

VERY ACCURATE MCHF CALCULATIONS OF OSCILLATOR STRENGTHS IN LIGHT ATOMS. THE BORON (B II) LINE AT 1362 Å.

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ABSTRACT

A new method to deal with non-orthogonalities in transition calculations has been implemented and tested. Large-scale transition calculations using the multiconfiguration Hartree-Fock (MCHF) method have been performed for the resonance line of B II at 1362 Å. In these calculations the orbital sets of the initial and final state wave functions have not been assumed to be equal, but have been optimized independently. The calculated weighted oscillator strength $gf = 0.999$ has an estimated uncertainty of less than 0.2 %. Together with the previously calculated isotope shift and hyperfine structure all atomic parameters needed for a detailed modelling of the B II resonance line in high-resolution spectra are now available with high accuracy.

Subject headings: atomic data - line: identification - Galaxy: evolution - ultraviolet: general

1 INTRODUCTION

The cosmic abundance of the light elements lithium, beryllium, and boron is of particular interest as these are not natural products of nucleosynthesis reactions inside stars. These elements are instead believed to be produced in primordial (big bang) nucleosynthesis. Being a very complicated process, different models have been proposed. Recently, two reactions not usually included in primordial nucleosynthesis were considered: ${}^7\text{Li}({}^3\text{H}, n){}^9\text{Be}$ and ${}^9\text{Be}({}^3\text{H}, n){}^{11}\text{B}$ (Kajino & Boyd 1990). With these reactions included, theoretical calculations show that considerably higher abundances of ${}^9\text{Be}$, ${}^{10}\text{B}$, and ${}^{11}\text{B}$ are produced in the nonuniform density model (NDM) than in the standard model (SM) for large intervals of the parameters associated with these models of primordial nucleosynthesis. The difference in abundance is especially large for ${}^{10}\text{B}$ where the SM predicts a dramatic decrease in production at a baryon-to-photon ratio η of 10^{-9} , whereas the NDM predicts a monotonic increase with η . Other processes, such as spallation of CNO nuclei and neutrino induced reactions within the helium and carbon shells in supernovae, have also been proposed for the nucleosynthesis of ${}^{10}\text{B}$ and ${}^{11}\text{B}$. The former process leads to production of both isotopes whereas the latter process produces only ${}^{11}\text{B}$ and could be a possible explanation of the high solar ${}^{11}\text{B}/{}^{10}\text{B}$ isotopic ratio.

To check the proposed production processes it is of importance to determine the ${}^{10}\text{B}$ and ${}^{11}\text{B}$ abundances, and specially the isotopic ratio, in various objects. The B I lines at 2090 Å, having an isotope shift of 25 mÅ, have been suggested for this purpose (Johansson et. al. 1993). However, the ionization balance in moderate temperature stars as well as in the interstellar medium (ISM) suggests that B II is much more abundant than B I and, in this perspective, lines in B II are therefore more suitable for abundance determinations. The resonance line of B II appears at 1362 Å and was recently observed in medium resolution spectra of the ISM toward ζ Ophiuchi obtained with the Goddard High Resolution Spectrograph (GHRS) aboard the Hubble Space Telescope (HST) (Federman et. al. 1993). After the successful repair of the GHRS in December 1993 it should now be possible to observe the transition also in high resolution.

To determine the abundances of ${}^{10}\text{B}$ and ${}^{11}\text{B}$ from the resonance line of B II a detailed modeling of the observed line profile has to be done, requiring accurate values of the oscillator strength, isotope shift and hyperfine structure. Recent progress in large-scale multiconfiguration Hartree-Fock (MCHF) calculations, together with today's powerful computers, has made it possible to calculate hyperfine structures and isotope shifts in light atoms with very high accuracy (see e.g. Sundholm & Olsen 1991a,b, Jönsson & Froese Fischer 1993, 1994). In a previous *letter* the isotope shift and hyperfine structure in the resonance transition of B II have been calculated with an estimated uncertainty of less than 1 % (Jönsson et. al. 1994). By contrast, the calculation of accurate transition values, such as oscillator strengths, has remained difficult. To evaluate the transition matrix elements using standard Racah algebra techniques the two states involved in the transition have to be described by the same orbital set (Robb 1973, see also Froese Fischer et. al. 1991 who have relaxed the orthogonality condition slightly). A high-quality wave function, however, demands orbitals optimized for the specific electronic state, and it is usually not possible to obtain an accurate description when the same orbital set is used for two different states. This problem can be overcome, as proposed by Malmqvist (1986), and it is now possible to perform large-scale transition calculations where the orbital sets of the two wave functions are not assumed to be equal, but can be optimized independently (Olsen et. al. 1994). Using the active space method, where the configuration spaces for the initial and final state are generated by excitations from two separate active sets of orbitals, the convergence of the calculated oscillator strength can be studied as the active sets are increased in a systematic way. From the convergence pattern the uncertainty of the calculated oscillator strength can then be estimated. A further check on the accuracy of the

calculated oscillator strengths can be obtained by comparing the length and velocity form of the oscillator strength. These two forms should give the same result provided exact wave functions are used for both the initial and final states. A disagreement between them for approximate wave functions indicates that important correlation effects have been left out.

