A study of the isotope shift in chromium
by Charles Albert Lincoln

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Physics
Montana State University

Abstract:
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The experimentally observed shift was 85±5 mK. The volume effect shift was calculated to be 4 mK. The normal mass effect was calculated to be 7.7 mK. The residual shift was then 81±5 mK.

A three prism Steinheil-Streander spectrograph with a Fabry-Perot interferometer was used. A hollow cathode discharge tube (cooled in liquid air) with chromium trioxide on the surface of the hollow cathode comprised the remaining important features of the experimental set-up.

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Approved:

Irving C. Dayton
Head, Major Department

Roy V. Wiegand
Chairman, Examining Committee

Doris O. Smith
Dean, Graduate Division

MONTANA STATE COLLEGE
Bozeman, Montana

June, 1964

ACKNOWLEDGMENT

This Thesis represents the extension of some work
done by Dr. Hack Arroe. It was largely by means of his
patience and understanding help that the thesis was completed.
Dr. Roy Wiegand took much of his time in constructive crit-
icism and made many useful remarks. Drs. Joseph Ball and
E. Miller Layton also read the thesis and offered constructive
criticism.

The author is extremely thankful to the above-mentioned
individuals for their help. Also, thanks are due to Mrs.
Harlan Wilhelm for the excellent typing.

A special word of thanks is given to the author's wife
for her much-appreciated encouragement.

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ABSTRACT

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INTRODUCTION

Optical spectroscopy has been the major tool in the analysis of atomic structure.[1] With the advent of high resolution spectroscopy, first used by Michelson in 1892,[2] and the development of a theory to explain the hyperfine structure of the multiplet lines in the atomic spectra which were subsequently observed, optical spectroscopy has become an important tool in the analysis of nuclear structure.[3] In 1924, Pauli[4] proposed that the hyperfine structure (HFS) results from a magnetic coupling between the nucleus and its orbital electrons. Pauli's explanation was soon shown to be essentially correct, but some HFS experiments yielded anomalous values. These anomalies were later interpreted as due to an effect called isotope shift. This paper contains a brief review of the theories dealing with the HFS and with isotope shift. Since isotope shift and HFS utilize similar assumptions on the nucleus, both are treated here.

In the Bohr theory of the atom,[5] the nucleus is assumed to be a point charge, and the interaction between the nucleus and the electrons is a coulomb type. This simple assumption is useful as a first approximation and serves to describe the gross structure of the atom. The intrinsic spin and magnetic

moment of the electron is required for an explanation of the observed fine structure in atomic spectra. If it is also assumed that the nucleons have an intrinsic spin and that the nucleus has a resultant angular momentum and magnetic moment, then the HFS can be related to the resulting interactions between the magnetic multipole moments of the nucleus and the electrons.

The energy levels contributing to the production of HFS are due, in general, to the magnetic interaction mentioned above. However, the levels may be modified by the addition of a factor, which is usually small, arising from an electrostatic interaction between the nucleus and the electrons. Some of the results from the analysis of fine structure apply to hyperfine structure since they arise from similar effects. Among these are the Lande interval rule,[3] and the selection rules.[3] HFS also exhibits Zeemann and Paschen-Back effects similar to those found in fine structure and are treated in a similar manner.[6] Experimentally, hyperfine structure is observed only if the nucleus has non-zero angular momentum. This condition is satisfied in atoms with odd-even, even-odd, and odd-odd nuclei. That is, with an odd number of protons and an even number of neutrons, etc.. Hyperfine structure

will be discussed more completely in part II.

The isotope shift studies fall naturally into two categories; the mass and the volume effects. The mass effect is further divided into the normal and specific mass effects. These effects are described in part III. The volume effect has many aspects and gives much insight into the structure of the nucleus. The experimental data on the volume effect would indicate that the term shift is caused mainly by s electrons, the sign of the shift being obtained by assuming that the s electron raises the level of the heavier isotope relative to the lighter one. Experiments also show that the spectral lines of the even isotopes are always arranged in the order of their mass numbers, and separations tend to be of the same order of magnitude for different isotopes in a particular spectral line. Odd-even staggering is observed i.e. the lines of the odd isotopes are shifted towards the isotope of lower atomic number. These features are shown graphically in Fig. 1. Mack and Arroe[7] have written an excellent review which includes a survey of the literature of the isotope shift studies to 1956. The volume effect will be discussed more completely in part IV.

