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MASTER

THE ZEEMAN SPECTRUM OF SCANDIUM

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(Ph.D. thesis)

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This Thesis is dedicated to

My Father

and

the Memory of my Mother (1926-1971)

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ABSTRACT

The spectra of Sc I, Sc II, Sc III, and Sc IV are analyzed through the use of the Zeeman effect. A sliding spark of the author's design is used in conjunction with a 27 kilogauss electromagnet. The spectra have (reciprocal) dispersions of 0.2 to 0.5 Å/mm.

10 Sc I levels, 16 Sc II levels and 5 Sc III levels show Zeeman splitting. No Sc IV Zeeman patterns were observed. 2 Sc I, 4 Sc II, and all of the Sc III level data are new.

CHAPTER I

HISTORICAL PERSPECTIVE

Spectroscopy can be said to date from the year 1672, when Isaac Newton discovered that white light is composed of different colors. It was many years, however, before spectral lines were observed, this observation reported by the Scotsman Thomas Melville in 1752. The first systematic investigation of spectral physics was carried out by the German optician Joseph Fraunhofer, who in 1814 observed several hundred lines in the solar spectrum. Fraunhofer was the first to observe the spectra of Mars, Venus, and several stars. This prolific worker also invented the diffraction grating.

The development of atomic theory by such men as Dalton, Lavoisier, and Gay-Lussac had advanced to the point where the concept of element had gained a respectable scientific following. Various workers in the period 1800-1859 had inklings of the connection between an element and its spectrum, but it was not until the year 1859 that a definitive explanation was forthcoming. In that year Gustav Kirchhoff and Robert Bunsen of Heidelberg stated each element had its own characteristic spectrum, and the absorption and emission spectra of a given element have the same structure. These concepts fostered an explosion of spectroscopic research which was to last for decades.

In the decades following the announcement of Kirchhoff and Bunsen's theory of spectra, experimenters made good use of photography, which was developed during the 1830's.

The next major advance in spectroscopy was due essentially to one man--Henry Rowland of Johns Hopkins. In 1882 he invented the concave reflection grating. In 1888, Rowland published a list of over 15,000 solar spectrum lines, measured and classified according to element.

Rowland's accurate gratings permitted spectra to be measured much more precisely, and in 1885 J. Balmer of Basel published his now famous formula for the Balmer series of Hydrogen. In 1890, J. Rydberg of Lund found that many spectral series had a simple mathematical form if expressed in terms of the wavenumber rather than wavelength. Experiments on the structure of atoms were moving ahead during this period, Zeeman discovering his effect in 1896, J. J. Thomson discovering the electron in 1897, and Wien the proton in 1898.

CHAPTER II

THEORY OF THE ZEEMAN EFFECT

Atomic Hamiltonian

A model Hamiltonian for an N electron atom can be given by (Bethe, 1973, Sakurai, 1967):

$$H_0 = \sum_{i=1}^N (\underline{\sigma}_i \cdot \underline{p}_i) (\underline{\sigma}_i \cdot \underline{p}_i) / 2m - \sum_{i=1}^N Ze^2 / |\underline{r}_i| + \sum_{i=j}^N e^2 / |\underline{r}_i - \underline{r}_j|$$

where $H_0 \Psi = E_0 \Psi$. Z is the nuclear charge, m the electron mass, and $\underline{\sigma}$ the Pauli spin matrices.

In the presence of an electromagnetic field, the Hamiltonian is modified by the rule of minimal coupling:

$$\underline{p}_i \rightarrow \underline{p}_i - q \underline{A}(\underline{r}_i, t) / c, \quad E_0 \rightarrow E_0 - q \sum_{i=1}^N \phi(\underline{r}_i, t).$$

For a static, homogeneous magnetic field B, we have

$$\phi = 0, \quad \underline{A}(\underline{r}_i, t) = \frac{1}{2} \underline{B} \times \underline{r}_i.$$

Working in the Coulomb gauge ($\nabla \cdot \underline{A} = 0$), we obtain

$$H = H_0 + \sum_{i=1}^N \frac{e}{mc} \underline{A}(\underline{r}_i) \cdot \underline{p}_i - \sum_{i=1}^N \frac{ie}{2mc} \underline{\sigma} \cdot (\underline{p}_i \times \underline{A}(\underline{r}_i)) \\ + \sum_{i=1}^N \frac{e^2}{2mc^2} \underline{A}^2(\underline{r}_i).$$

Now

$$\vec{\ell}_i = \vec{r}_i \times \vec{p}_i, \quad \vec{S}_i = \hbar \vec{\sigma}_i / 2, \quad \vec{B} = \vec{\nabla} \times \vec{A}$$

so H can be rewritten as

$$H = H_0 + \frac{e}{2mc} \sum_{i=1}^N (\vec{\ell}_i + 2\vec{S}_i) \cdot \vec{B} + \frac{e^2}{2mc^2} \sum_{i=1}^N A^2(\vec{r}_i).$$

For magnetic fields of 50 kilogauss or less, the third term in the above Hamiltonian is much smaller than the second term. We therefore neglect it.

Writing

$$\vec{L} = \sum_{i=1}^N \vec{\ell}_i, \quad \vec{S} = \sum_{i=1}^N \vec{S}_i, \quad B = B_z, \quad \vec{J} = \vec{L} + \vec{S},$$

we get

$$H = H_0 + \frac{eB}{2mc} (J_z + S_z).$$

Energy Eigenvalues of H

The shift in energy of the unperturbed eigenstates is given by first order perturbation theory (we work in the E_0, J, M basis):

$$\begin{aligned} \Delta E_0 &= \frac{eB}{2mc} \langle E_0, J, M | J_z + S_z | E_0, J, M \rangle \\ &= \frac{e\hbar B}{2mc} (M + \langle E_0, J, M | S_z | E_0, J, M \rangle / \hbar). \end{aligned}$$

The matrix element of S_z can be simplified with the help of the Wigner-Eckart theorem (Merzbacher, 1970):

$$\begin{aligned} \langle J, M | \underline{S}_z | J, M \rangle &= 0 & J = 0 \\ &= \langle J, M | \underline{J} \cdot \underline{S} | J, M \rangle \langle J, M | \underline{J}_z | J, M \rangle / \hbar^2 J(J+1) & J \neq 0 \end{aligned}$$

Now $\underline{J} \cdot \underline{S}$ is a scalar, so its matrix element cannot depend on M .

Therefore we have

$$\Delta E_o = \frac{e\hbar B}{2mc} M g_J$$

where

$$\begin{aligned} g_J &= 1 & J = 0 \\ &= 1 + \langle J, M | \underline{J} \cdot \underline{S} | J, M \rangle / \hbar^2 J(J+1) & J \neq 0 \end{aligned}$$

If L, S coupling is valid we get

$$\begin{aligned} g_J &= 1 & J = 0 \\ &= 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \end{aligned}$$

Energy Eigenstates of H

The eigenstates of H can be expanded in the eigenstates of H_o by the use of first order perturbation theory. In general, states of the same M , and J 's which differ by 0 or ± 1 will be mixed by the interaction Hamiltonian. In Scandium, the energy difference between states of different J is much larger than the Zeeman splitting. Consequently,

the mixing of states of different J is small and will be neglected.

We therefore consider the eigenstates of H to coincide with those of H_0 in the discussion that follows.

Radiative Transitions between Eigenstates of H

The transition probability per unit time per unit solid angle is given (to first order in H_{int}) by Fermi's Golden Rule (Sakurai, 1967):

$$\frac{d\omega}{d\Omega} = \frac{2\pi}{h} |\langle f | H_{int} | i \rangle|^2 \rho(\hbar\omega)$$

where we require

$$E_f - E_i = \hbar\omega$$

In our case

$$H_{int} = \sum_{i=1}^N \tilde{j} \cdot \tilde{A} d^3 \tilde{r}_i$$

with

$$\tilde{A} = c \sqrt{\hbar/2\pi\omega} \hat{e} \exp i(\tilde{k} \cdot \tilde{r} - \omega t)$$

$$\tilde{j} = -\frac{e}{mc} \sum_{i=1}^N \left[\tilde{p}_i + \frac{i}{\hbar} (\tilde{p}_i \times \tilde{s}_i) \right]$$

($\hat{e}$ is the photon polarization vector.)

