

A Complete Bacher and Goudsmit Method

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A complete Bacher and Goudsmit method for the calculation of atomic energy states in terms of the experimentally observed energies of ions of higher ionization is developed. The method has been extended to include configurations containing electrons of any angular momentum. A term in d^4 is calculated as an example.

I. INTRODUCTION

BACHER and Goudsmit¹ developed a theoretical method for finding the term values in atomic spectra from the experimental term values of the higher ions. Their results applied to configurations of s and p electrons only. Using the coefficients of fractional parentage of Racah² and Meshkov,³ it is now possible to give a direct method for obtaining Bacher and Goudsmit's results and to extend these results to configurations containing electrons of higher angular momentum than $l=1$.

II. CONFIGURATION CONTRIBUTIONS TO TOTAL ENERGY

A term in a given configuration is expressed as a linear combination of the terms of the configurations of the ions on which it is built. Our problem is to find the coefficients of this linear combination. First, we remove one electron from the original configuration and obtain the configurations of the next higher ion. The contribution of each of these configurations is proportional to the number of ways of forming it from the original configuration. If the original configuration has only equivalent electrons, then we get only one ion configuration; the number of ways of forming this higher ion configuration is $\binom{n}{n-1} = n$. If the original con-

figuration is of the form $l^{n-1}l'$, then there are $\binom{n-1}{n-2} = n-1$ ways of forming the configuration, $l^{n-2}l'$, and there is but one way to form the configuration l^{n-1} .

Again, we obtain $\binom{n}{n-1} = n$ ways of forming configurations of the ion. In general, for any configuration of n electrons, there are n ways of choosing configurations, and the sum of the coefficients of the terms of any configuration will be equal to the number of times this configuration occurs.

Each higher ion is broken up into its higher ions in a similar way. The number of ways of obtaining configurations for the ion with $n-2$ electrons is $\binom{n}{n-2}$,

and the coefficient of each configuration is equal to the number of times the configuration occurs. This process is continued until the ion consists of a single electron outside closed shells. In general, there are $\binom{n}{r}$ ways of choosing configurations of r electrons, and the coefficient of each configuration will be equal to the number of times this configuration occurs. The energies contributed by the different stages of ionization are in the ratio of the number of ways of obtaining configurations for each ion, i.e., in the ratio

$$\binom{n}{n-1} : \binom{n}{n-2} : \cdots : \binom{n}{r} : \cdots : n.$$

When the configurations of each successive ion are added to obtain the total energy of the term of the original configuration, each ion occurs with alternating signs. The alternation happens because it is necessary to transpose terms to obtain the energy in terms of the observed values of the energies of the successive ions, as was done in (15) of Bacher and Goudsmit.

As an example of the procedure so far, consider a d^4 configuration. The energy of a term may be written in terms of the experimentally observed energies of d^3 , d^2 , and d . The $d^3:d^2:d$ energy ratios are determined by the coefficients of the binomial expansion. There are four ways to group four electrons, three at a time; six, to group four electrons, two at a time; and four, to group four electrons, one at a time. Therefore, we write in the approximation used by Bacher and Goudsmit

$$W(d^4) = 4W(d^3) - 6W(d^2) + 4W(d). \quad (1)$$

Similarly, for five electrons,

$$W(d^5) = 5W(d^4) - 10W(d^3) + 10W(d^2) - 5W(d). \quad (2)$$

III. INDIVIDUAL TERM CONTRIBUTIONS TO TOTAL ENERGY

Having obtained the contributions of the electron configurations of all the ions to the energy, the next step is to express the energy of each configuration as a linear combination of the observed energies of its terms. The coefficients of this linear combination are obtained by using coefficients of fractional parentage together with (16) of M-I. We denote by $1R$ the energy of the term we are computing as given by (16) of M-I.

¹ R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934).

² G. Racah, Phys. Rev. **63**, 367 (1943), referred to as R-III.

³ S. Meshkov, Phys. Rev. **91**, 871 (1953), referred to as M-I. The fractional parentage coefficients are normalized such that the sum of the squares of all the coefficients in any row of a table equals one.

We must find how many R 's of energy there are in each stage of ionization.

In the first stage of ionization, we found that the sum of the coefficients of the terms of the configurations with $n-1$ electrons is n . The energy of n electrons is made up of the sum of the energies of $\binom{n}{n-2} = n(n-1)/2$ electron pairs. The energy of $n-1$ electrons is made up of the sum of the energies of $\binom{n-1}{n-3} = (n-1)(n-2)/2$ electron pairs. The energy of n electrons is thus $n/(n-2)$ times the energy of $n-1$ electrons. Therefore, in one R of energy the sum of the coefficients of the terms of the $n-1$ configuration is $n/(n-2)$. We now require x R 's of energy to obtain n , the sum of the coefficients of the terms of the $n-1$ configuration. Therefore,

$$xn/(n-2) = n, \quad (3)$$

and

$$x = n-2. \quad (4)$$

In all our discussion, except in special examples, we assume we are considering n electrons, with no specification of equivalence or nonequivalence.

