

*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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¹I. L. Thomas, Phys. Rev. **185**, 90 (1969).

²See for example, R. G. Parr, *Quantum Theory of Molecular Electronic Structure* (W. A. Benjamin, Inc., New York, 1963), pp. 21–30.

³I. L. Thomas, Phys. Rev. A **2**, 728 (1970).

⁴*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1964).

⁵I. L. Thomas, Chem. Phys. Letters **3**, 705 (1969).

⁶I. L. Thomas, Phys. Rev. A **2**, 72 (1970).

⁷P. S. Bagus, I. L. Gilbert, K. D. Cohen, and C. C. J. Roothaan, Bull. Am. Phys. Soc. **9**, 624 (1964).

⁸E. Clementi, IBM J. Res. Develop. **9**, 2 (1965).

Atomic Bethe-Goldstone Calculations of the Hyperfine Structure of B(²P)

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(Received 7 April 1970)

A variational generalization of Brueckner's theory has been applied to the calculation of hyperfine parameters for the ²P ground state of atomic boron. The computational method makes use of a hierarchy of *n*th-order (or *n*-particle) variational Bethe-Goldstone equations defined in terms of configurational excitations of a Hartree-Fock reference state. Hyperfine parameters are computed as the sum of net increments defined at each level of the hierarchy. Orbital basis sets are extrapolated to practical completeness for each one- and two-particle net increment. Three-particle net increments are found to be small but not negligible. Computed magnetic hyperfine constants are within roughly 1% of experiment. The electric field gradient is computed, and its relative accuracy is estimated from that of the magnetic hyperfine constants. Combined with experimental quadrupole coupling constants, this implies values of the nuclear quadrupole moments $Q(\text{B}^{10}) = 0.08472(56)$ b and $Q(\text{B}^{11}) = 0.04065(26)$ b, with the indicated precision.

I. INTRODUCTION

The hyperfine structure of atomic energy levels arises from the interaction between nuclear moments and the static electric and magnetic fields produced at the nucleus by the atomic electrons. A nuclear magnetic moment $\vec{\mu}$ interacts with the electrons through an effective Hamiltonian

$$h a_J \vec{I} \cdot \vec{J}, \quad (1)$$

where \vec{I} is the nuclear spin and \vec{J} is the electronic total angular momentum. If both \vec{I} and \vec{J} are expressed in atomic units (angular momentum divided by \hbar) then a_J is in frequency units (energy divided by h). There are three contributions to a_J of different tensorial character.¹ For light atoms, when the electronic wave function has definite quantum numbers L and S , the Fermi contact, spin-dipolar, and orbital contributions to a_J , in the state $J=L+S$, can be expressed in the form, respectively,^{1,2}

$$\begin{aligned} a_{J,c} &= \gamma_{JI} \frac{1}{2} g_e X_c, \\ a_{J,\text{dip}} &= \gamma_{JI} \frac{1}{2} g_e X_{\text{dip}}, \\ a_{J,\text{orb}} &= \gamma_{JI} X_{\text{orb}}, \end{aligned} \quad (2)$$

such that

$$a_J = a_{J,c} + a_{J,\text{dip}} + a_{J,\text{orb}}.$$

Here we have

$$g_e = 2.00232, \quad (3)$$

$$\gamma_{JI} = G_{en} \mu_I / JI, \quad (4)$$

where μ_I is the nuclear magnetic moment in nuclear magnetons, I is the nuclear spin quantum number, and

$$G_{en} = 95.4129 \text{ MHz}, \quad (5)$$

using recently tabulated values of fundamental constants.³

The dimensionless constants X_c , X_{dip} , and X_{orb} in Eqs. (2) are operator mean values computed for the electronic wave function of the state with $M_L = L$, $M_S = S$, and $M_J = L + S = J$:

$$\begin{aligned} \hbar a_0^{-3} X_c &= [\vec{s} \delta] = \langle 8\pi \sum_i s_{zi} \delta(\vec{r}_i) \rangle_{LS}, \\ \hbar a_0^{-3} X_{\text{dip}} &= [\vec{s} \vec{C}^{(2)}] = \langle 2 \sum_i s_{zi} r_i^{-3} C_0^{(2)}(\theta_i) \rangle_{LS}, \\ \hbar a_0^{-3} X_{\text{orb}} &= [\vec{l}] = \langle \sum_i r_i^{-3} l_{zi} \rangle_{LS}. \end{aligned} \quad (6)$$

Here $C_0^{(2)}$ is the spherical tensor function

$$C_0^{(2)}(\theta) = \left(\frac{4}{3}\pi\right)^{1/2} Y_2^0(\theta\phi) = P_2(\cos\theta) ,$$

defined in terms of the normalized spherical harmonics $Y_l^m(\theta, \phi)$. Two other mean values evaluated in the present work are

$$\begin{aligned} [\delta] &= \langle 4\pi \sum_i \delta(\vec{r}_i) \rangle_{LS} , \\ [\vec{C}^{(2)}] &= \langle \sum_i r_i^{-3} C_0^{(2)}(\theta_i) \rangle_{LS} . \end{aligned} \quad (7)$$

The mean value $[\vec{s}\delta]$ is sometimes denoted by f and referred to as the Fermi contact parameter.