Electric Dipole Approximation

We make the following approximations:

$$\lambda_{\text{photon}} = 1/|k| \gg r_{\text{atom}}$$

so

$$\underline{A} \cong c \sqrt{\hbar/2\pi\omega} \hat{\underline{e}} \quad (\text{dipole transition})$$

$$\underline{j} \cong -e/mc \underline{p}_i \quad (1 \text{ electron transition, neglect magnetic dipole}) .$$

Using the above we get

$$\frac{d\omega}{d\Omega} = \frac{e^2 \omega^3}{8\pi \hbar c} \left| \langle f | \underline{r} \cdot \hat{\underline{e}} | i \rangle \right|^2 .$$

Explicitly

$$|i\rangle = |E_i, J_i, M_i\rangle \quad |f\rangle = |E_f, J_f, M_f\rangle$$

with

$$E_i = E_{oi} + \frac{ehB}{2mc} M_i g_{Ji} \quad E_f = E_{of} + \frac{ehB}{2mc} M_f g_{Jf} .$$

Selection Rules

The Wigner-Eckart theorem tells us that $\langle i | \underline{r} | f \rangle$ is non-zero only for $\Delta J = 0, \pm 1$, $\Delta M = 0, \pm 1$. Also, since $\underline{r}$ is odd under parity, $|i\rangle$ and $|f\rangle$ must have opposite parity.

Polarization

The polarization of the emitted radiation is contained in the matrix element $\langle f | \underline{r} \cdot \hat{\underline{e}} | i \rangle$. If we limit ourselves to viewing photons emitted perpendicularly to B ($\theta = \pi/2$), the results are easily derived. (See Fig. 1).

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Fig. 1. Polarization Geometry

$$\hat{\epsilon}_{\parallel} = \cos \theta \hat{x} - \sin \theta \hat{z} = -\hat{z} \quad \hat{\epsilon} = \hat{y}$$

$$\underline{r} = x\hat{x} + y\hat{y} + z\hat{z} = \left(\frac{r_+ + r_-}{2}\right) \hat{x} + \left(\frac{r_+ - r_-}{2i}\right) \hat{y} + r_o \hat{z}$$

|| case (π polarization)

$$\underline{r} \cdot \hat{\epsilon}_{\parallel} = -r_o \Rightarrow \Delta M = 0$$

⊥ case (σ polarization)

$$\underline{r} \cdot \hat{\epsilon}_{\perp} = \left(\frac{r_+ - r_-}{2i}\right) \Rightarrow \Delta M = \pm 1$$

Intensity

The intensity of the emitted radiation is proportional to

$$|\langle f | \underline{r} \cdot \hat{\epsilon} | i \rangle|^2$$

This quantity can be simplified by the application of the Wigner-Eckart theorem. We derive one case, $\Delta J = 0$, $M \rightarrow M \pm 1$, and list the complete results in Tables 1 and 2.

The matrix elements of the raising and lowering operators are given in most quantum mechanics textbooks (Merzbacher, 1970):

$$\langle J, M-1 | r_+ | J, M \rangle = 0$$

$$\langle J, M+1 | r_- | J, M \rangle = 0$$

$$\langle J, M+1 | r_+ | J, M \rangle = \sqrt{(J-M)(J+M+1)} \quad \langle J || r_+ || J \rangle$$

$$\langle J, M-1 | r_- | J, M \rangle = \sqrt{(J+M)(J-M+1)} \quad \langle J || r_- || J \rangle$$

so we get

Table 1. Electric dipole transition intensities ($\theta = \pi/2$).

$J \rightarrow J$	$\sigma : M \rightarrow M + 1$	$\frac{1}{4} (J \mp M) (J \pm M + 1)$
	$\pi : M \rightarrow M$	M^2
$J \rightarrow J - 1$	$\sigma : M \rightarrow M \pm 1$	$\frac{1}{4} (J \mp M) (J \mp M - 1)$
	$\pi : M \rightarrow M$	$(J^2 - M^2)$
$J \rightarrow J + 1$	$\sigma : M \rightarrow M \pm 1$	$\frac{1}{4} (J \pm M + 1) (J \pm M + 2)$
	$\pi : M \rightarrow M$	$(J + 1)^2 - M^2$

Table 2.

J_i	J_f	Relative Intensities (π components in parenthesis)
$1/2 \rightarrow 1/2$		1, (1), (1), 1
$1/2 \rightarrow 3/2$		3, 1, (4), (4), 1, 3
$3/2 \rightarrow 1/2$		1, 3, (4), (4), 3, 1
$3/2 \rightarrow 3/2$		3, 4, 3, (9), (1), (1), 3, 4, 3
$3/2 \rightarrow 5/2$		10, 6, 3, 1, (8), (12), (12), (8), 1, 3, 6, 10
$5/2 \rightarrow 3/2$		1, 3, 6, 10, (8), (12), (12), (8), 10, 6, 3, 1
$5/2 \rightarrow 5/2$		5, 8, 9, 8, 5, (25), (9), (1), (1), (9), (25), 5, 8, 9, 8, 5
$5/2 \rightarrow 7/2$		21, 15, 10, 6, 3, 1, (12), (20), (24), (24), (20), (12), 1, 3, 6, 10, 15, 21
$7/2 \rightarrow 5/2$		1, 3, 6, 10, 15, 21, (12), (20), (24), (24), (20), (12), 21, 15, 10, 6, 3, 1
$0 \rightarrow 1$	1	1 (2) 1
$1 \rightarrow 0$		
$1 \rightarrow 1$		1, 1, (2), (0), (2), 1, 1
$2 \rightarrow 1$		1, 3, 6, (6), (8), (6), 6, 3, 1
$1 \rightarrow 2$		6, 3, 1, (6), (8), (6), 1, 3, 6
$2 \rightarrow 2$		2, 3, 3, 2, (8), (2), (0), (2), (8), 2, 3, 3, 2

 $\lambda \rightarrow$

$$g_f > g_i$$

$$\left| \langle J, M \pm 1 | \frac{\mathbf{r}_+ - \mathbf{r}_-}{2i} | J, M \rangle \right|^2 = \frac{1}{4} (J \mp M) (J \pm M + 1) \left| \langle J \| \frac{\mathbf{r}_+ - \mathbf{r}_-}{2i} \| J \rangle \right|^2 .$$

Splitting of Spectral Lines

Because the magnetic field lifts the degeneracy in M , spectral lines are split when a magnetic field is applied:

$$\Delta E = \Delta E_0 + \epsilon (g_{J_i} M_{J_i} - g_{J_f} M_{J_f}) \quad , \quad \epsilon \equiv ehB/2mc > 0 \quad .$$

For emission, $\Delta E = E_f - E_i < 0$, giving

$$\frac{1}{\Delta E} \cong \frac{1}{\Delta E_0} \left[1 - \frac{\epsilon}{\Delta E_0} (g_{J_i} M_{J_i} - g_{J_f} M_{J_f}) \right]$$

and

$$\Delta \lambda = \lambda - \lambda_0 \cong \frac{\epsilon \lambda_0^2}{hc} (g_{J_f} M_{J_f} - g_{J_i} M_{J_i}) \quad .$$

For electric dipole transitions $\Delta J = 0, \pm 1$ so $M_{J_f} = M_{J_i}, M_{J_i} \pm 1$:

$$J : M \rightarrow M$$

$$\Delta \lambda = \frac{\epsilon \lambda_0^2}{hc} M (g_{J_f} - g_{J_i}) \quad -J_{\min} \leq M \leq J_{\min}$$

$$J : M \rightarrow M \pm 1$$

$$\Delta \lambda = \frac{\epsilon \lambda_0^2}{hc} \left[M (g_{J_f} - g_{J_i}) \pm g_{J_f} \right]$$

$$\text{i) } J_i < J_f$$

$$-J_i \leq M \leq J_i$$

$$\text{ii) } J_i = J_f$$

$$-J_f \mp 1 \leq M \leq J_f \mp 1, \quad M \rightarrow M \pm 1$$

$$\text{iii) } J_i > J_f$$

$$-J \leq M \leq J - 1, \quad M \rightarrow M + 1$$

$$-J + 1 \leq M \leq J, \quad M \rightarrow M - 1$$

Using the above, we construct Fig. 2.

