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Large-scale multiconfiguration Hartree-Fock calculations of hyperfine-interaction constants for low-lying states in beryllium, boron, and carbon

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Multiconfiguration Hartree-Fock (MCHF) calculations of hyperfine constants for the $2s2p$ ^3P states of beryllium and the ground states of boron and carbon are reported. The capacity of a recently developed configuration-interaction program [Froese Fischer and Tong (unpublished); Stathopoulos and Froese Fischer (unpublished)], allowing for large configuration expansions, is explored. Using a systematic active-space MCHF approach, combined with large multireference configuration-interaction calculations, it is shown that hyperfine constants can be calculated very accurately. To reliably account for spin-polarization of the $1s$ and $2s$ shells in boron and carbon, three-particle effects had to be included in a systematic way. The relativistic, finite-nuclear-size- and finite-nuclear-mass-corrected values of the hyperfine constants are compared with experimental values and with the most accurate theoretical values obtained with other methods.

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I. INTRODUCTION

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 ($\mathbf{J}$) and nuclear ($\mathbf{I}$) 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

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

and

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

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, and Fermi contact parameters (a_l, a_{sd}, and a_c) [1]:

$$A_J=G_{M1}\frac{\mu_I}{I}\left[\frac{\langle\mathbf{L}\cdot\mathbf{J}\rangle}{LJ(J+1)}g_l a_l+\frac{[3\langle\mathbf{S}\cdot\mathbf{L}\rangle\langle\mathbf{L}\cdot\mathbf{J}\rangle-L(L+1)\langle\mathbf{S}\cdot\mathbf{J}\rangle]}{SL(2L-1)J(J+1)}\frac{g_s}{2}a_{sd}+\frac{\langle\mathbf{S}\cdot\mathbf{J}\rangle}{SJ(J+1)}\frac{g_s}{6}a_c\right], \tag{3}$$

where, for an N-electron atom,

$$a_l=\left\langle\gamma LSLS\left|\sum_{i=1}^{N}l_0^{(1)}(i)r_i^{-3}\right|\gamma LSLS\right\rangle, \tag{4}$$

$$a_{sd}=\left\langle\gamma LSLS\left|\sum_{i=1}^{N}2C_0^{(2)}(i)s_0^{(1)}(i)r_i^{-3}\right|\gamma LSLS\right\rangle, \tag{5}$$

$$a_c=\left\langle\gamma LSLS\left|\sum_{i=1}^{N}2s_0^{(1)}(i)r_i^{-2}\delta(r_i)\right|\gamma LSLS\right\rangle \tag{6}$$

and

$$\langle\mathbf{L}\cdot\mathbf{J}\rangle=\tfrac{1}{2}[J(J+1)+L(L+1)-S(S+1)], \tag{7}$$

$$\langle\mathbf{S}\cdot\mathbf{J}\rangle=\tfrac{1}{2}[J(J+1)-L(L+1)+S(S+1)], \tag{8}$$

$$\langle\mathbf{S}\cdot\mathbf{L}\rangle=\tfrac{1}{2}[J(J+1)-L(L+1)-S(S+1)], \tag{9}$$

μ_I is the nuclear magnetic dipole moment, $g_l = (1 - m_e/M_{\text{atom}})$ the orbital electron g factor, and $g_s = 2.002\,32$ the QED corrected electron-spin g factor. The electric-quadrupole hyperfine constants B_J are proportional to the electric-field gradient b_q:

$$B_J = -G_{E2}Q\frac{[6\langle\mathbf{L}\cdot\mathbf{J}\rangle^2 - 3\langle\mathbf{L}\cdot\mathbf{J}\rangle - 2L(L+1)J(J+1)]}{L(2L-1)(J+1)(2J+3)}b_q ,\qquad(10)$$

where

$$b_q = \left\langle\gamma LSLS\left|\sum_{i=1}^{N}2\mathbf{C}_0^{(2)}(i)r_i^{-3}\right|\gamma LSLS\right\rangle\qquad(11)$$

and Q is the nuclear electric-quadrupole moment.

In the formulas above, hyperfine parameters are evaluated in atomic units using LS-coupled wave functions with $M_L = L$ and $M_S = S$. For hyperfine constants in the customary experimental unit of MHz, $G_{M1} = 95.4107$ and $G_{E2} = 234.965$.

The diagonal magnetic dipole and electric-quadrupole hyperfine constants have been determined very accurately with the atomic-beam magnetic-resonance technique [2–5] for the states in beryllium, boron, and carbon investigated here. Since accurate nuclear magnetic dipole moments μ_I are known for these atoms [6], precise comparisons between experimental and theoretical values of the magnetic dipole hyperfine constants are possible. Such comparisons cannot be made for the electric-quadrupole hyperfine constants, since the corresponding nuclear quadrupole moments Q are not known from direct nuclear experiments, at least not with high precision [6]. More accurate values of the nuclear quadrupole moments can instead be obtained by combining the experimental values of the electric-quadrupole hyperfine constants (in MHz) with the calculated electric-field gradients b_q (in a.u.) [7].

It is in general a very demanding task to calculate hyperfine structures accurately. Polarization of the closed shells in the core, due to the Coulomb interaction with open shells, can have a large effect on the hyperfine structure. Polarization of s shells is especially important. If the two s electrons in the same shell have different spin densities at the nucleus, a contact interaction is induced. Since inner s electrons have high densities at the nucleus, a very small unbalance is sufficient to cause a net interaction which is comparable to that of an open outer shell. Already in lithium, a seemingly simple three-electron system, large configuration expansions, including triple excitations, have to be used to describe the spin-polarization of the $1s$ shell accurately [8]. In a Hylleraas calculation, the energy must approach the nonrelativistic limit to give reliable values of the hyperfine parameters. For boron and carbon the situation is more difficult since the contributions from the spin-polarized $1s$ and $2s$ shells are both large, but nearly cancel. To compute an accurate value of the Fermi contact term, as noted by Bauschlicher in a recent study of the related nitrogen atom [9], virtually all of the correlation energy must be obtained. In particular, the correlation of the $1s$ and $2s$ shells must be correctly balanced. Thus, very extensive treatments are required for the calculations. The Fermi contact term in boron has been studied with a number of theoretical methods, but the calculated values differ significantly from each other and from the experimental value. However, the Fermi contact term is small and contributes little to the total magnetic dipole hyperfine constants. In carbon the situation is different. Here the Fermi contact term is of crucial importance for the magnetic dipole hyperfine constant in the $J = 1$ state due to the strong cancellation between the spin-dipole and orbital terms.

