,3)4} = 8\sqrt{35} \left[\prod_{n=-3}^3 (2l_2+1+n)^{-\frac{1}{2}} \right] \sum_{i \in l_2} V^{(4)}[\mathbf{s}_i \otimes V^{(3)}(\mathbf{l}_i)], \quad (\text{E.46})$$

$$W^{(1,4)3} = 24\sqrt{35} \left[\prod_{n=-4}^4 (2l_2+1+n)^{-\frac{1}{2}} \right] \sum_{i \in l_2} V^{(3)}[\mathbf{s}_i \otimes V^{(4)}(\mathbf{l}_i)], \quad (\text{E.47})$$

or

$$W^{(1,4)3} = \frac{6}{\sqrt{2(2l_2+1)}} [C_{l_2 0; 40}^{l_2 0}]^{-1} \sum_{i \in l_2} V^{(3)}[\mathbf{s}_i \otimes \mathbf{C}^{(4)}(\hat{\mathbf{r}}_i)], \quad (\text{E.48})$$

$$W^{(1,5)4} = 48\sqrt{77} \left[\prod_{n=-5}^5 (2l_2+1+n)^{-\frac{1}{2}} \right] \sum_{i \in l_2} V^{(4)}[\mathbf{s}_i \otimes V^{(5)}(\mathbf{l}_i)]. \quad (\text{E.49})$$

Appendix F

The Equivalence between $V^{(2n)}(1)$ and $C^{(2n)}(\hat{\mathbf{r}})$.

From the Wigner-Eckart theorem, we know that

$$\langle \alpha j m | T_q^{(k)} | \alpha' j' m' \rangle = (-1)^{j-m} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \langle \alpha j || T^{(k)} || \alpha' j' \rangle \quad (\text{F.1})$$

Applying this theorem to the tensor operators in an l -shell, we obtain the following relation between the operators $V^{(2n)}(1)$ and the operators $C^{(2n)}(\hat{\mathbf{r}})$, that is

$$\frac{V^{(2n)}(1)}{C^{(2n)}(\hat{\mathbf{r}})} = \frac{V^{(k)}(\mathbf{s} \otimes V^{(2n)}(1))}{V^{(k)}(\mathbf{s} \otimes C^{(2n)}(\hat{\mathbf{r}}))} = \frac{\langle l || V^{(2n)}(1) || l \rangle}{\langle l || C^{(2n)}(\hat{\mathbf{r}}) || l \rangle}. \quad (\text{F.2})$$

This relation does not hold between $V^{(2n+1)}(1)$ and $C^{(2n+1)}(\hat{\mathbf{r}})$ since

$$\langle l || C^{(2n+1)}(\hat{\mathbf{r}}) || l \rangle = 0. \quad (\text{F.3})$$

In particular, we have

$$\frac{V^{(2)}(1)}{C^{(2)}(\hat{\mathbf{r}})} = \frac{V^{(k)}(\mathbf{s} \otimes V^{(2)}(1))}{V^{(k)}(\mathbf{s} \otimes C^{(2)}(\hat{\mathbf{r}}))} = -\frac{(2l+3)(2l-1)}{\sqrt{6}}, \quad (\text{F.4})$$

and

$$\frac{V^{(4)}(1)}{C^{(4)}(\hat{\mathbf{r}})} = \frac{V^{(k)}(\mathbf{s} \otimes V^{(4)}(1))}{V^{(k)}(\mathbf{s} \otimes C^{(4)}(\hat{\mathbf{r}}))} = \frac{\frac{1}{4\sqrt{70}} \prod_{n=-4}^4 (2l+1+n)^{\frac{1}{2}}}{\sqrt{2l+1} C_{l0;40}^{l0}}. \quad (\text{F.5})$$

Appendix G

Rotation Matrix Elements $D_{m,n}^{(j)}(\alpha, \beta, \gamma)$

As we know from rotation-group theory the rotated functions in the axes-fixed system are expressed as

$$\begin{aligned}\psi_m^{(j)'}(\mathbf{r}) &= P_R(\alpha, \beta, \gamma)\psi_m^{(j)}(\mathbf{r}) = \psi_m^{(j)}(R^{-1}(\alpha, \beta, \gamma)\mathbf{r}) \\ &= \sum_{m'} \psi_{m'}^{(j)}(\mathbf{r}) D_{m',m}^{(j)}(\alpha, \beta, \gamma)\end{aligned}\quad (\text{G.1})$$

Also, if we assume that functions are fixed, but axes are rotated, we have

$$\begin{aligned}\psi_m^{(j)}(\mathbf{r}) &= \psi_m^{(j)}[R(\alpha, \beta, \gamma)\mathbf{r}_0] \\ &= \sum_{m'} \psi_{m'}^{(j)}(\mathbf{r}_0) [D^{(j)}(\alpha, \beta, \gamma)]_{m',m}^{-1} \\ &= \sum_{m'} D^{(j)}(\alpha, \beta, \gamma)_{m,m'}^* \psi_{m'}^{(j)}(\mathbf{r}_0)\end{aligned}\quad (\text{G.2})$$

where a vector $\mathbf{r}_0$ is rotated to $\mathbf{r} = R(\alpha, \beta, \gamma)\mathbf{r}_0$. α , β , and γ are the Euler angles, and the rotation matrices are given as follows[23]

$$\begin{aligned}D_{m,n}^{(j)}(\alpha, \beta, \gamma) &= \langle jm | \exp^{-i\alpha J_z} \exp^{-i\beta J_y} \exp^{-i\gamma J_z} | jn \rangle \\ &= \exp^{-i(\alpha m + \gamma n)} \langle jm | \exp^{-i\beta J_y} | jn \rangle \\ &= \exp^{-i(\alpha m + \gamma n)} d_{m,n}^{(j)}(\beta)\end{aligned}\quad (\text{G.3})$$

$$\begin{aligned}d_{m,n}^{(j)}(\beta) &= \sum_t (-1)^t \frac{[(j+m)!(j-m)!(j+n)!(j-n)!]^{\frac{1}{2}}}{(j+m-t)!(j-n-t)!t!(t+n-m)!} \\ &\quad \times \left(\cos\frac{\beta}{2}\right)^{2j+m-n-2t} \left(\sin\frac{\beta}{2}\right)^{2t+n-m}\end{aligned}\quad (\text{G.4})$$

where the sum is taken over all values of t which lead to non-negative factorials.
(Formulae for $d_{m,n}^{(j)}(\beta)$ for $j = 1$, and 2 are given in Table G.1).

These rotation operators are unitary

$$D^\dagger(\alpha, \beta, \gamma) = D^{-1}(\alpha, \beta, \gamma) = D(-\gamma, -\beta, -\alpha), \quad (\text{G.5})$$

$$\det[D(\alpha, \beta, \gamma)] = 1, \quad (\text{G.6})$$

and they are reduced to spherical harmonics when m or $n = 0$

$$\begin{aligned} D_{m,0}^{(l)}(\alpha, \beta, \gamma) &= \sqrt{\frac{4\pi}{2l+1}} Y_m^{(l)}(\beta, \alpha)^*, \\ D_{0,m}^{(l)}(\alpha, \beta, \gamma) &= \sqrt{\frac{4\pi}{2l+1}} Y_m^{(l)}(\beta, \gamma). \end{aligned} \quad (\text{G.7})$$

Table G.1: Formulas for $d_{m,n}^j(\beta)$ for $j = 1$ and 2.