When recalibrated for the current value of the proton magnetic moment³ (2.792 782 μ_N), the magnetic moments of the two stable isotopes of boron, in μ_N , are⁴

$$\begin{aligned} \mu(\text{B}^{10}) &= 1.800\ 84 , \quad I=3 \\ \mu(\text{B}^{11}) &= 2.688\ 56 , \quad I=\frac{3}{2} . \end{aligned} \quad (8)$$

Then the constant in Eqs. (2), for $J=\frac{3}{2}$, is

$$\begin{aligned} \gamma_{JI}(\text{B}^{10}) &= 38.1830 \text{ MHz} , \\ \gamma_{JI}(\text{B}^{11}) &= 114.0103 \text{ MHz} . \end{aligned} \quad (9)$$

The natural atomic units used in *ab initio* atomic calculations set the reduced mass of the electron equal to unity. Thus the units depend on the ratio of the electronic mass m to the nuclear mass M . Because the Bohr radius a_0 is defined for infinite nuclear mass, the computed mean values $[\vec{s}\delta]$ and $[\vec{s}\vec{C}^{(2)}]$ must be multiplied by a factor

$$\gamma_{sp} = (1+m/M)^{-3} , \quad (10)$$

the mass correction for a_0^{-3} . In the case of the orbital hyperfine interaction, the Bohr magneton also depends on the electronic reduced mass, requiring a mass correction to the constant G_{en} of Eq. (4). This can be combined with the correction for a_0^{-3} by multiplying $[\vec{I}]$ by the factor

$$\gamma_{orb} = (1+m/M)^{-2} . \quad (11)$$

In C^{12} mass units, the electronic and isotopic masses are^{3,5}

$$\begin{aligned} m &= 0.548\ 593 , \\ M(\text{B}^{10}) &= 10.012\ 94 , \\ M(\text{B}^{11}) &= 11.009\ 31 . \end{aligned} \quad (12)$$

Then the mass correction factors, to be multiplied into the computed hyperfine parameters, are

$$\begin{aligned} \gamma_{sp}(\text{B}^{10}) &= 0.999\ 835\ 6 , \\ \gamma_{sp}(\text{B}^{11}) &= 0.999\ 850\ 5 , \\ \gamma_{orb}(\text{B}^{10}) &= 0.999\ 890\ 4 , \\ \gamma_{orb}(\text{B}^{11}) &= 0.999\ 900\ 3 . \end{aligned} \quad (13)$$

These factors should be included in any results quoted to four or more significant decimals. For the sake of consistency, they have been included in the conversion factors used for all data considered in the present work.

In the 2P ground state of boron, with numerical values for the coefficients as discussed above, Eqs. (2) give the three independent contributions to $a_{3/2}$. The $J=\frac{1}{2}$ coupling constants, derived from the Wigner-Eckart theorem,¹ are

$$\begin{aligned} a_{1/2,c} &= -a_{3/2,c} , \\ a_{1/2,dip} &= -10a_{3/2,dip} , \\ a_{1/2,orb} &= 2a_{3/2,orb} . \end{aligned} \quad (14)$$

A nuclear electric quadrupole moment eQ interacts with atomic electrons through the mean value $[\vec{C}^{(2)}]$. Hyperfine structure due to this interaction is determined by the quadrupole coupling constant eQq , where

$$q = -2e[\vec{C}^{(2)}] \quad (15)$$

is the electric field gradient at the nucleus due to the atomic electrons.

The 2P ground state of boron, with electronic configuration $1s^2 2s^2 2p$, provides a simple example of polarization of nominally closed orbital subshells by the unbalanced spin and nonspherical spatial distribution of an unfilled valence shell. Within the Hartree-Fock approximation, the self-consistent field acting on the $1s$ and $2s$ electrons is spin dependent and nonspherical.⁶ Unless specific constraints are imposed, this has the effect of inducing a nonzero net spin density in the $1s^2$ and $2s^2$ shells, and of mixing the $1s$ and $2s$ orbitals with virtual orbitals of d symmetry.⁶ This spin polarization of the inner shells introduces a nonzero Fermi contact hyperfine interaction,⁷ and the virtual d/s excitation has an important effect on all of the hyperfine interaction parameters. To examine these effects, it is necessary to carry out calculations of greater complexity than traditional Hartree-Fock calculations with the usual orbital symmetry and equivalence constraints.^{6,8} Calculations on the 2^2P excited state of Li, whose configuration $1s^2 2p$ is similar to that of 2P boron, indicate that specific electronic correlation effects must be taken into account, in addition to spin and orbital polarization, in order to compute hyperfine interactions with high enough accuracy for useful comparison with experimental data.^{2,9}

There are several calculations of the hyperfine parameters of $\text{B}(^2P)$ that go beyond the traditional Hartree-Fock approximation. Results of three of these calculations, converted from the original atomic units to MHz, using the constants given here in Eqs. (2), (9), and (13), are shown in Table I.

Goodings¹⁰ has carried out a Hartree-Fock calculation without the traditional constraint requiring the $1s\beta$ or $2s\beta$ spatial orbital to be identical with the $1s\alpha$ or $2s\alpha$ spatial orbital, respectively. Although referred to by Goodings as a UHF (unrestricted Hartree-Fock) calculation, this terminology is inappropriate, because the constraint of neglecting d/s polarization was imposed, even though the 2P state of boron had been discussed previously as an example of such polarization.⁶ The structure of Gooding's wave function causes $[\vec{s}\vec{C}^{(2)}]$ and $[\vec{1}]$ to depend on a single parameter, the mean value $\langle r^{-3} \rangle$ for the occupied $2p$ orbital. With a more accurate wave function this interdependence of the hyperfine parameters is broken down by d/s polarization and by electronic correlation effects. Despite these limitations, Gooding's values of $a_{1/2}$ and $a_{3/2}$, shown in Table I, are in reasonable agreement with experiment.

