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Isotope Shift in Boron

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Mrozowski's microphotometer curves for the lines λ2497, 2498 of B I due to $2^2P_{\frac{1}{2},1\frac{1}{2}}-3^2S_{\frac{1}{2}}$ and λ3451 of B II due to $(2s)(2p)\,{}^1P_1-(2p)^2\,{}^1D_2$ showed asymmetries which he resolved into isotope shifts arising from the isotopes 10 and 11. Subtraction of the corresponding normal shift from each of his observed values leads to observed specific shifts of -0.373 cm^{-1} for λ2497, -0.366 cm^{-1} for λ2498, and $+0.734$ cm^{-1} for λ3451. The present note gives a calculation of these specific shifts with the aid of Morse, Young, Haurwitz wave functions. The results are -0.3665 cm^{-1} for either member of λ2497, 2498 of B I and $+0.566$ cm^{-1} for λ3451 of B II. Reasons are suggested why the agreement with experiment is better in the case of the B I lines than in the case of the B II line, and also why the present calculation for the B I lines agrees better than that due to Opechowski and DeVries, who calculated -0.33 cm^{-1} for λ2497, 2498. The possible spread due to nuclear spin is estimated with the use of triplet separations and Morse, Young, Haurwitz functions and found to be of the order 0.03 cm^{-1} in each case, thus explaining on the basis of smallness the absence of nuclear spin h.f.s. in Mrozowski's plates.

MROZOWSKI[1] has recently investigated with high resolving power apparatus the boron spectrum excited in a hollow cathode discharge. Photometric investigation of the doublet lines λ2497 and λ2498 of B I, due to $2^2P_{\frac{1}{2}}-3^2S_{\frac{1}{2}}$ and $2^2P_{1\frac{1}{2}}-3^2S_{\frac{1}{2}}$, respectively, and of the line λ3451 of B II due to $(2s)(2p)^1P_1-(2p)^2\,{}^1D_2$ showed in each case an asymmetry. This asymmetry Mrozowski interpreted as indication of an isotope shift. Resolution of the photometric curve of each line into two symmetrical components, each of the typical shape due to Doppler effect, led to values for the abundance ratio B^{11}/B^{10} in good agreement with mass-spectrograph values. Letting $\Delta\nu\equiv\nu_{11}-\nu_{10}$, we may summarize his results as follows:

B I, λ2497: $\Delta\nu=-0.175\pm0.012$ cm^{-1},
B I, λ2498: $\Delta\nu=-0.168\pm0.010$ cm^{-1},
B II, λ3451: $\Delta\nu=0.877\pm0.004$ cm^{-1}.

There was no indication of h.f.s. splitting due to nuclear spin.

It is the purpose of this note to give a theoretical calculation of the expected isotope shifts due to nuclear motion and an estimate of the possible spreads due to nuclear spin. The notation of the author's paper on isotope shift in Mg I[2] will be followed. Thus for the line $A\rightarrow B$, $\Delta\nu=(\Delta\nu)_N+(\Delta\nu)_\sigma$, where the normal shift $(\Delta\nu)_N=(1/11-1/10)1838^{-1}(\tau_A-\tau_B)$, where, e.g., τ_A is the term value in cm^{-1} of level A, and the specific shift $(\Delta\nu)_\sigma=-(1/11-1/10)1838^{-1}\,2\,\mathrm{Ry}(k_A-k_B)=1.0855(k_A-k_B)$ cm^{-1}. From the observed term values we have, to sufficient accuracy, $(\Delta\nu)_N=0.198$ cm^{-1} for either λ2497 or λ2498 of B I, and $(\Delta\nu)_N=0.143$ cm^{-1} for λ3451 of B II. These values lead to specific shifts of -0.373 cm^{-1} for λ2497, -0.366 cm^{-1} for λ2498, and 0.734 cm^{-1} for λ3451.

For the doublet λ2497, 2498 of B I, the level A is $(1s)^2(2s)^2 3s\,{}^2S_{\frac{1}{2}}$ and B is $(1s)^2(2s)^2 2p\,{}^2P_{\frac{1}{2},1\frac{1}{2}}$. From reference 2, Eqs. (1), (4), (5), and the relation $\bar{\sigma}\equiv-2(m/M)\,\mathrm{Ry}\,k$, we obtain:

$$k_A=0$$
$$k_B=\tfrac{1}{3}[J^2(2p,1s)+J^2(2p,2s)]. \qquad (1)$$

In deducing (1) the fact has been used that it is valid to calculate $\bar{\sigma}$ in the SLM_LM_S representation, in which the wave functions in the above simple cases are single determinants corresponding, respectively, to the configurations $1s^+1s^-2s^+2s^-3s^\pm$ and $1s^+1s^-2s^+2s^-2p^\pm{}_m$. In evaluating the J's the variational radial functions of Morse, Young, and Haurwitz[3] will be used. Use of the parameters for $(1s)^2(2s)^2 2p\,{}^2P$ as given by them leads, after some simple integrations, to $J^2(2p,1s)=0.7590$ and $J^2(2p,2s)=0.2539$,

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[1] S. Mrozowski, Zeits. f. Physik **112**, 223 (1939).