$d_{1,1}^{(1)} = d_{-1,-1}^{(1)} = \cos^2(\frac{\beta}{2})$	$d_{2,-1}^{(2)} = d_{1,-2}^{(2)} = -d_{-2,1}^{(2)}$
$d_{1,-1}^{(1)} = d_{-1,1}^{(1)} = \sin^2(\frac{\beta}{2})$	$= -d_{-1,2}^{(2)} = \frac{1}{2}\sin\beta(\cos\beta - 1)$
$d_{0,1}^{(1)} = d_{-1,0}^{(1)} = -d_{1,0}^{(1)}$	$d_{2,-2}^{(2)} = d_{-2,2}^{(2)} = \sin^4(\frac{\beta}{2})$
$= -d_{0,-1}^{(1)} = \frac{\sin\beta}{\sqrt{2}}$	$d_{1,1}^{(2)} = d_{-1,-1}^{(2)}$
$d_{2,2}^{(2)} = d_{-2,-2}^{(2)} = \cos^4(\frac{\beta}{2})$	$= \frac{1}{2}(2\cos\beta - 1)(\cos\beta + 1)$
$d_{2,1}^{(2)} = -d_{1,2}^{(2)} = -d_{-2,-1}^{(2)}$	$d_{1,-1}^{(2)} = d_{-1,1}^{(2)}$
$= d_{-1,-2}^{(2)} = -\frac{1}{2}\sin\beta(1 + \cos\beta)$	$= \frac{1}{2}(2\cos\beta + 1)(1 - \cos\beta)$
$d_{2,0}^{(2)} = d_{0,2}^{(2)} = d_{-2,0}^{(2)}$	$d_{1,0}^{(2)} = d_{0,-1}^{(2)} = -d_{0,1}^{(2)}$
$= d_{0,-2}^{(2)} = \sqrt{\frac{3}{8}}\sin^2\beta$	$= -d_{-1,0}^{(2)} = -\sqrt{\frac{3}{2}}\sin\beta\cos\beta$
	$d_{0,-1}^{(2)} = \frac{1}{2}(3\cos^2\beta - 1)$

These unitary rotation matrices also obey the following orthogonality relations

$$\int_0^{2\pi} \int_0^{2\pi} \int_0^\pi (D_{m',n'}^{(j')}(\alpha, \beta, \gamma))^* D_{m,n}^{(j)}(\alpha, \beta, \gamma) \sin\beta \, d\beta \, d\alpha \, d\gamma = \frac{8\pi^2}{2j+1} \delta_{j,j'} \delta_{m,m'} \delta_{n,n'}. \quad (\text{G.8})$$

Appendix H

Scattering Operator $F_{q(EL)}^{(k)}$ in a SLJ -Coupled System.

In the fast colision approximation, the scattering operator $F_{q(EL)}^{(k)}$ is proportional to the spin-orbital coupled moment $M_{q(EL)}^{(k)}$ (Section 2.2),

$$F_{q(EL)}^{(k)} = R(l_1 j_{\pm}; L; l_2) \sqrt{\frac{2L+1}{2k+1}} M_q^{(k)}(l_1 j_{\pm}; L; l_2). \quad (\text{H.1})$$

From the Wigner-Eckart theorem, we have

$$\langle l_2^{\nu} SLJM \mid M_q^{(k)} \mid l_2^{\nu} S' L' J' M' \rangle = \frac{1}{\sqrt{2J+1}} C_{J'M';kq}^{JM} \langle l_2^{\nu} SLJ \parallel M^{(k)} \parallel l_2^{\nu} S' L' J' \rangle. \quad (\text{H.2})$$

Also, since

$$[V_q^{(k)}(\mathbf{J}), \mathbf{J}^2] = [V_q^{(k)}(\mathbf{J}), \mathbf{L}^2] = [V_q^{(k)}(\mathbf{J}), \mathbf{S}^2] = 0, \quad (\text{H.3})$$

$$\langle l_2^{\nu} SLJM \mid V_q^{(k)}(\mathbf{J}) \mid l_2^{\nu} S' L' J' M' \rangle =$$

$$\delta_{S,S'} \delta_{L,L'} \delta_{J,J'} \frac{1}{\sqrt{2J+1}} C_{J'M';kq}^{JM} \langle l_2^{\nu} SLJ \parallel V^{(k)}(J) \parallel l_2^{\nu} S' L' J' \rangle. \quad (\text{H.4})$$

Therefore, for a scattering in a manifold of a good J ($\mid l_2^{\nu} SLJM \rangle \rightarrow \mid l_2^{\nu} SLJM' \rangle$), the scattering operator $F_{q(EL)}^{(k)}$ is proportional to the tensor operator $V^{(k)}(\mathbf{J})$

$$F_q^{(k)} = R \sqrt{\frac{2L+1}{2k+1}} \frac{\langle l_2^{\nu} SLJ \parallel M^{(k)} \parallel l_2^{\nu} SLJ \rangle}{\langle J \parallel V^{(k)}(\mathbf{J}) \parallel J \rangle} V_q^{(k)}(\mathbf{J}). \quad (\text{H.5})$$

and

$$M_q^{(k)} = \frac{\langle l_2^{\nu} SLJ \parallel M^{(k)} \parallel l_2^{\nu} SLJ \rangle}{\langle J \parallel V^{(k)}(\mathbf{J}) \parallel J \rangle} V_q^{(k)}(\mathbf{J}). \quad (\text{H.6})$$

Here $V_q^{(k)}(\mathbf{J})$ and $\langle J || V^{(k)}(\mathbf{J}) || J \rangle$ are obtained by replacing $\mathbf{l}$ by $\mathbf{J}$ in $V^{(k)}(\mathbf{l})$ (in Appendix E), and $\langle l_2^\nu SLJ || M^{(k)}(j_\pm) || l_2^\nu SLJ \rangle = -\frac{j_\pm + \frac{1}{2}}{2l_1 + 1} c_k \langle || \bar{W}^{(0,k)} || \rangle$

$$\begin{aligned} & \pm [d_{k,|k-1|} \langle || W^{(1,k-1)k} || \rangle \\ & + d_{k,|k+1|} \langle || W^{(1,k+1)k} || \rangle] \end{aligned} \quad (\text{H.7})$$

$\langle || W^{(\kappa,l)k} || \rangle = \langle l_2^\nu SLJ || W^{(\kappa,l)k} || l_2^\nu SLJ \rangle$, $\bar{W}^{(0,k)} = W^{(0,k)}$ for $k \neq 0$, $\bar{W}^{(0,0)} = W^{(0,0)} - \sqrt{2(2l_2 + 1)}$, and where c_k and d_{kl} are given by Eq.(2.18).

The reduced matrix elements for the orbital moments $W^{(0,k)}$ are given by

$$\begin{aligned} \langle l_2^\nu SLJ || W^{(0,k)} || l_2^\nu SLJ \rangle &= \sqrt{\frac{2k+1}{2}} (-1)^{L+S+J+k} (2J+1) \begin{Bmatrix} J & k & J \\ L & S & L \end{Bmatrix} \\ &\times \langle l_2^\nu SL || U^{(k)} || l_2^\nu SL \rangle, \end{aligned} \quad (\text{H.8})$$

where

$$U^{(k)} = \sum_{i \in l_2} \mathbf{u}_i^{(k)}. \quad (\text{H.9})$$

Here $\mathbf{u}^{(k)}$ are the symmetric unit tensor operators ($\langle l_2 || \mathbf{u}^{(k)} || l_2 \rangle = 1$). In particular,

$$\langle l_2^\nu SLJ || \bar{W}^{(0,0)} || l_2^\nu SLJ \rangle = -(4l_2 + 2 - \nu) \sqrt{\frac{2J+1}{2(2l_2+1)}}. \quad (\text{H.10})$$

The rest of the reduced matrix elements $\langle l_2^\nu SL || U^{(k)} || l_2^\nu SL \rangle$ for p , d and f subshells have been tabulated by Nielson and Koster[24].