For the second stage of ionization, we require y R 's to yield $n(n-1)/2$ terms. To find y , the number of R 's, which, when converted to the energies of $n-2$ electrons, are subtracted, we change the energy of n electrons to the energy of $n-1$ electrons and finally to the energy of $n-2$ electrons. To express an n electron energy in terms of the $n-2$ electron energies, we write

$$y \left(\frac{n}{n-2} \right) \left(\frac{n-1}{n-3} \right) = \frac{n(n-1)}{2}, \quad (5)$$

where $n/(n-2)$ is obtained in going from n to $n-1$ electrons and $(n-1)/(n-3)$ is obtained in going from $n-1$ to $n-2$ electrons. Therefore,

$$y = (n-2)(n-3)/2. \quad (6)$$

In general, the number of R 's to be added or subtracted is given by $\binom{n-2}{r-2}$, where r is the number of n electrons considered at a time.

For example, in the d^4 configuration, we first find how many R 's of energy, expressing d^4 in terms of d^3 , we must have. From (1) there are four d^3 energies. From (4), $x = n-2 = 2$ for $n=4$. Therefore, we must have two R 's of d^4 energy expressed in terms of d^3 energies.

To find the number of R 's, which, when converted to d^2 energies, are subtracted, we change d^4 energies to d^3 energies and finally to d^2 energies. From (6),

$$\begin{aligned} y &= (n-2)(n-3)/2 \\ &= 1 \text{ for } n=4. \end{aligned} \quad (7)$$

Therefore, one R of d^4 energy expressed in terms of d^2 energy must be subtracted. The final result is

$$W(d^4) = 2R(d^3) - R(d^2) + 4d. \quad (8)$$

IV. ENERGY OF (d^4 4^1I)

A specific illustration of the general Bacher and Goudsmit method is the calculation of the term energy $W(d^4$ 4^1I). From (8), we need two R 's of energy expressed in terms of d^3 energies. Using Tables II and III of R-III and (16) of M-I we get

$$\begin{aligned} 2R(d^3; d^4 \text{ } 4^1I) &= 2 \cdot 2 \cdot [(3/10)W(d^3 \text{ } 3^2G) \\ &\quad + (7/10)W(d^3 \text{ } 3^2H)] \\ &= (6/5)W(d^3 \text{ } 3^2G) + (14/5)W(d^3 \text{ } 3^2H). \end{aligned} \quad (9)$$

To obtain $1R(d^2; d^4 \text{ } 4^1I)$, we first take $1R(d^3; d^4 \text{ } 4^1I)$ from (9) and transform each d^3 energy into d^2 energies

$$\begin{aligned} W(d^3 \text{ } 3^2G) &= (3/42)[10W(d^2 \text{ } 2^1D) + 21W(d^2 \text{ } 2^3F) \\ &\quad + 11W(d^2 \text{ } 2^1G)], \end{aligned} \quad (10)$$

$$W(d^3 \text{ } 3^2H) = (3/2)[W(d^2 \text{ } 2^3F) + W(d^2 \text{ } 2^1G)]. \quad (11)$$

Substituting (10) and (11) into $R(d^3; d^4 \text{ } 4^1I)$ which is obtained in (9), we find

$$\begin{aligned} 1R(d^2; d^4 \text{ } 4^1I) &= (3/7)W(d^2 \text{ } 2^1D) + 3W(d^2 \text{ } 2^3F) \\ &\quad + (18/7)W(d^2 \text{ } 2^1G). \end{aligned} \quad (12)$$

Substituting (9) and (12) into (8), we find

$$\begin{aligned} W(d^4 \text{ } 4^1I) &= (6/5)W(d^3 \text{ } 3^2G) + (14/5)W(d^3 \text{ } 3^2H) \\ &\quad - (3/7)W(d^2 \text{ } 2^1D) - 3W(d^2 \text{ } 2^3F) \\ &\quad - (18/7)W(d^2 \text{ } 2^1G) + 4W(d^2 \text{ } 2D). \end{aligned} \quad (13)$$

Although we have illustrated the method for configurations of equivalent electrons, configurations of nonequivalent electrons can be treated in similar fashion.

V. COMMENTS

When terms of the same kind appear, the method gives the elements of the energy matrix rather than the term values themselves. It is therefore necessary to devise a scheme to calculate the values of the matrix elements in terms of the observed energies. A possible method for the calculation of these matrix elements has been applied to the d^3 and d^4 configurations of vanadium.⁴

One drawback to calculating absolute energies by the Bacher and Goudsmit method is the lack of precise experimental values for the ionization potentials of many atoms. However, the method will give the separations of the terms of the same ions, since the separations are independent of ionization potentials.

Some of these ideas have been developed independently by Trees.⁵

⁴ S. Meshkov, Phys. Rev. **93**, 270 (1954).

⁵ R. E. Trees (private communication).