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ACCURATE MULTICONFIGURATION HARTREE-FOCK 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 nonorthogonalities 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 wavefunctions have not been assumed to be equal but have been optimized independently. The calculated weighted multiplet oscillator strength $gf = 0.999$ has an estimated uncertainty of less than 0.5%. Together with the previously calculated isotope shift and hyperfine structure (Jönsson, Johansson, & Froese Fischer 1994), all the important atomic parameters needed for a detailed modeling of the B II resonance line in high-resolution astrophysical spectra are now available with high accuracy.

Subject headings: atomic data — fundamental parameters — stars: abundances — 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. Because this is very complicated process, different models have been proposed. Recently, two reactions not usually included in primordial nucleosynthesis were considered: ^{7}Li(^{3}H, *n*)^{9}Be and ^{9}Be(^{3}H, *n*)^{11}B (Kajino & Boyd 1990). With these reactions included, theoretical calculations show that considerably higher abundances of ^{9}Be, ^{10}B, and ^{11}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}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}B and ^{11}B. The former process leads to production of both isotopes, whereas the latter process produces only ^{11}B and could be a possible explanation of the high solar ^{11}B/^{10}B isotopic ratio.

To check the proposed production processes, it is of importance to determine the ^{10}B and ^{11}B abundances, and especially the isotopic ratio, in various objects. The B I lines at 2090 Å, having isotope shifts 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 Oph 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 1993 December it should now be possible to observe the transition also in higher resolution ($R \approx 100{,}000$).

To determine the abundances of ^{10}B and ^{11}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 paper 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, Johansson, & Froese Fischer 1994). By contrast, the calculation of accurate values of transition parameters, 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, Godefroid, & Hibbert 1991, who have relaxed the orthogonality condition slightly). A high-quality wavefunction, 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 wavefunctions are not assumed to be equal but can be optimized independently (Olsen et al. 1995). 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

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

In this article we report on calculations of the weighted multiplet oscillator strength of the resonance transition of B II with an estimated uncertainty of less than 0.5%. The calculated weighted multiplet oscillator strength $gf = 0.999$ is outside the error bars 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).

2. THEORY

In the nonrelativistic MCHF approach (Froese Fischer 1991) the wavefunction 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 (CSFs) with the same LS term:

$$\psi(\gamma LS) = \sum_j c_j \Phi(\gamma_j LS) . \tag{1}$$

The configuration state functions Φ are antisymmetrized linear combinations of products of spin orbitals

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

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

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

In the multiconfiguration self-consistent field (MC-SCF) procedure both the orbitals and the expansion coefficients are optimized to self-consistency. When core orbitals are fixed at their Hartree-Fock value, we refer to the approximation as a fixed-core MCHF calculation.

The weighted multiplet oscillator strength, or 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 forms, respectively (Cowan 1981, p. 395; Froese Fischer et al. 1991):

$$gf_l = \frac{2}{3} (E_{\gamma' L' S'} - E_{\gamma LS}) \left| \left\langle \gamma LS \middle\| \sum_{i=1}^{N} r_i \boldsymbol{C}^{(1)}(i) \middle\| \gamma' L' S' \right\rangle \right|^2 , \tag{4}$$

$$gf_v = \frac{2}{3} (E_{\gamma' L' S'} - E_{\gamma LS})^{-1} \left| \left\langle \gamma LS \middle\| \sum_{i=1}^{N} \boldsymbol{\nabla}^{(1)}(i) \middle\| \gamma' L' S' \right\rangle \right|^2 . \tag{5}$$

Here $C_q^{(1)} = (4\pi/3)^{1/2} Y_{1q}$ is the normalized spherical harmonic and $\nabla_q^{(1)}$ the tensor form of the gradient operator. The two forms of the gf-value give the same result for exact nonrelativistic wavefunctions. For approximate wavefunctions, 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:

$$\psi(\gamma' L' S') = \sum_j c'_j \Phi(\gamma'_j L' S') , \tag{6}$$

$$\psi(\gamma LS) = \sum_k c_k \Phi(\gamma_k LS) , \tag{7}$$

the calculation of the gf-value reduces to the evaluation of transition matrix elements between arbitrarily LS-coupled CSFs:

$$\left\langle \gamma_k LS \middle\| \sum_{i=1}^{N} r_i \boldsymbol{C}^{(1)}(i) \middle\| \gamma'_j L' S' \right\rangle , \tag{8}$$

$$\left\langle \gamma_k LS \middle\| \sum_{i=1}^{N} \boldsymbol{\nabla}^{(1)}(i) \middle\| \gamma'_j L' S' \right\rangle . \tag{9}$$