The reduced matrix elements for the spin coupled orbital moments $W^{(1,l)k}$ are given by

$$\begin{aligned} \langle l_2^\nu SLJ || W^{(1,l)k} || l_2^\nu SLJ \rangle &= (2J+1) \begin{Bmatrix} S & S & 1 \\ L & L & l \\ J & J & k \end{Bmatrix} \sqrt{2(2l+1)(2k+1)} \\ &\times \langle l_2^\nu SL || V^{(l,1)} || l_2^\nu SL \rangle, \end{aligned} \quad (\text{H.11})$$

where the double tensor operators $V^{(l,1)}$ are

$$V^{(l,1)} = \sum_{i \in l_2} \mathbf{u}_i^{(l)} \mathbf{s}_i. \quad (\text{H.12})$$

The values of $\langle l_2^{\nu}SL || V^{(l,1)} || l_2^{\nu}SL \rangle$ have also been tabulated by Nielson and Koster[24] for the p , d and f subshells.

Appendix I

The Generalized Scattering Operator $\bar{S}_{LM';LM}$.

The scattering operator $F_{LM';LM}^{(e)}(\omega)$ is defined by Eq.(2.3)

$$F_{LM';LM}^{(e)} = K \sum_{all\ m,m'} \frac{\langle R_{ncl_1j_1} | r^L | R_{nl_2m'_s} \rangle \langle R_{nl_2m_s} | r^L | R_{ncl_1j_1} \rangle}{[\Delta E_{IO}(m_s) - \hbar\omega - i\Gamma/2]} \times \bar{\rho}_{m_2m_s;m'_2m'_s} D_{m'_2m'_s;m_2m_s}, \quad (I.1)$$

where $K(l_1 L l_2)$ is given by Eq.(2.10),

$$D_{m'_2m'_s;m_2m_s} = C_{l_1m'_1;\frac{1}{2}m'_S}^{j_1m_j} C_{l_1m_1;\frac{1}{2}m_S}^{j_1m_j} C_{l_1m'_1;LM'}^{l_2m'_2} C_{l_1m_1;LM}^{l_2m_2}, \quad (I.2)$$

and the hole-density matrix-elements

$$\bar{\rho}_{m_2m_s;m'_2m'_s} = \hat{a}_{m'_2m'_s}^\dagger \hat{a}_{m_2m_s}. \quad (I.3)$$

The hole matrix is complimentary to the density matrix

$$\rho_{m_2m_s;m'_2m'_s} = \hat{a}_{m_2m_s}^\dagger \hat{a}_{m'_2m'_s}, \quad (I.4)$$

and from the anticommutation relations, we have

$$\rho + \bar{\rho} = I. \quad (I.5)$$

Also the density matrices are hermitian

$$\rho = \rho^\dagger, \text{ and } \bar{\rho} = \bar{\rho}^\dagger. \quad (I.6)$$

Consider there is an exchange splitting Δ between the spin-up and the spin-down valence shell (Δ is not necessarily small),

$$\Delta E_{IO}(m_s = \pm \frac{1}{2}) = \Delta E_{IO} \mp \frac{\Delta}{2}, \quad (\text{I.7})$$

and different radial matrix-elements to these states,

$$\langle r^L(m_s = \pm \frac{1}{2}) \rangle = \langle r^L \rangle (1 \pm \frac{\delta}{2}). \quad (\text{I.8})$$

Then, $F_{LM';LM}^{(e)}$ becomes, valid to order δ ($\delta \ll 1$),

$$\begin{aligned} F_{LM';LM}^{(e)} &= K \sum [\frac{|\langle r^L \rangle^{(+)}|^2}{(\Delta E_{IO} - \frac{\Delta}{2} - \hbar\omega - i\Gamma/2)} \bar{\rho}_{m_2 \uparrow; m'_2 \uparrow} D_{m'_2 \uparrow; m_2 \uparrow} \\ &\quad + \frac{|\langle r^L \rangle^{(-)}|^2}{(\Delta E_{IO} + \frac{\Delta}{2} - \hbar\omega - i\Gamma/2)} \bar{\rho}_{m_2 \downarrow; m'_2 \downarrow} D_{m'_2 \downarrow; m_2 \downarrow} \\ &\quad + \frac{|\langle r^L \rangle^{(-)}| |\langle r^L \rangle^{(+)}|}{(\Delta E_{IO} - \frac{\Delta}{2} - \hbar\omega - i\Gamma/2)} \bar{\rho}_{m_2 \uparrow; m'_2 \downarrow} D_{m'_2 \downarrow; m_2 \uparrow} \\ &\quad + \frac{|\langle r^L \rangle^{(+)}| |\langle r^L \rangle^{(-)}|}{(\Delta E_{IO} + \frac{\Delta}{2} - \hbar\omega - i\Gamma/2)} \bar{\rho}_{m_2 \downarrow; m'_2 \uparrow} D_{m'_2 \uparrow; m_2 \downarrow}] \\ &= \bar{R} \frac{1}{(1 - \bar{\Delta}^2)} \bar{S}_{LM';LM}(j_{\pm}), \end{aligned} \quad (\text{I.9})$$

where

$$\bar{R} = K \frac{|\langle r^L \rangle|^2}{(\Delta E_{IO} - \hbar\omega - i\Gamma/2)}, \quad (\text{I.10})$$

$$\bar{\Delta} = \frac{\Delta}{\Gamma(X - i)}, \quad (\text{I.11})$$

$$X = (\Delta E_{IO} - \hbar\omega)/(\Gamma/2), \quad (\text{I.12})$$

and

$$\begin{aligned}
\bar{S}_{LM';LM} = & \sum[(1+\delta)(1+\bar{\Delta})\bar{\rho}_{m_2\uparrow;m'_2\uparrow}D_{m'_2\uparrow;m_2\uparrow} \\
& +(1-\delta)(1-\bar{\Delta})\bar{\rho}_{m_2\downarrow;m'_2\downarrow}D_{m'_2\downarrow;m_2\downarrow} \\
& +(1+\bar{\Delta})\bar{\rho}_{m_2\uparrow;m'_2\downarrow}D_{m'_2\downarrow;m_2\uparrow} \\
& +(1-\bar{\Delta})\bar{\rho}_{m_2\downarrow;m'_2\uparrow}D_{m'_2\uparrow;m_2\downarrow}].
\end{aligned} \tag{I.13}$$

At $j_1 = j_- (l_1 - \frac{1}{2})$, let $\epsilon = (\bar{\Delta} + \delta)$,

$$\begin{aligned}
\bar{S}_{LM';LM}(j_-) = & \sum\{[(1+\epsilon+\bar{\Delta}\delta)\bar{\rho}_{m_2\uparrow;m'_2\uparrow}\frac{l_1-m_1}{2l_1+1} \\
& +(1-\epsilon+\bar{\Delta}\delta)\bar{\rho}_{m_2\downarrow;m'_2\downarrow}\frac{l_1+m_1}{2l_1+1}]C_{l_1m_1;LM'}^{l_2m'_2}C_{l_1m_1;LM}^{l_2m_2} \\
& +\frac{\sqrt{2l_1(l_1+1)}}{2l_1+1}[(1+\bar{\Delta})\bar{\rho}_{m_2\uparrow;m'_2\downarrow}C_{l_1m_1;11}^{l_1(m_1+1)}C_{l_1(m_1+1);LM'}^{l_2m'_2}C_{l_1m_1;LM}^{l_2m_2} \\
& -(1-\bar{\Delta})\bar{\rho}_{m_2\downarrow;m'_2\uparrow}C_{l_1m_1;1,-1}^{l_1(m_1-1)}C_{l_1(m_1-1);LM'}^{l_2m'_2}C_{l_1m_1;LM}^{l_2m_2}]\} \\
= & S_{LM';LM}(j_-) + \epsilon E_{LM';LM}(j_-) + \bar{\Delta}\delta Q_{LM';LM}(j_-) \\
& +\bar{\Delta}U_{LM';LM}(j_-),
\end{aligned} \tag{I.14}$$