The purpose of this work is to explore the capacity of a recently developed configuration-interaction (CI) program, allowing for large configuration expansions, and to study the convergence of the hyperfine parameters using sequences of active spaces. Special attention has been paid to the large and cancelling contributions to the Fermi contact term from the spin-polarized $1s$ and $2s$ shells in boron and carbon, where three-particle effects are very important and must be included in a systematic way.

II. METHOD OF CALCULATION

The wave functions were generated with the MCHF atomic structure package of Froese Fischer [10,11], where the wavefunction ψ for a state labeled γLSJ is expanded in terms of configuration-state functions (CSF's) $\phi_j(\gamma_j LSJ)$ with the same LS term:

$$\psi(\gamma LSJ) = \sum_j c_j\phi_j(\gamma_j LSJ) .\qquad(12)$$

In the numerical multiconfiguration Hartree-Fock (MCHF) approach, the CSF's 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 (MCSCF) procedure, both the orbitals and the expansion coefficients (c_j) are optimized to self-consistency. The subsequent CI calculations were performed with a recently developed program, using a sparse representation of the lower triangular part of the Hamiltonian matrix [12,13]. With this program, expansions with up to 40 000 CSF's could be handled on a DEC workstation with 32-Mbyte internal memory, the limit set by the available disk space. The calculation of the parameters (4)–(6) and (11) from the MCHF wave functions was done with a hyperfine structure program [14], part of the MCHF atomic structure package of Froese Fischer.

The configuration expansions were obtained with the active-space method, where CSF's of a particular parity and LS symmetry are generated by excitations from one or more reference configurations to an active set of orbitals. The active set is then increased in a systematic way, allowing the convergence of the hyperfine parameters to be studied. If all possible excitations to the active set are allowed, the configuration-state expansion, referred to as the complete active space (CAS), grows very rapidly with

the increasing active set. By imposing different restrictions on the allowed excitations, the number of configuration states can be kept down and orbitals can be targeted to describe different electron-correlation effects. This method has been utilized by the quantum chemists in the restricted-active-space (RAS) approach for some time [15,16]. In their notation, the size of the active set of orbitals is specified by the number of orbitals of a given symmetry since the principal quantum numbers do not have physical significance. The active set is increased not one orbital at a time, but by adding a group of new orbitals. We refer to the new group as a shell of active orbitals. The set of configurations states generated from the active set under certain rules is called the active space.

For smaller configuration expansions, where most of the orbitals are spectroscopic, a stationary requirement with respect to orbital rotations speeds up the convergence in the MCSCF procedure considerably [17]. In the improvement of an approximate orbital basis, pairs of radial functions with the same l quantum number were then allowed to rotate:

$$\begin{bmatrix} P_j(r) \\ P_{j'}(r) \end{bmatrix} \rightarrow \begin{bmatrix} 1 & \eta \\ -\eta & 1 \end{bmatrix} \begin{bmatrix} P_j(r) \\ P_{j'}(r) \end{bmatrix} \bigg/ \sqrt{1+\eta^2} , \qquad (13)$$

changing the energy

$$E \rightarrow E + \eta \Delta E + \eta^2 \Delta^2 E . \qquad (14)$$

The solution for which the energy is stationary with respect to small variations in η was then selected. However, for the larger expansions in this study the orbital rotations introduced instabilities in the MCSCF procedure and more stable convergence was obtained when the rotational analysis was turned off.

III. RESULTS AND DISCUSSION

A. $1s^2 2s 2p$ ^3P in ^{9}Be

With current codes, it is not possible to do a complete active-space calculation for beryllium, that is, to include all single, double, triple, and quadruple excitations (SDTQ excitations) to the active sets of increasing size.

Since the number of configurations must be kept rather small in an MCHF calculation, only SD excitations from the reference configuration were allowed to the larger active sets. To capture the most important three- and four-particle effects, CSF's obtained by triple and quadruple excitations to the smaller active set $4s3p2d1f$ augmented the CSF's obtained from SD excitations to the large active sets. In Table I the results of the active-space calculations are shown. For the sets up to $4s3p2d1f$, where all SDTQ excitations were included, convergence was very good and all orbitals could be optimized simultaneously. When further shells of active orbitals were added, to which only SD excitations were allowed, stability problems occurred in the MCSCF procedure, and so the previous shells had to be frozen and only the new ones optimized. The orbital, spin-dipole, and Fermi contact terms converge smoothly with increasing active space, and the extrapolations to the nonrelativistic $spdf$ limits are obvious. The convergence with increasing active space for the electric-field gradient is slow and oscillatory, and the extrapolation to the $spdf$ limit is more uncertain.

To estimate the contributions from higher symmetries, g orbitals were added to the active sets and another set of MCHF calculations were performed; the results are shown in Table II. From these calculations g-shell corrections to the $spdf$ limits could be derived. It is interesting to see how slow the g-shell contributions build up and that a relatively large number of orbitals is needed to get the correct contributions. As expected from the tensorial form of the hyperfine operators, the g-shell correction is most important for the orbital term and least important for the Fermi contact term. Finally, to account for the remaining three-particle effects, a set of CI calculations was performed where CSF's obtained from triple excitations to increasing active sets were augmented to the $12s11p10d9f$ space from the MCHF calculation. In Table III the results of the CI calculations are shown. It can be seen that triple excitations to the $5s4p3d2f$ set are important, but as further triple excitations are included, the resulting changes in the hyperfine parameters are small. The three-particle contributions

TABLE I. The hyperfine parameters and total energies (in a.u.) of the $1s^2 2s 2p$ ^3P term in ^{9}Be for different active sets of orbitals.

