

PRECISE ATOMIC MASSES AND MASS DIFFERENCES FOR

Hf, Ta, W and Re

by

Kumar Satish Sharma, B.Sc.(Hon.)

A THESIS

Submitted to The Faculty of Graduate Studies

In Partial Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

Department of Physics

University of Manitoba

Winnipeg, Manitoba

June, 1979

PRECISE ATOMIC MASSES AND MASS DIFFERENCES FOR

Hf, Ta, W and Re

BY

KUMAR SATISH SHARMA

A dissertation submitted to the Faculty of Graduate Studies of  
the University of Manitoba in partial fulfillment of the requirements  
of the degree of

DOCTOR OF PHILOSOPHY

©1979

Permission has been granted to the LIBRARY OF THE UNIVERSITY OF MANITOBA to lend or sell copies of this dissertation, to the NATIONAL LIBRARY OF CANADA to microfilm this dissertation and to lend or sell copies of the film, and UNIVERSITY MICROFILMS to publish an abstract of this dissertation.

The author reserves other publication rights, and neither the dissertation nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

Doctor of Philosophy (1979)

University of Manitoba

Physics

Winnipeg, Manitoba

TITLE: Precise Atomic Masses and Mass Differences for  
Hf, Ta, W and Re

AUTHOR: Kumar Satish Sharma, B.Sc.(Hon.), University of Manitoba

SUPERVISOR: Professor R.C. Barber

PAGES: vi, 92

SCOPE AND CONTENTS:

The stability of operation and the sensitivity of the Manitoba II spectrometer have been significantly improved through changes and modifications of the instrumentation. This has made it possible to redetermine the results for two doublets involving the rare nuclides  $^{180}\text{W}$  and  $^{174}\text{Hf}$ . The mass difference  $^{181}\text{Ta} - ^{180}\text{Ta}$  has also been determined for the first time by a mass spectrometric technique.

A total of 16 new doublet spacings have been determined in this work. These new results, when combined with a few other precise measurements, constitute for the first time a completely over determined set of mass differences between the naturally occurring isotopes of Hf, Ta, W and Re. A set of self consistent masses and mass differences was derived from these data and the systematic properties of the calculated  $S_{2n}$  values have been interpreted in terms of Nilsson single particle levels. The data are also used to determine the groundstate energy level structure at  $A = 180$ .

## CONTENTS

	<u>Page</u>
List of Tables	iv
List of Figures	v
<u>CHAPTER 1</u>	INTRODUCTION
1-0	Introduction 1-1
1-1	Standards of Mass 1-2
1-2	The Importance of Atomic Mass Determinations 1-4
1-3	Methods of Atomic Mass Determination 1-5
1-4	Tables of Atomic Data 1-8
<u>CHAPTER 2</u>	HISTORY AND DEVELOPMENT OF MASS SPECTROMETRY
2-0	Introduction 2-1
2-1	Early Instruments 2-1
2-2	Positive Ion Optics 2-3
2-3	Elements of Mass Spectrometry 2-9
<u>CHAPTER 3</u>	THE MANITOBA II MASS SPECTROMETER
3-0	Instrument Geometry 3-1
3-1	The Ion Source Region 3-2
3-2	The Electrostatic Analyser Region 3-5
3-3	Magnetic Analyser Region 3-7
3-4	Peak Matching on Manitoba II 3-10
3-5	Hardware Associated with Peak Matching 3-17
<u>CHAPTER 4</u>	NEW ATOMIC MASS DETERMINATIONS
4-0	Introduction 4-1
4-1	Experimental Details 4-1
4-2	Description of the Least Squares Evaluation 4-5
4-3	Supplementary Data 4-6
4-4	Results of the Least Squares Evaluation 4-9
4-5	Conclusion 4-13
<u>APPENDIX 1</u>	A-1
<u>REFERENCES</u>	R-1

LIST OF TABLES

	<u>Page</u>
2-1 Ion Optical coefficients (1st order focussing)	2-15
2-2 Current high resolution mass spectrometers	2-16
4-1 New Atomic mass differences	4-15
4-2 Auxiliary data	4-16
4-3 Other relevant doublets measured by this group	4-17
4-4 Additional data used for the calculation	4-18
4-5 Input/Output from adjustment	4-19
4-6 Calculated masses and comparison values	4-20
4-7 $S_{2n}$ , $S_n$ values in comparison with '77 Mass Evaluation	4-21