where $S_{LM';LM}(j_-)$ is given by Eq.(B.10-B.13),

$$E_{LM';LM}(j_-) = \sum [\bar{\rho}_{m_2\uparrow;m'_2\uparrow}\frac{l_1-m_1}{2l_1+1} - \bar{\rho}_{m_2\downarrow;m'_2\downarrow}\frac{l_1+m_1}{2l_1+1}]C_{l_1m_1;LM'}^{l_2m'_2}C_{l_1m_1;LM}^{l_2m_2}, \tag{I.15}$$

$$Q_{LM';LM}(j_-) = \sum [\bar{\rho}_{m_2\uparrow;m'_2\uparrow}\frac{l_1-m_1}{2l_1+1} + \bar{\rho}_{m_2\downarrow;m'_2\downarrow}\frac{l_1+m_1}{2l_1+1}]C_{l_1m_1;LM'}^{l_2m'_2}C_{l_1m_1;LM}^{l_2m_2}, \tag{I.16}$$

and

$$U_{LM';LM}(j_-) = \sum [\bar{\rho}_{m_2\uparrow;m'_2\downarrow}C_{l_1m_1;11}^{l_1(m_1+1)}C_{l_1(m_1+1);LM'}^{l_2m'_2}C_{l_1m_1;LM}^{l_2m_2}$$

$$+\bar{\rho}_{m_2\downarrow;m_2'\uparrow}C_{l_1m_1;1,-1}^{l_1(m_1-1)}C_{l_1(m_1-1);LM'}^{l_2m_2'}C_{l_1m_1;LM}^{l_2m_2}]\frac{\sqrt{2l_1(l_1+1)}}{2l_1+1}. \quad (\text{I.17})$$

Since

$$\begin{aligned} U_{LM;LM}(j_-) &= \frac{\sqrt{2l_1(l_1+1)}}{2l_1+1} \sum [\bar{\rho}_{m_2\uparrow;(m_2+1)\downarrow}C_{l_1m_1;11}^{l_1(m_1+1)}C_{l_1(m_1+1);LM}^{l_2(m_2+1)}C_{l_1m_1;LM}^{l_2m_2} \\ &\quad +\bar{\rho}_{m_2\downarrow;(m_2-1)\uparrow}C_{l_1m_1;1,-1}^{l_1(m_1-1)}C_{l_1(m_1-1);LM}^{l_2(m_2-1)}C_{l_1m_1;LM}^{l_2m_2}], \end{aligned} \quad (\text{I.18})$$

these two terms cancel each other,

$$\begin{aligned} (\text{second term}) &= \sum \bar{\rho}_{(m_2+1)\downarrow;m_2\uparrow}C_{l_1(m_1+1);1,-1}^{l_1m_1}C_{l_1m_1;LM}^{l_2m_2}C_{l_1(m_1+1);LM}^{l_2(m_2+1)} \\ &= -\sum \bar{\rho}_{(m_2+1)\downarrow;m_2\uparrow}C_{l_1m_1;1,1}^{l_1(m_1+1)}C_{l_1m_1;LM}^{l_2m_2}C_{l_1(m_1+1);LM}^{l_2(m_2+1)} \\ &= -(\text{first term}). \end{aligned} \quad (\text{I.19})$$

due to $\bar{\rho}_{(m_2+1)\downarrow;m_2\uparrow} = [\bar{\rho}_{m_2\uparrow;(m_2+1)\downarrow}]^\dagger = \bar{\rho}_{m_2\uparrow;(m_2+1)\downarrow}$. We can neglect $U_{LM';LM}$ terms.

Following the similar procedures as in Appendix B, we obtain

$$E_{LM';LM}(j_\pm) = \sum_{l=0}^{2L} [-a_l^{(\pm)} A_{LM}(l) \bar{W}_0^{(1,l)} \mp b_l B_{LM}^{(0)}(l)_m \bar{W}_m^{(0,l)}], \quad (\text{I.20})$$

and

$$Q_{LM';LM}(j_\pm) = \sum_{l=0}^{2L} [-a_l^{(\pm)} A_{LM}(l) \bar{W}_m^{(0,l)} \mp b_l B_{LM}^{(0)}(l)_m \bar{W}_0^{(1,l)}], \quad (\text{I.21})$$

Then we have proved Eq.(3.4)

$$\begin{aligned} \bar{S}_{LM';LM} &= \sum_{l=0}^{2L} \left\{ -\frac{(j_\pm + \frac{1}{2})}{(2l_1+1)} c_l [(1 + \bar{\Delta}\delta) \bar{W}_q^{(0,l)} + \epsilon \bar{W}_{0q}^{(1,l)}] C_{LM';lq}^{LM} \right. \\ &\quad \left. \pm \sum_{k=|l-1|(\neq l)}^{l+1} d_{kl} [\bar{W}_q^{(1,l)k} + (\epsilon \bar{W}_q^{(0,l)} + \bar{\Delta}\delta \bar{W}_{0q}^{(1,l)}) C_{lq;10}^{kq}] C_{LM';kq}^{LM} \right\}. \end{aligned} \quad (\text{I.22})$$

Appendix J

Multipole Moments $\overline{M}^{(k)}$.

From Appendix I and Eq.(3.9), we have

$$\begin{aligned}\overline{M}^{(0)}(l_1 j_{\pm}; 1; l_2) &= -\alpha_0(j_{\pm})[(1 + \overline{\Delta}\delta)\overline{W}^{(0,0)} + \epsilon\overline{W}_0^{(1,0)}] \\ &\quad \pm \gamma_0[\overline{W}^{(1,1)0} + (\epsilon\overline{W}_0^{(0,1)} + \overline{\Delta}\delta\overline{W}_{0\ 0}^{(1,1)})C_{10;10}^{00}],\end{aligned}\quad (\text{J.1})$$

$$\begin{aligned}\overline{M}_q^{(1)}(l_1 j_{\pm}; 1; l_2) &= \alpha_1(j_{\pm})[(1 + \overline{\Delta}\delta)\overline{W}_q^{(0,1)} + \epsilon\overline{W}_{0\ q}^{(1,1)}] \\ &\quad \pm \beta_1[\overline{W}_q^{(1,0)} + (\epsilon\overline{W}^{(0,0)} + \overline{\Delta}\delta\overline{W}_0^{(1,0)})C_{00;10}^{1q}], \\ &\quad \pm \gamma_1[\overline{W}_q^{(1,2)1} + (\epsilon\overline{W}_q^{(0,2)} + \overline{\Delta}\delta\overline{W}_{0\ q}^{(1,2)})C_{2q;10}^{1q}],\end{aligned}\quad (\text{J.2})$$

$$\begin{aligned}\overline{M}_q^{(2)}(l_1 j_{\pm}; 1; l_2) &= -\alpha_2(j_{\pm})[(1 + \overline{\Delta}\delta)\overline{W}_q^{(0,2)} + \epsilon\overline{W}_{0\ q}^{(1,2)}] \\ &\quad \pm \beta_2[\overline{W}_q^{(1,1)2} + (\epsilon\overline{W}_q^{(0,1)} + \overline{\Delta}\delta\overline{W}_0^{(1,1)})C_{1q;10}^{2q}], \\ &\quad \pm \gamma_2[\overline{W}_q^{(1,3)2} + (\epsilon\overline{W}_q^{(0,3)} + \overline{\Delta}\delta\overline{W}_{0\ q}^{(1,3)})C_{3q;10}^{2q}],\end{aligned}\quad (\text{J.3})$$

where α , β and γ are given by Table 2.1.