Define $\Lambda = \frac{e\hbar B}{2mc} \frac{\lambda_0^2}{hc}$, $\Delta g = |g_i - g_f|$

$$J_i = J_f$$

$$J_i \neq J_f$$

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Fig. 2. Typical Zeeman Patterns

CHAPTER III

DESCRIPTION OF EQUIPMENT

Spectrograph

This experiment made use of a Jarell-Ash 3.4 meter Ebert spectrograph (see Fig. 3). Photons enter the spectrograph's entrance slit, strike a 15 cm wide by 6.3 cm high concave mirror (at normal incidence), are reflected to a 18 cm by 6 cm plane grating, are diffracted back to a 41 cm by 6.3 cm concave mirror, and lastly reflected to the film holder. The holder can accommodate two 25 cm by 5 (or 10) cm glass film plates. The wavelength region observed is chosen by rotating the diffraction grating.

At large angles of incidence, the images of spectral lines at the film plate are slightly tilted. This is compensated for by rotating the entrance slit; the slit jaws are no longer parallel to the grating rulings.

The spectrograph is focused by moving the entrance slit parallel to the instrument's longest axis.

Magnet

We used a Spectromagnetic Industries water cooled electromagnet, along with its model TC 200-300 regulated power supply (see Fig. 4). This magnet is current regulated to 0.01%. The magnet and power supply both require 0.1 liter/sec water flow for cooling. Power consumption at full power is 60 kW. With Permendur tapered pole pieces, 10.16 cm diameter face and 2.86 cm gap, the magnet will produce up to 27 kG.

SIDE VIEW

θ = Angle of incidence

TOP VIEW

XBL 808-1819

Fig. 3. Spectrograph Geometry

ELECTROMAGNET

XBL 808-1813

Fig. 4. Electromagnet

Thorium Standards Lamp

Standards are provided by a thorium electrodeless lamp. The lamp is a 2 cm high by 0.5 cm diameter quartz capsule filled with thorium iodide. The discharge is excited by a Burdick model MW/200 microwave (2450 MHz) diathermy unit.

Scandium Source

We modified the standard sliding spark source to allow operation of the source in a magnetic field. To the author's knowledge, no published description of such a modified source exists.

The electrodes are held in place by a quartz spacer (see Fig. 5 and 6). The spark jumps between the two electrodes and the light escapes through the conical viewing hole. The light then passes through a large quartz window, which is attached to the pyrex envelope by black sealing wax. A 10 cm diffusion pump provides the vacuum.

The spark is powered by an LRC circuit (see Fig. 7). A d.c. power supply charges the capacitor C, typically to 1000 V. The repetition rate is chosen electronically. A mercury ignition switch closes the circuit and a current pulse flows through the source. The details of the power supply can be found in Van Deurzen (1973). The subject of sliding sparks is dealt with in the review article by Beverly (1978).

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Fig. 5a. Spark Source Side View.

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Fig. 5b. Spark Source Side View.

Fig. 5c. Spark Source Top View.

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XBL 808-1820

Fig. 6. Quartz spacer.

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Fig. 7. Spark Source Circuit

CHAPTER IV

EXPERIMENTAL PROCEDURE

Grating

In order to get the greatest possible dispersion, we selected an 18 cm wide grating, 295 lines/mm, blaze angle 56° . This grating gives a plate factor $d\lambda/ds$ of 0.4 Å/mm (in 10th order) in the 2000 to 5000 Å region. The resolving power is given by $\lambda/\Delta\lambda = m$ 53100, where m is the order.

Filters

Preliminary exposures at 5 Å/mm showed the Scandium source to be very dim, particularly when operated in a strong magnetic field. To keep exposure times within reason, we decided not to use a pre-disperser. Our pre-disperser cuts intensity by 85%. To aid in the separation of orders, we used filters, which only reduced intensity by 20%.

We decided to look at the ten strongest lines of Sc I, II, III, IV, for a total of 40 lines. These lines are found in the region 2400 to 4500 Å. We chose a Dow Corning 0-52 filter for the region 3500 to 4700 Å, and a 7-54 filter for the 2350 to 4050 Å region. The Thorium standards were photographed in 13th order through a 4000 Å high pass and a 4500 Å low pass Optics Technology interference filters.

HP-67 Program

In order to find the optimum settings for maximum coverage of the Scandium I, II, III, IV, spectra, a table of λ and $d\lambda/ds$ vs. θ and m (derived from data) was approximated by a set of polynomial equations. The following least squares cubic fits were made:

$m\lambda(\theta)$	$md\lambda/ds(\theta)$	$md\lambda/ds(m\lambda)$
$\theta(m\lambda)$	$\theta(md\lambda/ds)$	$m\lambda(md\lambda/ds)$

(See Table 3).

In calculating the least squares cubic fits, the author tried the most straight forward (and naive) method: inverting a 4 by 4 matrix. This was tried on the Hewlett Packard HP-67 hand held programmable calculator, and then the CDC 7600 (about as far away from a hand held calculator as one can get.) Both trys gave nonsense results. It turns out that the matrix in question is very close to a submatrix of the infamous Hilbert matrix (Forsythe, 1968), which looks reasonable but is in fact exceedingly ill conditioned. Using the IBM routine MATINV (Bevington, 1969) required double precision on the CDC 7600, which has 60 bit words!

Also fit (by eye) was a set of points giving the brightest order for a given wavelength.

The coefficients obtained were used in a program written for the HP-67. We key in λ and get out θ , m , λ_{LO} , λ_{HI} , $d\lambda/ds$, λ_{BPLO} , λ_{BPHI} where λ_{BPLO} to λ_{BPHI} is the bandpass needed to pass only one order. Also available is $d^2\lambda/ds^2(\lambda)$, $\theta(\theta)$, and the bandpasses for 3, 5, 7, etc. orders.

Six different grating settings were needed to provide the desired coverage. The proper slit rotation and focus position were found. (See Table 4).