The following explanation of figure 1 is taken from

the review article by Mack and Arroe;[7] "Figure 1a shows a term

shrinkage that occurs in all spectra, and is the only shift

in the spectra in the hydrogen-like isoelectronic sequence:

the shift (measured from the value postulated for an infinitely

massive nucleus) tends to reduce the term differences and is

strictly proportional to the term value and to the reciprocal

of the mass of the atom or ion; thus the separation between

adjacent mass numbers is approximately inversely proportional

to the square of the average mass. This universal term

shrinkage is completely accounted for as the normal mass

effect. For simplicity it is not shown in the other parts

of figure 1, all of which show selective shifts, i.e., shifts

occurring only in certain levels.

"In its simplest manifestation (Fig. 1b), from Z=2

through about the first third of the atomic table, the

selective shift of a level may be either sign, depending on

the electron quantum numbers; and the magnitude of the shift

per unit mass change for those levels that are most strongly

affected in any spectrum is somewhat smaller than the normal

mass effect and varies from element to element in roughly the

same way, i.e., inversely as the mass squared, or approxi-

mately linearly in the mass when the mass differences are

small compared with the mass itself. This shift is identified with the specific mass effect.

"All of the following phenomena are attributed to the field effect, and the usual hypothetical reference level is not that with infinite mass but that with zero volume (zero mass). About where the specific mass effect becomes in-appreciable (10^{-3}K, where K stands for Kayser, or cm^{-1}) there begins to be noticeable, but only among certain levels (Fig. 1c), an increase in the energy with increasing mass. The energy change depends only upon the configuration, and is greatest in the case of a configuration with a single un-balanced s electron; but for a $p_{\frac{1}{2}}$-electron it grows to about one-fifth this magnitude in heavy atoms. Notice that the only characteristic distinctions to be observed experi-mentally between the specific mass effect (Fig. 1b) and the field effect when the latter is approximately linear (Fig. 1c) are that the former may have either sign while the latter is always negative; also, the two effects differ markedly with respect to their dependence upon the electronic quantum numbers.

"Figure 1d illustrates odd-even staggering (. . .).

"Figure 1e shows the most general situation, which is

beginning to be recognized as the usual one in the field effect region of the atomic table; even for increases of 2 in N (i.e., when N stays odd or stays even) the position of the level is appreciably nonlinear in N."

Fig. 1

General Features of Atomic Isotope Shifts
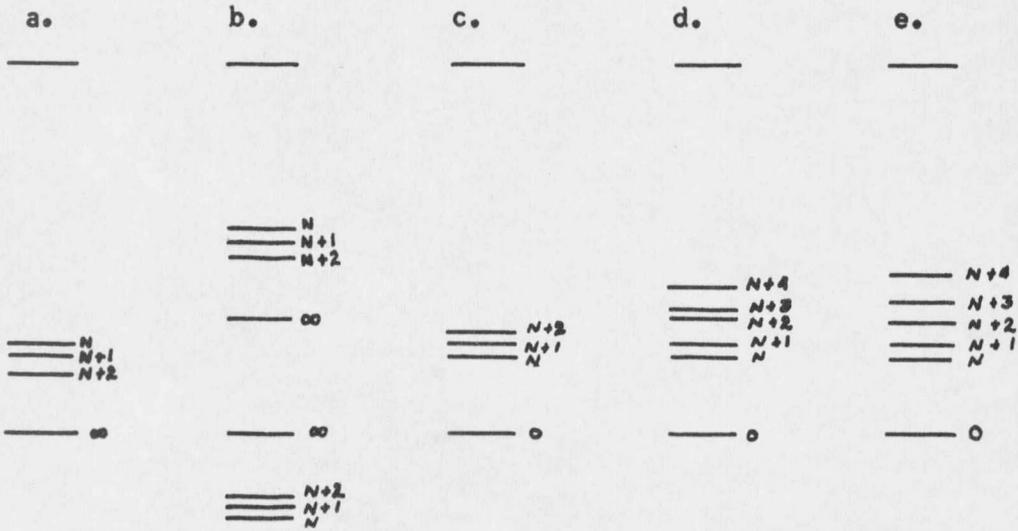
a. Normal Mass Effect

