High-Precision Calculations of the Hyperfine Constants for the Low-Lying Excited ^{2}S States of Be$^{+\dagger}$

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High-precision Hylleraas-type calculations of the hyperfine constants for the four lowest excited 3 ^{2}S, 4 ^{2}S, 5 ^{2}S, and 6 ^{2}S states of the ^{9}Be$^+$ ion are reported. Small adjustments to the hyperfine constants arising from effects that include the finite nuclear mass, the magnetization density distribution over the nucleus, the Breit−Rosenthal correction for finite nuclear size, and lowest-order relativistic and quantum electrodynamic corrections are considered. The final values obtained for the hyperfine constants for the n ^{2}S states were: −158.78, −62.43, −30.66, and −17.29 MHz for n = 3, 4, 5, and 6, respectively.

I. Introduction

The lithium atom has long served as a target for testing various theoretical approaches to the evaluation of numerous properties. The few-electron nature of this species makes it amendable to very high-precision calculations. In particular, for the hyperfine coupling, the lithium atom has proved to be a rather attractive target, and considerable work using a variety of computational techniques has been reported.[1−17]

The beryllium positive ion, ^{9}Be$^+$, is an even more attractive target. The ground state of this atomic ion has been studied by laser fluorescence spectroscopy in an ion trap,[18] resulting in a hyperfine constant having 11 digits of precision, making it one of the most accurately known hyperfine constants of any species that has been investigated. The determination of the hyperfine structure constants for the excited states of ^{9}Be$^+$ has received far less experimental attention. The only experimental results available are two studies on the low-lying P states of this atomic ion.[19,20]

The objective of the present work is to report the results of high-precision nonrelativistic calculations of the four lowest excited doublet S states of the ^{9}Be$^+$ ion. The Hylleraas approach that is employed in the present study has proved to be particularly successful for studying few-electron atomic and molecular systems. This technique has also yielded high-precision results for low-lying excited states. In essence, the entire correlation energy is captured in the present calculations: the correlation energy not accounted for is expected to be below $\sim 5 \times 10^{-7}$% of the total correlation energy.

The target property of interest is the hyperfine constant. The accurate calculation of this quantity requires the wave function in the vicinity of the nucleus to be accurately described. This provides a suitable theoretical challenge, particularly for the excited states of even small atomic and molecular systems. Beyond the nonrelativistic regime, a number of small corrections contribute to the hyperfine constant. Often, one or more of these corrections are ignored. In the present study, all of the key small corrections are estimated for each excited state investigated.

II. Theory

The nonrelativistic Hamiltonian for an n-electron atomic system can be written in the following form

$$H = -\sum_{i=1}^{n} \frac{1}{2\mu_i}\nabla_i^2 - \frac{1}{M}\sum_{i=1}^{n}\sum_{j>i}^{n}\nabla_i\cdot\nabla_j + Z\sum_{i=1}^{n}\frac{q_i}{r_i} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{q_i q_j}{r_{ij}} \quad (1)$$

For atomic systems, the nucleus is taken to be the principal reference particle. In eq 1, r_i designates the electron−nuclear separation distance for electron i, r_{ij} is the interelectron separation distance, M and Z are the mass and charge of the nucleus, and $q_i = -1$ for the electrons (in au). The reduced mass relative to the nucleus is $\mu_i = m_i M/(m_i + M)$, where the particle mass is $m_i = 1$ for the electrons (in au). Adopting the infinite nuclear mass approximation, the Hamiltonian for the S states of an atomic three-electron system can be written as[1−3]

$$H_S = -\sum_{i=1}^{3}\left(\frac{1}{2}\frac{\partial^2}{\partial r_i^2} + \frac{1}{r_i}\frac{\partial}{\partial r_i} + \frac{Z}{r_i} + \frac{\partial^2}{\partial u_i^2} + \frac{2}{u_i}\frac{\partial}{\partial u_i} - \frac{1}{u_i}\right) - \frac{1}{2}\sum_{P_{ijk}}\left(\frac{r_i^2 + u_k^2 - r_j^2}{r_i u_k}\frac{\partial^2}{\partial r_i \partial u_k} + \frac{1}{2}\frac{u_i^2 + u_k^2 - u_j^2}{2 u_i u_k}\frac{\partial^2}{\partial u_i \partial u_k}\right) \quad (2)$$

where P_{ijk} indicates that the summation is over the six permutations $\begin{pmatrix} 1 & 2 & 3 \\ i & j & k \end{pmatrix}$, and the notational simplifications $u_1 = r_{23}$, $u_2 = r_{31}$, and $u_3 = r_{12}$ are employed. The contribution of the mass polarization term, the term involving the double sum over $\nabla_i\cdot\nabla_j$ in eq 1, will be addressed in Section V.A. The form of the Hamiltonian given in eq 2 turns out to be particularly useful when a Hylleraas basis set is employed. The impact of finite nuclear mass for the calculated target property will be considered in Section V.A.