Active set	a_l	a_{sd}	a_c	b_q	Energy
HF	0.295 21	−0.059 04	7.8182	−0.118 09	−14.511 502
$2s1p$	0.295 80	−0.059 16	7.8297	−0.118 32	−14.511 577
$3s2p1d$	0.298 87	−0.061 82	9.0900	−0.122 82	−14.553 679
$4s3p2d1f$	0.302 88	−0.068 51	9.0444	−0.107 67	−14.560 100
$5s4p3d2f$	0.303 44	−0.063 34	9.1527	−0.112 91	−14.563 946
$6s5p4d3f$	0.304 63	−0.068 46	9.2254	−0.119 91	−14.565 325
$7s6p5d4f$	0.304 11	−0.064 71	9.2376	−0.111 78	−14.565 841
$8s7p6d5f$	0.304 31	−0.066 94	9.2268	−0.119 04	−14.566 132
$9s8p7d6f$	0.303 67	−0.066 03	9.2293	−0.116 06	−14.566 232
$10s9p8d7f$	0.303 73	−0.065 78	9.2317	−0.115 48	−14.566 295
$11s10p9d8f$	0.303 68	−0.065 96	9.2298	−0.115 98	−14.566 319
$12s11p10d9f$	0.303 70	−0.065 91	9.2316	−0.115 67	−14.566 333
Extrapolated	0.303 69	−0.065 94	9.2310	−0.115 82	

TABLE II. The hyperfine parameters and total energies (in a.u.) of the $1s^2 2s 2p\ ^3P$ term in ^{9}Be for increasing active sets including g orbitals.

Active set	a_l	a_{sd}	a_c	b_q	Energy
HF	0.295 21	−0.059 04	7.8182	−0.118 09	−14.511 502
$2s1p$	0.295 80	−0.059 16	7.8297	−0.118 32	−14.511 577
$3s2p1d$	0.298 87	−0.061 82	9.0900	−0.122 82	−14.553 679
$4s3p2d1f$	0.302 88	−0.068 51	9.0444	−0.107 67	−14.560 100
$5s4p3d2f1g$	0.303 45	−0.063 34	9.1530	−0.112 92	−14.563 969
$6s5p4d3f2g$	0.304 70	−0.068 47	9.2252	−0.119 92	−14.565 533
$7s6p5d4f3g$	0.304 22	−0.064 73	9.2377	−0.111 83	−14.566 119
$8s7p6d5f4g$	0.304 45	−0.066 94	9.2278	−0.119 09	−14.566 441
$9s8p7d6f5g$	0.303 82	−0.066 05	9.2307	−0.116 11	−14.566 560

were added to the extrapolated values from the MCHF calculations to give the final *spdf* limits. Remaining four-particle effects were found to be very small and were neglected. In Table IV the final values of the hyperfine parameters are compared with values from other calculations. From the diagonal magnetic dipole hyperfine constants, an experimental value of the spin-dipole parameter can be obtained. The theoretical hyperfine parameters have to be corrected for relativistic, finite-nuclear-size and finite-nuclear-mass effects before they are compared with the experimental values. The finite nuclear mass $M_{9_{Be}}$ leads to a scaling of the Schrödinger equation. The effect of this scaling is accounted for by multiplying the nonrelativistic hyperfine parameters with the factor

$$(1-m_e/M_{9_{Be}})^3 = 0.999\,82 \ .$$

The most important effect of relativity is the contraction of the valence orbitals. This is in part counterbalanced by the effect of the finite nuclear size. Besides orbital contraction, relativistic effects also lead to a deviation from LS coupling which manifests itself in a small change of the intermediate-coupling coefficients $c_1 = \sqrt{\frac{1}{3}}$ and $c_2 = \sqrt{\frac{2}{3}}$ in the LS-jj transformation:

$$\Psi(^3P_2) = |(\tfrac{1}{2}, \tfrac{3}{2})2\rangle \ , \tag{15}$$

$$\Psi(^3P_1) = c_1 |(\tfrac{1}{2}, \tfrac{3}{2})1\rangle + c_2 |(\tfrac{1}{2}, \tfrac{1}{2})1\rangle \ . \tag{16}$$

If the deviation from LS coupling is neglected, the relativistic effects on the different hyperfine parameters a_l, a_{sd}, a_c, and b_q can be estimated by looking at hydrogen-like relativistic corrections for the electric and magnetic hyperfine integrals [18]. This was done by Sundholm and Olsen [19] using the tables of Ref. [18]. In Table V the relativistic and finite-nuclear-mass-corrected values are

compared with the experimental values. The final value of the spin-dipole parameter agrees perfectly with the experimental value. Our values also agree very well with the finite-element MCHF (FE MCHF) values of Sundholm and Olsen. The Fermi contact term differs by only 0.069%, whereas the differences for the other terms are on the order of a few parts in a thousand. A possible explanation for these differences could be different f- and g-shell contributions. Whereas we calculate the *spdf* limits and estimate the g-shell contribution, Sundholm and Olsen calculated the *spd* limits and estimated the f- and g-shell contributions. Considering the slow buildup, these contributions can easily be underestimated.