[2] J. P. Vinti, Phys. Rev. **56**, 1120 (1939).

[3] P. M. Morse, L. A. Young, and E. S. Haurwitz, Phys. Rev. **48**, 948 (1935). This paper is subsequently referred to as MYH; the radial factors of the MYH functions are written explicitly in reference 2.

with the result that $k_B=0.3376$, so that $k_A-k_B=-0.3376$ and $(\Delta\nu)_\sigma=-0.3665$ cm^{-1}. Thus for each member of the doublet line $(1s)^2(2s)^2 3s\ {}^2S \rightarrow (1s)^2(2s)^2 2p\ {}^2P$ there results the calculated specific shift -0.3665 cm^{-1}, as against Mrozowski's observed values of -0.373 cm^{-1} for λ2497 and -0.366 cm^{-1} for λ2498. At this point it should be mentioned that a calculation by Opechowski and DeVries[4] of this shift gave a value -0.33 cm^{-1}. Their calculation was carried out with the aid of Hartree radial functions obtained by Brown, Bartlett, and Dunn.[5] Thus their radial functions correspond to the solution of a variational problem in which the trial function has as much flexibility as is consistent with the requirement that it be a product of single-electron wave functions. The MYH functions, on the other hand, although not so flexible as the Hartree functions, take proper symmetry into account at the very start. This fact may account for the better agreement with observation obtained with the use of the MYH functions.

For λ3451 of B II the transition is $(1s)^2(2p)^2\ {}^1D_2 \rightarrow (2s)(2p)^1P_1$. For $(1s)^2(2p)^2\ {}^1D_2$ we use the fact that $\bar{\sigma}$ is the same in the SLM_LM_S representation as in the $SLJM_J$ representation, and that its value in the SLM_LM_S representation is independent of M_S or M_L. We may then compute its value for $M_S=0$, $M_L=2$, for which the wave function is the single determinant corresponding to the configuration $1s^+1s^-2p^+{}_1 2p^-{}_1$. Then from Eqs. (1), (4), and (5) of reference 2 and the relation connecting $\bar{\sigma}$ and k, we have:

$$k_A=\tfrac{2}{3}J^2(2p,\ 1s), \tag{2}$$

where the subscript A refers to the initial level $(2p)^2\ {}^1D_2$. For the final level $B\equiv(1s)^2(2s)(2p)^1P_1$ we make use of the diagonal sum rule, in the manner of reference 2. In the use of this method we have to assume that a given single orbit function, e.g. $2p$, is the same for $(2s)(2p)^1P$ and $(2s)(2p)^3P$; in the final formulas for the singlet and triplet, however, we may use the proper (different) values of the parameters as found by MYH. This procedure is justified by the fact that if we actually wrote the wave function in each case as the proper linear combination of determinants and then calculated $\bar{\sigma}$, we should obtain essentially the same formulas as would be given by the method of sums, the only difference being that the correct (different) parameters would appear in the final formulas. The method of sums here goes very much as it does for $(3s)(3p)$ of Mg I, for which the process was given in reference 2, p. 1124; thus for the triplet:

$$\bar{\sigma}_t=-\tfrac{2}{3}(m/M)\ \mathrm{Ry}\ [J^2(2p,\ 1s)+J^2(2p,\ 2s)] \tag{3}$$

and for the sum for singlet and triplet:

$$\bar{\sigma}_t+\bar{\sigma}_s=-(4/3)(m/M)\ \mathrm{Ry}\ J^2(2p,\ 1s). \tag{4}$$

By difference, we obtain:

$$\bar{\sigma}_s=-\tfrac{2}{3}(m/M)\ \mathrm{Ry}\ [J^2(2p,\ 1s)-J^2(2p,\ 2s)], \tag{5}$$

so that

$$k_B=\tfrac{1}{3}[J^2(2p,\ 1s)-J^2(2p,\ 2s)]. \tag{6}$$

Using in Eq. (2) the MYH parameters for $(2p)^2\ {}^1D$ and in Eq. (6) the MYH parameters for $(2s)(2p)^1P$, we find after some simple integrations that $k_A=0.8019$ and $k_B=0.2804$. These values give $(\Delta\nu)_\sigma=+0.566$ cm^{-1}, as compared with Mrozowski's observed value of $+0.734$ cm^{-1}, a discrepancy of 23 percent. The fact that the agreement is less satisfactory for the B II line than for the B I lines may possibly be due to the MYH functions. Examination of the term values given by the B I and B II functions of MYH shows that the wave functions for B I are probably much better than those for B II, MYH finding indeed that their term value discrepancies are always much less when there is only one electron in the outermost shell than when there are two or more.