Since $C_{\frac{1}{2}\frac{1}{2};10}^{\frac{1}{2}\frac{1}{2}} = -C_{\frac{1}{2},-\frac{1}{2};10}^{\frac{1}{2},-\frac{1}{2}} = \frac{1}{\sqrt{3}}$, we have

$$\begin{aligned}\overline{W}_{0\ q}^{(1,l)} &= W_{0\ q}^{(1,l)} = \sqrt{\frac{3(2l+1)}{2(2l_2+1)}} \sum_{m_2 m'_2 m_s m'_s} \hat{a}_{m_2 m_s}^{\dagger} \hat{a}_{m'_2 m'_s} C_{\frac{1}{2} m'_s;10}^{\frac{1}{2} m_s} C_{l_2 m'_2;lm}^{l_2 m_2} \\ &= \sqrt{\frac{(2l+1)}{2(2l_2+1)}} \sum_{m_2 m'_2} (\hat{a}_{m_2 \uparrow}^{\dagger} \hat{a}_{m'_2 \uparrow} - \hat{a}_{m_2 \downarrow}^{\dagger} \hat{a}_{m'_2 \downarrow}) C_{l_2 m'_2;lm}^{l_2 m_2}\end{aligned}$$

$$= \overline{W}_q^{(0,l)}(\uparrow) - \overline{W}_q^{(0,l)}(\downarrow) = \overline{W}_q^{(0,l)(s)}. \quad (\text{J.4})$$

Then,

$$\overline{W}_0^{(1,0)} = \sqrt{\frac{2}{2l_2 + 1}} S_z(l_2), \quad (\text{J.5})$$

$$\begin{aligned} \overline{W}_0^{(1,1)} &= \frac{\sqrt{\frac{3}{2}}}{\sqrt{l_2(l_2 + 1)(2l_2 + 1)}} [L_q(\uparrow) - L_q(\downarrow)] \\ &= \frac{\sqrt{\frac{3}{2}}}{\sqrt{l_2(l_2 + 1)(2l_2 + 1)}} L_q^{(s)}(l_2), \end{aligned} \quad (\text{J.6})$$

$$\overline{W}_0^{(1,2)} = \frac{\sqrt{15}}{\sqrt{l_2(l_2 + 1)(2l_2 + 3)(2l_2 + 1)(2l_2 - 1)}} \sum_{i \in l_2} [V_q^{(2)}(\mathbf{l}_i \otimes \mathbf{l}_i)^{(s)}]. \quad (\text{J.7})$$

Here, the operators $\hat{O}^{(s)}$ indicate the difference of the spin-up $\hat{O}(\uparrow)$ and spin-down $\hat{O}(\downarrow)$,

$$\hat{O}^{(s)} = \hat{O}(\uparrow) - \hat{O}(\downarrow) = \sum_{m_s} (-1)^{1-2m_s} \hat{O}(m_s). \quad (\text{J.8})$$

From $(\hat{\mathbf{z}})_\mu = 0$, unless $\mu = 0$, $(\hat{\mathbf{z}})_0 = 1$,

$$C_{lq;10}^{kq} W_q^{(0,l)} = \sum_{m,\mu} C_{lm;1\mu}^{kq} (\hat{\mathbf{z}})_\mu W_m^{(0,l)} = V_q^{(k)} [\hat{\mathbf{z}} \otimes W^{(0,l)}], \quad (\text{J.9})$$

where $\hat{\mathbf{z}}$ is the unit vector of the local field direction. We have

$$\begin{aligned} \overline{W}_0^{(0,1)} C_{10;10}^{00} &= V_0^{(0)} [\hat{\mathbf{z}} \otimes W^{(0,1)}] \\ &= -\frac{1}{\sqrt{3}} [\hat{\mathbf{z}} \cdot W^{(0,1)}] \\ &= -\frac{1}{\sqrt{3}} \frac{\sqrt{\frac{3}{2}}}{\sqrt{l_2(l_2 + 1)(2l_2 + 1)}} L_z(l_2) \\ &= -\frac{1}{\sqrt{2l_2(l_2 + 1)(2l_2 + 1)}} L_z(l_2), \end{aligned} \quad (\text{J.10})$$

$$\overline{W}^{(0,0)} C_{00;10}^{10} = \frac{-N_h(l_2) \hat{\mathbf{z}}}{\sqrt{2(2l_2 + 1)}}, \quad (\text{J.11})$$

$$\begin{aligned}
\overline{W}_q^{(0,2)} C_{2q;10}^{1q} &= \frac{\sqrt{15}}{\sqrt{l_2(l_2+1)(2l_2+3)(2l_2+1)(2l_2-1)}} \sum_{i \in l_2} [\hat{\mathbf{z}} \otimes V^{(2)}(\mathbf{l}_i \otimes \mathbf{l}_i)]_q^1. \\
&= \sqrt{\frac{l_2(l_2+1)}{(2l_2+3)(2l_2+1)(2l_2-1)}} \sum_{i \in l_2} [(\hat{\mathbf{z}} - \frac{3\{l_z, l_q\}_+}{2l_2(l_2+1)})_i]. \quad (\text{J.12})
\end{aligned}$$

$$\overline{W}_q^{(0,1)} C_{1q;10}^{2q} = \frac{\sqrt{\frac{3}{2}}}{\sqrt{l_2(l_2+1)(2l_2+1)}} \sum_{i \in l_2} [V_q^{(2)}(\hat{\mathbf{z}} \otimes \mathbf{l}_i)]. \quad (\text{J.13})$$

Also from

$$\overline{W}_{0\ q}^{(1,l)} C_{lq;10}^{kq} = V_q^{(k)}(\hat{\mathbf{z}} \otimes \overline{W}^{(0,l)})^{(s)}, \quad (\text{J.14})$$

We have

$$\begin{aligned}
\overline{W}_{0\ 0}^{(1,1)} C_{10;10}^{00} &= -\frac{1}{\sqrt{2(2l_2+1)l_2(l_2+1)}} L_z^{(s)} \\
&\equiv \frac{-\sqrt{2}}{\sqrt{(2l_2+1)l_2(l_2+1)}} [\sum_{i \in l_2} (s_z l_z)_i], \quad (\text{J.15})
\end{aligned}$$

$$\overline{W}_{0\ q}^{(1,2)} C_{2q;10}^{1q} = \sqrt{\frac{l_2(l_2+1)}{(2l_2+3)(2l_2+1)(2l_2-1)}} \sum_{i \in l_2} [(\hat{\mathbf{z}} - \frac{3\{l_z, l_q\}_+}{2l_2(l_2+1)})_i^{(s)}]. \quad (\text{J.16})$$

$$\overline{W}_{0\ q}^{(1,1)} C_{1q;10}^{2q} = \frac{\sqrt{\frac{3}{2}}}{\sqrt{l_2(l_2+1)(2l_2+1)}} \sum_{i \in l_2} [V_q^{(2)}(\hat{\mathbf{z}} \otimes \mathbf{l}_i)^{(s)}]. \quad (\text{J.17})$$