Table 3. 56 degree grating

$$y = ax^3 + bx^2 + cx + d$$

$y = m \lambda (\text{\AA})$	$x = \theta (\text{deg})$	$y = m d \lambda / ds (\text{\AA}/\text{mm})$	$x = \theta (\text{deg})$
$a = 0.32407718$		$a = 5.20837754 \times 10^{-5}$	
$b = -64.533269$		$b = -9.78578990 \times 10^{-3}$	
$c = 4824.4661$		$c = 0.46422454$	
$d = -69487.112$		$d = 1.0047757$	
error in $y = \pm 3$		$\Delta y = \pm 5 \times 10^{-4}$	

$y = \theta (\text{deg})$	$x = m \lambda (\text{\AA})$	$y = \theta (\text{deg})$	$x = m d \lambda / ds (\text{\AA}/\text{mm})$
$a = -3.80756158 \times 10^{-13}$		$a = -0.15256238$	
$b = 9.93751377 \times 10^{-8}$		$b = 2.1206180$	
$c = -5.94157920 \times 10^{-3}$		$c = -16.570502$	
$d = 145.18771$		$d = 108.08841$	
$\Delta y = \pm 0.004$		$\Delta y = \pm 0.004$	

$y = m d \lambda / ds (\text{\AA}/\text{mm})$	$x = m \lambda (\text{\AA})$	$y = m \lambda (\text{\AA})$	$x = m d \lambda / ds (\text{\AA}/\text{mm})$
$a = 1.61109805 \times 10^{-13}$		$a = -248.42626$	
$b = -3.41966088 \times 10^{-8}$		$b = 3305.8655$	
$c = 2.08290283 \times 10^{-3}$		$c = -18443.969$	
$d = -32.412037$		$d = 97808.065$	
$\Delta y = \pm 0.001$		$\Delta y = \pm 7$	

(deviations quoted are deviations from Van Deurzen's table)

Table 4. Expense information

θ	Film	Filter B.P.	LO	λ MID	Hi	Slit Rotate	Slit Focus	Orders Appearing
58.73	F	3500-4700	4277	4378	4473	5.25°	17.5 mm	12-16
57.00	F	3500-4700	4191	4296	4396	5.25°	17.5 mm	12-16
59.75	103a 0	2350-4050	4326	4424	4517	5.25°	17.5 mm	14-24
58.09	103a 0	2350-4050	4246	4348	4445	5.25°	17.5 mm	14-24
58.87	103a 0	2350-4050	4284	4384	4479	5.25°	17.5 mm	14-24
59.89	103a 0	2350-4050	4333	4430	4523	5.25°	17.5 mm	14-24

Optics

The setups for the illumination of the slit by the Sc and Th sources are given in Fig. 8. As long as the grating is fully illuminated, the irradiance at the film plate is independent of what optics are used in front of the slit (assuming, of course, 100% transmittance for the optical elements). The reason for the conical viewing hole in the spacer and the flared glass envelope is to provide a brighter image at the slit. This is a great aid in maintaining proper alignment. The Scandium image was magnified because the viewing hole in the spacer is very small (1.3 mm diameter).

Magnetic Field

The magnetic field strength was measured with a Bell 620 Hall effect gaussmeter. The results (reproducible to 0.05%) are given in Table 5. The magnetic field did not vary more than 0.1% throughout a 1 cm^3 volume in the center of the magnet. We operated at 210 amps, giving $B = 27243$ Gauss.

Exposures

The Thorium lamp was so bright that a 1 sec exposure was sufficient. The Scandium source was operated at a pulse rate of 3 Hz. This rate was chosen so as not to overload the diffusion pump. At all six settings of the grating, exposures were taken with inductance $L = 133 \text{ } \mu\text{H}$, capacitance $C = 25 \text{ } \mu\text{F}$, and resistance $R = 5 \text{ } \Omega$. This gave a peak current $I_{\text{max}} = 250 \text{ amp}$, and a duration $\Delta t = 200 \text{ } \mu\text{sec/pulse}$. These values were chosen to accentuate the Sc III spectrum (Van Deurzen, 1973).

4.5 cm dia.
10 cm F.L. UV quartz lens

magnification = 1

THORIUM LAMP

4.5 cm dia.
15 cm F.L. UV quartz lens

magnification = 3

SCANDIUM SOURCE

Fig. 8. Optical Geometry

XBL 808-1810

Table 5. Magnetic field strength vs. magnetic current.

Current (amp)	B (gauss)
30	9518
60	18667
90	24042
120	25616
150	26313
180	26814
210	27243
240	27614
270	27950
300	28250

At the grating angle setting of 58.09° , a plate was taken with peak current $I_{\max} = 150$ amp, duration $\Delta t = 400$ μ sec. At grating angle 58.87° , another plate was taken with peak current $I_{\max} = 500$ amp, duration $\Delta t = 100$ μ sec. This was done to accentuate the spectra of Sc I, II, and Sc IV, respectively. The source would not operate in a magnetic field with $I_{\max} < 150$ amp. Above 500 amp, the source would quickly go out due to the accumulation of debris in the spark path. A 35 micron slit width was used throughout.

Typical exposure times are 1 min for Sc when $B = 0$. When $B = 27000$ Gauss, the intensity of the source is greatly reduced. It is further reduced by the Nicol prism polarizer which is used to separate the σ and π components of the Sc Zeeman spectrum. Exposures usually run 30 min for each component of polarization.

Film

We used Kodak 103a F plates in the region 3500 to 4700 Å, and Kodak 103a0 plates in the region 2350 to 4050 Å. The film was developed for 5 min in Kodak D-76, put in a dilute acetic acid stop bath for 30 sec, then placed in Kodak Rapid Fix for 3 min. The plates were then washed for 10 min in ordinary tap water.

CHAPTER V

DATA ANALYSIS

Wavelength Determination

The plates are measured by hand on a Grant optical comparator. This instrument measures positions to ± 2 microns. Press a button and a punched card is produced containing the position and any other auxiliary information which may be put in manually, such as suspected wavelength, lineshape, intensity, etc.

The cards produced are then run through our group's program POLYSIG, which fits λ vs. position with a 6th degree polynomial curve. Typically 30 Thorium lines per plate are required to make a good fit. We use the secondary Thorium standards as proposed by Giachetti et al. (Giachetti, 1970).

Order Searching

The output of POLYSIG assigns a wavelength to each measured line, assuming that the line is observed in 13th order (same order as Thorium). To find the true wavelength, we must search different orders. All the brightest lines of Sc I, II, III, IV are known, so this task is not impossible. A list was made up of the following spectral lines:

C I - 20	II - 30	III - 28	IV - 15	
Sc I - 27	II - 44	III - 33	IV - 34	V - 24
Si I - 21	II - 33	III - 36	IV - 14	
Sc I - 46	II - 46	III - 11	IV - 17	

The wavelengths were obtained from the CRC Handbook (Weast, 1978). The list was compared with the output of POLYSIG by the author's modestly named program BLSEARCH. The details of searching are given in Appendix I. The results were such that virtually every unknown line was identified as a Scandium or impurity line. A tolerance of 0.1 Å was used for identification because the Sc lines of the Zeeman spectrum are very broad. The number of multiple identifications was nil. Also, the expected number of accidental coincidences was much lower than the actual number identified. This is possible only because of the low density of lines in the Sc spectra. The above method would fail miserably if applied to Uranium, for example.

Zeeman Data

In our chapter on the theory of the Zeeman effect, we show that the separation (in wavelength) between individual σ or π components is given by $(ehB/2mc) \lambda_0^2/hc |g_1 - g_2|$ and that the separation of the centers of the two σ groups is given by $(ehB/2mc) \lambda_0^2/hc (g_1 + g_2/2)$. A measurement of the distances between Zeeman components, together with the dispersion, $d\lambda/ds$ evaluated at λ_0 , allows one to calculate g_1 and g_2 .

In general, the number of independent distances measured in a given Zeeman pattern will be greater than two, leading to an over determined set of equations for g_1 and g_2 . A least squares technique was used to solve for g_1 and g_2 . This problem is examined in Appendix II.

The Zeeman pattern separations are measured three times by hand on a Grant optical comparator. The separations (in mm) are recorded on punch cards. The dispersion at a given wavelength is obtained by taking the derivative of the sixth degree polynomial for $\lambda(s)$ provided by the program POLYSIG. The resulting polynomial is then truncated after the linear term, giving an expression for $d\lambda/ds$ that is linear in s .

The actual calculations outlined in Appendix II are done on a Hewlett-Packard HP-67 calculator.

Discussion of Zeeman Results

For Sc I, the level 41474.84 was assigned the value $J = 5/2$ in the literature. Our work shows that $J = 3/2$ is the correct value.