A more recent calculation, by Goddard,¹¹ uses a wave function that allows for limited electronic correlation in the $1s^2$ and $2s^2$ subshells as well as for spin polarization of these shells by the $2p$ valence orbital. No d orbitals are included in the calculation, so d/s polarization and correlation involving virtual excitation of d orbitals are neglected. The computed magnetic hyperfine constants, shown in Table I, are further from the experimental values than are Goodings's spin-polarized Hartree-Fock results.

The effect of virtual excitation including d orbitals has been considered by Schaefer, Klemm, and Harris.¹² Their variational wave function, used for calculations of the hyperfine parameters of $B({}^2P)$, consisted of a superposition of the Hartree-Fock function Φ_0 with all singly excited configurations obtained from a given orbital basis set. This wave function is expected to give an internally consistent treatment of polarization effects but not of the detailed effect of electronic correlation. As shown in Table I, the computed magnetic hyperfine constants are within approximately 2% of experiment.

In order to consider the quantitative effects of electronic correlation as well as polarization, a theoretical method is needed that provides internal criteria of accuracy and convergence and that is free of obvious constraints such as those incorporated in the traditional Hartree-Fock approximation or its immediate generalizations. The method used in the present work is to carry out calculations based on a convergent hierarchy of Bethe-Goldstone equations, where an n -particle Bethe-Goldstone equation is defined as the Schrödinger equation for $n \leq N$ particles of an N -particle system, with the wave function constrained by orthogonality to $N-n$ orbital functions of an assumed

TABLE I. Results of previous calculations. Data for B^{11} only (MHz).

	Goodings ^a	Goddard ^b	SKH ^c	Expt
$a_{1/2,c}$	-8.22	-17.31	-3.51	
$a_{1/2,dip}$	178.49	180.89	189.45	
$a_{1/2,orb}$	178.27	181.10	174.97	
$a_{1/2}$	348.54	344.68	360.91	366.077 ^d
$a_{3/2,c}$	8.22	17.31	3.51	
$a_{3/2,dip}$	-17.85	-18.09	-18.94	
$a_{3/2,orb}$	89.14	90.54	87.48	
$a_{3/2}$	79.51	89.76	72.05	73.347 ^e

^aD. A. Goodings, Phys. Rev. **123**, 1706 (1961).

^bW. A. Goddard, III, Phys. Rev. **182**, 48 (1969).

^cH. F. Schaefer, III, R. A. Klemm, and F. E. Harris, Phys. Rev. **176**, 49 (1968).

^dH. Lew and R. S. Title, Can. J. Phys. **38**, 868(1960).

^eG. Wessel, Phys. Rev. **92**, 1581 (1953).

Hartree-Fock Fermi sea.¹³ This method is based on the many-particle theory of Brueckner.¹⁴ To avoid convergence difficulties indicated in earlier hyperfine structure calculations by this method,¹⁵ which was originally described in terms of virtual excitations of individual orbitals (one-electron functions), the method has been restated in terms of *configurational* excitations in a recent application to the 2^2P state of Li.² Earlier calculations by an equivalent method were carried out on the 2P ground state of B by Schaefer and Harris.¹⁶ The contact hyperfine interaction in $B({}^2P)$ was computed by this method,¹⁷ but with orbital basis sets less complete than those considered here. A detailed comparison of results will be given below.

The calculations reported here are based on configurational excitations. In contrast to the procedure used earlier, the wave functions obtained variationally at each stage of computation are eigenfunctions of \vec{L}^2 and \vec{S}^2 . This has the effect of preventing spurious contributions to the hyperfine interaction parameters from appearing at a low level in the hierarchy or results, only to be canceled out at a higher level after laborious computations.

Details of the calculations will be given in Sec. II, and results for the magnetic hyperfine interaction parameters will be described in Sec. III. An important result of the present work is to compute $[\vec{C}^{(2)}]$ and hence the electric field gradient q to an accuracy not previously attained. In Sec. IV this result is used to determine the nuclear quadrupole moments of B^{10} and B^{11} from experimental data on the quadrupole coupling constant.

II. COMPUTATIONAL DETAILS

The procedure followed in the present work has been described in detail in an earlier paper.² A given set of basis orbital functions generates a Hilbert space $[\Phi]$ of N -electron wave functions, whose basis is the set of normalized Slater determinants defined by virtual excitation of a reference state determinant Φ_0 , usually taken to be an approximate Hartree-Fock function. Individual orbital functions are designated by the quantum numbers (l, n, m_s, m_l) , where l, m_s , and m_l have their usual meaning, as does the principal quantum number n for occupied orbitals of Φ_0 . For unoccupied orbitals, always a finite set of normalized functions, n is just a counting index. Sets of basis functions are used that can be extended to countable complete sets. Virtual excitations of Φ_0 are defined in terms of replacement of occupied by unoccupied orbitals. Unless m_s, m_l are specified, excitations refer to configurational excitations. For example, relative to the ground-state configuration $1s^2 2s^2 2p$ of boron, the excitation $(nd/2s)$ denotes the configuration $1s^2 2s nd 2p$. Only determinants with given values of M_L and M_S are considered.