The trial Hylleraas wave function involves an expansion in terms of explicit factors of the electron−electron separation distances of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \mathscr{A} \sum_{\mu=1}^{N} C_\mu r_1^{i_\mu} r_2^{j_\mu} r_3^{k_\mu} r_{12}^{l_\mu} r_{13}^{m_\mu} r_{23}^{n_\mu} e^{-a_\mu r_1 - b_\mu r_2 - c_\mu r_3} \chi_\mu$$

(3)

where $\mathscr{A}$ is the three-electron antisymmetrizer, C_μ denotes the expansion coefficients, χ_μ is a spin eigenfunction, and N represents the number of terms in the expansion. The constants a_μ, b_μ, and c_μ are greater than 0, and the integer indices $\{i_\mu, j_\mu, k_\mu, l_\mu, m_\mu, n_\mu\}$ are each greater than or equal to 0.

The Hylleraas approach just sketched is well known and has a long history in calculations on atomic systems. It is apparently not as well known that this same atomic-like technique can be employed for very high-precision non-Born–Oppenheimer (BO) calculations on molecular systems. This approach avoids the evaluation of two-center integrals in elliptical coordinates that arise in the more traditional molecular calculations using explicit r_{ij} factors. The size of the molecular systems that can be currently attacked is limited entirely by the mathematical problem of resolving the correlated integrals with multiple r_{ij} factors that arise. For non-BO calculations involving Slater-type-orbital basis functions, progress has been considerably limited because of the severe mathematical integration problems that arise. Recent work over the past few years by Adamowicz and colleagues using correlated Gaussian functions has been particularly successful using this atomic-like approach.[21–24]

The Fermi contact operator is given by the following expression

$$H_F = \frac{2}{3} \mu_0 g_e g_I \mu_B \mu_N \mathbf{I} \cdot \sum_{i=1}^{3} \delta(\mathbf{r}_i) \mathbf{s}_i$$

(4)

where μ_0 is the vacuum permeability, g_e is the electronic g factor, which includes the electron magnetic moment anomaly, g_I is the nuclear g factor, μ_B and μ_N are the Bohr and nuclear magneton, respectively, $\mathbf{I}$ is the nuclear spin operator, $\mathbf{s}_i$ is the electron spin operator for electron i, and $\delta(\mathbf{r}_i)$ is the Dirac delta distribution. The Fermi contact Hamiltonian can be written as an effective operator in the following form

$$H_F = h A_J \mathbf{I} \cdot \mathbf{J}$$

(5)

where h denotes Planck's constant, $\mathbf{J}$ is the total angular momentum operator, and A_J is the hyperfine constant (in hertz). In the following discussion, the subscript J on A will be dropped to avoid a proliferation of subscripts. For the ^{2}S states of ^{9}Be$^+$, the energy splitting occurs between $F = 1$ (upper level) and $F = 2$ (lower level), where F is the total spin (nuclear plus electronic) of the ^{9}Be$^+$ ion. The hyperfine constant can be expressed in terms of the experimental hyperfine frequency, $\Delta\nu$, by the following result

$$A = -\frac{1}{2} \Delta\nu$$

(6)

It is common practice to report the expectation value of the Fermi contact term in the form

$$f = \langle\psi| 4\pi \sum_{i=1}^{3} \delta(r_i) \sigma_{z_i} |\psi\rangle$$

(7)

where the operator σ_{z_i} acts on the electron spin states $\alpha(i)$ and $\beta(i)$ in the following manner: $\sigma_{z_i}\alpha(i) = \alpha(i)$ and $\sigma_{z_i}\beta(i) = -\beta(i)$, ψ is characterized by the quantum numbers L, S, M_L, and M_S, and $M_L = L$ and $M_S = S$. The relationship between the nonrelativistic contribution to the hyperfine constant and f can be written as

$$A_{NR} = \frac{\mu_0 \mu_B \mu_N}{2\pi h a_0^3} \frac{g_e \mu_I}{3I} f \equiv C \frac{g_e \mu_I}{3I} f$$

(8)

where a_0 is the Bohr radius and I is the nuclear spin. The constant C isolates a group of fundamental constants that can be re-expressed in terms of fundamental constants that are known collectively with greater accuracy so that

$$C = \frac{\mu_0 \mu_B \mu_N}{2\pi h a_0^3} = \alpha^2 c R_\infty (m_e/m_p) = 95.41066037(14) \text{ MHz}$$

(9)

where α is the fine structure constant, c is the speed of light, R_∞ is the Rydberg constant, and m_e and m_p are the mass of the electron and proton, respectively. The numerical result for C reported in eq 9 is based on the most recent recommended values of the fundamental constants given in the CODATA report.[25] The associated error estimate is reported in parentheses. The nuclear moment needed to evaluate eq 8 was taken from ref 26.

