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Published in:
Physical Review A (Atomic, Molecular and Optical Physics)

DOI:
10.1103/PhysRevA.50.3080

1994

Citation for published version (APA):
Jönsson, P., & Fischer, C. F. (1994). Large-scale Multiconfiguration Hartree-fock and Configuration-interaction Calculations of Isotope Shifts and Hyperfine Structures In Boron. *Physical Review A (Atomic, Molecular and Optical Physics)*, *50*(4), 3080-3088. https://doi.org/10.1103/PhysRevA.50.3080

Total number of authors:
2

PHYSICAL REVIEW A VOLUME 50, NUMBER 4 OCTOBER 1994

Large-scale multiconfiguration Hartree-Fock and configuration-interaction calculations of isotope shifts and hyperfine structures in boron

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(Received 17 June 1994)

A new isotope shift program, part of the multiconfiguration Hartree-Fock (MCHF) atomic structure package, has been written and tested. The program calculates the isotope shift of an atomic level from MCHF or configuration-interaction (CI) wave functions. The program is specially designed to be used with very large CI expansions, for which angular data cannot be stored on disk. To explore the capacity of the program, large-scale isotope shift calculations were performed for the $1s^22s^22p\ ^2P$, $1s^22s^23s\ ^2S$, and $1s^22s2p^2\ ^2D$ levels in boron. From the isotope shifts of these levels the transition isotope shifts were calculated for the two resonance transitions. The calculated transition isotope shifts are in very good agreement with experimental shifts. As an additional test of the quality of the CI wave functions, the hyperfine structure was calculated for all levels.

PACS number(s): 31.20.Tz, 31.30.Gs, 31.20.Di

I. INTRODUCTION

Since the Hubble Space Telescope (HST) was launched in April 1990 there has been an increasing interest in isotope shift and hyperfine structure among astrophysicists. The high resolution of stellar spectra obtained with the Goddard High Resolution Spectrograph aboard the HST makes it possible to resolve the isotope shift and hyperfine structure in many spectral lines. For most lines, however, these small structures cannot be completely resolved, and instead they shift and broaden the lines. This may lead to erroneous interpretation of lines of special astrophysical interest where, for example, the unresolved isotope shift can be misinterpreted as a Doppler broadening [1,2]. In order to correctly interpret high-resolution stellar spectra it is necessary to include isotope shift and hyperfine structure in a theoretical modeling of the line profiles. For many lines there are no laboratory values of the isotope shift and hyperfine structure and the modeling of the line profiles has to rely on calculated values [3]. It is therefore of importance to develop reliable computational methods for both isotope shift and hyperfine structure that can support the analysis of astrophysical spectra.

Many-body perturbation theory (MBPT) has, with great success, been applied to hyperfine structure for many years [4]. More recently large-scale multiconfiguration Hartree-Fock (MCHF) calculations have been reported for a number of atoms [5–9]. Using these two methods it is now possible to calculate hyperfine structure very accurately for a large number of states in different atoms. For many excited states, not available to the extremely accurate resonance methods, the calculated values are often more accurate than the experimental values.

For isotope shift calculations the situation is different. In atoms, where the specific mass shift is important, it has been shown to be exceedingly difficult to calculate isotope shifts accurately and, compared with the large number of hyperfine structure calculations, few isotope shift calculations have been performed.

MBPT calculations of isotope shifts were pioneered by Mårtensson-Pendrill and Salomonson in 1982 [10]. Since then, calculations on effective one- and two-electron systems have been performed, notably by Mårtensson-Pendrill and co-workers [11–13]. MBPT calculations of isotope shifts in light atoms have been performed by Veseth [14]. Using a third-order algebraic approach good agreement with experimental shifts was found, although discrepancies remained in some cases. The MCHF studies of isotope shift performed so far have, in many cases, given discouraging results due to the rather limited number of configurations included in the wave-function expansion. Isotope shift is known to be very sensitive to electron correlation and it is, in general, necessary to use large configuration expansions to obtain accurate values [15,16]. Recent progress in variational calculations, together with today's powerful computers, has now made it possible to perform large-scale MCHF and configuration-interaction (CI) calculations where the configuration space can be increased in a systematic way, allowing the convergence of different parameters to be studied [17]. The purpose of this work is to explore the capacity of a newly written isotope shift program [18], designed to be used with very large CI expansions, and to see how accurately large-scale MCHF and CI calculations can predict isotope shifts. As a test the ^{11}B-^{10}B isotope shifts in the $1s^22s^22p\ ^2P - 1s^22s^23s\ ^2S$ and $1s^22s^22p\ ^2P - 1s^22s2p^2\ ^2D$ transitions were calculated. The isotope shifts in these transitions are of astrophysical importance and have been proposed as a possible diagnostic of the cosmic ^{11}B:^{10}B ratio [19,20]. Both shifts were recently determined with high accuracy from vacuum ultraviolet Fourier transform spectra [20]. As an additional check on the quality of the wave functions the hyperfine structure was calculated for all of the involved levels.