b. Specific Mass Effect

c. Linear Volume Effect

d. Odd-Even Staggering

e. General Volume Effect

II. HYPERFINE STRUCTURE

The following is a review of the magnetic and electro-static interactions between a nucleus and the core electrons. The results are qualitatively the same as those obtained from a rigorous quantum mechanical treatment with only a few minor alterations. A more thorough treatment is to be found in the literature.[3]

A. Magnetic Dipole Interaction between Atomic Nucleus and Orbital Electrons

From classical electrodynamics, it is seen that the energy of magnetic interaction between an atomic nucleus and orbital electrons is given by[8]

$$U = - \int_V \vec{A} \cdot \vec{j} \, dv$$

where $\vec{A}$ is the nuclear vector potential, $\vec{j}$ is the current density of the electrons, and V indicates the volume of the atom. To a first approximation, the nucleus is considered a magnetic dipole and the vector potential is then given by,

$$\vec{A} = \vec{\mu} \times \vec{r} / r^3$$

where $\vec{\mu}$ is the magnetic moment of the nucleus. A better

approximation would be given by expanding $\vec{A}$ in powers of r^{-1}. This would resolve the nuclear magnetic field into monopole, dipole, quadrupole, and multipole components of higher order. However, poles of even order would not be symmetrical in the nucleus with respect to the nuclear equatorial plane, and, therefore, they cannot exist.* The magnetic octupole interaction contributes very little to the energy and there is no conclusive evidence that this interaction has been observed in optical spectroscopy. Neglecting terms higher than dipole, the interaction energy is written

$$U = -\int_V \frac{\vec{\mu} \times \vec{r}}{r^3} \cdot \vec{J} \, dv = -\int_V \vec{\mu} \cdot \frac{\vec{r} \times \vec{J}}{r^3} \, dv$$

The magnetic field of the electrons at the nucleus is[9]

$$H(0) = \int_V \frac{\vec{r} \times \vec{J}}{r^3} \, dv$$

The expression for the energy may be simplified by utilizing the relationship between the magnetic moment μ_I and the nuclear spin $\vec{I}$, $\mu_I = \frac{e}{2M} \hbar \vec{I} \, g_I$ where g_I is the nuclear

---

*See H. Kopferman[3] page 5. In particular; when the vector potential outside of the nucleus is expanded in powers of r^{-1}, then the first-order point source is the magnetic counterpart of the electric dipole. Second-order magnetic point sources correspond to the electric quadrupole.

gyromagnetic ratio and M is the proton mass. Using units of

the nuclear magneton, $\mu_B \frac{m}{M} = \mu_m$, the relation is con-

cisely written as

$$\mu_I = \frac{e}{2M} \hbar \vec{I} g_I \frac{m}{M} = \mu_B \vec{I} g_I \frac{m}{M}$$

which implies that

$$\frac{\mu_I}{\mu_m} = \vec{I} g_I$$

In order to obtain the shift of the energy levels, it is

necessary to take the time average over the unperturbed

electronic motion, that is:

$$\Delta W = -\mu_I \overline{H(o)} \cos(\vec{\mu}_I, \vec{H}(o)) ,$$

$\vec{H}(0)$ and $\vec{J}$ are anti-parallel for a single electron. The

orbital angular momentum of the electron, $\vec{l}$, is directed

opposite to the magnetic field that it produces at the

nucleus, $\vec{H}_l(o)$. The intrinsic magnetic moment of the elec-

tron, $\vec{\mu}_s$, can be considered as being located on the electron

orbit and increases or decreases the field $\vec{H}_l(o)$ depending

on whether $\vec{s}$ and $\vec{l}$ are parallel or anti-parallel. When $\vec{H}(o)$

and $\vec{J}$ are anti-parallel and g_I is positive, μ_I is most stable

when it is parallel to $\vec{H}(o)$, then $\cos(I,J) = -1$. This means

that the change in energy level is

$$\Delta W = \Delta W_{IJ} = A\,IJ \cos(\vec{I},\vec{J}) \ .$$

$\vec{I}$ and $\vec{J}$ precess jointly about the total angular momentum of the atom, $\vec{F}$, so that