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
2-1	Magnetic Analyser	2-17
2-2	Electrostatic Analyser	2-18
3-1	The Manitoba II Mass Spectrometer	3-20
3-2	Geometry of the Manitoba II Spectrometer	3-21
3-3	Ion Source	3-22
3-4	Electrostatic Analyser Supply System	3-23
3-5a	Current Supply for the Magnetic Analyser	3-24
3-5b	Regulator for short term variations in the Magnetic Field	3-25
3-6	Sweep Amplifier	3-26
3-7	Electron Multiplier Preamplifier	3-27
3-8a,b	Error Signal generated with the Visual Null Method	3-28
3-9	Relative positions of the peaks collected in each quadrant for the Centroid Method (normal, add, forward mode)	3-29
3-10a	Waveforms for the Visual Null Method	3-30
3-10b	Waveforms for the Centroid Method	3-31
3-11	Synchronization and Control System	3-32
4-1	Input data	4-22
4-2a	Groundstate energy levels at $A = 180$ as given by Greenwood (1975)	4-23
4-2b	Groundstate energy levels at $A = 180$ as determined by these results	4-24
4-3	$S_{2n}$ Systematics	4-25

ACKNOWLEDGMENT

This research has been supported by the National Research Council.

I wish to thank my supervisor, Dr. R.C. Barber, for his guidance and support during the course of this research and I am grateful for the helpful comments and suggestions made by Dr. H.E. Duckworth. Thanks are also due to the members of the "Mass Spectrometry Group" for their invaluable assistance.

I thank my wife who helped support me for the last few years and has endured the many delays resulting from my diversions. I also wish to thank Dr. D.P. Shelton, Mr. P. Dickof, Dr. B. Chait and Mr. M. Neuman for initiating these diversions.

Thanks are also due to my father for taking the photographs used in this thesis and both of my parents for their encouragement and support. I also wish to thank Mrs. Janice Smith who typed the manuscript.

## CHAPTER 1

### INTRODUCTION

#### 1-0. INTRODUCTION

The atomic view of matter began as a result of speculations by the ancient Greek philosophers. Empedocles (430 B.C.) and later Democritus (400 B.C.) attempted to construct a doctrine which explained the many and varied properties of materials in terms of a set of tiny indivisible particles. This theory, though briefly revived by Roman philosophers, lay dormant until the 1800's. At this time it was once again revived by Dalton and other chemists in an attempt to explain the law of proportions in chemistry. Dalton proposed that in a chemical reaction a fixed number of identical particles of one type combine with a fixed number of particles of another type to produce a composite particle. The law of proportions then reflected the numbers of particles involved and their masses. This theory represents a fairly accurate model of chemical reactions in terms of interactions between atoms, except that the possibility of the existence of isotopes was not considered.

In the chemist's view, the atom was no more than a convenient model to explain certain chemical phenomena. It was generally accepted that atoms were microscopic indivisible particles that could not be created, destroyed or changed in any manner. As a result of investigations by Goldstein (1886), Wien (1898) and Thomson (1913), features like the charge to mass ratio and the first details of the structure of atoms began to emerge.



The current view of the atom as a physical particle having the properties of mass, charge and extension in space and a fairly complex structure has developed over roughly the last 100 yrs. It is with the property of mass that this work is mainly concerned.

#### 1-1. STANDARDS OF MASS

Mass, like the quantities of length and time, escapes definition except in terms of a prescription for its measurement. This prescription usually takes the form of comparing the mass of the object in question with the mass of a second object which is taken to be the standard. Similar prescriptions are used in the definitions of length and time.

The mass of an object may be compared to the standard by examining the accelerations of the object and the standard when subjected to a particular force. The property measured in this case is called "inertial mass". Comparisons between the object and standard may also be made on the basis of the gravitational interaction between each of them and a third mass. In this case the "gravitational mass" is said to be measured. The equality between inertial and gravitational mass has been established by Eotvos and Dicke (as described by Roll, 1964) to an accuracy of  $1/10^{11}$ .

A standard of mass, in the form of a solid, platinum - iridium (90/10) alloy, cylinder with height equal to its diameter has been defined as 1 kilogram and is kept at the Bureau International des poids et mesures in France. Copies of the standard kilogram may be compared to the original to a precision of  $1/10^8$ .