II. THEORY

A. Isotope shift

The isotope shift observed in atomic transitions can be separated into a mass and a field shift. The mass shift is due to differences in the nuclear mass of the isotopes and is the dominating effect for light atoms. The field or volume shift is connected to the extension of the nuclear charge and is important for heavy atoms. The isotope shift in a transition is given as the difference between the shift for the upper and the lower level. The individual shifts are often large, but cancel, and therefore it is necessary to calculate them very accurately in order to get a reliable value of the difference. Below, the operators for the mass and field shifts of an atomic level are given. The corresponding energy shifts are evaluated in first-order perturbation theory with wave functions obtained from the zeroth-order Hamiltonian $\mathcal{H}_0$, where the nucleus is assumed to be a point charge of infinite mass[1]

$$\mathcal{H}_0 = \sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2m} - \frac{Z}{r_i}\right) + \sum_{i<j}^{N}\frac{1}{r_{ij}} \ . \tag{1}$$

1. Mass shift

For a finite nuclear mass M, the kinetic energy of the nucleus must be considered. Using the momentum conservation law in the center-of-mass coordinate system, the operator for the internal kinetic energy of an N-electron atom becomes [21]

$$\mathcal{H}_{\rm kin} = -\sum_{i=1}^{N}\frac{\nabla_i^2}{2\mu} - \frac{1}{M}\sum_{i<j}^{N}\boldsymbol{\nabla}_i\cdot\boldsymbol{\nabla}_j . \tag{2}$$

The first term includes a correction to the electron mass in which the mass m is replaced by the reduced mass $\mu = Mm/(M+m)$. The resulting correction to the energy level E_0 is then given by

$$E_{\rm NMS} = -E_0\frac{m}{M+m} \ . \tag{3}$$

This is the normal mass shift (NMS). The inclusion of the second term leads to an additional energy correction known as the specific mass shift (SMS):

$$E_{\rm SMS} = -\left\langle\psi\left|\frac{1}{M}\sum_{i<j}^{N}\boldsymbol{\nabla}_i\cdot\boldsymbol{\nabla}_j\right|\psi\right\rangle \ . \tag{4}$$

In the tables the specific mass shift parameter S is given by

$$S = -\left\langle\psi\left|\sum_{i<j}^{N}\boldsymbol{\nabla}_i\cdot\boldsymbol{\nabla}_j\right|\psi\right\rangle \ . \tag{5}$$

This parameter represents the expectation value of the mass-independent factor of the specific mass shift operator.

2. Field shift

The field shift of an atomic energy level is due to the extended nuclear charge distribution. The field inside the nucleus deviates from the Coulomb field of a point charge and this is reflected in the calculated levels. For light atoms the resulting correction to the level E_0 is expressed in terms of the nonrelativistic electron probability $|\psi(0)|^2$ at the origin

$$E_{\rm FS} = \frac{2\pi}{3}Z\langle r^2\rangle|\psi(0)|^2 \ , \tag{6}$$

where $\langle r^2\rangle$ is the mean square radius of the nucleus. For heavier atoms ($Z > 10$) it becomes necessary to include a relativistic correction factor.

B. Hyperfine structure

The hyperfine structure of atomic energy levels is caused by the interaction between the electrons and the electromagnetic multipole moments of the nucleus. The leading terms of this interaction are the magnetic dipole and electric quadrupole moments.

The hyperfine interaction couples the electronic (**J**) and nuclear (**I**) angular momenta to a total momentum $\mathbf{F} = \mathbf{I} + \mathbf{J}$. In the $|\ \gamma IJFM_F\rangle$ representation the diagonal hyperfine energy corrections are given by

$$W_{M1}(J,J) = \frac{1}{2}A_J C \tag{7}$$

and

$$W_{E2}(J,J) = B_J\frac{\frac{3}{4}C(C+1) - I(I+1)J(J+1)}{2I(2I-1)J(2J-1)} \ , \tag{8}$$

where $C = F(F+1) - J(J+1) - I(I+1)$.

The magnetic dipole hyperfine constants A_J can be written as linear combinations of the orbital, spin-dipole,

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[1] In atomic units $m = 1$, but we include it explicitly to avoid misunderstandings. The nuclear mass M is usually given in units of the unified atomic mass (u) and must be converted to atomic units before being used in the formulas below. 1 u = 1822.888 51 a.u.

and Fermi contact parameters (a_l, a_{sd}, and a_c) [22] where, for an N-electron atom,

$$a_l = \left\langle \gamma LSLS \left| \sum_{i=1}^{N} l_0^{(1)}(i) r_i^{-3} \right| \gamma LSLS \right\rangle \ , \tag{9}$$

$$a_{\mathrm{sd}} = \left\langle \gamma LSLS \left| \sum_{i=1}^{N} 2C_0^{(2)}(i) s_0^{(1)}(i) r_i^{-3} \right| \gamma LSLS \right\rangle \ , \tag{10}$$

$$a_c = \left\langle \gamma LSLS \left| \sum_{i=1}^{N} 2s_0^{(1)}(i) r_i^{-2} \delta(r_i) \right| \gamma LSLS \right\rangle \ . \tag{11}$$

The electric quadrupole hyperfine constants B_J are proportional to the electric field gradient b_q,

$$b_q = \left\langle \gamma LSLS \left| \sum_{i=1}^{N} 2C_0^{(2)}(i) r_i^{-3} \right| \gamma LSLS \right\rangle \ . \tag{12}$$

In the formulas above hyperfine parameters are evaluated using LS coupled wave functions with $M_L = L$ and $M_S = S$.