In this *letter* we have calculated the oscillator strength of the resonance transition of B II with an estimated uncertainty of less than 0.2 %. The calculated oscillator strength $gf = 0.999$ is outside the errorbars of the most accurate experimental value, obtained by isoelectronic smoothing of experimental (measured by the beam-foil technique) line strengths in the beryllium isoelectronic sequence (Reistad & Martinson 1986). This indicates that the experimental values suffer from systematic errors, or that the given errorbars after the smoothing procedure of Reistad and Martinson are too small.

2 THEORY

In the non-relativistic MCHF approach (Froese Fischer 1991) the wave function ψ for a state labelled γLS , where γ represents the configuration and any other quantum numbers required to specify the state, is expanded in terms of configuration state functions (CSF's) with the same LS term.

$$\psi(\gamma LS) = \sum_j c_j \Phi_j(\gamma_j LS) \quad (1)$$

The configuration state functions Φ are anti-symmetrized linear combinations of products of spin-orbitals

$$\phi_{nlm_l m_s} = \frac{1}{r} P_{nl}(r) Y_{lm_l}(\theta, \varphi) \xi_{m_s}(\sigma) \quad (2)$$

where the radial functions $P_{nl}(r)$ are represented by their numerical values at a number of grid-points. The radial functions are required to be orthonormal within each l -symmetry

$$\int_0^\infty P_{n'l}(r) P_{nl}(r) dr = \delta_{n'n} \quad (3)$$

In the multiconfiguration self-consistent field (MC-SCF) procedure both the orbitals and the expansion coefficients are optimized to self-consistency.

The gf value for a transition between a level $\gamma' L' S'$ and the level γLS can be written in two forms, the length and velocity form, respectively (Cowan 1981, Froese Fischer et. al. 1991)

$$gf_l = \frac{2}{3} (E_{\gamma' L' S'} - E_{\gamma LS}) |\langle \gamma LS || \sum_{i=1}^N r_i \mathbf{C}^{(1)}(i) || \gamma' L' S' \rangle|^2 \quad (4)$$

$$gf_v = \frac{2}{3} (E_{\gamma' L' S'} - E_{\gamma LS})^{-1} |\langle \gamma LS || \sum_{i=1}^N \nabla_i^{(1)}(i) || \gamma' L' S' \rangle|^2 \quad (5)$$

Here $C_q^{(1)} = \sqrt{4\pi/3} Y_{1q}$ is the normalized spherical harmonic and $\nabla_q^{(1)}$ the tensor form of the gradient operator. The reduced matrix elements are defined through the relation

$$\langle \gamma J M | T_Q^{(K)} | \gamma' J' M' \rangle = (-1)^{J-M} \begin{pmatrix} J & K & J' \\ -M & Q & M' \end{pmatrix} \langle \gamma J || \mathbf{T}^{(K)} || \gamma' J' \rangle \quad (6)$$

where $T^{(K)}$ is a spherical tensor operator of rank K and J a general angular momentum. The two forms of the gf value give the same result for exact non-relativistic wave functions. For approximate

wave functions, however, they will differ and this can be used as a measure of the accuracy of the calculated values.

In the MCHF approach, where both states in the transition are given as configuration state expansions

$$\psi(\gamma' L' S') = \sum_j c'_j \Phi_j(\gamma' L' S') \quad (7)$$

$$\psi(\gamma L S) = \sum_k c_k \Phi_k(\gamma L S) \quad (8)$$

the calculation of the gf value reduces to the evaluation of transition matrix elements between arbitrarily LS coupled CSF's

$$\langle \gamma_k L S \| \sum_{i=1}^N r_i \mathbf{C}^{(1)}(i) \| \gamma'_j L' S' \rangle \quad (9)$$

$$\langle \gamma_k L S \| \sum_{i=1}^N \nabla^{(1)}(i) \| \gamma'_j L' S' \rangle \quad (10)$$

This can be done with standard Racah-algebra assuming that both left and right configurations are formed from the *same* orthonormal set of spin-orbitals (Robb 1973). This is a very severe restriction since a high-quality wave function demands orbitals optimized for the specific electronic state. However, Malmqvist (1986) has shown that for very general configuration expansions, where the initial and final state are described by different orbital sets, it is possible to change the wave function representation of the two states in such a way that the standard Racah-algebra can be used for the evaluation of the matrix elements in the new representation. This procedure for the calculation of gf values can be summarized as follows.