The sheer size of the kilogram, which is approximately  $10^{25}$  times the mass of an atom, coupled with the difficulty in designing experiments to compare masses of atoms with the standard kilogram makes this mass standard an unsuitable one for use in atomic mass determinations. Moreover this standard is not universally available to all experimenters. Therefore, a second standard of mass has been adopted for use in the atomic domain.

Before 1960 two scales of atomic mass were in use: the chemical scale in which the gram atomic weight of Oxygen (of natural isotopic composition) was chosen to be exactly 16 g. and the physical scale in which the atomic mass of  $^{16}\text{O}$  was chosen to be exactly 16 atomic mass units (16 amu). These two scales were replaced by a single scale (Mattauch, 1960 and Wichers, 1962) in which a single atom of  $^{12}\text{C}$  has a mass of exactly 12 mass units (12 u). This standard has the advantage of being available to any investigator and in particular facilitates the determination of atomic masses by mass spectrometric methods.

Thus, one may express the unit of atomic mass as

$$1 \text{ u} = 1/12 (\text{mass of } ^{12}\text{C}). \quad (1-1)$$

Combining this definition with the definition of a gram-atomic weight and Avogadro's number,  $N_A$ , it is possible to define the atomic mass unit in terms of the standard kilogram as follows

$$1 \text{ u} = 1/N_A \text{ g}. \quad (1-2)$$

A connection between the atomic mass scale and the energy scale (electron volts) may be established by means of the now well known relation between mass and energy presented by Einstein in 1905 viz.

$$E = mc^2. \quad (1-3)$$

Combining Eqns. 1-2 and 1-3 with the definition of an electron volt yields,

$$1 \text{ u} = c^2 / N_A e \text{ eV} \quad (1-4)$$

where  $e$  is the charge of the electron (in coulombs) and  $c$  is the speed of light (in m/sec).

Recently Avogadro's number has been determined to a precision of 1 part per million, in a beautiful experiment, by Deslattes (1974, 1976). A standard value for general metrological use has been recommended by the Consultative Committee on the Definition of the Metre (Cohen, 1976) which gives the speed of light with a precision of  $4/10^9$ . These results and others have been combined in a least squares adjustment by Cohen (1976) and a self consistent set of fundamental constants obtained. The quantities in equations 1-2 and 1-4 may be calculated from the results of this adjustment as,

$$1 \text{ u} = 1.660 \ 565 \ 5 \pm 86 \cdot 10^{-27} \text{ kg.} \quad (1-5a)$$

$$1 \text{ u} = 931.501 \ 6 \pm 26 \text{ MeV} \quad (1-5b)$$

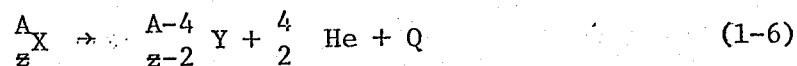
## 1-2. THE IMPORTANCE OF ATOMIC MASS DETERMINATIONS

Inasmuch as a knowledge of the mass of macroscopic objects is useful in understanding their nature and behaviour so also it is with atoms. It is found that the masses of atoms (measured on the  $^{12}\text{C}$  scale) differ from whole numbers by less than 0.1 u. This is a good indication that atoms are composite structures made up of the same constituent parts. Moreover the magnitude of this deviation from whole numbers provides a wealth of information about the binding energies of the constituent parts of the atom. Many modern techniques exist (some

of which are discussed below) which allow the experimenter to evaluate atomic masses and mass differences to a precision of  $\sim 1$  keV. While this is not enough to study effects involving atomic electrons, nuclear binding energy effects which are typically of the order of several MeV may be easily investigated. In particular, the variation in these binding energies from one nuclide to another provides a picture of the interactions between the nucleons in the nucleus. A few of the methods used to determine atomic masses and mass differences are outlined below.