$$\cos(\vec{I},\vec{J}) = (F^2 - I^2 - J^2)/2\,IJ \ .$$

In the quantum mechanical treatment, $\vec{\mu}_I$ is replaced by the component along the z axis, μ_{I_z} and $\vec{H}(o)$ by $H_z(o)$, F^2, J^2, and I^2 are replaced by $F(F+1)$, $J(J+1)$, and $I(I+1)$ respectively. $\vec{F}$ can take on all values $F = |I+J|$, $|I+J-1|$, ..., $|I-J|$. The change in energy levels is finally given by

$$\Delta W_{IJ} = A/2 \left[F(F+1) - I(I+1) - J(J+1) \right]$$

with

$$A = \mu_I \,\overline{H(o)} /IJ = \mu_m\, g_I \,\overline{H(o)} / J \ .$$

B. Electrostatic Quadrupole Interaction between Nucleus and Orbital Electrons

The difference between the electrostatic interaction energies for a nucleus with finite volume and one of point

charge is

$$\Delta u = e \int_V \rho_m \psi_e \, dv - z e^2 \int_V \frac{\rho_e}{r} \, dv$$

where $e\rho_m$ is the charge density of the nucleus, $e\rho_e$ the

charge density of the electrons and ψ_e is the electrostatic

potential of the orbital electrons. For electrons with zero

charge density at the center of gravity of the nuclear charge,

ψ_e may be expanded in powers of (x,y,z) about the origin

which is taken as the center of gravity of the nuclear charge.

This gives, using an ordinary Taylor series expansion in

three variables where, for example $\psi_z = \frac{\partial \psi}{\partial z}$ etc. an energy of

$$\Delta u = e \int_V \rho_m \psi_e(0) \, dv + e \int_V \rho_m \left[x \, \psi_x(0) + \cdots + z \, \psi_z(0) \right] dv$$

$$+ \, e/2 \int_V \rho_m \left[x^2 \, \psi_{xx}(0) + xy \, \psi_{xy}(0) + \cdots \right] dv - z e^2 \int_V \frac{\rho_e}{r} \, dv \, .$$

But $\psi(0) = \frac{ze}{r}$ and $\rho_m x$ corresponds to an electric dipole

which vanishes in the nucleus from symmetry considerations.

Thus the energy shift may be simplified to

$$\Delta u = \frac{1}{2} \left[\psi_{xx}(0) \, e \int_V \rho_m x^2 \, dv + \psi_{xy}(0) \, e \int_V \rho_m xy \, dv + \cdots + \psi_{zz}(0) \, e \int_V \rho_m z^2 \, dv \right].$$

This is merely the double scalar product of two second rank

tensors Q_{ij} and φ_{ij} where

$$Q_{ij} = \int_V \rho_m \, \varkappa_i \, \varkappa_j \, dv \quad .$$

Transforming to a coordinate system with (ξ, η, ζ) specifically for the representation of the nuclear charge distribution and (x, y, z) for the electrostatic field, with symmetry about ζ and z respectively, the change of potential becomes

$$\Delta U_Q = e/2 \left[Q_{xx} \varphi_{xx} + Q_{yy} \varphi_{yy} + Q_{zz} \varphi_{zz} \right] \quad .$$

Note that from the cylindrical symmetry about the z axis and the fact that at the nucleus, $\nabla^2 \varphi = 0$ and $\varphi_{zz} = -2\varphi_{xx} = -2\varphi_{yy}$ that ΔU_Q may be written as

$$\Delta U_Q = \varphi_{zz} \, e/4 \int_V (3z^2 - r^2) \rho_m \, dv$$

and also that

$$\int_V (3z^2 - r^2) \rho_m \, dv = \int_V (3\zeta^2 - r^2) \rho_m \, dv \left(\tfrac{3}{2} \cos^2 \gamma - \tfrac{1}{2} \right)$$

where γ is the angle between ζ and z. The expression,

$$e \int_V (3\zeta^2 - r^2) \rho_m \, dv \quad ,$$

is called the quadrupole moment.