Our data for the singlet levels of Sc II did not suffice to determine the g values uniquely (an undetermined set of equations). We therefore used Neufeld's value of g for the level a^1D_2 to determine the heretofore unknown g values for b^1D_2 and $z^1F^o_3$. The asterisks in Table 6IIb are to remind the reader of this fact.

The results for Se III are not as clean as the results for Sc I and II. Consequently, we can only quote values of $\bar{g}$ for various pairs of transitions. On one plate, the transition $4p^2P^o_{1/2}$ to $4s^2S_{1/2}$ was resolved into the individual Zeeman components. The pattern clearly showed that $M_J = 0$, $J \geq 2$. The quotation marks in Table 6III are to remind the reader of this fact.

The errors in the quoted g values are unfortunately rather large. This is due in part to the fact that we used a 3.4 m rather than 10 m spectrograph. The values for g given in Table 6 are claimed to have errors of 2 percent.

XBL 808-1818

Fig. 9. Sc I Doublet

XBL 808-1817

Fig. 10. Sc III Doublet.

Fig. 11. Sc II Singlet.

XBL 808-1816

Fig. 12. Sc II Triplet.

XBL 808-11546

XBL 808-1815

Fig. 13. Sc I Quartet.

Table 6.

Observed Transitions

D	Ion	Wavelength	M	Initial	Final	δ_{LS} I	δ_{LS} F	Pattern	
								Pre	Obs
1	SC1	4359.08	13	24P05/2	{F4P3/2}	1.6000	1.7333	3	3
2	SC1	4082.40	14	(Y2P01/2+)	AZD5/2	0.6667	1.2000	5	5
3	SC1	4054.55	14	(Y2P01/2+)	AZD3/2	0.6667	0.8000	5	5
4	SC1	4023.69	14	Y2D05/2	AZD5/2	1.2000	1.2000	4	4
5	SC1	4020.40	14	Y2D03/2	AZD3/2	0.8000	0.8000	4	4
6	SC1	3996.61	14	Y2D05/2	AZD3/2	1.2000	0.8000	3	3
7	SC1	3911.81	14	(Y2F07/2)	AZD5/2	1.1429	1.2000	2	4
8	SC1	3907.49	14	Y2F05/2	AZD3/2	0.8571	0.8000	3	4
9	SC1	3273.63	17	X2P03/2	AZD5/2	1.3333	1.2000	2	4
10	SC1	2988.95	19	Y2D03/2	AZD5/2	0.8000	1.2000	3	4
1	SC2	4670.40	12	(Z1F03)	(B1D2)	1.0000	1.0000	4	4
2	SC2	4415.56	13	Z3F02	A3F2	0.6667	0.6667	4	4
3	SC2	4400.37	13	Z3F03	A3F1	1.0833	1.0833	4	4
4	SC2	4374.46	13	Z3F04	(A3P4)	1.2500	1.2500	4	4
5	SC2	4354.61	13	Z3F04	A3F3	1.2500	1.0833	3	4
6	SC2	4325.01	13	Z3D01	A3F2	0.5000	0.6667	3	4
7	SC2	4320.74	13	Z3D02	A3F3	1.1667	1.0833	2	4
8	SC2	4314.09	13	Z3D03	(A3P4)	1.3333	1.2500	2	4
9	SC2	4305.71	13	Z3D02	A3F2	1.1667	0.6667	1	1
10	SC2	4294.77	13	Z3D03	A3F3	1.3333	1.0833	1	1
11	SC2	4246.83	13	Z3D02	A1D2	1.0000	1.0000	4	4
12	SC2	3651.80	16	Z3P02	A3D2	0.6667	1.1667	1	1
13	SC2	3645.31	15	Z3F03	A3D3	1.0833	1.3333	1	1
14	SC2	3642.79	15	Z3F02	A3D1	0.6667	0.5000	3	4
15	SC2	3630.75	15	Z3F03	A3D2	1.0833	1.1667	2	4
16	SC2	3613.84	16	Z3F04	A3D3	1.2500	1.3333	2	4
17	SC2	3590.48	16	Z3D02	A3D3	1.1667	1.3333	3	3
18	SC2	3589.64	16	Z3D01	A3D2	0.5000	1.6667	3	3
19	SC2	3580.94	16	Z3D01	A3D1	0.5000	0.5000	4	4
20	SC2	3576.35	16	Z3D02	A3D2	1.1667	1.1667	4	4
21	SC2	3572.53	16	Z3D03	A3D3	1.3333	1.3333	4	4
22	SC2	3567.70	16	Z3D02	A3D1	1.1667	0.5000	3	3
23	SC2	3558.55	16	Z3D03	A3D2	1.3333	1.6667	3	3
24	SC2	3535.73	16	Z1P01	A1D2	1.0000	1.0000	4	4
25	SC2	3372.15	17	Z1P02	A3D3	1.3333	1.3333	4	4
26	SC2	3368.95	17	Z3P01	A3D2	1.5000	1.1667	2	5
27	SC2	3361.94	17	Z3P00	A3D1	1.0000	0.5000	2	4
28	SC2	3359.68	17	Z3P02	A3D2	1.1667	1.1667	4	1
29	SC2	3353.73	17	(Z1F03)	A1D2	1.0000	1.0000	4	4
30	SC2	3343.28	17	(E3D3)	Z3P04	1.3333	1.2500	2	4
31	SC2	3065.11	19	(E3G5)	Z3P04	1.2000	1.2500	2	1
1	SC3	4309.47	13	(5G2G7/5+)	(4F2F05/2+)	0.8889	0.8571	5	4
2	SC3	4068.66	14	(4F2F07/2)	(4D2D5/2)	1.1429	1.2000	2	4
3	SC3	4061.21	14	(4F2F05/2)	(4D2D3/2)	0.8571	0.8000	3	1
4	SC3	2734.05	21	(4P2P01/2)	(4S2S1/2)	0.6667	2.0000	1	1
5	SC3	2699.07	21	(4P2P03/2)	(4S2S1/2)	1.3333	2.0000	2	1

 1 2 3 4 5 other

Zeeman Patterns
 M = order

Table 6I. Sc I.

Configuration	Designation	Level	Observed g
$3d4s^2$	$a^2D_{3/2}$	0.00	1.027
	$a^2D_{5/2}$	168.34	0.989
$3d4s(a^3D)4p$	$z^4P^o_{5/2}$	18571.38	1.321
$3d4s(a^3D)4p$	$y^2D^o_{3/2}$	24866.19	0.580
	$y^2D^o_{5/2}$	25014.20	1.423
$3d4s(a^3D)4p$	$y^2F^o_{5/2}$	25584.63	0.801
	$y^2F^o_{7/2}$	25724.68	1.139
$4s^2(a^1S)4p$	$x^2P^o_{3/2}$	30706.63	1.203
$3d^2(a^3F)4p$	$x^2D^o_{3/2}$	33614.87	1.071
$3d4s(a^3D)4d$	$f^4P_{3/2}$	41474.84	0.935

Table 6IIa. Sc II.

Configuration	Designation	Level	Observed g
3d(² D)4s	a ³ D ₁	0.00	0.867
	a ³ D ₂	67.73	1.078
	a ³ D ₃	177.75	1.530
3d ²	a ³ F ₂	4802.82	1.236
	a ³ F ₃	4883.56	1.053
	a ³ F ₄	4987.76	0.944
3d(² D)4p	z ³ F ^o ₂	27443.73	0.404
	z ³ F ^o ₃	27602.45	0.932
	z ³ F ^o ₄	27841.28	1.522
3d(² D)4p	z ³ D ^o ₁	27917.79	0.448
	z ³ D ^o ₂	28021.27	1.506
	z ³ D ^o ₃	28161.12	1.311
3d(² D)4p			--
	z ³ P ^o ₁	29742.16	0.814
3d(² D)5s	e ³ D ₃	57743.88	0.768
			--

Table 6IIb. Sc II.