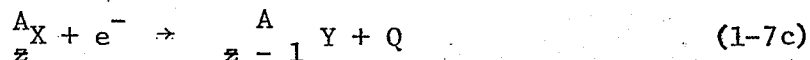
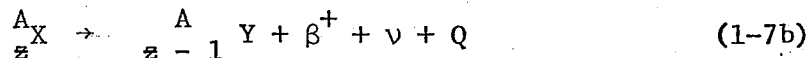
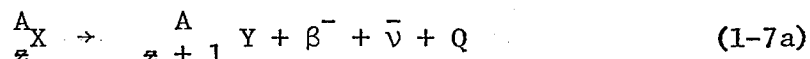
### 1-3. METHODS OF ATOMIC MASS DETERMINATION

A.  $\alpha$  - decay: The  $\alpha$  - decay of a nucleus may be represented by the reaction



By measuring the energy of the  $\alpha$  - particle and calculating the related recoil energy of the parent nucleus, the mass difference between X and Y may be determined. Such energy measurements are usually performed with a magnetic analyser which is calibrated by means of  $\alpha$  - particles of a known energy ( $\alpha$  - particles emitted in the decay of isotopes of polonium are commonly used). This type of measurement is responsible for the determination of most of the atomic mass differences among nuclei heavier than Pb. Uncertainties as low as 50 eV have been reported by Rytz (1972) in the determination of the energies of some of the standards used. In addition to magnetic analysers surface barrier detectors may also be employed to measure  $\alpha$  - particle energies. In this case the uncertainty of a typical measurement is  $\sim 20$  keV.

B.  $\beta$  - decay: The  $\beta$  - decay of a nucleus involves one of the following reactions



In the first two cases (Eqns. 1-7a,b) the energy released in the decay is shared by the  $\beta$  - particle and the neutrino. The  $\beta$  - particles are therefore seen to have a continuous spectrum of energies. The Q-value must therefore be estimated as the maximum possible  $\beta$  - particle energy from the observed energy spectrum. This is called the end-point of the  $\beta$  - particle spectrum. A knowledge of the energies of any accompanying  $\gamma$  - rays is also essential. Precisions of  $\sim 0.1$  keV have been attained in some cases (e.g. with the large iron free magnetic spectrometer at Chalk River) but typical uncertainties are  $\sim 10$  keV.

The energy released in the third process (Eqn. 1-7c) is difficult to measure accurately. In this process an atomic electron (usually from the inner shell) is captured by the nucleus and one or more X-rays are emitted. The energy released in the course of this reaction is deduced from the sum of the energies of the X-rays observed. The low energies and the number of X-rays involved make it difficult to measure accurately the energy released in this process.

C. Nuclear reactions: Nuclear reactions induced by charged particle beams and neutrons are also used to determine mass differences. In this method a target nucleus (X) is bombarded by a projectile (a) resulting in the formation of a product nucleus (Y) and an outgoing

projectile (b). Such reactions are customarily written in the form  $X(a,b)Y$ . In this case the energy released or Q-value is defined as

$$Q = (M_x + M_a - M_y - M_b) c^2 \quad (1.8)$$

This quantity may be evaluated experimentally by measuring the energies of a, b and Y. The most precise measurements of this type are in (n,  $\gamma$ ) reactions involving thermal neutrons, for which uncertainties < 1 keV are frequently attained. Other reactions yield results ranging from 1-10 keV.

D. Mass spectrometric methods: In this method the absolute mass of an atom X may be determined directly by comparing the mass of the atom with the mass of a hydrocarbon fragment in a mass spectrometer. The resulting mass difference enables a direct calculation of the mass of X. The absolute masses of a number of nuclides have been determined to a high degree of precision (uncertainties of  $\sim 100$  eV) in this manner. These masses, some of which are listed in Table 4-2, may be used as secondary standards for mass determinations. Uncertainties of 1 - 5 keV are typically obtained.

Ionic species containing atoms X and Y as part of their constituents may also be compared using this technique. By selecting ions constituted of atoms whose masses are known precisely and X and Y and measuring the mass difference between them the mass difference between X and Y can be determined. This method, which has been in use at many laboratories, yields results whose precision approaches 1 keV in most cases. Precisions as high as 65 eV have been attained by some investigators.

Until recently mass spectrometric determinations have been

carried out only among the naturally occurring nuclides while data on the unstable nuclides was obtained through nuclear reaction and decay Q-values. More recently Klapisch and his associates (Thibault et al, 1975) at Orsay and Wollnik (1975) at Lohengrin have utilized mass spectrometric techniques to study short-lived, unstable nuclides produced in charged particle reactions. In this laboratory (Manitoba I and II) a helium jet transport system is currently under construction (Venkatasubramanian et al, 1979). This system will be used to transport short-lived nuclides, produced by (p, xn) reactions, in the University of Manitoba cyclotron vault, to the mass spectrometry laboratory, some 100 m away, for analysis.