III. METHOD OF CALCULATION

The wave functions were generated with the MCHF atomic structure package of Froese Fischer [23], where the wave function ψ for a state labeled γLS is expanded in terms of configuration state functions (CSFs) with the same LS term

$$\psi(\gamma LS) = \sum_j c_j \phi_j(\gamma_j LS) \ . \tag{13}$$

In the numerical MCHF approach the CSFs are sums of products of spin orbitals, where the radial part of the spin orbital is represented by its numerical values at a number of grid points. In the multiconfigurational self-consistent field procedure both the orbitals and the expansion coefficients are optimized to self-consistency.

Once the optimized orbital basis was obtained from the MCHF calculations, a number of large CI calculations were performed. In the CI calculations the wave function is expanded in CSFs where only the expansion coefficients are determined. This is done by diagonalizing the Hamiltonian matrix. Using a sparse matrix representation large CI expansions can be used. On a modern workstation expansions with more than 100 000 CSFs can easily be handled, the limit usually set by the available disk space. Direct CI techniques also exist in which the explicit storage of the Hamiltonian matrix is avoided. For these techniques only the Hamiltonian matrix times a vector has to be stored and therefore extremely large expansions can be used [24]. The calculations of the specific mass shift parameter and the hyperfine structure constants from the CI wave functions were done with the isotope shift and hyperfine structure programs [18,25] which are part of the MCHF atomic structure package.

The configuration expansions were obtained with the active space method [26,27], where CSFs of a particular parity and LS symmetry are generated by excitations from the reference configurations to an active set of orbitals. The active set was then increased in a systematic way, allowing the convergence of the specific mass shift and hyperfine parameters to be studied. In the MCHF calculations only single and double (SD) excitations from the most important configurations to the active set were allowed. This can be considered as the zeroth-order wave function. Since the specific mass shift operator couples configurations that differ with up to two electrons, it is necessary to include the most important triple and quadruple excitations to improve the wave function further. This was done in the CI calculations using multireference (MR) expansions where the SD excitations to the active set of orbitals were done from all configurations in the preceding MCHF calculations with expansion coefficients larger than a certain cutoff.

IV. RESULTS AND DISCUSSION

A. Isotope shift

As a starting point a number of MCHF calculations were performed. In Tables I–III the obtained values of the specific mass shift parameter, the electron density at the nucleus, and the total energy are shown for the $1s^22s^22p\ ^2P$, $1s^22s^23s\ ^2S$, and $1s^22s2p^2\ ^2D$ terms. The MCHF expansions were generated from SD excitations from the two or three most important configurations to the active set of orbitals. 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. Of course, principal quantum numbers have no significance other than defining the order in which the orbitals are introduced.

Previous convergence studies of the specific mass shift parameter in lithium [17] showed the importance of including orbitals of high angular momenta in the active set. In this calculation, mainly targeted on the isotope shift, higher orbital symmetries were included each time the active set was increased. This is in sharp contrast to hyperfine structure calculations, where accurate values of the parameters mainly rely on a large orbital basis consisting of orbitals with low angular momenta.

A common feature of the MCHF calculations for all three terms is the sudden increase of the specific mass shift parameter with about 0.6 a.u. after the first few correlation orbitals have been included. An analysis of the contributions to the specific mass shift parameter from all pairs of CSFs showed that this increase occurs when the added p orbitals start to correlate the $1s$ subshell. The corresponding correlation in the $2s$ subshell was found to be much less important. In Table IV the leading contributions to the specific mass shift parameter are shown for each term. As the specific mass shift parameter for the $1s^22s^22p\ ^2P$ and $1s^22s2p^2\ ^2D$ terms are mainly built up from two large, but canceling, contributions, they are sensitive to correlation effects. For the

TABLE I. The specific mass shift parameter, electron density at the nucleus, and the total energy (in a.u.) for the $1s^22s^22p\ ^2P$ term from MCHF calculations. The configuration expansions were obtained from SD excitations to the active sets from the reference configurations $1s^22s^22p$ and $1s^22p^3$.

Active set	S (a.u.)	$\vert\psi(0)\vert^2$	E_0 (a.u.)	Number of configurations
HF	-0.4049	71.9214	-24.529 061	1
$2s1p$	-0.4105	71.7851	-24.560 354	6
$3s2p1d$	0.2939	71.7916	-24.621 891	129
$4s3p2d1f$	0.2404	71.8618	-24.638 480	520
$5s4p3d2f1g$	0.2566	71.8519	-24.645 478	1301
$6s5p4d3f2g1h$	0.2544	71.8562	-24.648 728	2584
$7s6p5d4f3g2h1i$	0.2533	71.8593	-24.650 290	4479
$8s7p6d5f4g3h2i1k$	0.2521	71.8606	-24.651 009	7096

TABLE II. The specific mass shift parameter, electron density at the nucleus, and the total energy (in a.u.) for the $1s^22s^23s\ ^2S$ term from MCHF calculations. The configuration expansions were obtained from SD excitations to the active sets from the reference configurations $1s^22s^23s$, $1s^22p^23s$, and $1s^22s2p^2$.