From the hyperfine parameters, the nuclear spin $I = \frac{3}{2}$ and the nuclear magnetic dipole moment $\mu_I = -1.177\,492(17)\mu_N$ [6] values of the diagonal magnetic dipole hyperfine constants were calculated. Before being compared with experiment, these values must be corrected for relativistic, finite-nuclear-size, and finite-nuclear-mass effects. More accurate corrections for the hyperfine constants than the ones resulting from the correction of the hyperfine parameters were obtained by multiplying the nonrelativistic values of the magnetic dipole hyperfine constants with the ratio of the Dirac-Fock (DF) and Hartree-Fock values, where in the Dirac-Fock calculation a Fermi charge distribution was used [20,21,8]. By this procedure the neglected deviation from LS coupling as well as the effect of finite nuclear size are properly accounted for. In Table VI the final values of the magnetic dipole hyperfine constants are compared with results from other calculations and experiment.

The total relativistic corrections for the diagonal magnetic dipole hyperfine constants resulting from the parameter corrections are −0.223 and −0.218 MHz for the $J=1$ and 2 states, respectively. This should be com-

TABLE III. The hyperfine parameters and total energies (in a.u.) of the $1s^2 2s 2p\ ^3P$ term in ^{9}Be from CI calculations also including triple excitations. The CSF's obtained from triple excitations to the second active set (following //) augmented the SD expansion to $12s11p10d9f$.

Active set	a_l	a_{sd}	a_c	b_q	Energy
$12s11p10d9f$	0.303 70	−0.065 91	9.2316	−0.115 67	−14.566 333
$12s11p10d9f//5s4p3d2f$	0.303 21	−0.065 82	9.2406	−0.115 45	−14.566 386
$12s11p10d9f//6s5p4d3f$	0.303 16	−0.065 82	9.2407	−0.115 50	−14.566 404

TABLE IV. The hyperfine parameters (in a.u.) of the $1s^2 2s 2p\ ^3P$ term in ^{9}Be compared with litera-
ture values.

Method	a_l	a_{sd}	a_c	b_q	Reference
spdf limit	0.303 14	−0.065 85	9.2401	−0.115 65	This work
Δg correction	0.000 15	−0.000 02	0.0015	−0.000 05	This work
Final values	0.303 29	−0.065 87	9.2416	−0.115 70	This work
FE MCHF	0.302 61	−0.065 64	9.2349	−0.115 0	[19]
LC MBPT[a]	0.304 78	−0.064 90	9.2319	−0.115 6	[30,31]
HF + SDCI[b]	0.300 14	−0.066 56	9.2738	−0.109 7	[32]

[a]Linked-cluster many-body perturbation theory.
[b]Hartree-Fock and CI allowing all SD excitations to correlation orbitals of Slater type.

pared with the relativistic and finite-nuclear-size correc-
tions of −0.177 and −0.140 MHz from the ratio of the
Dirac-Fock and Hartree-Fock values. Although small,
these differences are important at the present level of ac-
curacy, showing that the nonrelativistic limit of the cal-
culations essentially has been reached and that much of
the uncertainty is hidden in these corrections. In order
to improve the result further, relativity and the finite-
nuclear-size effects have to be taken into account in a
more rigorous way. This can, in principle, be done in the
fully relativistic multiconfiguration Dirack-Fock ap-
proach with a realistic model of the nuclear charge distri-
bution [20–22]. However, the computer power required
to do large-scale MCDF calculations is presently large,
making the calculations unfeasible on a workstation.

Combined with the experimental electric-quadrupole
hyperfine constant $B_2 = 1.429(8)$ MHz, the corrected
value $b_q = -0.1157$ a.u. gives a nuclear quadrupole mo-
ment of $Q(^9$Be$) = 0.052\,56$ b. This is slightly smaller than
the value of $Q(^9$Be$) = 0.052\,88$ b obtained by Sundholm
and Olsen.

B. $1s^2 2s^2 2p\ ^2P$ in ^{11}B

The Fermi contact term is very difficult to calculate
due to the large and cancelling contributions from the
spin-polarization of the $1s$ and $2s$ shells. When only
energy-optimized orbitals were used, the behavior of the
Fermi contact term was extremely oscillatory. In order
to reduce the oscillations and to include spin-polarization
at an early stage of the calculation, we augmented three
spin-polarization orbitals to the active set of orbitals. All
SD excitations were then allowed to the augmented set.

To construct the polarization orbitals, we started from
frozen Hartree-Fock orbitals. Only single excitations
were allowed to the polarization shells, which were opti-
mized. The spin-polarization orbitals were then kept
frozen in the subsequent calculations in which all the oth-
er orbitals were optimized simultaneously. In Table VII
the hyperfine parameters and total energies are shown as
a function of the increasing active space. Spin-
polarization orbitals are preceded by a slash in the tables.
Even though three spin-polarization s shells have been
augmented to the active set, the behavior of the Fermi
contact term is still oscillatory in the beginning, but
starts to stabilize after the seventh energy-optimized s
shell has been added. The orbital term converges
smoothly with increasing active space, but the spin-dipole
term and electric-field gradient converge more slowly and
it would have been desirable to add a few more shells to
the active set. Doing so, the limit set by the internal
memory of the computer is passed and the MCSCF pro-
cedure is slowed down due to heavy swapping to the
external disk. The practical limit for the MCHF expan-
sions is around 5500 CSF's on a machine with 32-Mbyte
internal memory.

In contrast to beryllium, triple excitations contribute a
great deal to the Fermi contact term. This can be under-
stood by looking at the result of the first CI calculation in
Table VIII, where the $1s$ shell was kept closed. By com-
paring it with the equivalent CI calculation in which ex-
citations from the $1s$ shell were allowed, the separate con-
tributions to the Fermi contact term from the $1s$ and $2s$
shells can be estimated. Since these contributions are
large and have different sign, a small unbalance due to
the three-particle effects can change the total value

TABLE V. The relativistic and finite-nuclear-mass-corrected hyperfine parameters (in a.u.) of the
$1s^2 2s 2p\ ^3P$ term in ^{9}Be compared with values from other calculations and experiment.