#### 1-4. TABLES OF ATOMIC DATA

The results from the various laboratories represent a large number of determinations of atomic mass differences and a much smaller number of absolute mass determinations. These data usually provide several ways of evaluating any particular mass difference, not all of which will agree with other data. All of these measurements may be written as a linear combination of the atomic masses. Thus a system of linear equations, each equation representing a mass or mass difference, with the set of atomic masses representing the unknown quantities may be set up. This system of equations is overdetermined for many nuclides as the number of measurements greatly exceeds the number of nuclides considered. A least squares solution for this system of equations is extracted in a manner originated by Mattauch (1965) and continued to recent years by Wapstra and his collaborators Gove (1971)

and Bos (1977). The resulting set of self-consistent masses and mass differences is published approximately every 5 yrs. in the form of the so-called Mass Evaluations. These compilations have the advantage that in the course of the calculation grossly inconsistent data may be recognized and removed to further enhance the reliability of the calculated results.



## CHAPTER 2

### HISTORY AND DEVELOPMENT OF MASS SPECTROMETRY

#### 2-0. INTRODUCTION

In 1886, while working with discharge tubes, Goldstein discovered positive rays. These rays were subsequently deflected by Wien (1898) with electric and magnetic fields and shown to have an  $e/m$  ratio that was much smaller than that of the electron. In order to investigate further the nature of these rays Thomson (1913) built his famous positive ray parabola apparatus at Cambridge. This device, which consisted of parallel, coterminous electric and magnetic fields, analysed the ion beam presented to it into a family of parabolas, each parabola corresponding to a particular  $e/m$ . With this apparatus Thomson (1912) was able to identify the constituents of the positive rays as ionized molecules of the discharge tube gas and found strong evidence that neon exists in two isotopic forms.

#### 2-1. EARLY INSTRUMENTS

Under the encouragement of Thomson, Aston, then a research student at Cambridge, designed and built an instrument, which he called a "mass spectrograph", to be used in the study of stable isotopes (Aston, 1919). This instrument had many of the characteristics of the deflection instruments which came later.

In general, in a deflection instrument, an ion source is used to illuminate an entrance or object slit. This slit is used as the object for an arrangement of electric and magnetic fields which

produce a set of images, each of which corresponds to a different  $e/m$  value at a photographic plate or at an exit slit which selects a particular mass for detection. The sharpness of each image, and hence the resolution of the apparatus, depends on the focussing properties of the apparatus, the variations in the velocities of the ions and the angular divergence of the ion beam used.

In Aston's instrument a highly collimated beam of ions was deflected first by an electric field and then by a magnetic field (in the same plane) and then detected on a photographic plate. The instrument had the property of "velocity focussing" i.e. that ions having different velocities did not contribute to the broadening of the image at the photographic plate.

At almost the same time Dempster (1918) built an instrument at Chicago to perform the same function. This instrument did not have the velocity focussing property but instead had a direction focussing property. That is, the apparatus focussed a monoenergetic ion beam, which initially diverged in direction, at an exit slit, and thereby greatly reduced the need for collimating the ion beam. In this instrument, different mass spectral lines were brought to a focus at the exit slit by changing the magnetic field. Bainbridge (1933) added a Wien velocity filter to a Dempster type instrument to reduce the effects caused by variations in the ionic velocity.

Herzog (1934) presented a general analysis of the focussing properties of electric and magnetic fields which lead to the construction of several instruments having both velocity and direction focussing. A summary of the ion optical properties of the two major

constituent fields used in mass spectrometers is briefly presented below.

## 2-2. POSITIVE ION OPTICS

The trajectories of ions of mass,  $m$  and charge,  $q$  as they traverse electric ( $E$ ) and magnetic ( $B$ ) fields are defined by the Lorentz force equation.

$$F = q (E + V \times B) \quad (2-1)$$

where  $V$  is the velocity of the ion considered. This relationship was applied to the particular field geometries and yielded the results summarized below.

A. Magnetic Analysers: One of the major components of mass spectrometers is the sector shaped homogenous magnetic field (see Fig. 2-1). If the magnetic field is constant and perpendicular to the velocity of an ion entering it, then the trajectory of the ion is a circle of radius  $a_m$  such that

$$a_m = \frac{MV}{qB} \quad (2-2)$$

in a plane perpendicular to the applied field.