Active set	S (a.u.)	$\vert\psi(0)\vert^2$	E_0 (a.u.)	Number of configurations
HF	0.0000	72.7158	-24.352 104	1
$3s2p1d$	0.6402	72.4613	-24.438 718	92
$4s3p2d1f$	0.6280	72.5349	-24.456 608	379
$5s4p3d2f1g$	0.6257	72.5397	-24.464 056	943
$6s5p4d3f2g1h$	0.6030	72.5425	-24.467 945	1854
$7s6p5d4f3g2h1i$	0.6030	72.5435	-24.469 218	3182
$8s7p6d5f4g3h2i1k$	0.6018	72.5443	-24.469 860	4997

TABLE III. The specific mass shift parameter, electron density at the nucleus, and the total energy (in a.u.) for the $1s^22s2p^2\ ^2D$ term from MCHF calculations. The configuration expansions were obtained from SD excitations to the active sets from the reference configurations $1s^22s2p^2$ and $1s^22s^23d$.

Active set	S (a.u.)	$\vert\psi(0)\vert^2$	E_0 (a.u.)	Number of configurations
HF	-0.73672	70.5526	-24.311 869	1
$2s1p$	-0.73566	70.5519	-24.311 921	4
$3s2p1d$	-0.67012	70.7397	-24.379 506	157
$4s3p2d1f$	-0.06550	70.8733	-24.416 497	812
$5s4p3d2f1g$	-0.06585	70.8413	-24.424 768	2320
$6s5p4d3f2g1h$	-0.06609	70.8188	-24.429 451	5004
$7s6p5d4f3g2h1i$	-0.06950	70.8186	-24.431 353	9161

TABLE IV. The dominating contributions in the summation of the specific mass shift parameter.

Term	CSF	Weight	Matrix element	Value
$1s^22s^22p\ ^2P$	$\vert 1s^22s^22p\ ^2P\rangle$	$c_1 = 0.9638$	$c_1^2\langle 1s^22s^22p\ ^2P\vert H_{\mathrm{SMS}}\vert 1s^22s^22p\ ^2P\rangle$	-0.394
	$\vert 3p^22s^22p\ ^2P\rangle$	$c_2 = 0.0225$	$2c_1c_2\langle 1s^22s^22p\ ^2P\vert H_{\mathrm{SMS}}\vert 3p^22s^22p\ ^2P\rangle$	0.478
$1s^22s^23s\ ^2S$	$\vert 1s^22s^23s\ ^2S\rangle$	$c_1 = 0.9523$	$c_1^2\langle 1s^22s^23s\ ^2S\vert H_{\mathrm{SMS}}\vert 1s^22s^23s\ ^2S\rangle$	0.000
	$\vert 3p^22s^23s\ ^2S\rangle$	$c_2 = 0.0218$	$2c_1c_2\langle 1s^22s^23s\ ^2S\vert H_{\mathrm{SMS}}\vert 3p^22s^23s\ ^2S\rangle$	0.451
$1s^22s2p^2\ ^2D$	$\vert 1s^22s2p^2\ ^2D\rangle$	$c_1 = 0.9011$	$c_1^2\langle 1s^22s2p^2\ ^2D\vert H_{\mathrm{SMS}}\vert 1s^22s2p^2\ ^2S\rangle$	-0.586
	$\vert 4p^22s2p^2\ ^2D\rangle$	$c_2 = 0.0198$	$2c_1c_2\langle 1s^22s2p^2\ ^2D\vert H_{\mathrm{SMS}}\vert 4p^22s2p^2\ ^2D\rangle$	0.359

$1s^22s^23s\ ^2S$ term there is only one dominating contribution since the specific mass shift parameter is zero at the Hartree-Fock level. The specific mass shift parameter of this term should therefore be less sensitive to correlation effects.