III. Computational Details

From the form of the Hamiltonian given in eq 2 and the choice of Hylleraas wave function in eq 3, it can be readily demonstrated that all of the integrals required for the evaluation of matrix elements of the Hamiltonian and the hyperfine operator take the following form

$$I(i, j, k, l, m, n, \alpha, \beta, \gamma) = \iiint r_1^i r_2^j r_3^k r_{12}^l r_{13}^m r_{23}^n e^{-ar_1 - br_2 - cr_3} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\mathbf{r}_3$$

(10)

where $a > 0$, $b > 0$, and $c > 0$. The individual integer indices $\{i, j, k, l, m, n\}$ must be greater than -2 for this integral to be convergent. For an evaluation of the nonrelativistic (NR) energy (E_{NR}) expectation value

$$E_{NR} = \langle\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)| H_S |\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\rangle$$

(11)

where ψ is the normalized wave function obtained from a variational calculation based on H_S, and for the evaluation of the Fermi contact expectation value, the only integral cases that arise have indices $\{l, m, n\}$ each greater than or equal to -1. The evaluation of more complicated expectation values, for example, those arising in lower-bound calculations for the state energies or the evaluation of certain relativistic contributions leads to integral cases with members of the set $\{l, m, n\}$ taking values of -2. These cases are considerably more complicated to evaluate. An introductory account on the evaluation of correlated integrals with r_{ij} factors for two-, three-, and four-electron systems can be found in ref 27.

Extensive optimization of the nonlinear exponents in eq 3 was carried out. The optimization was done as each basis term was added to the basis set. A stochastic optimization approach

TABLE 1: Convergence Behavior of the Nonrelativistic Energies for the Low-Lying Excited n ^{2}S States of Be^{+a}

	E_{NR} (hartree)			
N	3 ^{2}S	4 ^{2}S	5 ^{2}S	6 ^{2}S
100	−13.922 465 919	−13.797 873 636	−13.740 424 783	−13.709 376 659
300	−13.922 780 497	−13.798 703 473	−13.744 609 204	−13.716 207 500
600	−13.922 788 485	−13.798 715 281	−13.744 629 490	−13.716 280 185
1000	−13.922 789 111	−13.798 716 367	−13.744 631 457	−13.716 285 677
1300		−13.798 716 497	−13.744 631 722	−13.716 286 039
1330	−13.922 789 202			
1600		−13.798 716 542	−13.744 631 784	−13.716 286 148
1888		−13.798 716 573		
1940			−13.744 631 827	
2058				−13.716 286 244

a The number of basis functions employed is denoted by N.

TABLE 2: Comparison of Different Literature Values for E_{NR} for the n ^{2}S States of Be^{+a}

state	nonrelativistic energy	size	author/year/reference
3 ^{2}S	−13.922 72	170	Pipin and Woźnicki (1982) (28)
	−13.922 764	447	King (1991) (29)
	−13.922 788 6		Wang, Zhu, and Chung (1992) (30)
	−13.922 789 267 4	8000	Stanke et al. (2008) (31)
	−13.922 789 268 554 2	∼10 000	Puchalski and Pachucki (2008) (32)
	−13.922 789 268 559^b		Puchalski and Pachucki (2008) (32)
	−13.922 789 20	1330	present work
4 ^{2}S	−13.798 662	501	King (1991) (29)
	−13.798 714 4		Wang, Zhu, and Chung (1992) (30)
	−13.798 716 609 2	8000	Stanke et al. (2008) (31)
	−13.798 716 57	1888	present work
5 ^{2}S	−13.744 577	522	King (1991) (29)
	−13.744 630 6		Wang, Zhu, and Chung (1992) (30)
	−13.744 631 82	1940	present work
6 ^{2}S	−13.716 286 24	2058	present work

a The number of basis functions employed by each author is indicated in the size column. *b* Energy eigenvalue based on extrapolation to infinite basis set.