Bringing all these results into Eq.(J.1-J.3), we obtain

$$\begin{aligned}
A_0 &= [(1 + \overline{\Delta}\delta)\overline{W}^{(0,0)} + \epsilon\overline{W}_0^{(1,0)}] \\
&= \frac{(-1)}{\sqrt{2(2l_2+1)}} [(1 + \overline{\Delta}\delta)N_h(l_2) - 2\epsilon\mathbf{S}_z(l_2)], \quad (\text{J.18})
\end{aligned}$$

$$C_0 = [\overline{W}^{(1,1)0} + (\epsilon\overline{W}_0^{(0,1)} + \overline{\Delta}\delta\overline{W}_{0\ 0}^{(1,1)})C_{10;10}^{00}]$$

$$= -\frac{\sqrt{2}}{\sqrt{(2l_2+1)l_2(l_2+1)}}\left[\sum_{i \in l_2}(\mathbf{s}_i \cdot \mathbf{l}_i) + \frac{\epsilon}{2}L_z + \frac{\overline{\Delta}\delta}{2}L_z^{(s)}\right], \quad (\text{J.19})$$

$$\begin{aligned} \mathbf{A}_1 &= [(1 + \overline{\Delta}\delta)\overline{W}^{(0,1)} + \epsilon\overline{W}_0^{(1,1)}] \\ &= \frac{\sqrt{\frac{3}{2}}}{\sqrt{(2l_2+1)l_2(l_2+1)}}[(1 + \overline{\Delta}\delta)\mathbf{L}(l_2) + \epsilon\mathbf{L}^{(s)}], \end{aligned} \quad (\text{J.20})$$

$$B_{1q} = [\overline{W}_q^{(1,0)} + (\epsilon\overline{W}^{(0,0)} + \overline{\Delta}\delta\overline{W}_0^{(1,0)})C_{00;10}^{1q}]$$

$$\mathbf{B}_1 = \sqrt{\frac{2}{2l_2+1}}\left[\mathbf{S} - \frac{\epsilon}{2}N_h(l_2)\hat{\mathbf{z}} + \overline{\Delta}\delta S_z\hat{\mathbf{z}}\right], \quad (\text{J.21})$$

$$C_{1q} = [\overline{W}_q^{(1,2)1} + (\epsilon\overline{W}^{(0,2)} + \overline{\Delta}\delta\overline{W}_0^{(1,2)})C_{2q;10}^{1q}]$$

$$\begin{aligned} \mathbf{C}_1 &= \sqrt{\frac{4l_2(l_2+1)}{(2l_2+3)(2l_2+1)(2l_2-1)}}\left[\sum_{i \in l_2}\left[(\hat{\mathbf{s}} - \frac{3\{\mathbf{s} \cdot \mathbf{l}, \mathbf{l}\}_+}{2l_2(l_2+1)})_i\right.\right. \\ &\quad \left.+\frac{\epsilon}{2}\sum_{i \in l_2}\left[(\hat{\mathbf{z}} - \frac{3\{l_z, \mathbf{l}\}_+}{2l_2(l_2+1)})_i\right] + \frac{\overline{\Delta}\delta}{2}\sum_{i \in l_2}\left[(\hat{\mathbf{z}} - \frac{3\{l_z, \mathbf{l}\}_+}{2l_2(l_2+1)})_i^{(s)}\right]\right]. \end{aligned} \quad (\text{J.22})$$

$$\begin{aligned} A_{2q} &= [(1 + \overline{\Delta}\delta)\overline{W}_q^{(0,2)} + \epsilon\overline{W}_0^{(1,2)}] \\ &= \frac{\sqrt{15}}{\sqrt{(2l_3+1)(2l_2+1)(2l_2-1)l_2(l_2+1)}} \\ &\quad \times \sum_{i \in l_2}[(1 + \overline{\Delta}\delta)V_q^{(2)}(\mathbf{l}_i \otimes \mathbf{l}_i) + \epsilon V_q^{(2)}(\mathbf{l}_i \otimes \mathbf{l}_i)^{(s)}], \end{aligned} \quad (\text{J.23})$$

$$B_{2q} = [\overline{W}_q^{(1,1)2} + (\epsilon\overline{W}_q^{(0,1)} + \overline{\Delta}\delta\overline{W}_0^{(1,1)})C_{1q;10}^{2q}]$$

$$\begin{aligned}
&= \sqrt{\frac{6}{(2l_2+1)l_2(l_2+1)}} \sum_{i \in l_2} [V_q^{(2)}(\mathbf{s}_i \otimes \mathbf{l}_i) \\
&\quad + \frac{\epsilon}{2} V_q^{(2)}(\hat{\mathbf{z}} \otimes \mathbf{l}_i) + \frac{\bar{\Delta}\delta}{2} V_q^{(2)}(\hat{\mathbf{z}} \otimes \mathbf{l}_i)^{(s)}],
\end{aligned} \tag{J.24}$$

$$\begin{aligned}
C_{2q} &= [\bar{W}_q^{(1,3)2} + (\epsilon \bar{W}_q^{(0,3)} + \bar{\Delta}\delta \bar{W}_0^{(1,3)}) C_{3q;10}^{2q}] \\
&= 8\sqrt{35} \left[\prod_{n=-3}^3 (2l_2+1+n)^{-\frac{1}{2}} \sum_{i \in l_2} [V_q^{(2)}(\mathbf{s}_i \otimes V^{(3)}(\mathbf{l}_i)) + \frac{\epsilon}{2} V_q^{(2)}(\mathbf{z} \otimes V^{(3)}(\mathbf{l}_i)) \right. \\
&\quad \left. + \frac{\bar{\Delta}\delta}{2} V_q^{(2)}(\mathbf{z} \otimes V^{(3)}(\mathbf{l}_i))^{(s)}] \right]
\end{aligned} \tag{J.25}$$

From these we get $\bar{M}^{(k)}(l_1 j_{\pm}; 1; l_2)$ in Eq.(3.15)

$$\begin{aligned}
M^{(0)}(l_1 j_{\pm}; 1; l_2) &= \alpha'_0(j_{\pm})[(1 + \bar{\Delta}\delta)N_h(l_2) - 2\epsilon S_z] \\
&\quad \mp \gamma'_0 \left[\sum_{i \in l_2} (\mathbf{s}_i \cdot \mathbf{l}_i) + \frac{\epsilon}{2} L_z + \frac{\bar{\Delta}\delta}{2} L_z^{(s)} \right],
\end{aligned} \tag{J.26}$$

$$\begin{aligned}
M^{(1)}(l_1 j_{\pm}; 1; l_2) &= \alpha'_1(j_{\pm})[(1 + \bar{\Delta}\delta)\mathbf{L} + \epsilon \mathbf{L}^{(s)}] \\
&\quad \pm \beta'_1 \left[\mathbf{S} - \left(\frac{\epsilon}{2} P_{hole} - \bar{\Delta}\delta S_z \right) \mathbf{z} \right] \\
&\quad \pm \gamma'_1 \sum_{i \in l_2} \left[\left(\mathbf{s} - \frac{3\{\mathbf{s} \cdot \mathbf{l}, \mathbf{l}\}_+}{2l_2(l_2+1)} \right)_i + \frac{\epsilon}{2} \left(\mathbf{z} - \frac{3\{l_z, \mathbf{l}\}_+}{2l_2(l_2+1)} \right)_i \right. \\
&\quad \left. + \frac{\bar{\Delta}\delta}{2} \left(\mathbf{z} - \frac{3\{l_z, \mathbf{l}\}_+}{2l_2(l_2+1)} \right)_i^{(s)} \right],
\end{aligned} \tag{J.27}$$

$$\begin{aligned}
M^{(2)}(l_1 j_{\pm}; 1; l_2) &= -\alpha'_2(j_{\pm}) \sum_{i \in l_2} [(1 + \bar{\Delta}\delta)V^{(2)}(\mathbf{l}_i \otimes \mathbf{l}_i) + \epsilon V^{(2)}(\mathbf{l}_i \otimes \mathbf{l}_i)^{(s)}] \\
&\quad \pm \beta'_2 \sum_{i \in l_2} [V^{(2)}(\mathbf{s}_i \otimes \mathbf{l}_i) + \frac{\epsilon}{2} V^{(2)}(\mathbf{z} \otimes \mathbf{l}_i) + \frac{\bar{\Delta}\delta}{2} V^{(2)}(\mathbf{z} \otimes \mathbf{l}_i)^{(s)}] \\
&\quad \pm \gamma'_2 \sum_{i \in l_2} [V^{(2)}(\mathbf{s}_i \otimes V^{(3)}(\mathbf{l}_i)) + \frac{\epsilon}{2} V^{(2)}(\mathbf{z} \otimes V^{(3)}(\mathbf{l}_i))
\end{aligned}$$

$$+\frac{\overline{\Delta}\delta}{2}V^{(2)}(\mathbf{z}\otimes V^{(3)}(\mathbf{l}_i))^{(s)}] \tag{J.28}$$

where α' , β' and γ' are given in Table 2.2.