The most important three- and four-particle effects were taken into account in the CI calculations. In Tables V–VII the values of the specific mass shift parameter, the electron density at the nucleus, and the total energy are shown for the $1s^22s^22p\ ^2P$, $1s^22s^23s\ ^2S$, and $1s^22s2p^2\ ^2D$ terms. The CI expansions were obtained from SD excitations to the active set from all configurations in the MCHF expansion with weights larger than 0.01. Even if only the most important three- and four-particle effects are taken into account in this way, the multireference CI expansions contain CSFs that are unimportant. Thus the expansions can be condensed without significant loss of accuracy [28]. For the $1s^22s^22p\ ^2P$ term the expansion generated from the $6s5p4d3f2g1h$ active set was condensed by deleting CSFs with expansion coefficients smaller than 0.000 001. The deleted expansion contains only 17 672 CSFs compared with 39 623 CSFs for the full expansion and gives the same value of all the parameters including the total energy. To avoid the CI expansions from growing unmanageably large for the $7s6p5d4f3g2h1i$ and $8s7p6d5f4g3h2i1k$ active sets, SD excitations to these sets were done only from the three most important configurations in the multireference set, i.e., $1s^22s^22p$, $1s^22p^3$, and $1s^22s2p3d$. These expansions were then added to the condensed expansion generated from the $6s5p4d3f2g1h$ active set. For the $1s^22s2p^2\ ^2D$ term the expansion generated from the $5s4p3d2f1g$ active set was condensed. Also in this case the condensed and the full expansion give the same value of all the parameters. For the $6s5p4d3f2g1h$ and $7s6p5d4f3g2h1i$ active sets SD excitations were done from $1s^22s2p^2, 1s^22s^23d$, and $1s^22p^23d$. These expansions were added to the condensed expansion generated from the $5s4p3d2f1g$ active set.

Comparing Tables I and V it is seen that the three- and four-particle effects included in the CI expansion increase the specific mass shift parameter of the $1s^22s^22p\ ^2P$ term by 8%. As seen from Tables III and VII this change is even larger for the $1s^22s2p^2\ ^2D$ term where the increase is almost 50%.

Since the isotope shift in a transition is determined by the difference of the level isotope shift for the upper and lower level, it is interesting to monitor the difference of the specific mass shift parameters, the electron densities at the nucleus, and the energies for the two levels. In Tables VIII and IX these differences for the $1s^22s^23s\ ^2S$ and $1s^22s^22p\ ^2P$ terms as well as for the $1s^22s2p^2\ ^2D$ and $1s^22s^22p\ ^2P$ terms are shown as a function of the increasing active set of orbitals. Although the individual specific mass shift parameters for the upper and the lower state change very much with the increasing active set of orbitals, the difference is comparatively constant and even rather small expansions give acceptable values. The exception is the very large value of ΔS for $1s^22s2p^2\ ^2D$ and $1s^22s^22p\ ^2P$ for the $3s2p1d$ active set. At this level the newly introduced p orbital has started to correlate the $1s$ subshell in the $1s^22s^22p\ ^2P$ term leading to an increase in the specific mass shift parameter whereas the corresponding increase for the $1s^22s2p^2\ ^2D$ term occurs first at the $4s3p2d1f$ level. The transition energies are not yet converged, but show a monotonic trend towards the experimental values as the active set is increased.

From the parameters in Tables VIII and IX the isotope-dependent transition energies, in atomic units, can be calculated as

$$\Delta E_M = \Delta E_0 - \Delta E_0 \frac{m}{M+m} + \frac{\Delta S}{M} + \frac{2\pi}{3} Z \Delta |\psi(0)|^2 \langle r_M^2 \rangle \ , \tag{14}$$

where M is the nuclear mass of the isotope and $\langle r_M^2 \rangle$ the root mean square nuclear radii, both expressed in atomic units. The isotope shift is then obtained as the difference between the transition energies for the two isotopes

TABLE V. The specific mass shift parameter, electron density at the nucleus, and the total energy (in a.u.) for the $1s^22s^22p\ ^2P$ term from multireference CI calculations as a function of the increasing active set of orbitals. The multireference set consisted of all CSFs in the MCHF expansions with weights larger than 0.01.

Active set	S (a.u.)	$\lvert\psi(0)\rvert^2$	E_0 (a.u.)	Number of configurations
$2s1p$	-0.4105	71.7851	-24.560 354	6
$3s2p1d$	0.3090	71.7911	-24.622 672	366
$4s3p2d1f$	0.2585	71.8645	-24.639 807	4 520
$5s4p3d2f1g$	0.2758	71.8552	-24.647 000	16 525
$6s5p4d3f2g1h$	0.2741	71.8587	-24.650 392	39 623
$6s5p4d3f2g1h$[a]	0.2741	71.8587	-24.650 392	17 672
$7s6p5d4f3g2h1i$[b]	0.2733	71.8615	-24.651 991	24 082
$8s7p6d5f4g3h2i1k$[b]	0.2723	71.8626	-24.652 725	32 456

[a] The $6s5p4d3f2g1h$ MR CI expansion is condensed. Only CSFs with expansion weight larger than 0.000 001 are included.

[b] CSFs obtained by SD excitations from $1s^22s^22p$, $1s^22p^3$, and $1s^22s2p3d$ have been added to the condensed $6s5p4d3f2g1h$ MR CI expansion.

TABLE VI. The specific mass shift parameter, electron density at the nucleus, and the total energy (in a.u.) for $1s^22s^23s\ ^2S$ in B I from multireference CI calculations as a function of the increasing active set of orbitals. The multireference set consisted of all CSFs in the MCHF expansions with weights larger than 0.01.