The shift in energy level may be found by averaging over all of the unperturbed eigenvalues. (It must be kept in mind that this treatment is suitable only for cylindri-cally symmetric charge distributions, not for spherically symmetric distributions whose quadrupole moments are zero.) Thus ΔW_Q is given as

$$\Delta W_Q = e/4 \; Q \; \overline{\varphi_{zz}(0)} \; \left(\tfrac{3}{2}\cos^2\Omega - \tfrac{1}{2}\right) = B/4 \left[\tfrac{3}{2}\cos^2(I,J) - \tfrac{1}{2}\right]$$

where

$$B = e \; Q \; \overline{\varphi_{JJ}(0)} \quad,$$

in the limit of large quantum numbers. Casimir[10] has shown that

$$\left[\tfrac{3}{2}\cos^2(I,J) - \tfrac{1}{2}\right] = \tfrac{3}{2}\left[C(C+1) - 2I(I+1)J(J+1)\right] / IJ(2J-1)(2I-1)$$

for small quantum numbers, where C is determined by

$$C = F(F+1) - I(I+1) - J(J+1) \quad.$$

C. Determination of HFS Splittings

The total energy of a given level with quantum number F

may be represented by

$$W_F = W_J + AC/2 + B/4 \frac{3/2\, C(C+1) - 2\, IJ(I+1)(J+1)}{IJ(2J-1)(2I-1)} \quad .$$

The separation (in wave numbers) between any pair of levels
(1,2) is given as σ_{12} ,

$$\sigma_{12} = \frac{1}{2} A(C_1 - C_2) + \frac{3}{8} B[C_1(C_1+1) - C_2(C_2+1)]/I(2I-1)J(2J-1) \quad .$$

Thus A and B may be determined from any two unperturbed
intervals,[11] although more intervals may be used as a check
on accuracy. When B is negligible the splitting of the levels
is given by $W_F = W_J + AC/2$ and the total width of the split-
ting is given by

$$\Delta W = AI(2J+1) \text{ for } J \geq I , \quad \Delta W = AJ(2I+1) \text{ for } I \geq J ,$$

where ΔW is the interval from $|J+I|$ to $|J-I|$. The interval
rule, however, always holds for HFS term differences. The
intervals are in the ratio $(I+J):(I+J-1):(I+J-2):$ etc..

D. Determination of μ_s from A

It is desirable, in many cases, to know the value of the
nuclear magnetic moment. This may be found from the A values
in HFS splitting. The change in energy level is regarded as

the sum of the change in energy level from the orbital

magnetic field and from the spin magnetic field, that is

$$\Delta W_{IJ} = \Delta W_{I\ell} + \Delta W_{Is} \ .$$

Using a treatment similar to that part A above the respective

magnetic interactions are written

$$\Delta W_{I\ell} = -\mu_I H_\ell(o) \cos(\mu_I, H_\ell(o)) = -\mu_I H_\ell(o) \cos(I,\ell) \ .$$

However,

$$H_\ell(o) = \frac{e (\vec{r} \times \vec{v})}{r^3}$$

and since angular momentum is quantized, $m(\vec{r} \times \vec{v}) = \vec{\ell}\, \hbar$,

this implies that

$$\vec{H}_\ell(o) = \frac{e}{m}\, \hbar\, \frac{\ell}{r^3}\, \vec{\ell} \ .$$

Regarding the electron and the nucleus as small magnets

gives to a first approximation,

$$\Delta W_{Is} = \frac{\mu_I \mu_s}{r^3} \Big[\cos(I,s) - 3\cos(I,r)\cos(r,s) \Big] \ .$$

Combining these expressions, the resulting energy change is

$$\Delta W_{IJ} = \frac{1}{2} \left(\frac{e}{m}\hbar \right)^2 \frac{1}{r^3}\, g_I \Big[I\ell \cos(I,\ell) - Is \cos(I,s) + 3 Is \cos(I,r)\cos(r,s) \Big].$$

Goudsmit[17] has shown that this may be written as

$$\Delta W_{IJ} = A/2 \left[F(F+1) - I(I+1) - j(j+1) \right]$$

where

$$A = 2 \mu_B^2 \frac{\ell(\ell+1)}{j(j+1)} \frac{1}{r^3} g_I \quad .$$

Thus μ may be found from the HFS splitting factor.