TABLE 3: Comparison of Different Literature Values for the Fermi Contact Expectation Value for the n ^{2}S States of Be^{+a}

state	f (nonrelativistic) au	size	author/year/reference
3 ^{2}S	3.172	447	King (1991) (29)
	3.18087		Guan and Wang (1998) (33)
	3.1766719		Godefroid, Fischer, and Jönsson (2001) (13)
	3.1769		Yerokhin (2008) (17)
	3.1778	1330	present work
4 ^{2}S	1.252	501	King (1991) (29)
	1.25071		Guan and Wang (1998) (33)
	1.2488773		Godefroid, Fischer, and Jönsson (2001) (13)
	1.2494	1888	present work
5 ^{2}S	0.618	522	King (1991) (29)
	0.61419		Guan and Wang (1998) (33)
	0.6137	1940	present work
6 ^{2}S	0.3460	2058	present work

a The number of basis functions employed by each author is indicated in the size column.

was used with a generous search grid employed for the exponent parameters. Orbital exponent sets within the search grid were randomly selected. The energy for each set of exponents was determined. The optimal energy set was then selected. Further refinements were made using a Newton search. To simplify the optimization the choice, $a_\mu = b_\mu$ was used to restrict the computer cost. Each electronic state was separately optimized. This is an essential approach if high-precision results are to be obtained for the excited states.

IV. Nonrelativistic Results

In Table 1, the behavior of the nonrelativistic energy for each of the states studied is shown as a function of the size of the basis set. These results provide support for the level of convergence of the energy level calculations. A comparison of the E_{NR} values of the present calculations with a selection of results from previous theoretical work is displayed in Table 2. The result obtained for E_{NR} for 5 ^{2}S improves upon previously published work. No accurate values for the 6 ^{2}S state appear to be available for comparison with the present calculation. The value obtained in the present calculations for the 3 ^{2}S state is ∼69 nanohartrees above the most recent results of Puchalski and Pachucki,[32] and for the 4 ^{2}S state, it is ∼67 nanohartrees

above the recent calculation of Stanke et al.[31] The basis sets employed by these authors are larger than those used in the present study by factors of approximately 7.5 and 4 for the 3 ^{2}S and 4 ^{2}S states, respectively. With the very large basis sets employed by Puchalski and Pachucki, it was necessary to employ multiple precision arithmetic to do the integral evaluations. This was done to avoid near-linear dependence problems that can arise in the Hylleraas basis set expansion.

Given some of the uncertainties for the small corrections that will be discussed in the next section, we feel that the nonrelativistic component of the calculations is sufficiently accurate so as not to be the limiting factor in the overall precision of the reported values for the hyperfine constants.

The values for the expectation value of the Fermi contact operator, f, are summarized in Table 3. Some accurate results from previous calculations are also summarized in this table. For the 3 ^{2}S state, the present result is approximately 0.036% above the result of Godefroid et al.[13] and 0.097% below the result of Guan and Wang.[33] For the 4 ^{2}S state, the present result for f is about 0.042% higher than the result of Godefroid et al.[13] and 0.10% below the result of Guan and Wang.[33] The result of the present calculation for the 5 ^{2}S state agrees with the theoretical result of Guan and Wang to within approximately 0.080%.[33] No accurate results appear to be available for comparison with the 6 ^{2}S state.

V. Small Corrections to the Hyperfine Coupling

Beyond the nonrelativistic calculation, there are a number of small corrections to the hyperfine constant that arise from the

TABLE 4: Input Values Used to Determine the Bohr−Weisskopf Correction to the Hyperfine Constants of Be$^+$

factors for Bohr−Weisskopf correction	value for ^{9}Be
nuclear spin	3/2
nuclear moment (nm)	-1.177432^a
$<r^2>^{1/2}$ (fm)	2.519^b
$<r^2>_M^{1/2}$ (fm)	2.67^c
spin g value (neutron)	-2.354864
asymmetry parameter ζ	1/5
α_S	1
α_L	0
$<K_S>$	0.000145
$<K_L>$	0.0000890
ε	0.000156

^{a} Ref 26. ^{b} Ref 54. ^{c} Average of several values reported in ref 54.

finite nuclear mass, relativistic effects, quantum electrodynamic (QED) corrections, and nuclear effects. A complete many-electron theory for all of these corrections for atomic and molecular systems is currently unavailable, and it is therefore necessary to resort to approximate one-electron models or simple nuclear models to estimate some of these corrections. There are difficulties in assigning meaningful error estimates to some of the approximate models that are employed to determine the following small corrections.