Active set	S (a.u.)	$\|\psi(0)\|^2$	E_0 (a.u.)	Number of configurations
$3s2p1d$	0.6404	72.4613	-24.438 727	150
$4s3p2d1f$	0.6328	72.5343	-24.456 917	1 734
$5s4p3d2f1g$	0.6313	72.5392	-24.464 460	5 909
$6s5p4d3f2g1i$	0.6090	72.5420	-24.468 409	13 431
$7s6p5d4f3g2h1i$	0.6095	72.5428	-24.469 729	25 183
$8s7p6d5f4g3h2i1k$	0.6085	72.543 3	-24.470 389	41 987

TABLE VII. The specific mass shift parameter, electron density at the nucleus, and the total energy (in a.u.) for $1s^22s2p^2\ ^2D$ in B I from multireference CI calculations as a function of the increasing active set of orbitals. The multireference set consisted of all CSFs in the MCHF expansions with weights larger than 0.01.

Active set	S (a.u.)	$\|\psi(0)\|^2$	E_0 (a.u.)	Number of configurations
$3s2p1d$	-0.668 33	70.7404	-24.380 038	449
$4s3p2d1f$	-0.039 40	70.8779	-24.418 061	7 237
$5s4p3d2f1g$	-0.039 01	70.8457	-24.426 635	32 012
$5s4p3d2f1g$[a]	-0.039 01	70.8457	-24.426 635	15 354
$6s5p4d3f2g1h$[b]	-0.038 47	70.8238	-24.431 399	21 674
$7s6p5d4f3g2h1i$[b]	-0.041 36	70.8245	-24.433 330	31 336

[a] The $5s4p3d2f1g$ MR CI expansion is condensed. Only CSFs with expansion weight larger than 0.000 001 are included.

[b] CSFs obtained by SD excitations from $1s^22s2p^2$, $1s^22s^23d$, and $1s^22p^23d$ have been added to the condensed $5s4p3d2f1g$ MR CI expansion.

TABLE VIII. The difference of specific mass shift parameters, electron densities at the nucleus, and total energies (in a.u.) for the $1s^22s^23s\ ^2S$ and $1s^22s^22p\ ^2P$ terms as a function of the increasing active set of orbitals. The differences were calculated from the CI values in Tables V and VI.

Active set	ΔS (a.u.)	$\Delta\|\psi(0)\|^2$	ΔE_0 (a.u.)
HF	0.4049	0.7944	0.176 96
$3s2p1d$	0.3314	0.6703	0.183 94
$4s3p2d1f$	0.3742	0.6698	0.182 89
$5s4p3d2f1g$	0.3556	0.6840	0.182 54
$6s5p4d3f2g1h$	0.3349	0.6834	0.181 98
$7s6p5d4f3g2h1i$	0.3362	0.6813	0.182 26
$8s7p6d5f4g3h2i1k$	0.3362	0.6807	0.182 34
Experiment[a]			0.182 44

[a] Reference [30].

TABLE IX. The difference of specific mass shift parameters, electron densities at the nucleus, and total energies (in a.u.) for the $1s^22s2p^2\ ^2D$ and $1s^22s^22p\ ^2P$ terms as a function of the increasing active set of orbitals. The differences were calculated from the CI values in Tables V and VII.

Active set	ΔS (a.u.)	$\Delta\|\psi(0)\|^2$	ΔE_0 (a.u.)
HF	-0.3319	-1.369	0.217 19
$3s2p1d$	-0.9773	-1.051	0.242 63
$4s3p2d1f$	-0.2979	-0.987	0.221 75
$5s4p3d2f1g$	-0.3148	-1.010	0.220 36
$6s5p4d3f2g1h$	-0.3126	-1.035	0.218 99
$7s6p5d4f3g2h1i$	-0.3147	-1.037	0.218 66
Experiment[a]			0.218 05

[a] Reference [30].

TABLE X. Transition isotope shift $\Delta E_{^{11}\mathrm{B}^{10}\mathrm{B}}$, in cm^{-1}, for the resonance transitions. The normal and specific mass shift as well as the field shift (FS) are shown together with the total value of the shift.

Transition	NMS	SMS	FS	Total shift	Method
$1s^22s^22p\ ^2P - 1s^22s^23s\ ^2S$	0.1986	-0.3661	-0.000 16	-0.1676	MR CI[a]
	0.1986	-0.293		-0.0944	MBPT[b]
				-0.174	Experiment[c]
$1s^22s^22p\ ^2P - 1s^22s2p^2\ ^2D$	0.2374	0.3415	0.000 25	0.5792	MR CI[a]
				0.569	Experiment[c]

[a] This work.
[b] Reference [14].
[c] Reference [20].

$$\begin{aligned}\Delta E_{M'M} &= \Delta E_{M'} - \Delta E_M \\ &= \Delta E_0\left(\frac{m}{M+m} - \frac{m}{M'+m}\right) \\ &\quad +\Delta S\left(\frac{1}{M'} - \frac{1}{M}\right) \\ &\quad +\frac{2\pi}{3}Z\Delta|\psi(0)|^2(\langle r^2_{M'}\rangle - \langle r^2_M\rangle)\ . \qquad (15)\end{aligned}$$