Configuration	Designation	Level	Observed g
3d(2D)4s	a^1D_2	2540.98	*
3d ²	b^1D_2	10944.60	0.989
3d(² D)4p	$z^1D^o_2$	26081.34	*
3d(² D)4p	$z^1P^o_1$	30815.70	*
3d(² D)4p	$z^1F^o_3$	32350.02	1.020

Table 6III. Sc III.

Transition	λ	$\bar{g}$
1	4309.47	not meaningful, too many levels mixed together
2	4068.66	1.068
3	4061.22	0.776
4	2734.05	" $4s^2S_{1/2} - 4p^2P^o_{1/2}$ " $g \approx 1.721$ $g \leq 1.435$ $\Delta J = 0, J \geq 2$
5	2699.07	0.999

CHAPTER VI

CONCLUSION

The use of the sliding spark in a magnetic field can extend the results obtained with an electrodeless lamp. In the first and second spectrum, transitions are observed in the sliding spark spectrum that cannot be seen in the arc spectrum. The third spectrum cannot be seen in an arc. Stark broadening diminishes the usefulness of the third spectrum, but some information can still be gained from the Zeeman pattern. The fourth spectrum disappears when the sliding spark is placed in a magnetic field.

Suggestions for further research include spacer and electrode geometry optimization for individual ionization states, along with circuit parameter optimization. Water cooling of the electrodes might also be useful.

APPENDIX I

WAVELENGTH IDENTIFICATION

The problem of searching for coincidences between two wavelength lists raises some theoretical questions to which we now turn.

Sampling from a Distribution

Consider a random variable x , distributed according to the probability distribution $f(x)$, with $0 \leq f(x)$, $\int_{-\infty}^{\infty} f(x)dx = 1$. The probability that a single observation of x will lie between x_1 and x_2 is given by

$$p = \int_{x_1}^{x_2} f(x)dx .$$

The probability that n out of N observations will lie in the region x_1 to x_2

$$P(n, N, x_1, x_2) = \binom{N}{n} p^n (1-p)^{N-n} .$$

The expected number observed between x_1 and x_2 is

$$\langle n \rangle = \sum_{n=1}^N n P(n, N, x_1, x_2) = Np$$

and the variance (defined as $\langle n^2 \rangle - \langle n \rangle^2$) is given by

$$\text{Var}(n) = Np(1-p)$$

(Bevington, 1969).

Some Specific Examples (see Fig. 14),

a) Small Bin

If $x_2 - x_1$ is sufficiently small, then

$$p \approx (x_2 - x_1) f(x) = \Delta x f(x) \quad \text{where } x_1 < x < x_2$$

$$\langle n \rangle \approx N \Delta x f(x)$$

$$\text{Var}(n) \approx N \Delta x f(x) \left[1 - \Delta x f(x) \right] \approx N \Delta x f(x) \quad .$$

b) Uniform Distribution

$$f(x) = 1/D \text{ for } x_{\min} < x < x_{\max}, \quad D = x_{\max} - x_{\min} \\ = 0 \quad \text{otherwise}$$

then

$$p = \Delta x / D \quad (x_{\min} < x_1, \quad x_2 < x_{\max})$$

$$\langle n \rangle = N \Delta x / D$$

$$\text{Var}(n) = N \Delta x / D (1 - \Delta x / D) \quad .$$

c) Triangular Distribution

$$f(x) = (1 - |x|/B)/2B \text{ for } |x| < B \\ = 0 \quad \text{otherwise}$$

then

$$p = (\Delta x / B)(1 - \bar{x}/B) \quad , \quad \bar{x} = (x_1 + x_2)/2 \quad , \quad 0 < x_1, x_2 < B$$

$$\langle n \rangle = (N \Delta x / B)(1 - \bar{x}/B)$$

$$\text{Var}(n) = (N \Delta x / B)(1 - \bar{x}/B) \left[1 - (\Delta x / B)(1 - \bar{x}/B) \right] \quad .$$

a) Small bin

b) Uniform distribution

c) Triangular distribution

Fig. 14. Some Examples

XBL 808-1826

Significance of the Triangular Distribution

Let the random variables x and y be distributed according to distributions $f(x)$ and $g(y)$, respectively. Then $w \equiv x+y$ and $x \equiv x-y$ are distributed according to

$$h(w) = \int_{-\infty}^{\infty} f(x)g(w-x)dx$$

$$j(x) = \int_{-\infty}^{\infty} f(x)g(x-z)dx$$

(Mood, 1974).

If $f(x)$ and $g(y)$ are uniform distributions, the above integrals give triangular distributions for $x+y$ and $x-y$.

Coincidence Searching

Consider the problem of searching for coincidences between two lists of wavelengths. Let list 1 have N_1 members, list 2, N_2 members. Further assume that both lists are uniformly distributed in the bandpass delimited by $\lambda_{\min}$, $\lambda_{\max}$. In this case, the number of expected coincidences is given by the preceding example c):

$$\langle n \rangle = 2N_1N_2 \frac{\delta\lambda}{\Delta\lambda} \left(1 - \frac{\delta\lambda}{\Delta\lambda} \right) \quad (\delta\lambda \equiv \lambda_{\max} - \lambda_{\min})$$

where we require $|\lambda_1 - \lambda_2| < \delta\lambda$ for a coincidence. Also

$$\text{Var}(n) = \langle n \rangle \left[1 - \frac{\delta\lambda}{\Delta\lambda} \left(1 - \frac{\delta\lambda}{2\Delta\lambda} \right) \right] .$$

In most cases of interest, $|\delta\lambda/\Delta\lambda| \ll 1$, and the above expressions simplify to

$$\langle n \rangle \approx 2N_1 N_2 \delta\lambda / \Delta\lambda$$

$$\text{Var}(n) \approx \langle n \rangle .$$

This is a reflection of the fact that if the bins are chosen small enough, n is Poisson (rather than binomially) distributed.

A Possible Complication

If one of the two wavelength lists, list 1 say, is not uniformly distributed, what are $\langle n \rangle$ and $\text{Var}(n)$? Let λ_2 be uniformly distributed:

$$f(\lambda_2) = 1/\delta\lambda \quad \lambda_{\min} < \lambda < \lambda_{\max} \quad (\Delta\lambda \equiv \lambda_{\max} - \lambda_{\min})$$

$$= 0 \quad \text{otherwise} .$$

The probability p of a coincidence (of tolerance $\delta\lambda$) at $\lambda_1(i)$ is

$$p = 2\delta\lambda / \Delta\lambda$$

and the most probable number $\langle n_i \rangle$ is given by

$$\langle n_i \rangle = N_2 p = 2N_2 \delta\lambda / \Delta\lambda .$$

Thus the total number of expected coincidences is given by summing over the wavelengths in list 1:

$$\langle n \rangle = \sum_{i=1}^{N_1} \langle n_i \rangle = 2N_1 N_2 \delta\lambda / \Delta\lambda .$$

Similarly

$$\text{Var}(n) = \langle n \rangle .$$

We see that the results derived from more restrictive assumptions still hold, provided we stick to the case of a small bin centered about $\lambda_1 - \lambda_2 = 0$, and one of the two wavelength distributions is uniform. This is usually the case in practice.

Order Conversion

If the true order of the lines in list 1 (say) were not known, then searching for true coincidences with list 2 is more complicated. Assume that the wavelengths in list 1 have assumed order m , and lie between (assumed) wavelengths λ_{lmin} , λ_{lmax} . If we require the true wavelength to lie in the bandpass λ_{min} , λ_{max} , then the true order for a given λ_1 could range from

$$m_{LOW} = \text{IFIX} (m\lambda_{lmin} / \lambda_{max})$$

to

$$m_{HIGH} = \text{IFIX} (m\lambda_{lmax} / \lambda_{min} + 1)$$

inclusive, where IFIX(r) means take the integer part of r . Thus we get the following results:

$$\langle n \rangle \approx 2N_1 N_2 (\delta\lambda / \Delta\lambda) (m_{HIGH} - m_{LOW} + 1)$$

$$\text{Var}(n) \approx \langle n \rangle .$$

This is a slight over estimate for $\langle n \rangle$, since not all wavelengths of a given order will lie in the bandpass region. It is only guaranteed that some wavelengths of a given order will lie in the given bandpass.