Appendix K

Spin Scattering Operator.

The scattering operator for E1 resonant scattering has been given in Eq.(2.34) as

$$F(j_{\pm}) = \frac{3}{2}\lambda_0 R[(\mathbf{e}_f^* \cdot \mathbf{e}_0)M_{(j_{\pm})}^{(0)} - \frac{i}{\sqrt{2}}(\mathbf{e}_f^* \times \mathbf{e}_0) \cdot M_{(j_{\pm})}^{(1)} - \sqrt{\frac{3}{5}}V^{(2)}(\mathbf{e}_f^* \otimes \mathbf{e}_0) \cdot M_{(j_{\pm})}^{(2)}], \quad (\text{K.1})$$

where $j_{\pm} = l_1 \pm \frac{1}{2}$, R is given by Eq.(2.10), and the $M_{(j_{\pm})}^{(k)}$'s are given in Eq.(2.35)

$$\begin{aligned} M_{(j_{\pm})}^{(0)} &= -\alpha_0(j_{\pm})\overline{W}^{(0,0)} \pm \gamma_0\overline{W}^{(1,1)0}, \\ M_{q(j_{\pm})}^{(1)} &= \alpha_1(j_{\pm})\overline{W}_q^{(0,1)} \pm \beta_1\overline{W}_q^{(1,0)} \pm \gamma_1\overline{W}_q^{(1,2)1}, \\ M_{q(j_{\pm})}^{(2)} &= -\alpha_2(j_{\pm})\overline{W}_q^{(0,2)} \pm \beta_2\overline{W}_q^{(1,1)2} \pm \gamma_2\overline{W}_q^{(1,3)2}, \end{aligned} \quad (\text{K.2})$$

The coefficients α , β and γ are given by Table 2.1.

In $La_{2-x}Sr_xCuO_4$, we assume that each Cu^{2+} has a single d hole of $x^2 - y^2$ symmetry, then, the ground state of a Cu^{2+} ion can be written as

$$|\Psi_{\sigma}\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{2\sigma} + \hat{a}_{-2\sigma})|0\rangle, \quad (\text{K.3})$$

where $|0\rangle$ is a full filled d shell, $|0\rangle = \prod_{m_2 m_s} \hat{a}_{m_2 m_s}^+ |Vacuum\rangle$. The effective spin-scattering operator $F_s(j_{\pm})$ is defined as

$$\langle \sigma' | F_s(j_{\pm}) | \sigma \rangle = \langle \Psi_{\sigma'} | F(j_{\pm}) | \Psi_{\sigma} \rangle, \quad (\text{K.4})$$

where $|\sigma\rangle = \hat{a}_{\sigma}|\tilde{0}\rangle$, and $|\tilde{0}\rangle$ is a nondegenerate orbital filled with both spin-up and spin-down electrons, $|\tilde{0}\rangle = \hat{a}_{\uparrow}^{\dagger}\hat{a}_{\downarrow}^{\dagger}|Vacuum\rangle$. We can prove that the following

identities hold

$$M^{(0)}(j_{\pm})_s = \frac{\alpha_0(j_{\pm})}{\sqrt{10}} I, \quad (\text{K.5})$$

$$M^{(1)}(j_{\pm})_s = \pm \left[\sqrt{\frac{2}{5}} \beta_1 s + \sqrt{\frac{2}{35}} \gamma_1 (s - 3s_z \hat{z}) \right], \quad (\text{K.6})$$

$$M_q^{(2)}(j_{\pm})_s = \frac{\alpha_2(j_{\pm})}{\sqrt{7}} \delta_{0,q} I, \quad (\text{K.7})$$

Proof of Eq.(K.5):

Since

$$\langle \sigma' | \overline{W}^{(0,0)} | \sigma \rangle = \langle \psi_{\sigma'} | \frac{1}{\sqrt{10}} \sum_{m_2 m_s} (-\hat{a}_{m_2 m_s} \hat{a}_{m_2 m_s}^\dagger) | \psi_{\sigma} \rangle = -\frac{1}{\sqrt{10}} \delta_{\sigma', \sigma}, \quad (\text{K.8})$$

$$\langle \sigma' | \overline{W}^{(1,1)0} | \sigma \rangle = 0, \quad (\text{K.9})$$

from Eq.(K.2), we obtain Eq.(K.5).

Proof of Eq.(K.6):

From Eq.(D.19)

$$W^{(1,0)} = \sqrt{\frac{2}{2l_2 + 1}} S(l_2) |_{l_2=2} = \sqrt{\frac{2}{5}} \mathbf{S}(l_2), \quad (\text{K.10})$$

and

$$\begin{aligned} \langle \sigma' | \overline{W}^{(1,2)1}_q | \sigma \rangle &= \langle \psi_{\sigma'} | \overline{W}^{(1,2)1}_q | \psi_{\sigma} \rangle \\ &= -\sqrt{\frac{3}{2}} \sum_{\mu, m} \sum_{m_2 m_s; m'_2 m'_s} C_{1\mu; 2m}^{1q} C_{2m'_2; 2m}^{2m_2} C_{\frac{1}{2}m'_s; 1\mu}^{\frac{1}{2}m_s} \\ &\quad \times \frac{1}{2} \langle 0 | (\hat{a}_{2\sigma'}^\dagger + \hat{a}_{-2\sigma'}^\dagger) \hat{a}_{m'_2 m'_s} \hat{a}_{m_2 m_s}^\dagger (\hat{a}_{2\sigma} + \hat{a}_{-2\sigma}) | 0 \rangle \end{aligned}$$

$$\begin{aligned}
&= \sqrt{\frac{3}{2}} \frac{1}{2} [C_{22,20}^{22} + C_{2,-2,20}^{2,-2}] C_{1q,20}^{1q} \\
&\quad \times (- \sum_{m_s m'_s} C_{\frac{1}{2}m'_s, 1q}^{\frac{1}{2}m_s} \langle \sigma' | \hat{a}_{m'_s} \hat{a}_{m_s}^\dagger | \sigma \rangle) \\
&= \sqrt{\frac{3}{2}} \frac{1}{2} \left(\frac{4}{\sqrt{14}} \right) \left[\frac{3q^2 - 2}{\sqrt{10}} \right] \frac{2}{\sqrt{3}} \langle \sigma' | S_q | \sigma \rangle \\
&= \sqrt{\frac{2}{35}} \left[\begin{array}{ll} \langle \sigma' | S_{\pm 1} | \sigma \rangle, & q = \pm 1, \\ -2 \langle \sigma' | S_z | \sigma \rangle, & q = 0 \end{array} \right. \\
&= \sqrt{\frac{2}{35}} \langle \sigma' | (\mathbf{S} - 3S_z \hat{\mathbf{z}}) | \sigma \rangle, \tag{K.11}
\end{aligned}$$

Here $C_{22,20}^{22} = C_{2,-2,20}^{2,-2} = \frac{2}{\sqrt{14}}$, $C_{1q,20}^{1q} = \frac{3q^2-2}{\sqrt{10}}$ and $(-\sum_{m_s m'_s} C_{\frac{1}{2}m'_s, 1q}^{\frac{1}{2}m_s} \langle \sigma' | \hat{a}_{m'_s} \hat{a}_{m_s}^\dagger | \sigma \rangle) = \frac{2}{\sqrt{3}} S_q$. Then bringing Eq.(K.10) and (K.11) into (K.2), Eq.(K.6) is proved.