The Hilbert space $[\Phi]$ is the direct sum of *disjoint* subspaces defined in terms of configurational excitations. For example, $(1s)$ denotes the subspace of configurations $(nl/1s)$ for all values of n and l represented in the given set of unoccupied orbitals; $(1s 2p)$ denotes the subspace of configurations $(nl, n'l'/1s, 2p)$ for all possible n, n' and l, l' . The reference configuration (containing Φ_0) is denoted by (0) . A *variational* subspace is defined as the direct sum of disjoint subspaces whose indices (sets of nl values) form subsets of the indices defining the variational subspace. For example, variational subspaces are defined by

$$[1s 2s] = (0) + (1s) + (2s) + (1s 2s) , \quad (16)$$

$$[1s^2 2p] = (0) + (1s) + (2p) + (1s^2) + (1s 2p) + (1s^2 2p) .$$

Variational calculations are carried out by finding the lowest eigenvalue of the electronic Hamiltonian matrix within each variational subspace. Mean values $\langle F \rangle$ of electronic operators are computed from the eigenvector, whose components are the coefficients of Slater determinants in the variational wave function. The *gross* increment ΔF of any mean-value property is defined as one of these variational mean values, with the reference state value F_{00} subtracted out. *Net* increments f are then defined by formulas of the same structure as the decomposition of the variational subspaces, exemplified by Eqs. (16). The corresponding formulas for gross and net increments of

some electronic mean value are

$$\Delta F_{1s 2s} = f_0 + f_{1s} + f_{2s} + f_{1s 2s} , \quad (17)$$

$$\Delta F_{1s 1s 2p} = f_0 + f_{1s} + f_{2p} + f_{1s 1s} + f_{1s 2p} + f_{1s 1s 2p} .$$

This has the effect of defining net increments

$$f_{1s 2s} = \Delta F_{1s 2s} - f_0 - f_{1s} - f_{2s} , \quad (18)$$

$$f_{1s 1s 2p} = \Delta F_{1s 1s 2p} - f_0 - f_{1s} - f_{2p} - f_{1s 1s} - f_{1s 2p} .$$

The general definition of a net increment with indices $n_1 l_1, n_2 l_2, \dots$, is the difference between the corresponding gross increment, directly computed from a variational wave function, and the sum of all distinct net increments of lower order whose indices are a subset of those given.

As a consequence of these definitions, the exact mean value $\langle F \rangle$ is expressed as the sum of F_{00} and of all net increments whose indices represent subsets of the occupied orbitals of the reference configuration, if the orbital basis set is extended to completeness. This decomposes $\langle F \rangle$ into a finite sum of net increments obtained by successive calculations in a hierarchy of variational subspaces of $[\Phi]$.

The orbital basis set shown in Table II was used as a base for extrapolation. It contains s and p orbitals from the Hartree-Fock calculation of Clementi *et al.*¹⁸ The two $3d$ exponents were obtained, respectively, by minimizing the energy of the $[2s]$ and $[1s]$ variational wave functions. Preliminary calculations indicated that f orbitals could be omitted from this starting basis set.

Extrapolations were carried out by augmenting the basis set of Table II with additional orbitals of s, p, d , and f symmetry. These extrapolations were carried out separately for each one- and two-particle set of net increments and for each l value. For virtual excitations of $1s$, the augmenting orbitals have a common exponent $\zeta_K = 10.085$; for virtual excitations of $2s$ and $2p$ the common exponent is $\zeta_L = 1.860$. These exponents were determined by variational calculations of electronic correlation energy net increments.¹³ When both K - and L -shell orbitals are excited, the basis set is augmented two orbitals at a time,

TABLE II. Exponents ζ for basis orbitals $r^{n-1} e^{-\zeta r} Y_l^m(\theta, \phi)$.

nl	ζ list
1s	4.4661, 7.8500
2s	0.8320, 1.1565, 1.9120, 3.5213
2p	0.8783, 1.3543, 2.2296, 5.3665
3d	1.428, 2.977

one with exponent ζ_K and one with ζ_L . For each exponent, basis orbitals were used in an increasing sequence of powers of r .

Extrapolation of the net increments was done with a standard formula equivalent to assuming geometric convergence.¹⁹ For virtual excitations within a single shell, five augmenting orbitals, added in succession, allowed two cycles of use of the three-term extrapolation formula. Because of the complexity of the calculations, fewer terms were computed in KL excitations. In cases of obviously irregular convergence, mean values computed for the final calculation in the sequence were used instead of extrapolated values.

The extrapolated corrections of the hyperfine parameters, obtained by a separate sequence of calculations for each l value, are listed in Table III and summed to give extrapolated estimates of the one- and two-particle net increments of the hyperfine parameters.

III. RESULTS FOR MAGNETIC HYPERFINE INTERACTIONS

Final computed values of the hyperfine parameters are listed in Table IV. The Hartree-Fock results, denoted by (0), are obtained with the s and p orbitals by the addition of basis functions with exponent ζ_L . The degree of convergence of the Hartree-Fock calculation is indicated by

$$\begin{aligned} \langle r^{-3} \rangle_{2p} &= 0.775\,266\,35, \quad H_{00} = 24.529\,052 \\ &\quad (6, 4 \text{ basis}), \\ \langle r^{-3} \rangle_{2p} &= 0.775\,604\,31, \quad H_{00} = 24.529\,053 \\ &\quad (6, 9 \text{ basis}), \end{aligned} \quad (19)$$

in a. u.