A. Finite Nuclear Mass Correction to the Hyperfine Coupling Constant. The finite nuclear mass impacts the calculations in three different ways. Two schemes can be used to evaluate the nonrelativistic mass corrections to the hyperfine constant. The first approach to the calculation of mass effects is to replace ψ in eq 11 by ψ_M, that is

$$E_{NR_M} = <\psi_M(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)|H|\psi_M(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)> \quad (12)$$

where ψ_M is normalized and is obtained in a variational calculation based on the Hamiltonian given in eq 1. The mass polarization term present in H can also be expressed in terms of partial derivatives with respect to the variables r_i and u_i in a fashion related to eq 2.[34] The Fermi contact term in eq 7 is then evaluated with ψ replaced by ψ_M.

The second approach is to obtain the principal mass correction to the hyperfine constant by multiplying f in eq 8 by a factor of $(1 - (\mu/M))^3$. This leads to a mass correction to the hyperfine constant of the form

$$\delta A_{mass} = -3\frac{\mu}{M}\left\{1 - \frac{\mu}{M} + \frac{1}{3}\left(\frac{\mu}{M}\right)^2\right\}A_{NR} \quad (13)$$

For the calculation of δA_{mass}, the atomic mass for ^{9}Be was taken from ref 35, and the calculated nuclear mass is $16424.203m_e$. The difference between the mass-corrected hyperfine constant using the factor $(1 - (\mu/M))^3$ and the hyperfine constant evaluated employing the wave function ψ_M leads to the mass polarization correction to the hyperfine constant. The values reported in Table 5 were determined in this manner. Because this correction arises from the difference in values that are very close, the uncertainty in the reported mass polarization corrections to the hyperfine constants is probably quite high. The mass polarization correction impacts the least significant digit reported for the final hyperfine constants by 0 to 2 for the four states considered.

Some of the relativistic and QED contributions to the hyperfine constant have a mass dependence.[36−38] These are at least an order of magnitude smaller than the least significant digits retained in the present calculations and are accordingly ignored in the present work.

B. Lowest-Order Relativistic Correction to the Hyperfine Constant. Pachucki[39] has given a general theoretical treatment of the relativistic corrections to the hyperfine splitting for a three-electron atomic system through order α^6, where α is the fine structure constant. The resulting formulas have a singular-like structure. No calculations based on these formulas have been published.

In place of the Pachucki analysis, a simplified one-electron model is commonly employed to treat the valence electron.[40−42] Employing the following parameters

$$\kappa = (-1)^{j+l+1/2}(j + 1/2), \; \gamma = \sqrt{\kappa^2 - \alpha^2 Z^2} \quad (14)$$

$$d = \sqrt{n^2 + 2(|\kappa| - n)(|\kappa| - \gamma)} \quad (15)$$

where j, l, and n are the total angular momentum, orbital angular momentum, and principal quantum numbers, respectively, the relativistic correction to the hyperfine constant is given by the following result

$$\delta A_{rel} = \left\{\frac{n^3(l + 1/2)(2j + 1)|2\kappa(n - |\kappa| + \gamma) - d|}{d^4\gamma(4\gamma^2 - 1)} - 1\right\}A_{NR} \quad (16)$$

It is common practice to present the preceding result in a series expansion form for an n s electron ($l = 0$, $j = 1/2$, $\kappa = -1$) in terms of αZ as

$$\delta A_{rel} = \left[\frac{11n^2 + 9n - 11}{6n^2}\right](\alpha Z)^2 + \left(\frac{189 - 330n - 134n^2 + 225n^3 + 203n^4}{72n^4}\right)(\alpha Z)^4 + O(\alpha^6 Z^6)A_{NR} \quad (17)$$

Some authors[8,12] evaluate the relativistic correction by replacing Z in the preceding formula with an effective nuclear charge Z_{eff}, where $Z_{eff} = Z - \sigma$, and σ denotes a suitable screening factor. Other authors, for example ref 10, do not include a screening constant. It is not immediately clear how the optimal screening factor should be accounted for in the present calculations. In the vicinity of the nucleus, the extent of screening is expected to be small. The effects of screening were determined by considering the calculated relativistic correction to the hyperfine constant using $\sigma = 0$, that is, no screening, and were then re-evaluated for each state using screening constants determined from Slater's rules. The changes from unscreened to screened values have the biggest impact for the 3 ^{2}S state, with deceasing impact in terms of actual contribution to the hyperfine corrections of the 4 ^{2}S, 5 ^{2}S, and 6 ^{2}S states. Specifically, the change in the 3 ^{2}S state is from -0.288 MHz for the unscreened value to -0.072 MHz for the screened value. For the 6 ^{2}S state, the change is from -0.030 (unscreened) to -0.0075 MHz (screened). The values reported in Table 5 are the screened values. The uncertainty introduced by a lack of precise knowledge of the appropriate screening is expected to be ~1 in the last reported digit for the hyperfine constants of the 5 ^{2}S and 6 ^{2}S states, ~1−4 in the final reported digit for