III. THE MASS EFFECT IN ISOTOPE SHIFT[12,13,14]

The total kinetic energy of the atom is

$$T = - \sum_{i=2}^{m} \frac{\hbar^2}{2m_i} \nabla_i^2 \psi_e - \frac{\hbar^2}{2m_1} \nabla_1^2 \psi_n$$

in cartesian coordinates, where ψ_e is the electronic wave function, and the atomic particles are numbered from 1 to n where m_1 would for example represent the mass of the nucleus. To eliminate the nuclear motion, center of mass coordinates are introduced whereby the kinetic energy takes on the form

$$T = \left[- \frac{\hbar^2}{2m_1} \nabla_1^2 - \sum_{i=2}^{m} \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_{j \neq i} \frac{\hbar^2}{2m_i} \nabla_i \cdot \nabla_j \right] \psi_e \ .$$

The first term in this expression represents the center of mass motion and is disregarded. By introducing the reduced mass, the expression becomes

$$T = \left[- \frac{\hbar^2}{2m_r} \sum \nabla_i^2 - \frac{\hbar^2}{2m_i} \sum_{j \neq i} \nabla_i \cdot \nabla_j \right] \psi_e \ .$$

Here the first term causes the normal mass effect and the second term is the specific mass effect.

A. The Specific Mass Effect

The specific mass effect expresses the mutual coupling of electrons and hence does not occur in one electron atoms.

The energy of the coupling may be regarded as a perturbation, giving the additional energy

$$\Delta W = -\frac{\hbar^2}{2m_i} \sum_{i \neq j} \int_V \psi^* (\nabla_i \cdot \nabla_j) \psi \, dv \quad .$$

This may be integrated by parts, leading to a perturbation energy

$$\Delta W = -\frac{\hbar^2}{2m_i} \sum_{i \neq j} \int_V \nabla_i \psi \cdot \nabla_j \psi^* \, dv \quad .$$

Following Kopfermann,[3] a simple example is the two electron problem in a central potential. The zero order eigenfunctions, in terms of the eigenfunctions of the individual electrons u and v, are given by[11]

$$\psi = \frac{1}{\sqrt{2}} \left[u(1) v(2) \pm v(1) u(2) \right] \quad .$$

The plus sign holds for the singlet system and the minus sign for the triplet system. Inserting this into the expression for the energy reduces the energy expression to a single term

$$\Delta W = \frac{\hbar^2}{2m} \left| \int u^* \nabla v \, dv \right|^2$$

since

$$\int u^* \nabla u \, dv = 0 \quad .$$

But from the form of the electronic eigenfunctions, ΔW has a non-zero value only if $\Delta l = \pm 1$. Kopfermann[3] has given values for some configurations and their agreement with experiment.

B. The Normal Mass Effect

The Bohr theory of the atom adequately describes the normal mass effect for the hydrogen atom. For example the second line of the Balmer series shows a normal mass shift between H^1 and H^2 of 5.600 K,* in agreement with calculation. The deuterium component is on the high wave number side. The energy levels in terms of the reduced mass are

$$W_{m_p} = \frac{R_\infty Z^2}{n^2}\left(1 - \frac{m}{m_p}\right) = T_\infty \left(1 - \frac{m}{m_p}\right).$$

This gives a line shift which is

$$\Delta\sigma \approx \frac{\sigma}{1836.12}\left(\frac{M_2 - M_1}{M_2 M_1}\right)$$

where M is the mass number of the nucleus, m_p the mass of the proton. It is easily seen that the normal mass shift is inversely proportional to M^2. For mass numbers on the order of 20 and larger, this effect is smaller than any observable HFS

*See the comments on figure 1.

splitting. Fig. 1 shows the main features of the normal and specific mass effects as well as the volume effect, which is treated in the following section. Fig. 2 shows graphically the normal mass effect as a function of the mass number as well as the line width due to the instrument and the line width due to Doppler broadening. The instrument line width and Doppler width are discussed in part V.