Net increments of the hyperfine parameters for all one- and two-particle configurational excitations possible for the configuration $1s^2 2s^2 2p$ are included in Table IV and summed to give the subtotal indicated by (total)₁. The $(2s^2 2p)$ net increments have been computed, using the orbital basis set 6420 of Table II without extrapolation. This is added into (total)₁ to give (total)₂ in the table. This three-particle contribution is not negligible, as can be seen from the table. The various three-particle net increments due to excitation of both K and L shells were estimated by carrying out calculations in which one- and two-particle excitations were allowed to interact, but explicit three-particle excitations were omitted from the variational Hilbert space. For example, a truncated variational subspace is defined by

$$\begin{aligned} [1s2s2p]_2 &= (0) + (1s) + (2s) + (2p) + (1s2s) \\ &\quad + (1s2p) + (2s2p) . \end{aligned} \quad (20)$$

This differs from $[1s2s2p]$ by omitting the disjoint subspace $(1s2s2p)$. The sum of intershell three-particle net increments, computed with the 6420 orbital basis, but in truncated variational subspaces as in Eq. (20), are added into (total)₂ to give (total)₃ in Table IV. In all cases the sum of intershell three-particle terms is smaller than the valence-shell term $(2s^2 2p)$. The sum $\sum_{(ijk)}$ in Table IV includes $(2s^2 2p)$.

These results are multiplied by the conversion constants discussed in the Introduction to give the magnetic hyperfine coupling constants listed in Table V. Comparison of the results for (total)₁ with either (total)₂ or (total)₃ shows that three-particle correlation effects are not negligible, although much smaller here than in previous calculations formulated in terms of individual orbital rather than configuration excitations.¹⁵ Despite large variations in $a_{J,c}$, the effect of the contact term is so small that the results of both (total)₂ and (total)₃ are in excellent agreement with the experimental hyperfine coupling constants. The largest relative error is 2% for $a_{3/2}$ from (total)₃. The sum $a_{1/2} + a_{3/2}$, which cancels out the effect of $a_{J,c}$, is in error by only 0.57% for (total)₂ and by 0.26% for (total)₃.

IV. NUCLEAR QUADRUPOLE MOMENTS

If the quadrupole coupling constant eqQ is known, then the nuclear quadrupole moment Q can be determined from a computed value of the field gradient q by the formula

$$Q(b) = eqQ(\text{MHz})/234.9649 q(e a_0^{-3}) . \quad (21)$$

The constant in this formula has been computed from recently tabulated values of fundamental constants.³ In atomic units, q is given by Eq. (15) as just $-2[\overline{C}^{(2)}]$, multiplied by the nuclear mass correction factor γ_{sp} given by Eq. (10) and (13) for the isotopes of boron. For B¹¹, this gives the values of q indicated in Table VI from the computed values of $[\overline{C}^{(2)}]$, Table IV.

The errors indicated for q in Table VI are obtained by assuming that the relative error is equal to that of the sum $a_{1/2} + a_{3/2}$. This is justified because the contact term $a_{J,c}$, which is subject to a loss of one significant decimal due to the near cancellation of $1s$ and $2s$ net increments, cancels out of this sum. The data in Table IV show that no comparable cancellation occurs for $[\overline{C}^{(2)}]$, $[\overline{s}\overline{C}^{(2)}]$, or $[\overline{I}]$ — all of which are dominated by the Hartree-Fock value. Hence the relative error in $[\overline{C}^{(2)}]$ or q should be comparable to that of $a_{1/2} + a_{3/2}$, a linear combination of $[\overline{s}\overline{C}^{(2)}]$ and $[\overline{I}]$. Thus the known error in the computed magnetic hyperfine interaction can be used to estimate the error in

TABLE III. Extrapolation for orbital basis set completeness. Net increments of hyperfine parameters (a.u.).

Increment	$[\delta]$	$[\vec{s}\delta]$	$[\vec{C}^{(2)}]$	$[\vec{s}\vec{C}^{(2)}]$	$[\vec{I}]$
1s base	-0.018 492	-0.748 697	0.000 750	-0.006 521	0.000 025
s	-0.000 629	-0.052 586	-0.000 000	-0.000 000	0.000 000
p	0.000 002	0.000 398	0.000 000	0.000 000	0.000 000
d	-0.000 525	-0.000 119	0.006 533	-0.000 711	0.000 015
f	0.0	0.0	0.0	0.0	0.0
Total	-0.019 644	-0.800 914	0.007 283	-0.007 232	0.000 040
2s base	-0.411 627	0.881 823	0.002 473	-0.001 683	-0.017 793
s	-0.012 306	-0.041 576	-0.000 000	0.000 000	0.000 002
p	0.000 119	0.000 179	0.000 000	0.000 001	-0.000 003
d	0.002 582	-0.007 611	0.000 321	-0.000 618	-0.000 159
f	0.0	0.0	0.0	0.0	0.0
Total	-0.421 232	0.832 815	0.002 794	-0.002 300	-0.017 953
2p base	0.0	0.0	0.0	0.0	-0.000 001
s	0.0	0.0	0.0	0.0	0.000 001
p	0.0	0.0	0.0	0.0	0.000 001
d	0.0	0.0	0.0	0.0	0.0
f	0.0	0.0	0.0	0.0	0.0
Total	0.0	0.0	0.0	0.0	0.000 001
1s ² base	0.707 331	-0.042 300	0.000 344	0.000 008	0.000 133
s	-0.743 039	0.007 716	-0.000 001	0.000 001	-0.000 001
p	0.495 681	0.000 026	-0.000 027	0.000 025	-0.000 105
d	-0.077 522	0.000 448	0.000 112	-0.000 107	-0.000 002
f	-0.027 090	0.000 135	-0.000 001	-0.000 001	-0.000 001
Total	0.355 361	-0.033 975	0.000 427	-0.000 074	0.000 024
1s2s base	0.302 214	0.082 455	0.000 488	0.000 168	0.000 935
s	-0.094 830	-0.010 130	-0.000 001	0.000 000	0.000 004
p	0.060 883	-0.001 992	-0.000 053	-0.000 002	-0.000 151
d	0.011 167	-0.003 487	-0.000 010	0.000 084	0.000 039
f	-0.000 253	0.000 024	0.000 000	0.000 002	-0.000 015
Total	0.279 181	0.066 870	0.000 424	0.000 252	0.000 812
1s2p base	-0.185 912	0.024 343	-0.003 565	-0.003 347	0.015 261
s	-0.020 009	0.004 692	-0.000 011	-0.000 013	0.000 061
p	-0.014 562	0.000 436	-0.000 042	-0.000 101	0.000 707
d	-0.011 646	0.002 296	-0.000 548	-0.000 365	0.002 621
f	-0.010 549	0.004 654	-0.000 192	-0.000 025	0.000 544
Total	-0.242 678	0.036 421	-0.004 358	-0.003 851	0.019 194
2s ² base	-0.840 067	0.116 831	0.009 257	0.000 420	-0.001 428
s	-0.048 475	-0.007 317	-0.000 004	0.000 001	0.000 002
p	0.024 719	0.000 266	-0.000 055	-0.000 006	-0.000 009
d	0.041 579	-0.010 903	0.000 119	-0.000 127	0.000 290
f	-0.000 080	0.000 213	-0.000 241	-0.000 142	-0.000 458
Total	-0.822 324	0.099 090	0.009 076	0.000 146	-0.001 603
2s2p base	0.095 936	-0.033 725	-0.005 422	-0.005 060	0.027 835
s	0.004 184	-0.004 533	-0.000 013	-0.000 008	0.000 051
p	-0.003 346	-0.002 178	-0.000 133	-0.000 116	0.000 763
d	0.004 183	-0.002 324	-0.000 331	0.000 086	0.000 469
f	0.001 809	-0.005 473	-0.000 305	0.000 055	0.000 880
Total	0.102 766	-0.048 233	-0.006 204	-0.005 043	0.029 998