The root mean square nuclear radii of the isotopes, needed for the evaluation of the field shift, were taken from pionic and muonic x-ray measurements of Olin *et al.* [29]: for ^{10}B, $\langle r^2\rangle^{1/2} = 2.44(6)$ fm, and for ^{11}B, $\langle r^2\rangle^{1/2} = 2.38(4)$ fm. The transition isotope shifts $\Delta E_{^{11}\mathrm{B}^{10}\mathrm{B}}$ (in cm^{-1}) are shown in Table X together with the experimental values. The calculated isotope shift for the $1s^22s^23s\ ^2S - 1s^22s^22p\ ^2P$ transition is $-0.1676\ \mathrm{cm}^{-1}$. This should be compared with the experimental shift of $-0.174\ \mathrm{cm}^{-1}$ [20]. The agreement is very satisfactory considering the fact that the normal and the specific mass shift have different sign and partly cancel (the field shift is much smaller and can be neglected). Using many-body perturbation theory within the algebraic approximation Veseth [14] calculated the shift to be $-0.0944\ \mathrm{cm}^{-1}$. The calculations, complete to third order, were based on both the Möller-Plesset and Epstein-Nesbet zeroth-order Hamiltonian. In Table XI the obtained specific mass shift parameters are compared with the CI values. Due to the large difference between the third-order Möller-Plesset and Epstein-Nesbeth values for the $1s^22s^22p\ ^2P$ term Veseth concluded that the most reliable value was obtained to second order. A comparison with the present CI value, however, shows that the best value is obtained in third order with the Epstein-Nesbeth Hamiltonian. More surprising is the large difference between the third-order MBPT values and the very well converged CI value for the $1s^22s^23s\ ^2S$ term.

The calculated shift for the $1s^22s2p^2\ ^2D - 1s^22s^22p\ ^2P$ transition is $0.5792\ \mathrm{cm}^{-1}$, which also agrees very well with the experimental shift of $0.569\ \mathrm{cm}^{-1}$ [20]. For this transition the normal and specific mass shift adds to

TABLE XI. The specific mass shift parameter in different orders for the MBPT calculation of Ref. [14] compared with the multireference CI values.

Term	Order	Möller-Plesset value	Epstein-Nesbet value	MR CI
$1s^22s^22p\ ^2P$	first	-0.4048	-0.4048	
	second	0.3959	0.3996	
	third	0.1727	0.2743	0.2723
$1s^22s^23s\ ^2S$	first	0.0000	0.0000	
	second	0.6570	0.7536	
	third	0.6652	0.6687	0.6086

TABLE XII. The orbital, spin-dipolar, Fermi contact, and electric quadrupole parameters (in a.u.) for the $1s^22s^22p\ ^2P$ term from multireference CI calculations as a function of the increasing active set of orbitals. The multireference set consisted of all CSFs in the MCHF expansions with weights larger than 0.01.

Active set	a_l	a_{sd}	a_c	b_q
HF	0.7756	-0.1551	0.000 00	-0.3102
$2s1p$	0.8109	-0.1622	-0.020 20	-0.3067
$3s2p1d$	0.8178	-0.1697	-0.618 61	-0.3108
$4s3p2d1f$	0.7584	-0.1697	0.042 10	-0.2602
$5s4p3d2f1g$	0.7739	-0.1652	0.242 14	-0.2730
$6s5p4d3f2g1h$	0.7819	-0.1665	0.050 76	-0.2898
$6s5p4d3f2g1h$[a]	0.7819	-0.1665	0.050 74	-0.2898
$7s6p5d4f3g2h1i$[b]	0.7808	-0.1681	0.067 48	-0.2848
$8s7p6d5f4g3h2i1k$[b]	0.7807	-0.1684	0.079 76	-0.2822
MCHF[c]	0.7807	-0.1671	0.085 71	-0.2844
FE MCHF[d]	0.7784	-0.1674	0.073 23	-0.2824

[a] The $6s5p4d3f2g1h$ MR CI expansion is condensed. Only CSFs with expansion weight larger than 0.000 001 are included.
[b] CSFs obtained by SD excitations from $1s^22s^22p$, $1s^22p^3$, and $1s^22s2p3d$ have been added to the condensed $6s5p4d3f2g1h$ MR CI expansion.
[c] Reference [9].
[d] Reference [6].

TABLE XIII. The Fermi contact term (in a.u.) for the $1s^22s^23s\ ^2S$ term from multireference CI calculations as a function of the increasing active set of orbitals. The multireference set consisted of all CSFs in the MCHF expansions with weights larger than 0.01.

Active set	a_c
HF	1.333
$3s2p1d$	1.301
$4s3p2d1f$	1.773
$5s4p3d2f1g$	2.078
$6s5p4d3f2g1h$	2.062
$7s6p5d4f3g2h1i$	2.045
$8s7p6d5f4g3h2i1k$	2.064

give the total shift, which can explain the smaller relative error compared with the error in the shift for the $1s^22s^23s\ ^2S - 1s^22s^22p\ ^2P$ transition.