Method	a_l	a_{sd}	a_c	b_q	Reference
MCHF[a]	0.303 46	−0.065 91	9.2566	−0.115 68	This work
FE MCHF[a]	0.302 78	−0.065 68	9.2499	−0.115 0	[19]
LC MBPT[a]	0.304 95	−0.064 94	9.2469	−0.115 6	[30,31]
HF + SDCI[a]	0.300 31	−0.066 60	9.2888	−0.109 7	[32]
Experiment[b]		−0.065 95			[2]

[a]The given uncorrected hyperfine parameters have been relativistic and finite-nuclear-mass corrected.
The relativistic correction is estimated from the tables of Ref. [18].
[b]Assuming *LS* coupling.

TABLE VI. The relativistic, finite-nuclear-size, and finite-nuclear-mass-corrected magnetic dipole constants (in MHz) for the $1s^2 2s 2p \; {}^3P_{1,2}$ states in ^{9}Be compared with values from other calculations and experiment.

Method	$2s2p \; {}^3P_1$	$2s2p \; {}^3P_2$	Reference
HF	-119.83	-106.55	This work
DF	-119.98	-106.67	This work
MCHF[a]	-139.35	-124.50	This work
FE MCHF[b]	-139.27	-124.50	[19]
LC MBPT[c]	-139.10	-124.47	[30,31]
HF + SDCI[c]	-139.77	-124.76	[32]
Experiment	$-139.373(12)$	$-124.5368(17)$	[2]

[a]Relativistic and finite-nuclear-size corrections using the ratio of the DF and HF values.
[b]Hydrogenlike relativistic corrections for the integrals of the hyperfine parameters.
[c]Calculated from given uncorrected hyperfine parameters with present relativistic and finite-nuclear-size corrections.

TABLE VII. The hyperfine parameters and total energies (in a.u.) of the $1s^2 2s^2 2p \; {}^2P$ term in ^{11}B as a function of the increasing active set. The /3s refers to three frozen core-polarization orbitals.

Active set	a_l	a_{sd}	a_c	b_q	Energy
HF	0.7756	-0.1551	0.00000	-0.3102	-24.529061
$3s2p1d/3s$	0.8284	-0.1714	0.26685	-0.3177	-24.623387
$4s3p2d1f/3s$	0.7630	-0.1693	0.04466	-0.2642	-24.637739
$5s4p3d2f1g/3s$	0.7795	-0.1660	0.04504	-0.2770	-24.643805
$6s5p4d3f2g/3s$	0.7850	-0.1663	0.03183	-0.2929	-24.646639
$7s6p5d4f3g/3s$	0.7843	-0.1682	0.03521	-0.2884	-24.647981
$8s7p6d5f4g/3s$	0.7841	-0.1686	0.03743	-0.2855	-24.648532
$9s8p7d6f5g/3s$	0.7842	-0.1674	0.03719	-0.2879	-24.648758

TABLE VIII. The hyperfine parameters and total energies (in a.u.) of the $1s^2 2s^2 2p \; {}^2P$ term in ^{11}B from MRCI calculations. The CSF's obtained by SDT excitations from $1s^2 2s^2 2p$ and $1s^2 2p^3$ to increasing active sets (preceded with //) augmented the CSF's obtained by SD excitations from $1s^2 2s^2 2p$ to $9s8p7d6f5g/3s$.

Active set	a_l	a_{sd}	a_c	b_q	Energy	Number of CSF's
$(1s)9s8p7d6f5g/3s$[a]	0.7646	-0.1575	0.81170	-0.2907	-24.601595	1 323
$9s8p7d6f5g/3s$	0.7842	-0.1674	0.03719	-0.2879	-24.648758	4 861
$9s8p7d6f5g/3s//3s2p1d/3s$	0.7833	-0.1673	0.05510	-0.2860	-24.650964	5 598
$9s8p7d6f5g/3s//4s3p2d1f/3s$	0.7813	-0.1678	0.06946	-0.2850	-24.651600	8 983
$9s8p7d6f5g/3s//5s4p3d2f1g/3s$	0.7811	-0.1670	0.07993	-0.2846	-24.652039	20 245
$9s8p7d6f5g/3s//6s5p4d3f2g/3s$[b]	0.7807	-0.1671	0.08571	-0.2844	-24.652143	36 924

[a]$1s$-shell closed, SD excitations from $2s^2 2p$ to $9s8p7d6f5g/3s$.
[b]SDT excitations from $1s^2 2s^2 2p$ to $6s5p4d3f2g/3s$ and from $1s^2 2p^3$ to $5s4p3d2f1g/3s$.

TABLE IX. The hyperfine parameters (in a.u.) of the $1s^2 2s^2 2p\ ^2P$ term in ^{11}B compared with values from other calculations.

Method	a_l	a_{sd}	a_c	b_q	Reference
CI(CIV3)	0.7752	−0.1670	0.098	−0.2953	[27]
Bethe-Goldstone	0.7789	−0.1674	0.047 62	−0.2822	[25,26]
FE MCHF	0.7784	−0.1674	0.073 23	−0.2824	[23]
MRCI	0.7807	−0.1671	0.085 71	−0.2844	This work