It still remains to be explained why no h.f.s. due to nuclear spin is observed in either case, since B^{10} and B^{11} both have nuclear magnetic moments. The obvious answer would be that the spread due to nuclear spin is too small to be resolved; this indeed turns out to be the case. The spread due to nuclear spin can be estimated for the line $3s\ {}^2S_{\frac{1}{2}} \rightarrow 2p\ {}^2P_j$ of B I; for B^{11} it is of the order 0.034 cm^{-1} for $j=\frac{1}{2}$, 0.022 cm^{-1} for $j=\frac{3}{2}$; for B^{10} it would be still smaller. For $(2p)^2\ {}^1D_2 \rightarrow (2s)(2p)^1P_1$ of B II it comes out 0.031 cm^{-1} for B^{11} and smaller for B^{10}. Since shifts

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[4] W. Opechowski and D. A. DeVries, Physica [6] **9**, 913 (1939).

[5] F. W. Brown, J. H. Bartlett, Jr., and C. G. Dunn, Phys. Rev. **44**, 296 (1933).

even of 0.7 cm^{-1} were not actually resolved by Mrozowski, but gave rise only to asymmetries in the microphotometer curves, it is clear that the splitting due to nuclear spin would be entirely unobservable in Mrozowski's plates.

Since Opechowski and DeVries[4] have indicated the method of estimating the nuclear spin spread for the doublet line of B I, we shall outline only the somewhat less obvious estimate for the B II line. We use the notation and methods of a paper by Goudsmit,[6] in which a or b denotes, respectively, the interaction parameter in the sense of Goudsmit's Eq. (3) for a single p electron or a single s electron with the nuclear magnetic moment, and $A(J)$ is the coupling coefficient occurring in the expression $A\,\mathbf{I}\cdot\mathbf{J}$ for the interaction energy of the electrons with the nucleus, where $\mathbf{I}$ is the nuclear spin and $\mathbf{J}$ the total electronic angular momentum. The single electron parameters a or b are given by the expression

$$\text{Ry}\,\alpha^2 g(I)1838^{-1}\langle 1/r^3\rangle_{\text{Av}} = (5.82)1838^{-1}g(I)\langle 1/r^3\rangle_{\text{Av}}\,\text{cm}^{-1}, \tag{7}$$

where Ry is the Rydberg energy, α the fine structure constant, $g(I)$ the nuclear gyromagnetic ratio, and r is expressed in units of the Bohr radius. For a hydrogenic nonpenetrating orbit $\langle 1/r^3\rangle_{\text{Av}}$ has the value $Z^{*3}/n^3l(l+\frac{1}{2})(l+1)$, Z^* being the effective nuclear charge.

For $(2s)(2p)$ we denote the singlet A by $A'(1)$ and the triplet A's for $J=1$ and 2 by $A(1)$ and $A(2)$. Then the method of sums gives:

$$\begin{aligned} A(2) &= \tfrac{2}{5}a+\tfrac{1}{4}b, \\ A(1)+A'(1) &= 2a+\tfrac{1}{4}b. \end{aligned} \tag{8}$$

Applying now the method of sums to the interaction energy of the orbital magnetic moments only with the nucleus and then to the interaction energy of the spin magnetic moments only with the nucleus, we find:

$$\begin{aligned} A_{\text{orb}}(2) &= \tfrac{1}{2}a, \\ A_{\text{orb}}(1)+A'_{\text{orb}}(1) &= 1\tfrac{1}{2}a, \end{aligned} \tag{9}$$

$$\begin{aligned} A_{\text{sp}}(2) &= -(1/10)a+\tfrac{1}{4}b, \\ A_{\text{sp}}(1)+A'_{\text{sp}}(1) &= \tfrac{1}{2}a+\tfrac{1}{4}b, \end{aligned} \tag{10}$$

where the meaning of the symbols is evident, so $A(2) = A_{\text{orb}}(2)+A_{\text{sp}}(2)$, etc. If we now apply Goudsmit's Eq. (33) for the $A(J)$ of a multiplet, we find:

$$\begin{aligned} A(2) &= \tfrac{1}{2}\lambda-\tfrac{1}{5}\sigma+\tfrac{1}{2}\beta, \\ A(1) &= \tfrac{1}{2}\lambda+\sigma+\tfrac{1}{2}\beta, \\ A'(1) &= \lambda. \end{aligned} \tag{11}$$