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the hyperfine constant of the 4 ^{2}S state, and ~1−10 in the last pair of digits for the 3 ^{2}S state. The correct answer on the issue of the extent of screening will depend on further theoretical developments on the many-electron relativistic corrections to the hyperfine constants along the lines of the contribution of Pachucki.[39]

The effect of the polarization of the paired electrons by the valence s electron via a Breit interaction has been investigated by Sushkov.[43] The total Breit correction to the hyperfine constant due to this polarization mechanism is

$$\delta A_{pol} = 0.681 Z\alpha^2 A_{NR} \qquad (18)$$

A Coulomb correction to the hyperfine constant was also derived by Sushkov and is given by

$$\delta A_C = -0.558 Z\alpha^2 A_{NR} \qquad (19)$$

This correction arises from the v/c (particle velocity to speed of light ratio) expansion of the electron−electron Coulomb interaction involving Dirac spinors and retains only terms of order $(v/c)^2$. Combining eqs 18 and 19 gives the total Sushkov correction to the hyperfine constant

$$\delta A_S = 0.123 Z\alpha^2 A_{NR} \qquad (20)$$

The values obtained for this correction are rather small and impact only the fifth or sixth significant digit for the calculated hyperfine constants of the excited S states of Be$^+$.

C. Quantum Electrodynamic Corrections to the Hyperfine Constant. The lowest-order QED correction is commonly split into two parts. One contribution is the Schwinger[44] correction to the electronic g factor, which takes the form $\alpha/(2\pi)$. This correction, along with some additional small corrections, is incorporated into the value of g_e. The remaining QED contributions to the hyperfine constant are based on a one-electron model and are given by[45,46]

$$\delta A_{QED} = \left(c_1\alpha(Z\alpha) + \frac{\alpha(Z\alpha)^2}{\pi}[c_{22}\{\ln(Z\alpha)^{-2}\}^2 + \right.$$
$$\left. c_{21}(n)\ln(Z\alpha)^{-2} + c_{20}(n)]\right) A_{NR} \quad (21)$$

where the state-independent constants take the following form

$$c_1 = \ln 2 - \frac{5}{2}, \quad c_{22} = -\frac{2}{3} \qquad (22)$$

and the state-dependent term, $c_{21}(n)$, for n S states is given by[38]

$$c_{21}(n) = -\frac{8}{3}\ln(2n) + \frac{1001}{360} - \frac{8}{3n} + \frac{2}{3n^2} + \frac{8}{3}\sum_{k=1}^{n-1}\frac{1}{k} \qquad (23)$$

In the case of $n = 1$, the sum in eq 23 is assigned to the value zero. The state-dependent terms $c_{20}(n)$ have been tabulated as numerical values by Jentschura and Yerokhin.[38] The results employed for $c_{20}(n)$ for the present calculations are: 10.417048,

9.719388, 9.312703, and 9.045565 for $n = 3, 4, 5$, and 6, respectively.

D. Bohr−Weisskopf Correction to the Hyperfine Constant. The impact of the finite size of the nucleus on the hyperfine coupling constant is taken into account by including in the expression for the hyperfine coupling constant a multiplicative factor, C_{NS}, that takes the following form[47]

$$C_{NS} = (1 - \delta)(1 - \varepsilon) \qquad (24)$$

In eq 24, δ is a direct correction for the finite nuclear size, and it is often referred to as the Breit−Rosenthal correction.[48] This term is discussed in Section V.E. The term ε accounts for a correction to the hyperfine constant due to the distribution of magnetization density over the extent of the nucleus. This contribution is referred to as the Bohr−Weisskopf correction,[49−51] and this subsection details how it is evaluated in the present study.

The most commonly employed procedure for evaluating the contribution to the hyperfine constant arising from the finite size of the nucleus is to use a result of Zemach.[52] In Zemach's model, a one-electron approximation is employed, and the hyperfine correction is evaluated as $-2a_0^{-1}<r>_{em}$, where $<r>_{em}$ is the first statistical moment of the convolution of the nuclear electric and magnetic distributions. In the present study, a different approach has been employed to account for the corrections to the hyperfine constant resulting from the finite nuclear size. The following theory can be adapted to deal with the case in which the odd nucleon is either a proton or a neutron and can also be employed to deal with both an odd proton and neutron. The general case is discussed, and the appropriate parameters for $^9_4$Be are tabulated.