dramatically. It is therefore necessary to include these excitations in a systematic way. This was done in a sequence of multireference CI (MRCI) calculations where CSF's generated by SDT excitations to smaller active sets augmented the CSF's obtained by SD excitations to the $9s8p7d6f5g/3s$ set. The most important near-degeneracy was included by allowing SDT excitations to the smaller active sets from the $1s^2 2p^3$ configuration. In Table VIII the hyperfine parameters, total energies, and number of CSF's are shown for the MRCI calculations. All parameters, except the spin-dipole, show a smooth monotonic convergence. The Fermi contact term is not quite converged, and the value $a_c = 0.085\,71$ a.u. should be considered as a lower limit. While the three-particle effects are almost negligible for the orbital and spin-dipole parameters, this is not the case for the Fermi contact term and the electric-field gradient. It is seen that the triple excitations, interpreted as polarization of the doubly excited configurations, give a larger total contribution to the Fermi contact term than the single and double excitations, and so it is not surprising that literature values of the Fermi contact term differ by a factor of 2 or more. The three-particle contribution to the electric-field gradient is much smaller, but still decreases the value by more than 1.2%. In Table IX the final nonrelativistic values of the hyperfine parameters are compared with values from other calculations. From the measured diagonal and off-diagonal magnetic dipole hyperfine constants, experimental values of all three hyperfine parameters can be deduced. The accuracy is limited by the off-diagonal constant which is known with error bars of 2.5% [4]. The theoretical hyperfine parameters have to be corrected for relativistic, finite-nuclear-size, and finite-nuclear-mass effects before being compared with the experimental values. We used the same corrections as Sundholm and Olsen [23] where the relativistic and finite-nuclear-size corrections were estimated by scaling the Li(^{2}P) hyperfine parameter corrections from Ref. [24]

with the square of the nuclear charge. The effect of the finite nuclear mass was corrected for by multiplying with the factor

$$(1 - m_e/M_{^{11}B})^3 = 0.999\,85 .$$

In Table X the corrected values are compared with the experimental values. It is interesting to note that all theoretical values of the spin-dipole term are in perfect agreement, but outside the error bars of the experimental value. By using the theoretical values for the spin-dipole parameter combined with the diagonal magnetic dipole hyperfine constants

$$A_{1/2} = 73.3496(4)\ \text{MHz}$$

and

$$A_{3/2} = 366.0765(15)\ \text{MHz}$$

(Refs. [3,4]), accurate semitheoretical values of the orbital and Fermi contact parameters can be deduced. This was done by Sundholm and Olsen who, using the calculated spin-dipole parameter

$$a_{sd} = 0.1675(3)\ \text{a.u.} ,$$

obtained $a_l = 0.7817(11)$ a.u. and $a_c = 0.0879(28)$ a.u. [23]. Our parameters agree closely with the semitheoretical ones, supporting the value

$$A_{1/2,3/2} = 17.32(21)\ \text{MHz}$$

of Sundholm and Olsen calculated from the latter. This semitheoretical value of the off-diagonal constant is outside the error bars of the experimental value

$$A_{1/2,3/2} = 16.44(40)\ \text{MHz} ,$$

indicating that the given error bars can be too small. The values of the electric-field gradient from the FE MCHF calculation of Sundholm and Olsen and the Bethe-

TABLE X. The relativistic, finite-nuclear-size, and finite-nuclear-mass-corrected hyperfine parameters (in a.u.) of the $1s^2 2s^2 2p\ ^2P$ term in ^{11}B compared with values from other calculations and experiment.

Method	a_l	a_{sd}	a_c	b_q	Reference
CI(CIV3)[a]	0.7752	−0.1671	0.098	−0.2953	[27]
Bethe-Goldstone[a]	0.7789	−0.1675	0.047 71	−0.2822	[25,26]
FE MCHF[a]	0.7784	−0.1675	0.073 32	−0.2824	[23]
MRCI[a]	0.7807	−0.1672	0.085 80	−0.2844	This work
Semitheoretical	0.7817(11)		0.087 9(28)		[23]
Experiment	0.7783(16)	−0.1686(5)	0.1016(62)		[3,4]

[a]The given uncorrected hyperfine parameters have been relativistic, finite-nuclear-size, and finite-nuclear-mass corrected. Relativistic and finite-nuclear-size corrections were made using scaled corrections from Li(^{2}P).

TABLE XI. The relativistic, finite-nuclear-size, and finite-nuclear-mass-corrected magnetic dipole constants (in MHz) for the $1s^2 2s^2 2p\ ^2P_{1/2,3/2}$ states in ^{11}B compared with values from other calculations and experiment.

Method	$2p\ ^2P_{1/2}$	$2p\ ^2P_{3/2}$	Reference
HF	353.9	70.72	This work
DF	354.3	70.69	This work
Unrestricted HF	362.6	79.8	[33]
FE MCHF[a]	365.9	72.42	[23]
MCHF[b]	365.9	73.15	This work
Bethe-Goldstone[c]	367.2	71.47	[25,26]
CI(CIV3)[c]	364.1	73.01	[27]
Experiment	366.0765(15)	73.3496(4)	[3,4]

[a]Relativistic and finite-nuclear-size corrected using scaled corrections from Li(^2P).
[b]Relativistic and finite-nuclear-size corrected using the ratio of the DF and HF values.
[c]Calculated from given uncorrected hyperfine parameters with present relativistic and finite-nuclear-size corrections.

Goldstone calculation [25,26] agree perfectly. Looking at the convergence patterns in Tables VII and VIII, it is reasonable to believe that the value $b_q = -0.2844$ a.u. from the largest MRCI calculation is too low, and a better value is obtained if the mean value of the two last calculations in Table VII is corrected for three-particle effects. This gives $b_q = -0.2832$ a.u., in better agreement with the FE MCHF and Bethe-Goldstone values. The CI(CIV3) value of Glass and Hibbert [27] differs by almost 5% from these values, which is surprising since the agreement for the orbital and spin-dipole parameters is good.

For the diagonal magnetic dipole hyperfine constants, more accurate relativistic and finite-nuclear-size corrections than the ones resulting from the scaled Li(^2P) corrections of the hyperfine parameters were obtained, as in beryllium, by multiplying the nonrelativistic values of the magnetic dipole hyperfine constants with the ratio of the Dirac-Fock and Hartree-Fock values, where in the Dirac-Fock calculation a Fermi charge distribution was used. In Table XI the corrected hyperfine constants, calculated with the nuclear spin $I = \frac{3}{2}$ and nuclear magnetic dipole moment

$$\mu_I = 2.688\ 648\ 9(10)\mu_N$$

[6], are compared with values from other calculations and experiment. The difference between the theoretical and

experimental values is less than three parts in a thousand for both the J states. The improvement compared to the FE MCHF and Bethe-Goldstone calculations lies in the more accurate value for the Fermi contact term.