B. Hyperfine structure

As pointed out before, there is a large difference between isotope shift and hyperfine structure calculations when it comes to the selection of the configuration expansion. The specific mass shift operator is a two-body operator and the expectation value is very dependent on core-core correlation effects. The hyperfine operators are one-body operators that are sensitive to core-valence correlation. As an additional difference orbitals with high angular momenta tend to be unimportant for hyperfine operators due to their r^{-3} radial dependence whereas for the specific mass shift operator they are not.

Core-core correlation is energetically much more important than core-valence correlation and in variational calculations where the configuration expansion is generated by SD excitation from an active set the first correlation orbitals will mainly describe the former effects. Not until the core-core correlation energy is saturated do the added orbitals start to describe core-valence correlation and as a result the values of the hyperfine structure parameters do not stabilize until a large number of orbitals, mainly with low angular momenta, have been added.

TABLE XIV. The orbital, spin-dipolar, Fermi contact, and electric quadrupole parameters (in a.u.) for the $1s^22s2p^2\ ^2D$ term from multireference CI calculations as a function of the increasing active set of orbitals. The multireference set consisted of all CSFs in the MCHF expansions with weights larger than 0.01.

Active set	a_l	a_{sd}	a_c	b_q
HF	1.5248	0.000 00	19.19	-0.6099
$3s2p1d$	1.4081	-0.029 79	21.08	-0.5689
$4s3p2d1f$	1.2816	-0.016 87	18.73	-0.5132
$5s4p3d2f1g$	1.3131	-0.015 29	18.66	-0.4763
$5s4p3d2f1g$[a]	1.3131	-0.015 28	18.66	-0.4763
$6s5p4d3f2g1h$[b]	1.3370	-0.014 70	18.89	-0.4939
$7s6p5d4f3g2h1i$[b]	1.3385	-0.015 70	18.95	-0.5188

[a] The $5s4p3d2f1g$ MR CI expansion is condensed. Only CSFs with expansion weight larger than 0.000 001 are included.

[b] CSFs obtained from SD excitations from $1s^22s2p^2$, $1s^22s^23d$, and $1s^22p^23d$ have been added to the condensed $5s4p3d2f1g$ expansion.

As a test of the overall quality of the CI wave functions the convergence of the hyperfine structure parameters was studied for all three terms; the results are shown in Tables XII–XIV. Although the present orbital basis was targeted for the specific mass shift parameter, the hyperfine parameters for the $1s^22s^22p\ ^2P$ term are in fair agreement with parameters from previous MCHF calculations [6,9]. The latter calculations focused only on the hyperfine structure and used orbital bases containing large numbers of s, p, and d orbitals. The Fermi contact parameter, which is built up from very large and canceling contributions arising from the spin polarization of the $1s$ and $2s$ subshells [9], has been shown to be extremely difficult to calculate accurately. This explains the comparatively large differences between the different MCHF calculations found for this parameter. The ^{11}B isotope has nuclear spin $I = 3/2$ and nuclear magnetic dipole moment $\mu = 2.688\,648\,9(10)\mu_N$ [31]. From the nuclear and hyperfine parameters the magnetic dipole interaction constants A_J were calculated. The relativistically corrected values $A_{1/2} = 367.6$ MHz and $A_{3/2} = 72.79$ MHz both agree within less than 0.8% with the experimental values $A_{1/2} = 366.0765(15)$ MHz and $A_{3/2} = 73.3496$ MHz.

There is, to our knowledge, no accurate experimental value of the magnetic coupling constant for the $1s^22s^23s\ ^2S_{1/2}$ state. From the Fermi contact parameter in Table XIII we obtain $A_{1/2} = 235.5$ MHz with an estimated error of less than 2%.

The hyperfine structure parameters for the $1s^22s2p^2\ ^2D$ term are not yet fully converged and it would be desirable to add more orbitals to get the spin-dipole parameter stabilized. The magnetic dipole interaction constants for the $J = 3/2$ and $J = 5/2$ states are, however, relatively insensitive to the value of the spin-dipole parameter. The calculated values $A_{3/2} = -291.4$ MHz and $A_{5/2} = 523.0$ MHz are therefore looking at the convergence patterns of the orbital and Fermi contact parameters, estimated to be correct to within less than 2%.

V. SUMMARY AND CONCLUSION

We report large-scale MCHF and multireference CI calculations of the specific mass shift parameter and the electron density at the nucleus for the $1s^22s^22p\ ^2P$, $1s^22s^23s\ ^2S$, and $1s^22s2p^2\ ^2D$ terms in boron. The configuration expansions were generated with the systematic active space approach and the largest CI expansion consisted of more than 40 000 CSFs. The calculated transition isotope shifts are in very good agreement with recent experimental values. By performing systematic large-scale MCHF and CI calculations it should be possible to obtain accurate isotope shifts for transitions in light atoms of importance for the interpretation of astrophysical spectra.

ACKNOWLEDGMENTS

This research has been supported by the Swedish Natural Science Research Council and the Division of Chemical Science, Office of Basic Energy Sciences, Office of Energy Science, U.S. Department of Energy. Valuable discussions with Dr. Jörgen Carlsson are gratefully acknowledged.

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