Suppose that ions of mass  $M_0$  and velocity  $V_0$  emerge from an object point,  $O$  (Fig. 2-1) with a half angular spread,  $\alpha$  ( $\alpha \ll 1$ ). An ion, following the median path, enters the magnetic field normally after traversing a distance  $l_m$ , where it follows a circular path of radius  $a_m$ . It emerges from the field normally and proceeds to an image point,  $I$ , a distance  $l'_m$  away from the field boundary, where the ion beam is focussed to a point. For normal entry and exit, the

points O, C and I all lie on the same straight line as stated in a rule by Barber (1933). A more complete geometrical method for locating O, C and I for cases of non-normal incidence and exit was given later by Cartan (1937).

An analysis of this situation, using methods commonly used in ion optics was presented by Herzog (1934). He considered displacements of the image  $b_m'$  resulting from small displacements of the object,  $b_m$ , a change in ionic mass from  $M_0$  to  $M_0 (1 + \gamma)$  and change in ionic velocity from  $V_0$  to  $V_0 (1 + \beta)$ . He found that when  $\beta$  and  $\gamma$  are small ( $\beta, \gamma \ll 1$ ) this displacement is given by:

$$b_m' = a_m (\beta + \gamma) B_1 - b_m B_2 \quad (2-3)$$

where  $B_1$  and  $B_2$  are constants dependent on the geometry of the apparatus (Table 2-1).

B. Electrostatic Analysers: Another common component of deflection type mass spectrometers is the electrostatic analyser. This analyser usually consists of a sector of a cylindrical condenser. A radial electric field is generated by applying a potential  $V$  between a pair of concentric cylindrical electrodes of radii  $a_e + k$  and  $a_e - k$  respectively (Fig. 2-2). The magnitude of this electric field  $E$  is given by

$$E \approx \frac{V}{2k} \quad (2-4a)$$

for  $k \ll a_e$ . As in the case of the magnetic analyser, discussed above, ions of mass  $M_0$  and velocity  $V_0$  start from an object point O (Fig. 2-2) with a half angular spread  $\alpha$  ( $\alpha \ll 1$ ). An ion following the median path traverses a distance  $l_e$  before entering the field normally where it follows a circular path of radius  $a_e$  such that

$$a_e = \frac{2k M_0 V_0^2}{q V} \quad (2-4b)$$

The ion exits the field normally and proceeds to an image point I at a distance  $l_e'$  where the ion beam is brought to a focus. The displacement of the image,  $b_e'$  as a result of small displacements of the object,  $b_e$ , a change in the ionic mass from  $M_0$  to  $M_0 (1 + \gamma)$  and change in the ionic  $V_0$  to  $V_0 (1 + \beta)$  has been given by Herzog as

$$b_e' = a_e (\beta + \frac{1}{2} \gamma) E_1 - b_e E_2 \quad (2-5)$$

where  $E_1$  and  $E_2$  are constants, dependent on the geometry of the apparatus (Table 2-1), and  $\beta, \gamma \ll 1$ .

C. Double focussing: It will be noticed that in Eqn. 2-5 the coefficient for  $\gamma$  differs from the coefficient for  $\beta$ . This is not the case for the isolated magnetic analyser (Eqn. 2-3). It is therefore possible to design a compound system using an electrostatic analyser and a magnetic analyser in which the velocity dispersions cancel while a mass dispersion remains.

Let us consider a compound system in which the image formed by the electrostatic analyser is presented as the object to the magnetic analyser which subsequently forms an image at the detector. Using Eqn. 2-3 and 2-5 we describe displacements of the final image,  $b'$ , for small displacements of the object  $b$ , changes in ionic mass from  $M_0$  to  $M_0 (1 + \gamma)$  and changes in ionic velocity from  $V_0$  to  $V_0 (1 + \beta)$  by

$$b' = a_m (\beta + \gamma) B_1 - [a_e (\beta + \frac{1}{2} \gamma) E_1 - b E_2] B_2 \quad (2-6)$$

This expression can be rewritten as

$$b' = \gamma (a_m B_1 - \frac{1}{2} a_e E_1 B_2) + \beta (a_m B_1 - a_e E_1 B_2) + b E_2 B_2 \quad (2-7)$$