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 wavefunction demands orbital optimized for the specific electronic state. However, Olsen et al. (1995) have shown that for very general configuration expansions, where the initial and final states are described by different orbital sets, it is possible to transform the wavefunction 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 wavefunctions are *not* assumed to be equal.
2. Change the wavefunction representation by transforming the two orbital sets to a biorthonormal basis, i.e., $\langle nl | n'l \rangle = \delta_{n,n'}$, where nl is an orbital from the initial configuration state and $n'l$ an orbital from the final configuration state. This is followed by a countertransformation of the expansion coefficients c'_j and c_k as to leave the total wavefunctions invariant.
3. Calculate the gf-values with the transformed wavefunctions for which the standard Racah algebra can now be used.

The details of the transformation are discussed in the articles of Malmqvist (1986) and Olsen et al. (1995).

The configuration expansions were obtained with the active space method (Roos, Taylor, & Siegbahn 1980; Olsen et al. 1988), where CSFs 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 in a fixed-core MCHF calculation, and the configuration expansions consisted of all CSFs of the form $1s^2nln'l'$, where $nln'l'$ 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 forms of the weighted multiplet oscillator strengths, for the transition, are shown as a

TABLE 1

Valence Correlation MCHF gf-Values in B II

	$1s^22s^2\ ^1S$		$1s^22s2p\ ^1P^0$		$1s^22s^2\ ^1S \rightarrow 1s^22s2p\ ^1P^0$		
Active Set	E(a.u.)	Ncfg[a]	E(a.u.)	Ncfg[a]	gf_l	gf_v	ΔE (cm^{-1})
HF	−24.237575	1	−23.912873	1	1.44934	0.73292	71260
$2s1p$	−24.296082	2	−23.912873	1	1.06474	0.78927	84100
$3s2p1d$	−24.298330	7	−23.956320	6	1.03593	1.06883	75059
$4s3p2d1f$	−24.298647	16	−23.960103	17	1.02566	1.05692	74298
$5s4p3d2f1g$	−24.298767	30	−23.961101	36	1.02296	1.05715	74105
$6s5p4d3f2g1h$	−24.298826	50	−23.961448	65	1.02218	1.05690	74042
$7s6p5d4f3g2h1i$......	−24.298852	77	−23.961607	106	1.02191	1.05683	74013
Experiment	...	...	...	...	...	...	73397

[a] Number of configurations.

function of the increasing active set. In our calculations the active sets for the initial and final states 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 forms of the oscillator strength have converged to within 2 parts in 10,000. 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, still a fixed-core MCHF calculation, outer correlation as well as polarization of the $1s$ subshell was included. In this case, the configuration expansions consisted of all CSFs of the form $1snln'l'n''l''$. In Table 2 the value of the total energy, as well as the length and velocity forms of the weighted multiplet 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 forms of the oscillator strength have converged for the largest active set of orbitals. In this case the two forms differ by only 2 parts in 1000, indicating that essentially all important correlation effects have been captured. Finally, a fully variational MCHF calculation was performed, where correlation within the $1s$ subshell was also included. In this calculation CSFs of the form $nln'l'n''l''n'''l'''$ were included in the expansion. This is referred to as a complete active space (CAS) expansion. When all CSFs 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, Jönsson, & Froese Fischer 1993; Froese Fischer 1993), and it is possible to impose restrictions on the allowed CSFs 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 forms of the weighted multiplet 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 forms 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 $1s$ subshell, 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, it is seen that the length and velocity forms are in perfect agreement, indicating that all correlation effects have been captured. For this case the transition energy shows a monotonous trend toward 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 multiplet oscillator strength is $gf = 0.999$, and, based on the convergence trends of Tables 2 and 3, the error is estimated to be well below five parts in a thousand. All the calculations have been performed in the nonrelativistic LS-coupled formalism, and the effect of relativity must be investigated. In transition calculations, relativistic effects enter in two ways: as a change of the transition energy and as a change in the transition matrix element. The former effect can easily be accounted for by using the experimental transition energy for the length form of the oscillator strength. Inserting the experimental transition energy instead of the calculated nonrelativistic one changes the gf-value in the