In the single-particle model, the correction ε can be determined using[53]

$$\varepsilon = \alpha_S <K_S> + \alpha_L <K_L> + \alpha_S\zeta(<K_S> - <K_L>) \quad (25)$$

In eq 25, α_S and α_L are the fractional spin and orbital contributions to the magnetic moment, respectively, and are given by

$$\alpha_S = \frac{g_S(g_I - g_L)}{g_I(g_S - g_L)}, \quad \alpha_L = 1 - \alpha_S \qquad (26)$$

where g_S and g_L are g factors for the spin and orbital momentum of individual nucleons, respectively. Normally, the assignment $g_L = 1$ for a proton and $g_L = 0$ for a neutron is made. The spin distribution asymmetry of the nucleus is described by the parameter ζ, defined by[50]

$$\zeta = \begin{cases} \dfrac{2I - 1}{4(I + 1)}, & \text{for } I = l + 1/2 \\ \dfrac{2I + 3}{4I}, & \text{for } I = l - 1/2 \end{cases} \qquad (27)$$

The expectation values $<K_S>$ and $<K_L>$ are determined from[53]

$$<K_S> = \int_0^\infty K_S(R)|u(R)|^2R^2\, dR \qquad (28)$$

and

$$\langle K_L \rangle = \int_0^\infty K_L(R)|u(R)|^2 R^2 \, dR \tag{29}$$

where the radial part of the probability density of the odd nucleon is assumed to be homogeneously distributed over the nuclear volume and is given by

$$|u(R)|^2 = \frac{3}{R_0^3} H(R_0 - R) \tag{30}$$

where $H(R)$ is a Heaviside step function. Approximate expressions for $K_S(R)$ and $K_L(R)$ for S states in the nonrelativistic limit have been developed by Shabaev[53]

$$K_S(R) = \frac{\alpha Z R_0}{\lambda_C}\left(\left(\frac{R}{R_0}\right)^2 - \frac{1}{10}\left(\frac{R}{R_0}\right)^4\right) \tag{31}$$

and

$$K_L(R) = \frac{3\alpha Z R_0}{5\lambda_C}\left(\left(\frac{R}{R_0}\right)^2 - \frac{1}{14}\left(\frac{R}{R_0}\right)^4\right) \tag{32}$$

where $R_0 = (5/3)^{1/2}\langle r^2 \rangle_M^{1/2}$, $\langle r^2 \rangle_M$ is the root-mean-square radius of the nuclear magnetization density distribution, and λ_C is the Compton wavelength: $\lambda_C = \hbar/(m_e c)$. One approximation is to assume that the root-mean-square radius of the nuclear magnetization density distribution is the same as the root-mean-square radius of the nuclear charge distribution, $\langle r^2 \rangle^{1/2}$. For the calculation of R_0 in this work, the average of several values of $\langle r^2 \rangle_M^{1/2}$ reported in ref 54 has been employed. The value for g_S was evaluated from the following formula

$$g_I = g_L \pm \frac{(g_S - g_L)}{(2l + 1)} \quad \text{for } I = l \pm \tfrac{1}{2} \tag{33}$$

In the case of $^9_4$Be, $g_L = 0$ and $l = 1$ so that $g_S = 2\mu_I$. The values of the parameters that determine ε and the calculated value of this quantity are summarized in Table 4. The result

reported for ε in Table 4 is in close agreement with the results of Yamanaka[12] and Yerokhin,[17] who obtain values of ε, adjusted for the opposite sign convention employed here, of 0.000160(12) and 0.000158(15), respectively. The Bohr−Weisskopf correction to the hyperfine constant is determined using $\delta A_{BW} = -\varepsilon A_{NR}$.

E. Breit−Rosenthal Correction to the Hyperfine Constant. The Breit−Rosenthal correction for the effect of finite nuclear size, δ, has been derived by Shabaev[53] for small Z values for S states as

$$\delta = \frac{3}{2}\alpha Z \frac{R_0}{\lambda_C} \tag{34}$$

This result assumes that a homogeneously charged sphere is adopted to model the nuclear charge distribution, and R_0 is given in terms of the root-mean-square nuclear charge radius as $R_0 = (5/3)^{1/2}\langle r^2 \rangle^{1/2}$. The value of $\langle r^2 \rangle^{1/2}$ employed in the present calculations is indicated in Table 4.

The Breit−Rosenthal correction to the hyperfine constant is given by the following result

$$\delta A_{BR} = \delta A_{NR} \tag{35}$$

and δ is obtained from eq 34. This correction impacts the fourth or fifth significant digit for the calculated hyperfine constants for the excited ^{2}S states of Be$^+$.