C. $1s^2 2s^2 2p^2\ ^3P$ in ^{13}C

For carbon, in contrast to boron, the Fermi contact term will be the most important term for the magnetic dipole hyperfine constant in the $J = 1$ state. This can be seen from Table XII, where the contributions (in MHz) to the dipole hyperfine constants from the orbital, spin-dipole, and Fermi contact terms are shown. On the Hartree-Fock level, the Fermi contact term is zero; the orbital and spin-dipole terms are both large, but cancel, leading to a hyperfine constant close to zero. The introduction of polarization and correlation effects will induce a Fermi contact term as well as change the degree of cancellation between the orbital and spin-dipole terms.

For carbon the same computational strategy was used as for boron. Here the number of CSF's in the MCHF expansions grows more rapidly, and the two last MCHF calculations had to be run on a computer with 64-Mbyte internal memory. In Table XIII hyperfine parameters and total energies are shown as a function of the active space. The orbital parameter and the electric-field gradient converge after the first few active spaces and remain very stable. For the spin-dipole and Fermi contact pa-

TABLE XII. Contributions to the total magnetic dipole hyperfine constants (in MHz) for the $1s^2 2s^2 2p^2\ ^3P_{1,2}$ states of ^{13}C from the orbital, spin-dipole, and Fermi contact terms.

Method	J	A_l	A_{sd}	A_c	A_J
HF	1	113.38	−113.51	0.00	−0.13
	2	113.38	22.70	0.00	136.08
SD MCHF	1	114.50	−120.94	5.27	−1.18
	2	114.50	24.19	5.27	143.95
SDT MRCI	1	114.31	−121.05	9.09	2.36
	2	114.31	24.21	9.09	147.62
Experiment	1				2.838
	2				149.055

TABLE XIII. The hyperfine parameters and total energies (in a.u.) of the $1s^2 2s^2 2p^2 {}^3P$ term in ^{13}C as a function of the increasing active set.

Active set	a_l	a_{sd}	a_c	b_q	Energy
HF	1.6918	0.3384	0.0000	0.6767	−37.688 619
$3s2p1d/3s$	1.6634	0.3424	0.3619	0.6360	−37.788 241
$4s3p2d1f/3s$	1.6942	0.3752	0.2377	0.6071	−37.821 515
$5s4p3d2f1g/3s$	1.7073	0.3651	0.2096	0.6147	−37.831 270
$6s5p4d3f2g/3s$	1.7089	0.3596	0.2302	0.6359	−37.835 674
$7s6p5d4f3g/3s$	1.7089	0.3609	0.2342	0.6399	−37.837 436
$8s7p6d5f3g/3s$	1.7085	0.3623	0.2371	0.6352	−37.838 110
$9s8p7d6f3g/3s$	1.7085	0.3605	0.2356	0.6353	−37.838 386

TABLE XIV. Number of CSF's in the MRCI calculation of the $1s^2 2s^2 2p^2 {}^3P$ term in ^{13}C.

Notation	Reference Configuration	Active set	Excitations	Number of CSF's
$9s8p7d6f3g/3s//3s2p1d/3s$	$1s^2 2s^2 2p^2$	$9s8p7d6f3g/3s$	SD	8 328
	$1s^2 2s^2 2p^2$	$3s2p1d/3s$	SDT	1 281
	$1s^2 2p^4$	$3s2p1d/3s$	SDT	881
			Total	9 554
$9s8p7d6f3g/3s//4s3p2d1f/3s$	$1s^2 2s^2 2p^2$	$9s8p7d6f3g/3s$	SD	8 328
	$1s^2 2s^2 2p^2$	$4s3p2d1f/3s$	SDT	7 358
	$1s^2 2p^4$	$4s3p2d1f/3s$	SDT	4 699
			Total	16 365
$9s8p7d6f3g/3s//5s4p3d2f/3s$	$1s^2 2s^2 2p^2$	$9s8p7d6f3g/3s$	SD	8 328
	$1s^2 2s^2 2p^2$	$5s4p3d2f/3s$	SDT	23 140
	$1s^2 2p^4$	$4s3p2d1f/3s$	SDT	4 699
			Total	31 381

TABLE XV. The hyperfine parameters and total energies (in a.u.) of the $1s^2 2s^2 2p^2 {}^3P$ term in ^{13}C from MRCI calculations. The CSF's obtained by SDT excitations from $1s^2 2s^2 2p^2$ and $1s^2 2p^4$ with active sets (preceded with //) of increasing size augmented the CSF's obtained by SD excitations from $1s^2 2s^2 2p^2$ to $9s8p7d6f3g/3s$.

Active sets	a_l	a_{sd}	a_c	b_q	Energy	Number of CSF's
$(1s)9s8p7d6f3g/3s^a$	1.6852	0.3444	2.9555	0.6465	−37.787 204	2 296
$9s8p7d6f3g/3s$	1.7085	0.3605	0.2356	0.6353	−37.838 386	8 328
$9s8p7d6f3g/3s//3s2p1d/3s$	1.7079	0.3606	0.2694	0.6342	−37.839 671	9 554
$9s8p7d6f3g/3s//4s3p2d1f/3s$	1.7063	0.3615	0.3817	0.6324	−37.841 073	16 365
$9s8p7d6f3g/3s//5s4p3d2f/3s$	1.7057	0.3608	0.4066	0.6319	−37.841 559	31 381

^{a}1s-shell closed, SD excitations from $2s^2 2p^2$ to $9s8p7d6f3g/3s$.