1. Perform MCHF calculations for the initial and the final state where the orbital sets of the two wave functions are *not* assumed to be equal.
2. Change the wave function representation by transforming the two orbital sets to a biorthonormal basis. This is followed by a counter-transformation of the expansion coefficients c'_j and c_k as to leave the total wave functions invariant.
3. Calculate the gf values with the transformed wave functions for which now the standard Racah-algebra can be used.

The details of the transformation are discussed in the articles of Malmqvist (1986) and Olsen et. al. (1994).

The configuration expansions were obtained with the active space method (Roos et al 1980 and Olsen et al 1988), where CSF's of a particular parity and LS symmetry are generated by excitations from the reference configuration to an active set of orbitals. The active set is then increased in a systematic way allowing the convergence of the oscillator strength to be studied. By imposing different restrictions on the way excitations can be done, orbitals can be targeted to describe different electron correlation effects.

3 RESULTS AND DISCUSSION

To illustrate the importance of different correlation effects, three separate sets of calculations of the oscillator strengths were done. In the first approach only outer correlation was included, and the configuration expansions consisted of all CSF's of the form $1s^2 nl n' l'$ where $nl n' l'$ belongs to

the active set of orbitals. In Table 1 the value of the total energy for the $1s^22s^2\ ^1S$ and $1s^22s2p\ ^1P$ terms of B II, as well as the length and velocity form of the weighted oscillator strengths, for the transition, are shown as a function of the increasing active set. In our calculations the active sets for the initial and final state contain the same number of orbitals of each l -symmetry and it is therefore necessary to specify the active set for only one of the states. The notation for the active set follows the conventions used in quantum chemistry. The set $3s2p1d$, for example, contains three s -orbitals, two p -orbitals and one d -orbital. It is seen that both the length and velocity form of the oscillator strength have converged to within two parts in tenthousand. The fact that the two forms differ by 3% shows that important correlation effects have been left out when including only outer correlation. In the second approach outer correlation as well as polarization of the $1s$ sub-shell was included. In this case the configuration expansions consisted of all CSF's of the form $1snln'l'n''l''$. In Table 2 the value of the total energy, as well as the length and velocity form of the weighted oscillator strengths, for the transition, are shown as a function of the increasing active set of orbitals. Also in this case the length and velocity form of the oscillator strength have converged for the largest active set of orbitals. In this case the two forms differ by only two parts in a thousand and showing that essentially all important correlation effects have been captured. Finally, a full correlation calculation was performed where also correlation within the $1s$ sub-shell was included. In the full correlation calculation CSF's of the form $nl'n'l'n''l''n'''l'''$ were included in the expansion. This is referred to as a complete active space (CAS) expansion. When all CSF's of this form are included, the size of the expansion grows very rapidly with the increasing active set. Many of these configurations have very small expansion coefficients and contribute very little to the total energy and the oscillator strengths (Tong et. al. 1993, Froese Fischer 1993), and it is possible to impose restrictions on the allowed CSF's without changing the final result. In our calculation we included only configurations where at least two of the orbitals had principal quantum numbers $n < 4$. In Table 3 the value of the total energy, as well as the length and velocity form of the weighted oscillator strengths, for the transition, are shown as a function of the increasing active set of orbitals. In this case the convergence of the length and velocity form is a little slower and a larger active set of orbitals was needed. The slower convergence rate in this case can be explained by the fact that many of the first orbitals will describe correlation within the $1s$ sub-shell, and first after these correlation effects have been saturated the orbitals start to describe core-valence correlation effects that are energetically unimportant but important for the oscillator strength. In this case, although more oscillatory, it is seen that the length and velocity form are in perfect agreement, showing that all correlation effects have been captured. For this case the transition energy shows a monotonous trend towards the experimental value of Ölme (1970). However, to make a more precise comparison between the theoretical and experimental transition energies the former has to be corrected for relativistic and finite mass effects.

The theoretical value of the weighted oscillator strength is $gf = 0.999$, and based on the convergence trends of Tables 2 and 3, the error is estimated to be below two parts in a thousand. Relativistic effects are very small and have been neglected. In Table 4 the oscillator strength is compared with values from other calculations and experiment. It is seen that our value lies outside the errorbars of the most accurate experimental value obtained by isoelectronic smoothing of experimental line strengths, measured by the beam-foil technique, in the beryllium isoelectronic sequence (Reistad & Martinson 1986). This indicates that the experimental values suffer from systematic errors, or that the given errorbars after the smoothing procedure of Reistad and Martinson are too small.