Here λ, σ, and β denote, respectively, parameters for interaction with the nucleus of the total orbital angular momentum $\mathbf{L}$, of the total spin $\mathbf{S}$, and of the spin of an "unbalanced" s electron such as occurs in sp. It is worth mention that Goudsmit's Eq. (33) can be derived very easily for all the special cases that are here considered. Equations (11) can now be decomposed as follows:

$$\begin{aligned} A_{\text{orb}}(2) &= \tfrac{1}{2}\lambda, & A_{\text{sp}}(2) &= -\tfrac{1}{5}\sigma+\tfrac{1}{2}\beta, \\ A_{\text{orb}}(1) &= \tfrac{1}{2}\lambda, & A_{\text{sp}}(1) &= \sigma+\tfrac{1}{2}\beta, \\ A'_{\text{orb}}(1) &= \lambda, & A'_{\text{sp}}(1) &= 0. \end{aligned} \tag{12}$$

Comparison of Eqs. (9), (10), and (12) leads to the relations $\lambda=a$, $\sigma=\frac{1}{2}a$, $\beta=\frac{1}{2}b$; thus the desired $A'(1)=a$. For $(2s)(2p)^1P_1$, therefore, we need only the p parameter a.

For $(2p)^2$ we denote the A of the ${}^1D_2$ by $A'(2)$ and the A's of the ${}^3P$ by $A(1)$ and $A(2)$. Then, from the method of sums:

$$\begin{aligned} A(2)+A'(2) &= (8/5)a, \\ A(1) &= 0, \end{aligned} \tag{13}$$

and from the general multiplet formula:

$$\begin{aligned} A'(2) &= \lambda, \\ A(1) &= \tfrac{1}{2}\lambda+\sigma, \\ A(2) &= \tfrac{1}{2}\lambda-\tfrac{1}{5}\sigma. \end{aligned} \tag{14}$$

Comparison of Eqs. (13) and (14) gives $\lambda=a$ and $\sigma=-a/2$, so that the desired $A'(2)=a$.

For $(2p)^2\,{}^1D_2$ the hydrogenic expression for $\langle 1/r^3\rangle_{\text{Av}}$ gives $a=5.82(Z^{*3}/24)g(I)/1838\ \text{cm}^{-1}$. From the work of Millman, Kusch, and Rabi,[7] $g(I)$ is known to have the value 1.788 for B^{11}; also Z^* may be estimated from the triplet separations for $(2p)^2\,{}^3P$ to be 2.80.[8] These values lead to $a=0.0052\ \text{cm}^{-1}$ for $(2p)^2\,{}^1D_2$. For $(2s)(2p)\ {}^1P_1$ we take Z^* from the triplet separation for $(2s)(2p)\ {}^3P$, *viz.* 2.82,[8] and obtain $a=0.0053\ \text{cm}^{-1}$. The $\langle 1/r^3\rangle_{\text{Av}}$ values may also be estimated from the MYH functions: for $(2p)^2\,{}^1D_2$ one finds $(\langle 1/r^3\rangle_{\text{Av}})_{2p}=\frac{1}{3}(1.385)^3=0.883$, leading to $a=0.0050$; for $(2s)(2p)\ {}^1P$ one finds $(\langle 1/r^3\rangle_{\text{Av}})_{2p}=\frac{1}{3}(1.335)^3=0.793$, leading to $a=0.0045$. The two methods check about as well as could be expected;[9] to obtain an upper limit for the spread in each case we take the slightly larger values of a obtained from the Z^*. Then since $A=a$ in each case, we have $A=0.0052\ \text{cm}^{-1}$ for $(2p)^2\,{}^1D_2$ and $A=0.0053\ \text{cm}^{-1}$ for $(2s)(2p)\ {}^1P_1$. Each hyperfine level is then given by

$$\delta\nu = A/2[F(F+1)-J(J+1)-I(I+1)], \tag{15}$$

where F is the hyperfine quantum number and I is the nuclear spin, for which the value $1\frac{1}{2}$ has been suggested[7] as the most reasonable value for B^{11}. Use of Eq. (15) for each level plus the selection rule leads to the hyperfine components; the spread is then given by the sum of the absolute values of the largest positive and largest negative $\delta\nu$'s. The result is $(0.0078+0.0232)\ \text{cm}^{-1}=0.031\ \text{cm}^{-1}$.

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[6] S. Goudsmit, Phys. Rev. **37**, 663 (1931).

[7] S. Millman, P. Kusch, and I. I. Rabi, Phys. Rev. **56**, 165 (1939).

[8] L. Pauling and S. Goudsmit *The Structure of Line Spectra* (McGraw-Hill, 1930), p. 101.

[9] For the level $2p\ {}^2P$ of B I an estimate of $(\langle 1/r^3\rangle_{\text{Av}})_{2p}$ from MYH functions leads to a value of A which is 10 percent larger than that estimated from doublet separations (the method of Opechowski and DeVries).