the computed electric field gradient. The experimental error in the magnetic hyperfine constants can be neglected in this context.

This estimated computational error is combined with the experimental errors in eqQ and the ratio $Q(B^{10})/Q(B^{11})$ to give final estimated errors in val-

ues of Q computed by Eq. (21). The resulting values of Q , for both isotopes, are shown in Table VI. If the estimate of the residual computational error is justified, the best result here [from (total)₃] represents a significant improvement on the accuracy of currently accepted values of the

TABLE IV. Net increments of hyperfine parameters (a. u.).

Increment	$[\delta]$	$[\bar{s}\delta]$	$[\bar{C}^{(2)}]$	$[\bar{s}\bar{C}^{(2)}]$	$[\bar{I}]$
0	0.0 ^a	0.0	-0.155 120	-0.155 120	0.775 604
1s	-0.019 644	-0.800 914	0.007 283	0.007 232	0.000 040
2s	-0.421 232	0.832 815	0.002 794	-0.002 300	-0.017 953
2p	0.0	0.0	0.0	0.0	0.000 001
1s ²	0.355 361	-0.033 975	0.000 427	-0.000 074	0.000 024
1s2s	0.279 181	0.066 870	0.000 424	0.000 252	0.000 812
1s2p	-0.242 678	0.036 421	-0.004 358	-0.003 851	0.019 194
2s ²	-0.822 324	0.099 090	0.009 076	0.000 146	-0.001 603
2s2p	0.102 766	-0.048 233	-0.006 204	-0.005 043	0.029 998
(total) ₁	-0.768 570 ^a	0.152 074	-0.145 678	-0.173 222	0.806 117
2s ² 2p	0.119 409	-0.056 652	0.003 944	0.004 177	-0.021 570
(total) ₂	-0.649 161 ^a	0.095 422	-0.141 734	-0.169 045	0.784 547
$\Sigma(i, j_k)$	0.025 869	-0.104 456	0.004 583	0.005 870	-0.027 218
(total) ₃	-0.742 701 ^a	0.047 618	-0.141 095	-0.167 352	0.778 899

^a Hartree-Fock value of $[\delta]$, 903.951 97 a. u., is not included.

quadrupole moments of B¹⁰ and B¹¹.

V. COMPARISON WITH PREVIOUS CALCULATIONS

The calculations by Goodings¹⁰ and Goddard,¹¹ whose results are shown in Table I, both use relatively simple wave functions that have a pre-determined structure. Comparison of Tables I and V shows the advantage of the present method. If the purpose is to obtain quantitative results, it is necessary to have a method such as that used here, which can be systematically pushed to ultimate convergence.

The calculation by Schaefer *et al.*,¹² included in Table I, also represents a wave function of pre-

determined form, but capable of representing all important physical effects of orbital polarization. The wave function is a variational function in the Hilbert space

$$[1s2s2p]_1 = (0) + (1s) + (2s) + (2p) , \quad (22)$$

representing all one-particle configurational excitations and the interactions among them. The orbital basis set used included *s*, *p*, and *d* orbitals and was carried to practical completeness for the assumed wave function. If $a_{1/2} + a_{3/2}$ is used as a criterion of accuracy, the computational error, neglecting the contact interaction, is 1.5% from the data in Table I. Schaefer *et al.* compute $[\bar{C}^{(2)}]$ and q , and deduce the nuclear quadrupole moments to be

$$Q(B^{10}) = 0.08035 \text{ b}, \quad Q(B^{11}) = 0.03856 \text{ b} , \quad (23)$$

with an estimated relative error of less than 2%. These numbers differ from the present results by approximately 5%. Because of the detailed and systematic treatment of electronic correlation in the present work, the present results are expected to be more reliable.