TYPICAL DATA ARISING IN ORDER SEARCHING

XBL 808-1824

Fig. 15. Typical Data

Fig. 16. Typical Data.

XBL 808-1823

Fig. 17. Typical Data.

XBL 808-1825

Fig. 18. Typical Data.

XBL 808-1814

APPENDIX II

SOLVING LINEAR EQUATIONS

Consider the following set of equations in the unknowns $\{x_i\}$:

$$\begin{array}{ccccccc} A_{11} x_1 + A_{12} x_2 & \dots & + A_{1n} x_n & = & b_1 \\ A_{21} x_1 + A_{22} x_2 & \dots & + A_{2n} x_n & = & b_2 \\ \vdots & & & & \vdots \\ A_{m1} x_1 + A_{m2} x_2 & \dots & + A_{mn} x_n & = & b_m \end{array}$$

These equations can be rewritten in the following three compact ways:

$$1) \quad A\tilde{x} = \tilde{b}$$

with $A: V_n \rightarrow V_m$ a rectangular mbyn matrix, $\tilde{x}$ an n dimensional column vector, $\tilde{b}$ an m dimensional column vector

$$2) \quad \tilde{u}_i \cdot \tilde{x} = b_i \quad i = 1, 2, \dots, m$$

where $\tilde{u}_i = (A_{i1}, A_{i2}, \dots, A_{in}) \in V_n$

$$3) \quad \sum_{i=1}^n \tilde{v}_i x_i = \tilde{b}$$

with $\tilde{v}_i = (A_{1i}, A_{2i}, \dots, A_{mi}) \in V_m$.

Given A and $\tilde{b}$, we desire $\tilde{x}$. If A is square and nonsingular, we get the familiar result $\tilde{x} = A^{-1}\tilde{b}$. If A is not square or not of full rank, the situation is more complicated. The complications are two: i) there exists an $\tilde{x}$ (or several $\tilde{x}$'s) such that $A\tilde{x} = \tilde{b}$, or ii) there exists no $\tilde{x}$ such that $A\tilde{x} = \tilde{b}$. Case i) occurs when the column vectors

$\underline{u}_i$ do not span V_n . If this is so, we can pick any $\underline{x}_0$ in V_n that is not in the span of $\underline{u}_i$ and get $A\underline{x}_0 = \underline{0}$. The general solution is given by $\underline{x} = \underline{x}_0 + \underline{x}_1$ where $A\underline{x}_1 = \underline{b}$, and $\underline{x}_1$ is unique.

Case ii) occurs when the row vectors $\{\underline{v}_i\}$ do not span V_m (i.e., the range of A is a proper subset of V_m). If $\underline{b}$ is not in the span of $\{\underline{v}_i\}$, then there is no $\underline{x}$ such that $A\underline{x} = \underline{b}$. In this case we must be content with finding an $\underline{x}$ (or $\underline{x}$'s) that minimize $S \equiv (A\underline{x} - \underline{b}) \cdot (A\underline{x} - \underline{b})$. Setting $\nabla_{\underline{x}} S = 0$ we obtain

$$A^t A \underline{x} = A^t \underline{b}, \text{ where } A^t \text{ is the transpose of } A.$$

(Some tedious algebra shows that the range of $A^t A$ is identical to the range of A^t , so that a solution to the above equation always exists. See Halmos (1974)).

If A is of full rank, $A^t A$ is nonsingular, so

$$\underline{x} = (A^t A)^{-1} A^t \underline{b}.$$

If A is square and nonsingular we reproduce

$$\underline{x} = A^{-1} (A^t)^{-1} A^t \underline{b} = A^{-1} \underline{b}.$$

If A is not of full rank, we are back to case i), with the replacements $A \rightarrow A^t A$, $\underline{b} \rightarrow A^t \underline{b}$.

Application to the Zeeman Effect

The technique used in this work is an improvement over that reported in the literature (Vander Sluis (1956), Neufeld (1970)). We present an example using both methods: Vander Sluis-Neufeld's and ours for the case $J = 5/2 \rightarrow J = 3/2$.

We first consider Vander Sluis' method (see Fig. 19). We have

$$\begin{matrix} A' & \underline{x}' & = & \underline{b} \end{matrix}$$

$$\begin{pmatrix} 2 & 3 \\ 2 & 1 \\ 2 & -1 \\ 2 & -3 \\ 0 & 3 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} - \\ \Lambda g \\ \Lambda \Delta g \end{pmatrix} = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6 \end{pmatrix}$$

where $\Lambda \equiv \frac{e\hbar B}{2mc} \frac{\lambda_0^2}{nc}$

$2g = g_1 + g_2$

$\Delta g = |g_1 - g_2|$

$a, b, c, \dots$ in Å

or

$$\begin{matrix} A & \underline{x} & = & \underline{b} \end{matrix}$$

$$\begin{pmatrix} 4 & -2 \\ 2 & 0 \\ 0 & 2 \\ -2 & 4 \\ 3 & -3 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} g > \\ g < \end{pmatrix} = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6 \end{pmatrix} \cdot 1/\Lambda$$

where $g > = \max(g_1, g_2)$

$g < = \min(g_1, g_2)$

Now A is of full rank, so

$$A^T A = \begin{pmatrix} 34 & -26 \\ -26 & 34 \end{pmatrix} \quad (A^T A)^{-1} = \frac{1}{480} \begin{pmatrix} 34 & 26 \\ 26 & 34 \end{pmatrix}$$

so

Fig. 19. Zeeman Pattern Example.

$$\begin{pmatrix} g > \\ g < \end{pmatrix} = \frac{1}{\Lambda 480} \begin{pmatrix} 84 & 68 & 52 & 36 & 24 & 8 \\ 36 & 52 & 68 & 84 & -24 & -8 \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6 \end{pmatrix}$$

If we assume that the errors in the b_i are uncorrelated and equal, the theory of least squares tells us that

$$\text{Covar}(\tilde{x}) = \sigma_b^2 (A^T A)^{-1}.$$

In this example

$$\sigma_{g>}^2 = \sigma_{g<}^2 = \sigma_s^2 \frac{34}{480}.$$

The above method can be improved upon because it does not utilize all the information available. In this example, there are 11 independent pieces of data. The choice of what data to use to minimize the errors in g_1 and g_2 is not straight forward, as the following will show.

If we have n components in a Zeeman pattern, we have our choice of which of the $n(n-1)/2$ separations we will measure. Which separations to measure can be decided by looking at the problem $u_i \cdot \tilde{x} = b_i$, $i = 1 \dots m$. With $x_1 = g >$, $x_2 = g <$, and $b_i = s_i$, these equations describe a set of lines in the $(g >, g <)$ plane. See Fig. 20. If the equations for g are consistent, the three lines will meet at a point g^* . Errors in the s_i will make the equations inconsistent, and g^* will be the point that minimizes the sum of the distances squared from g^* to each line. If the u_i are almost collinear, the lines for g will be almost parallel.

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Fig. 20. $g^<, g^>$ plane.

This situation can lead to a very long, narrow covariance ellipse for $\underline{g}$, and therefore large errors for $\underline{g}$. One should choose the s_i so that the slopes of the lines for $\underline{g}$ are as varied as possible. In particular, for each line of slope s , one should find another line with slope as close to $-1/s$ as possible (i.e., perpendicular lines are best). This will keep the covariance ellipse as round as possible. When choosing between lines of the same slope but different s_i , choose the line with the larger s_i . The larger s_i has a smaller relative uncertainty (assuming constant σ_s^2 of course) and will therefore contribute less uncertainty to $s_i/|u_i|$, the perpendicular distance from the origin to the line for $\underline{g}$. This will be true because $|u_i|$ is proportional to s_i (if there is no error in s_i). We now illustrate the above abstract considerations with two examples.