TABLE XVI. The hyperfine parameters (in a.u.) of the $1s^2 2s^2 2p^2 {}^3P$ term in ^{13}C compared with values from other calculations.

Method	a_l	a_{sd}	a_c	b_q	Reference
CI(CIV3)	1.6636	0.3580	0.726	0.6476	[27]
FE MCHF				0.6325	[28]
MRCI	1.7057	0.3608	0.4066	0.6319	This work

TABLE XVII. The relativistic, finite-nuclear-size, and finite-nuclear-mass-corrected magnetic dipole constants (in MHz) for the $1s^2 2s^2 2p^2\,^2P_{1,2}$ states in ^{13}C compared with values from other calculations and experiment.

Method	$2p^2\,^3P_1$	$2p^2\,^3P_2$	Reference
HF	−0.13	136.1	This work
DF		136.3	This work
Unrestricted HF	13.7	160.6	[33]
MCHF[a]	2.36	147.9	This work
CI(CIV3)[b]	7.63	152.0	[27]
Experiment	2.838(17)	149.055(10)	[5]

[a]The $J = 2$ state relativistic and finite-nuclear-size corrected using the ratio of the DF and HF values.
[b]Calculated from the given uncorrected hyperfine parameters with present relativistic and finite-nuclear-size corrections for the $J = 2$ state.

rameters, the convergence is oscillatory and slow, suggesting that there is an overcompensation each time the active space is increased.

Three-particle effects and near-degeneracies were included in systematic MRCI calculations. The CSF's obtained by SDT excitations from the $1s^2 2s^2 2p^2\,^3P$ and $1s^2 2p^4\,^3P$ configurations to smaller active sets were augmented to the CSFs obtained by SD excitations from the $1s^2 2s^2 2p^2\,^3P$ configuration to the $9s\,8p\,7d\,6f\,5g\,/3s$ set. To prevent the expansions from growing unmanageably large, some restrictions on the active sets to which SDT excitations were allowed had to be imposed. These restrictions together with the number of CSF's in the MRCI expansions are shown in Table XIV. The hyperfine parameters and total energies are shown in Table XV. The convergence trends are very similar to the ones in boron, but, although very important, the three-particle effects do not have the same dramatic effect on the Fermi contact term as in boron. This is explained by the relatively smaller cancelling $1s$ and $2s$-shell contributions compared to the total value. Since the off-diagonal magnetic dipole hyperfine constant has not been measured for carbon, experimental values for the individual hyperfine parameters cannot be deduced. Relatively few calculations have been done on carbon, but in Table XVI the final theoretical values of the hyperfine parameters are compared with the values from other calculations. The agreement between the MRCI and the CI(CIV3) [27] calculation is, except for the spin-dipole term, not very good. The Fermi contact term differs by about 80%, whereas for the orbital parameter and the electric-field gradient, the difference is between 2% and 3%. The electric-field gradient has recently been calculated with the FE MCHF method by Sundholm and Olsen [28], and the agreement with their value is excellent. From the measured electric-quadrupole hyperfine constant for the $J = 2$ state in ^{11}C, $B_2 = -4.949(28)$ MHz [29], the electric quadrupole moment can be calculated. Our value confirms the value

$$Q(^{11}C) = 0.033\,27(24)\ b$$

obtained by Sundholm and Olsen.

The magnetic dipole hyperfine constants have been calculated with the nuclear spin $I = \frac{1}{2}$ and the nuclear magnetic dipole moment

$$\mu_I = 0.702\,411\,8(14)\mu_N$$

(Ref. [6]). The relativistic and finite-nuclear-size correction is very difficult to determine for the $J = 1$ state since the hyperfine constant is zero at the Hartree-Fock level. However, the correction is small and can be neglected at the present level of accuracy. The correction for the $J = 2$ state was obtained by multiplying the nonrelativistic hyperfine constant with the ratio of the Dirac-Fock and Hartree-Fock values. In Table XVII the final hyperfine constants are compared with values from other calculations and experiment. The difference between the theoretical and experimental values for the $J = 2$ state is less than 1%, whereas the values for the $J = 1$ state differ by 20%. The large difference for the latter is not surprising considering the large and cancelling terms that are summed to give the final value. It can be interesting to note, in Table XII, that if only SD excitations are allowed to the $9s\,8p\,7d\,6f\,3g\,/3s$ active set, the $J = 1$ hyperfine constant does not even have the right sign. But, as three-particle effects are taken into account in the MRCI calculations, the sign changes and the value approaches the experimental one.

IV. SUMMARY AND CONCLUSIONS

We report large-scale MCHF and MRCI calculations, where the configuration expansions were generated with the systematic active-space approach. The largest MRCI expansion for the present calculations consists of almost 40 000 configuration states. The hyperfine parameters of the $2s2p\,^3P$ term in ^9Be converge slowly with an increasing number of active shells, but, using systematic sequences of active sets, extrapolation to the nonrelativistic limits is obvious. For beryllium the nonrelativistic limit is essentially reached and, to improve the calculations further, a fully relativistic approach with a realistic charge distribution has to be employed.

The necessity of a systematic approach is demonstrated in boron and carbon, where the Fermi contact term obtained from SD excitations to large active sets deviates by more than a factor of 2 from the correct value. To account accurately for the spin-polarization of the contact term, three-particle effects had to be included in a systematic way, leading to very large configuration expansions.

The relativistic, finite-nuclear-size- and finite-nuclear-mass-corrected values of the magnetic dipole hyperfine constants for the calculated states all agree very well with the extremely accurate experimental atomic-beam magnetic-resonance (ABMR) values. By performing systematic large-scale MCHF calculations, it should be possible to obtain accurate dipole hyperfine constants for states where experimental determinations are difficult. For many states, not accessible to the resonance methods, it should even be possible to calculate the hyperfine constants more accurately than they can be measured with existing techniques.

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