TABLE V. Hyperfine coupling constants (MHz).

		(total) ₁	(total) ₂	(total) ₃	Expt
B ¹⁰	$a_{1/2, c}$	-1.938	-1.216	-0.607	
	$a_{1/2, \text{dip}}$	66.207	64.610	63.963	
	$a_{1/2, \text{orb}}$	61.553	59.906	59.475	
	$a_{1/2}$	125.822	123.300	122.831	122.585 ^a
	$a_{3/2, c}$	1.938	1.216	0.607	
	$a_{3/2, \text{dip}}$	-6.621	-6.461	-6.396	
	$a_{3/2, \text{orb}}$	30.777	29.953	29.737	
	$a_{3/2}$	26.094	24.708	23.948	
	B ¹¹	$a_{1/2, c}$	-5.785	-3.630	-1.812
$a_{1/2, \text{dip}}$		197.690	192.923	190.991	
$a_{1/2, \text{orb}}$		183.793	178.875	177.587	
$a_{1/2}$		375.698	368.168	366.766	366.077 ^a
$a_{3/2, c}$		5.785	3.630	1.812	
$a_{3/2, \text{dip}}$		-19.769	-19.292	-19.099	
$a_{3/2, \text{orb}}$		91.897	89.437	88.794	
$a_{3/2}$		77.913	73.775	71.507	73.347 ^b

^aH. Lew and R. S. Title, Can. J. Phys. **38**, 868 (1960).

^bG. Wessel, Phys. Rev. **92**, 1581 (1953).

TABLE VI. Field gradients and nuclear quadrupole moments, including estimated errors.

	(total) ₁	(total) ₂	(total) ₃
q (a. u.)	0.291 31 (911)	0.283 43 (162)	0.282 15 (74)
$eqQ(B^{11})$ (MHz) ^a		2.695 (16)	
$Q(B^{10})/Q(B^{11})$ ^b		2.084 (2)	
$Q(B^{11})$ (b)	0.039 37 (125)	0.040 47 (33)	0.040 65 (26)
$Q(B^{10})$ (b)	0.082 05 (261)	0.084 34 (70)	0.084 72 (56)

^aG. Wessel, Phys. Rev. **92**, 1581 (1953).

^bH. G. Dehmelt, Z. Physik. **133**, 528 (1952).

All of the calculations considered here illustrate the difficulty in obtaining an accurate value of $a_{J,c}$, the Fermi contact interaction constant. One major source of this difficulty is the inherent cancellation between the (1s) and (2s) net increments of $[\vec{s}\delta]$, shown in Table IV. Moreover, because $[\vec{s}\delta]$ vanishes in the traditional Hartree-Fock approximation, the entire contact interaction is due to electronic polarization and correlation effects.

A calculation of the contact interaction by a method equivalent to that used here was carried out by Schaefer and Kaldor (SK).¹⁷ Their computed one- and two-particle net increments of $[\vec{s}\delta]$ are compared with the present results in Table VII. While the one-particle net increments and the two-particle increments (1s²) and (2s²) appear to be in reasonable agreement, there is a striking discrepancy in the two-particle cross terms, especially (1s2s). It is difficult to account for the large magnitude of the (1s2s) net increment in the SK calculation, since this is an intershell correlation effect. The corresponding net energy increment computed by Schaefer and Harris¹⁶ is an order of magnitude smaller than the largest pair correlation energies, (1s²) and (2s²). Although the SK calculations used an orbital basis set even larger than the set indicated here in Table II, the present results should be more accurate because of the systematic extrapolation to completeness summarized in Table III. The present values of $a_{J,c}$, from any of the results shown in Table V, are in reasonable agreement with the polarization function result of Schaefer *et al.*¹² in Table I, while the SK contact interaction is nearly twice as large as the largest of these values (total)₁.

VI. DISCUSSION

The present results, together with similar calculations on Li (2²P) reported earlier,² indicate that the method used here is capable of obtaining hyperfine interaction constants within an error of 1% of their experimental values. The Fermi contact interaction is obtained with considerably less

accuracy than this, but it makes only a small contribution to the magnetic hyperfine interaction in B(2P).

Since the electric field gradient q is obtained from the same computational procedure used for the magnetic hyperfine interactions, the computational error in q can be estimated from the relative error of the magnetic hyperfine constants. This value of q can be used to compute the nuclear electric quadrupole moment Q from experimental values of the quadrupole coupling constant eqQ . This combination of experimental measurements (of magnetic hyperfine structure and quadrupole coupling constants) with systematic computations of the hyperfine parameters provides values of Q together with an estimate of the relative error. The present method appears to give nuclear quadrupole moments for B¹⁰ and B¹¹ that are substantially more accurate than previously available values.

The formalism used here originates in Brueckner's many-particle theory,¹⁴ in the idea that each two-particle subsystem in an N -particle system can be dealt with exactly by solving the appropriate Bethe-Goldstone equation and then by adding the resulting pair correlation energies to give an estimate of the total correlation energy. This aspect of Brueckner's theory has been characterized as the "independent-pair model."²⁰

The present results on hyperfine structure make essential use of several innovations that go beyond the independent-pair model. Most important among these innovations are the concept of a hierarchy of variational Bethe-Goldstone equations, defining n -particle correlation effects for n different from 2, and the use of a configuration interaction formalism that makes possible the calculation of general mean-value electronic properties in addition to the energy.^{13,15} Following the work of Schaefer and Harris,¹⁶ the reformulation of this method in terms of configurational excitations² has helped to make accurate calculations of hyperfine interactions feasible. The extensive extrapolation of orbital basis sets to completeness carried out in the present work appears to be necessary in order to avoid individual calculations of impractical complexity.