Naive approach - more data $\neq$ better results

We try

$$\begin{pmatrix} 2 & 3 \\ 2 & 2 \\ 2 & 2 \\ 2 & 1 \\ 2 & 0 \\ 2 & 0 \\ 1 & 3 \\ 1 & 3 \\ 1 & 2 \\ 1 & 2 \end{pmatrix} \begin{pmatrix} x' \\ \Delta g \end{pmatrix} = \begin{pmatrix} s_1 \\ s_2 \\ s_2 \\ s_3 \\ s_4 \\ s_4 \\ s_8 \\ s_8 \\ s_9 \\ s_9 \end{pmatrix} \quad (\text{see Fig. 19})$$

or

$$\begin{array}{c}
 \mathbf{A} \\
 \left(\begin{array}{cc}
 4 & -2 \\
 3 & -1 \\
 3 & -1 \\
 2 & 0 \\
 2 & 0 \\
 1 & 1 \\
 1 & 1 \\
 7/2 & -5/2 \\
 7/2 & -5/2 \\
 5/2 & -3/2 \\
 5/2 & -3/2
 \end{array} \right)
 \end{array}
 \quad
 \begin{array}{c}
 \tilde{\mathbf{x}} = \tilde{\mathbf{b}} \\
 \begin{array}{c}
 g > \\
 g <
 \end{array}
 \mathbf{A} =
 \left(\begin{array}{c}
 s_1 \\
 s_2 \\
 s_2 \\
 s_2 \\
 s_3 \\
 s_4 \\
 s_4 \\
 s_4 \\
 s_8 \\
 s_8 \\
 s_9 \\
 s_9
 \end{array} \right)
 \end{array}$$

Thus

$$\begin{array}{c}
 \mathbf{A}^T \mathbf{A} = \begin{pmatrix} 81 & -37 \\ -37 & 25 \end{pmatrix} \quad (\mathbf{A}^T \mathbf{A})^{-1} = \frac{1}{656} \begin{pmatrix} 25 & 37 \\ 37 & 81 \end{pmatrix} \\
 \begin{pmatrix} g > \\ g < \end{pmatrix} \frac{1}{1656} \begin{pmatrix} 26 & 38 & 38 & 50 & 50 & 62 & 62 & -5 & -5 & 7 & 7 \\ -14 & 30 & 30 & 74 & 74 & 118 & 118 & -73 & -73 & -29 & -29 \end{pmatrix} \begin{pmatrix} s_1 \\ s_2 \\ s_2 \\ s_3 \\ s_4 \\ s_4 \\ s_4 \\ s_8 \\ s_8 \\ s_9 \\ s_9 \end{pmatrix} \\
 \sigma_{g>}^2 = \sigma_s^2 \frac{25}{656} \quad \sigma_{g<}^2 = \sigma_s^2 \frac{81}{656}
 \end{array}$$

Table 7 shows that the lines for g have their slopes clustered in the region 2 to ∞ .

Clever approach—More data = better results

We choose

$$\begin{array}{c}
 A' \\
 \left(\begin{array}{c} 2 \quad 3 \\ 2 \quad 2 \\ 2 \quad 1 \\ 2 \quad 0 \\ 2 \quad -1 \\ 2 \quad -2 \\ 2 \quad 3 \\ 1 \quad 3 \\ 1 \quad -2 \\ 1 \quad -3 \\ 0 \quad 3 \end{array} \right)
 \end{array}
 \begin{array}{c}
 \tilde{x}' \\
 \left(\begin{array}{c} \Lambda g \\ \Lambda \Delta g \end{array} \right)
 \end{array}
 =
 \begin{array}{c}
 \tilde{b} \\
 \left(\begin{array}{c} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \\ s_6 \\ s_7 \\ s_8 \\ s_{13} \\ s_{14} \\ s_{15} \end{array} \right)
 \end{array}$$

(see Fig. 19).

Table 7. $\underline{b} = A' \underline{x}' = A \underline{x}$.

$S_i =$	$a'_{i1}\bar{g} + a'_{i2}\Delta g =$	$a'_{i1}g> + a'_{i2}g<$	#i	slope _i	S'_i		
S_1	2	3	4	-2	1	2	13
S_2	2	2	3	-1	2	3	12
S_3	2	1	2	0	3	∞	11
S_4	2	0	1	1	4	-1	10
S_5	2	-1	0	2	3	0	9
S_6	2	-2	-1	3	2	1/3	8
S_7	2	-3	-2	4	1	1/2	7
S_8	1	3	7/2	-5/2	2	7/5	8
S_9	1	2	5/2	-3/2	4	5/3	7
S_{10}	1	1	3/2	-1/2	6	3	6
S_{11}	1	0	1/2	1/2	8	-1	5
S_{12}	1	-1	-1/2	3/2	6	1/3	4
S_{13}	1	-2	-3/2	5/2	4	3/5	3
S_{14}	1	-3	-5/2	7/2	2	5/7	2
S_{15}	0	3	3	-3	3	1	3
S_{16}	0	2	2	-2	6	1	2
S_{17}	0	1	1	-1	9	1	1

or

$$\begin{array}{c}
 \mathbf{A} \\
 \left(\begin{array}{cc}
 4 & -2 \\
 3 & -1 \\
 2 & 0 \\
 1 & 1 \\
 0 & 2 \\
 -1 & 3 \\
 -2 & 4 \\
 7/2 & -5/2 \\
 -3/2 & 5/2 \\
 -5/2 & 7/2 \\
 3 & -3
 \end{array} \right)
 \end{array}
 \begin{array}{c}
 \underline{\mathbf{x}} \\
 \left(\begin{array}{c}
 g > \\
 g <
 \end{array} \right)
 \end{array}
 =
 \begin{array}{c}
 \mathbf{b} \\
 \left(\begin{array}{c}
 s_1 \\
 s_2 \\
 s_3 \\
 s_4 \\
 s_5 \\
 s_6 \\
 s_7 \\
 s_8 \\
 s_{13} \\
 s_{14} \\
 s_{15}
 \end{array} \right)
 \end{array}
 \quad (\text{see Fig. 19}).$$

so

$$\begin{aligned}
 \mathbf{A}^T \mathbf{A} &= \begin{pmatrix} 64.75 & -51.25 \\ -51.25 & 68.75 \end{pmatrix} & (\mathbf{A}^T \mathbf{A})^{-1} &= \frac{1}{1825} \begin{pmatrix} 68.75 & 51.25 \\ 51.25 & 64.75 \end{pmatrix} \\
 \sigma_{g>}^2 &= \sigma_s^2 \frac{68.75}{1825} & \sigma_{g<}^2 &= \sigma_s^2 \frac{64.75}{1825}
 \end{aligned}$$

Comparison of Different Methods

Figure 21 shows the error ellipses generated by the covariance matrices of the three different methods. Clearly, the naive approach gives no better results than the Vander Sluis method. The clever approach clearly gives better results. If the Zeeman pattern image is truly symmetric, the Vander Sluis method and the clever method give the same answer for g , but the clever result will have a smaller variance. If the Zeeman image is not symmetric (often the case in practice), the clever method will give a more accurate answer for g as well as a smaller variance.

Also, the Vander Sluis method is not suitable for testing the hypothesis that a given pattern is produced by a transition having the assumed g values because the method assumes that the pattern is symmetric. It cannot therefore be used to check if a pattern is symmetric.

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"And further, by these, my son, be admonished: of making many books there is no end; and much study is a weariness of the flesh."

Ecclesiastes 12, 12

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