4 CONCLUSIONS

In the present *Letter* we report on an accurate calculation of the oscillator strength of the resonance line of B II at 1362 Å using a new method to deal with non-orthogonalities in the transition matrix elements. The theoretical value of the weighted oscillator strength is $gf = 0.999$, and the convergence pattern in the calculations implies an uncertainty of less than 0.2%. Determination of the boron abundance in various objects and in the interstellar medium is of great astrophysical and cosmological significance. Our results now provide the possibility to include the oscillator strength, together with the previously calculated isotope shift and hyperfine structure, in a detailed modelling of the B II resonance line in high-resolution spectra. To conclude we want to point out that the employed method to calculate oscillator strengths is completely general and that accurate calculations of other transitions in light atoms of astrophysical interest are in progress.

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Table 1. Valence correlation MCHF gf -values in B II.

active set	$1s^2 2s^2 \ ^1S$		$1s^2 2s 2p \ ^1P^o$		$1s^2 2s^2 \ ^1S \rightarrow 1s^2 2s 2p \ ^1P^o$		
	E (a.u.)	Ncfg	E (a.u.)	Ncfg	gf_l	gf_v	ΔE (cm^{-1})
HF	-24.237 575	1	-23.912 873	1	1.449 34	0.732 92	71 260
2s1p	-24.296 082	2	-23.912 873	1	1.064 74	0.789 27	84 100
3s2p1d	-24.298 330	7	-23.956 320	6	1.035 93	1.068 83	75 059
4s3p2d1f	-24.298 647	16	-23.960 103	17	1.025 66	1.056 92	74 298
5s4p3d2f1g	-24.298 767	30	-23.961 101	36	1.022 96	1.057 15	74 105
6s5p4d3f2g1h .	-24.298 826	50	-23.961 448	65	1.022 18	1.056 90	74 042
7s6p5d4f3g2h1i	-24.298 852	77	-23.961 607	106	1.021 91	1.056 83	74 013
Experiment ...							73 397

Table 2. Valence and core-valence correlation MCHF gf -values in B II

active set	$1s^22s^2\ ^1S$		$1s^22s2p\ ^1P^o$		$1s^22s^2\ ^1S \rightarrow 1s^22s2p\ ^1P^o$		
	E (a.u.)	Ncfg	E (a.u.)	Ncfg	gf_l	gf_v	ΔE (cm^{-1})
HF	-24.237 575	1	-23.912 873	1	1.449 34	0.732 92	71 260
2s1p	-24.296 373	3	-23.913008	3	1.065 33	0.792 79	84 135
3s2p1d	-24.300 685	23	-23.958 255	36	1.026 83	1.082 08	75 151
4s3p2d1f	-24.304 799	100	-23.966 961	185	1.005 65	0.997 67	74 143
5s4p3d2f1g	-24.305 673	318	-23.969 633	650	1.001 07	0.999 19	73 749
6s5p4d3f2g1h .	-24.305 998	831	-23.970 655	1810	1.000 59	0.998 89	73 595
7s6p5d4f3g2h1i	-24.306 153	1892	-23.971 064	4312	1.000 28	0.998 36	73 539
Experiment ...							73 397

Table 3. Full correlation MCHF gf -values in B II

active set	$1s^2 2s^2 \ ^1S$		$1s^2 2s 2p \ ^1P^o$		$1s^2 2s^2 \ ^1S \rightarrow 1s^2 2s 2p \ ^1P^o$		
	E (a.u.)	Ncfg	E (a.u.)	Ncfg	gf_l	gf_v	ΔE (cm^{-1})
HF	-24.237 575	1	-23.912 873	1	1.449 34	0.732 92	71 260
2s1p	-24.296 413	5	-23.913 062	4	1.065 22	0.791 43	84 132
3s2p1d	-24.334 812	63	-23.988 668	98	1.021 50	0.993 81	75 966
4s3p2d1f	-24.342 409	460	-24.001 844	713	1.018 60	1.025 82	74 741
5s4p3d2f1g	-24.346 046	1066	-24.008 886	2300	1.004 13	1.003 75	73 994
6s5p4d3f2g1h	-24.347 410	2306	-24.011 624	5211	1.000 75	0.999 78	73 693
7s6p5d4f3g2h1i ..	-24.347 943	4200	-24.012 990	9772	1.002 71	0.998 72	73 510
8s7p6d5f4g3h2i1k	-24.347 943	6865	-24.012 990	16298	0.999 03	0.999 15	73 449
Experiment							73 397

Table 4. The gf -values in B II compared with values from other calculations and experiment

Method	gf_l	gf_v	Ref.
MCHF	0.999(0.002)	0.999(0.002)	This work
CI	1.021	0.998	Hibbert (1974)
Beam-foil	0.971(0.079)		Bashkin et. al. (1985)
Isoelectronic-smoothing	0.965(0.020)		Reistad & Martinson (1986)

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