TABLE 2

Valence and Core-Valence Correlation MCHF gf-Values in B II

	$1s^22s^2\ ^1S$		$1s^22s2p\ ^1P^0$		$1s^22s^2\ ^1S \rightarrow 1s^22s2p\ ^1P^0$		
Active Set	E(a.u.)	Ncfg[a]	E(a.u.)	Ncfg[a]	gf_l	gf_v	ΔE (cm^{-1})
HF	−24.237575	1	−23.912873	1	1.44934	0.73292	71260
$2s1p$	−24.296373	3	−23.913008	3	1.06533	0.79279	84135
$3s2p1d$	−24.300685	23	−23.958255	36	1.02683	1.08208	75151
$4s3p2d1f$	−24.304799	100	−23.966961	185	1.00565	0.99767	74143
$5s4p3d2f1g$	−24.305673	318	−23.969633	650	1.00107	0.99919	73749
$6s5p4d3f2g1h$	−24.305998	831	−23.970655	1810	1.00059	0.99889	73595
$7s6p5d4f3g2h1i$......	−24.306153	1892	−23.971064	4312	1.00028	0.99836	73539
Experiment	...	...	...	...	...	...	73397

[a] Number of configurations.

TABLE 3

FULL CORRELATION MCHF gf-VALUES IN B II

ACTIVE SET	$1s^2 2s^2\ ^1S$		$1s^2 2s2p\ ^1P^0$		$1s^2 2s^2\ ^1S \rightarrow 1s^2 2s2p\ ^1P^0$		
	E(a.u.)	Ncfg[a]	E(a.u.)	Ncfg[a]	gf_l	gf_v	ΔE (cm^{-1})
HF	−24.237575	1	−23.912873	1	1.44934	0.73292	71260
$2s1p$	−24.296413	5	−23.913062	4	1.06522	0.79143	84132
$3s2p1d$	−24.334812	63	−23.988668	98	1.02150	0.99381	75966
$4s3p2d1f$	−24.342409	460	−24.001844	713	1.01860	1.02582	74741
$5s4p3d2f1g$	−24.346046	1066	−24.008886	2300	1.00413	1.00375	73994
$6s5p4d3f2g1h$	−24.347410	2306	−24.011624	5211	1.00075	0.99978	73693
$7s6p5d4f3g2h1i$	−24.347943	4200	−24.012990	9772	0.99924	0.99961	73510
$8s7p6d5f4g3h2i1k$	−24.348296	6865	−24.013636	16298	0.99903	0.99915	73449
Experiment	...	...	...	...	...	...	73397

[a] Number of configurations.

TABLE 4

gf-VALUES IN B II COMPARED WITH VALUES FROM OTHER CALCULATIONS AND EXPERIMENT

Method	gf_l	gf_v	Reference
MCHF	0.999(0.005)	0.999(0.005)	This work
R matrix	1.03	...	Opacity Project; Tully, Seaton, & Berrington 1990
CI[a]	1.021	0.998	Hibbert 1975
Beam foil	0.971(0.079)	...	Bashkin et al. 1985
Isoelectronic smoothing	0.965(0.020)	...	Reistad & Martinson 1986

[a] Configuration interaction.

length form from $gf_l = 0.99903$ to $gf_l = 0.99829$. To investigate the effect of relativity on the transition matrix elements, a number of small calculations were performed in the Breit-Pauli approximation. By comparing the transition matrix elements in the Breit-Pauli approximation with the corresponding nonrelativistic ones, the effect of relativity on the matrix elements was seen to be less than 2 parts in 10,000. Thus, the total effect of relativity on the gf-value is less than one part in a thousand and can be neglected.

In Table 4 the weighted multiplet oscillator strength is compared with values from other calculations and experiment. It is seen that our value lies outside the error bars 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).

4. CONCLUSIONS

In the present article we report on an accurate calculation of the weighted multiplet oscillator strength of the resonance line of B II at 1362 Å using a new method to deal with nonorthogonalities in the transition matrix elements. The theoretical value of the weighted multiplet oscillator strength is $gf = 0.999$, and the convergence pattern in the calculations implies an uncertainty of less than 0.5%. Determination of the boron abundance in various objects and in the ISM is of great astrophysical and cosmological significance. Our results now provide the possibility of including the oscillator strength, together with the previously calculated isotope shift and hyperfine structure, in a detailed modeling of the B II resonance line in high-resolution spectra. To conclude, we want to point out that the method employed 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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