The calculations reported here were carried out on an IBM 360/91 computer, using 64-bit arithmetic throughout.

ACKNOWLEDGMENT

The author is indebted to A. Routh for preparing and supervising the numerous computer runs required in this work.

TABLE VII. Comparison of computed net increments of contact parameter (a.u.).

Increment	Present ^a	SK ^b	Increment	Present ^a	SK ^b
0	0.0	0.0	1s2s	0.06687	0.53019
1s	-0.80091	-0.98334	1s2p	0.03642	0.06210
2s	0.83281	0.80809	2s ²	0.09909	0.09567
2p	0.0	0.0	2s2p	-0.04823	-0.19627
1s ²	-0.03398	-0.04109	Total	0.15207	0.27535

^a $[\vec{s}\delta]$ from Table IV.

^bH. F. Schaefer, III, and U. Kaldor, *J. Chem. Phys.* **49**, 468 (1968).

- ¹R. E. Trees, Phys. Rev. 92, 308 (1953); C. Schwartz, *ibid.* 97, 380 (1955).
- ²R. K. Nesbet, Phys. Rev. A 2, 661 (1970).
- ³B. N. Taylor, W. H. Parker, and D. N. Langenberg, Rev. Mod. Phys. 41, 375 (1969).
- ⁴N. F. Ramsey, *Molecular Beams* (Oxford U. P., New York, 1956), p. 172.
- ⁵*Handbook of Chemistry and Physics* (Chemical Rubber, Cleveland, 1969), 49th edition.
- ⁶R. K. Nesbet, Proc. Roy. Soc. (London) A230, 312 (1955).
- ⁷A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) A205, 135 (1951).
- ⁸D. R. Hartree, *The Calculation of Atomic Structures* (Wiley, New York, 1957).
- ⁹J. D. Lyons, R. T. Pu, and T. P. Das, Phys. Rev. 178, 103 (1969); 186, 266 (1969).
- ¹⁰D. A. Goodings, Phys. Rev. 123, 1706 (1961).
- ¹¹W. A. Goddard III, Phys. Rev. 182, 48 (1969).
- ¹²H. F. Schaefer III, R. A. Klemm, and F. E. Harris, Phys. Rev. 176, 49 (1968).
- ¹³R. K. Nesbet, Phys. Rev. 155, 51 (1967); 155, 56 (1967); 175, 2 (1968); Advan. Chem. Phys. 14, 1 (1969).
- ¹⁴K. A. Brueckner, Phys. Rev. 96, 508 (1954); 97, 1353 (1955); 100, 36 (1955); in *The Many-Body Problem*, edited by B. deWitt (Wiley, New York, 1959), pp. 47–241.
- ¹⁵R. K. Nesbet, in *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P. -O. Löwdin (Academic, New York, 1966), pp. 157–165; Colloq. Intern. Centre Natl. Rech. Sci. (Paris) 164, 87 (1967).
- ¹⁶H. F. Schaefer III and F. E. Harris, Phys. Rev. 167, 67 (1968).
- ¹⁷H. F. Schaefer III and U. Kaldor, J. Chem. Phys. 49, 468 (1968).
- ¹⁸E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. 127, 1618 (1962).
- ¹⁹D. R. Hartree, *Numerical Analysis* (Oxford U. P., New York, 1952), pp. 196–197.
- ²⁰L. C. Gomes, J. D. Walecka, and V. F. Weisskopf, Ann. Phys. (N. Y.) 3, 241 (1958).

PHYSICAL REVIEW A

VOLUME 2, NUMBER 4

OCTOBER 1970

Level-Crossing Measurement of Lifetime and hfs Constants of the ${}^2P_{3/2}$ States of the Stable Alkali Atoms*

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(Received 27 February 1970)

Measurements have been made of the hyperfine structure (hfs) constants and lifetimes of the first and second ${}^2P_{3/2}$ states of the stable alkali atoms, except lithium, using the pure magnetic field level-crossing technique. The results for Na²³ are

State	a (MHz)	b (MHz)	τ (nsec)
$3^2P_{3/2}$	18.9 ± 0.3	2.4 ± 0.3	16.0 ± 0.5
$4^2P_{3/2}$	6.2 ± 0.2	1.0 ± 0.1	95 ± 4

The results for K³⁹ have been reported previously. For Rb⁸⁵ and Cs¹³³, hfs constants were obtained that agreed with, but were less accurate than, previous work. The measured lifetimes are

Element	State	τ (nsec)
Rb ⁸⁵	$5^2P_{3/2}$	25.5 ± 0.5
	$6^2P_{3/2}$	118 ± 4
Cs ¹³³	$6^2P_{3/2}$	32.7 ± 1.5
	$7^2P_{3/2}$	134.5 ± 2.8

The error limits in these measurements are two standard deviations. The above results were obtained by fitting the observed level-crossing signal to a theoretical line shape computed from the Breit formula, using a , b , and τ as parameters.

I. INTRODUCTION

The stable alkali atoms continue to be the objects of widespread theoretical and experimental

study. Their importance stems from their utility as frequency standards¹ and magnetometers,² as probes of interaction processes such as atom-atom collisions³ and new effects such as light-