VI. Total Hyperfine Constant

The total hyperfine constant is the sum of the nonrelativistic component, A_{NR}, and the seven corrections indicated in the preceding subsections. Thus

$$A_{total} = A_{NR} + \delta A_{mass} + \delta A_{mass-pol} + \delta A_{rel} + \delta A_S + \\ \delta A_{QED} + \delta A_{BW} + \delta A_{BR} \tag{36}$$

The results for A_{total} and the component contributions are tabulated in Table 5 for the four excited ^{2}S states investigated.

VII. Discussion

For the 3 ^{2}S, 4 ^{2}S, and 5 ^{2}S states, there are other theoretical values for the hyperfine constant available for comparison. For the 3 ^{2}S state, the results of the present calculation of the hyperfine constant are in fairly close agreement with previous results: the deviation is about 0.07 to 0.08% from the most recent results of Yerokhin[17] and approximately 0.1% from the result of Blundell et al.[55] For the 4 ^{2}S state, the present calculation is in close agreement with the nonrelativistic calculations of Guan and Wang[33] and Godefroid et al.[13] For the 5 ^{2}S state, the result of the present study agrees very closely with the nonrelativistic result of Guan and Wang.[33] For the 6 ^{2}S state, there are apparently no other accurate computational results available for comparison.

Unfortunately, there are no experimental results available with which to compare the results of the present calculations. Given the potential to study the excited states of this species by high-resolution spectroscopy in an ion-trap configuration, perhaps the present theoretical work will inspire experimental interest in the hyperfine structure of the excited states of ^{9}Be$^+$.

One observation of note from the results presented in Table 5 is the partial cancellation that occurs when the small corrections to the hyperfine constant are summed. This clearly

TABLE 5: Theoretical Results for the Nonrelativistic and Small Corrections to the Hyperfine Constants of the Excited n ^{2}S States of Be$^+$

	A (MHz) ^{9}Be$^+$			
contribution	3 ^{2}S	4 ^{2}S	5 ^{2}S	6 ^{2}S
nonrelativistic	−158.844	−62.453	−30.677	−17.296
finite mass	0.0290	0.0114	0.0056	0.0032
mass polarization	−0.0285	−0.0114	−0.0056	−0.0032
relativistic	−0.0721	−0.0279	−0.0135	−0.0075
Sushkov	−0.0042	−0.0016	−0.0008	−0.0005
QED	0.0657	0.0256	0.0125	0.0070
Bohr−Weisskopf	0.0248	0.0098	0.0048	0.0027
Breit−Rosenthal	0.0586	0.0230	0.0113	0.0064
total	−158.78	−62.43	−30.66	−17.29
other theory	−158.6^a	−62.58^a	−30.9^a	
	−158.999^b	−62.518^b	−30.701^b	
	−158.79^c	−62.427^c		
	−158.98(2)^d			
	−158.897(7)^e			
	−158.905(7)^e			

^{a} Nonrelativistic results, ref 29. ^{b} Nonrelativistic results, ref 33. ^{c} Nonrelativistic results, ref 13. ^{d} Ref 55. ^{e} Ref 17.

indicates the need to include all of the major corrections rather than retaining just one of the key contributions. This partial cancellation provides a rationalization of why the nonrelativistic level of theory produces a fairly satisfactory result in reasonable agreement with the more refined theoretical approach adopted in the present work. A similar cancellation was noted in a related study for the corresponding states for different isotopes of the lithium atom.[16]

A direct consequence of the neglect of the many-electron nature of some of the small corrections to the hyperfine constant is the impossibility of making a meaningful estimate of the errors for some of these corrections. In some cases, this directly results from the simplified one-particle models employed. There is also a limitation in the accuracy with which certain nuclear structure information is known. As previously indicated, there is a partial cancellation of some of the small contributions to the hyperfine constants; however, the accumulated uncertainty from the small corrections is obviously additive. A somewhat approximate estimate of the errors, partially based on the uncertainty of the calculated nonrelativistic contribution and the possible uncertainty associated with screening issues discussed previously, indicates that there is expected uncertainty of about $10-14$ in the last two tabulated significant digits for A_{total} for the 3 ^2S state. For the 4 ^2S, 5 ^2S, and 6 ^2S states, the expected uncertainty is approximately $2-5$ in the last quoted digit for the total hyperfine constants for these three states.

A principal limitation to improving the present calculations is the nonmonotonic convergence behavior observed for the determination of the f values. This plays a role for each of the excited S states that was studied. Additional sources of error reside in the determination of the small corrections. In fact, the accuracy is limited because the many-electron nature of most of these corrections is not incorporated in the calculations. There is some variation in the reported values for the magnetic dipole moment, μ_I. Of the most accurate reported values for this quantity,[26,56] there is a spread of $\sim$50 ppm.

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