Proof of Eq.(K.7):

Bring

$$\begin{aligned}
\langle \sigma' | \overline{W}_q^{(0,2)} | \sigma \rangle &= \langle \psi_{\sigma'} | \overline{W}_q^{(0,2)} | \psi_\sigma \rangle \\
&= -\frac{1}{2\sqrt{2}} [C_{22,20}^{22} + C_{2,-2,20}^{2,-2}] \delta_{0,q} \delta_{\sigma',\sigma} \\
&= -\frac{1}{\sqrt{7}} \delta_{0,q} \delta_{\sigma',\sigma}, \tag{K.12}
\end{aligned}$$

$$\langle \sigma' | \overline{W}_q^{(1,1)^2} | \sigma \rangle = \langle \sigma' | \overline{W}_q^{(1,3)^2} | \sigma \rangle = 0 \tag{K.13}$$

into Eq.(K.2), we obtain Eq.(K.7).

Bring Eq.(K.5) to Eq.(K.7) into Eq.(K.1), Eq.(4.9) is proved.

$$\begin{aligned}
F_S(j_{\pm}) &= \frac{3}{2}\lambda_0 R\{[(\mathbf{e}_f^* \cdot \mathbf{e}_0)\frac{\alpha_0(j_{\pm})}{\sqrt{10}} - (3\mathbf{e}_{fz}^* \cdot \mathbf{e}_{0z} - \mathbf{e}_f^* \cdot \mathbf{e}_0)\frac{\alpha_2(j_{\pm})}{\sqrt{70}}] \\
&\quad \mp \frac{i}{\sqrt{2}}(\mathbf{e}_f^* \times \mathbf{e}_0) \cdot [\sqrt{\frac{2}{5}}\beta_1 \mathbf{S} + \sqrt{\frac{2}{35}}\gamma_1(\mathbf{S} - 3S_z \hat{\mathbf{z}})]\} \\
&= \frac{3}{2}\lambda R[A(j_{\pm}) \mp \sum_{\mu=-1}^1 (-1)^\mu B_{-\mu} S_\mu].
\end{aligned} \tag{K.14}$$

Similarly, if the last partially filled state is in the $d_{(3z^2-r^2)}$ orbital,

$$|\psi_\sigma\rangle = \hat{a}_{0\sigma} |0\rangle \tag{K.15}$$

then

$$\begin{aligned}
M_{(j_{\pm})}^{(0)} &= \frac{\alpha_0(j_{\pm})}{\sqrt{10}} I, \\
M_{q(j_{\pm})}^{(1)} &= \pm [\sqrt{\frac{2}{5}}\beta_1 \mathbf{S} - \sqrt{\frac{2}{35}}\gamma_1(\mathbf{S} - 3S_z \hat{\mathbf{z}})], \\
M_{q(j_{\pm})}^{(2)} &= -\frac{\alpha_2(j_{\pm})}{\sqrt{7}} \delta_{0,q} I,
\end{aligned}$$

and $F_s(j_{\pm})$ is given in Eq.(4.17)

$$\begin{aligned}
F_S(j_{\pm}) &= \frac{3}{2}\lambda_0 R\{[(\mathbf{e}_f^* \cdot \mathbf{e}_0)\frac{\alpha_0(j_{\pm})}{\sqrt{10}} + (3\mathbf{e}_{fz}^* \cdot \mathbf{e}_{0z} - \mathbf{e}_f^* \cdot \mathbf{e}_0)\frac{\alpha_2(j_{\pm})}{\sqrt{70}}] \\
&\quad \mp \frac{i}{\sqrt{2}}(\mathbf{e}_f^* \times \mathbf{e}_0) \cdot [\sqrt{\frac{2}{5}}\beta_1 \mathbf{S} - \sqrt{\frac{2}{35}}\gamma_1(\mathbf{S} - 3S_z \hat{\mathbf{z}})]\}.
\end{aligned} \tag{K.16}$$

Bibliography

- [1] D. Gibbs, D. K. Harshman, E. P. Isaacs, D. B. McWhan, D. Mills, and C. Vettier, *Phys. Rev. Lett.* **61**, 1241 (1988); D. Gibbs, G. Grübel, D. R. Harshman, E. D. Isaacs, D. B. McWhan, D. B. Mills, and C. Vettier, *Phys. Rev. B* **43**, 5663 (1991).
- [2] J. P. Hannon, G. T. Trammell, M. Blume, and D. Gibbs, *Phys. Rev. Lett.* **61**, 1245 (1988).
- [3] D. Gibbs, *Synchrotron Radiation News* **5**, no. 5, 18 (1992).
- [4] S. W. Lovesey, *Theory of Neutron Scattering From Condensed Matter*, Vol.2, (Clarendon Press, Oxford, 1984).
- [5] M. Blume and D. Gibbs, *Phys. Rev. B* **37**, 1779 (1988).
- [6] B. R. Judd, *Second Quantization and Atomic Spectroscopy*, (The Johns Hopkins Press, Baltimore, 1967); *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1963).
- [7] J. K. Lang, Y. Bauer, and P. A. Cox, *J. Phys. F* **11**, 121 (1981).
- [8] J. O. Dimmock and A. J. Freeman, *Phys. Rev. Lett.* **13**, 750 (1984); J. F. Herbert, D. N. Lowy, and R. E. Watson, *Phys. Rev. B* **6**, 1913 (1992).
- [9] M. O. Krause, J. H. Oliber, *J. Phys. Chem. Ref. Data* **8**, 329 (1979).
- [10] M. D. Hamrick, MA Thesis, Rice University (1991).

- [11] B. T. Thole, G. van der Laan, J. C. Fluggle, G. A. Sawatzky, R. C. Karnatak and J.-M. Esteve, *Phys. Rev. B* **32**, 5107 (1985).
- [12] B. T. Thole, P. Carra, F. Sette, and G. van der Laan, *Phys. Rev. Lett.* **68**, 1943 (1992).
- [13] P. Carra, B. T. Thole, M. Altarelli, and X. Wang, *Phys. Rev. Lett.* **70**, 694 (1993).
- [14] A. P. Yutsis, I. B. Levinson and V. V. Vanagas, *Mathematical Apparatus of the Theory of Angular Momentum*, (Israel Program for Scientific Translations, Jerusalem, 1962).
- [15] J. J. Sakurai, *Modern Quantum Mechanics* (Addison-Wesley Publishing Company, New York, 1985).
- [16] R. D. Cowan, *The Theory of Atomic Structure and Spectra*, (University of California Press, Berkley, 1981), sec.12.8.
- [17] T. E. Mason, G. Aepli, and H. A. Mook, *Phys. Rev. Lett.* **68**, 1414 (1992); S. W. Chang, et al, *Phys. Rev. Lett.* **67**, 1791 (1991).
- [18] B. Keimer, et al, *Phys. Rev. B* **46**,14034 (1992); G. Shirane et al., *Phys. Rev. Lett.* **63**,330 (1989); R. J. Birgeneau et al., *Phys. Rev. B* **38**, 6614 (1988); S. M. Hayden, et al.,*Physica B* **163**,1 (1990).
- [19] W. Weber, *Z. Phys. B* **70**, 323 (1988); W. Weber, *Phys. Rev. Lett.* **58**, 1371 (1987); A. K. McMahan, K. C. Hass, *Solid State Phys.* **42**, 213 (1989).
- [20] M. Blume, *J. Appl. Phys.* **57**,3615 (1985).
- [21] J. P. Hannon's notes (unpublished).

- [22] V. B. Berestetskii, E. M. Lifshitz and L. P. Pitaevskii, *Quantum Electrodynamics*, (Pergamon, Oxford, 1982); A. I. Akheizer and V. B. Berestetskii, *Quantum Electrodynamics*, (Interscience, New York, 1965); J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics*, (John Wiley & Sons, New York, 1952).
- [23] D. M. Brink and G. K. Satchler, *Angular Momentum*, (Clarendon Press, Oxford, 1968).
- [24] C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n , d^n , and f^n Configurations* (The M.I.T. Press, Cambridge, Mass., 1963); Ref.[16], section 11-9, 11-10 and Appendix H.