Calculations on the ^2S ground state of Be II

Frederick W. King
Department of Chemistry, University of Wisconsin–Eau Claire, Eau Claire, Wisconsin 54702
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Extensive variational calculations on the ^2S ground state of Be^+ are reported. Using a 401-term expansion of Hylleraas-type functions, the nonrelativistic ground-state energy is determined to be $-14.324\,760$ a.u., which is the lowest upper bound to the ground-state energy reported to date for this system. The Fermi contact interaction is determined to be 12.4980 a.u., which is in very close agreement with the experimental value of 12.503 88 a.u. The nuclear-magnetic shielding factor and the molar diamagnetic susceptibility are evaluated to be $\sigma=1.415\,401\times10^{-4}$ a.u. and $\chi=-5.154\,43\times10^{-6}$ cm^3 mol^{-1}, respectively. The electron density at the nucleus, the moments $\langle r_i^n\rangle$, $n=-1$, 1, 2, and 3, and $\langle r_{ij}^n\rangle$, $n=-1$, 1, and 2, are also reported. The specific mass shift (mass polarization contribution) is determined to be 2.758×10^{-5} a.u. The rate of convergence of the calculation is discussed. The role of one versus two spin eigenfunctions in the basis set is discussed with respect to its bearing on the calculation of the Fermi contact interaction.

I. INTRODUCTION

A major development in atomic physics over the last several years has been the emergence of ion-trapping techniques for making spectroscopic measurements of extremely high accuracy.[1–7] The Be^+ ion has been featured prominently in a number of these studies.[8–13] This ion has served as a prototype for the development of an improved atomic clock. A particular hyperfine transition of the ^2S ground state of Be^+ has recently been measured[12] with an uncertainty of approximately one part in 10^{13}. The high accuracy of this measurement has led Wineland to remark,[5] "In all of physics, only a few measurements can boast a higher accuracy; those experiments measure similar transitions in neutral cesium atoms."

In this study, detailed variational calculations on the ^2S ground state of the Be^+ ion are reported. The purpose of these calculations is to address several issues. A principal goal is the construction of a wave function of *near*-spectroscopic accuracy. Spectroscopic accuracy is taken by various workers to imply an error for the nonrelativistic energy of approximately 1 μhartree or less. For systems with more than two electrons, extremely few calculations approach the 1-μhartree level of inaccuracy.[14] At this limit, a meaningful comparison with experiment must include consideration of relativistic effects. A second objective is to provide information on the rates of convergence of the energy and a selected set of expectation values, as a function of the size of the basis set. One property of particular interest in this paper is the hyperfine coupling constant. A recent calculation of the hyperfine coupling constant for the ^2S ground state of Li I has been reported using as extended basis set of Hylleraas-type functions. An observation of that study was that the hyperfine coupling constant converged less satisfactorily, compared with several spin-independent properties.[15] Based on that finding, an attempt was made in the present study to assess to what extent the convergence of the hyperfine coupling constant might be improved, by using a better balance between the two spin eigenfunctions employed in the calculation.

The present investigation has two other goals. The high accuracy of the reported calculations should make them a useful benchmark for more approximate computational schemes. A longer-range goal is to obtain an indirect semiempirical evaluation of the Lamb shift using experimental ionization potentials. This can be achieved by equating the total ground-state energy to the sum of several energy terms, which in principle can be separately evaluated.[16–18] This goal awaits accurate calculations of the relativistic corrections, a project that has been initiated in the author's group.

II. THEORY

The theory underlying the present variational calculations has been reviewed in a number of sources of which the article by Hylleraas is particularly readable.[19] A brief sketch is as follows. The trial wave function employed is

$$\psi=\mathcal{A}\sum_{\mu=1}^{N}C_\mu\phi_\mu\chi_\mu\,, \tag{1}$$

where $\mathcal{A}$ is the antisymmetrizer and C_μ the variationally determined expansion coefficients. The basis functions are of the form

$$\phi_\mu(r_1,r_2,r_3,r_{23},r_{31},r_{12})=r_1^{i_\mu}r_2^{j_\mu}r_3^{k_\mu}r_{23}^{l_\mu}r_{31}^{m_\mu}r_{12}^{n_\mu}\exp(-\alpha_\mu r_1-\beta_\mu r_2-\gamma_\mu r_3)\,, \tag{2}$$

where the exponents i_μ, j_μ, k_μ, l_μ, m_μ, and n_μ are each ≥0. In Eq. (1) χ_μ denotes the doublet spin eigenfunctions, which take the form

$$\chi_\mu=\alpha(1)\beta(2)\alpha(3)-\beta(1)\alpha(2)\alpha(3) \tag{3a}$$

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or

$$\chi_\mu = 2\alpha(1)\alpha(2)\beta(3) - \beta(1)\alpha(2)\alpha(3) - \alpha(1)\beta(2)\alpha(3) \ . \tag{3b}$$

The nonrelativistic Hamiltonian employed is

$$H = \sum_{i=1}^{3} \left[-\tfrac{1}{2}\nabla_i^2 - \frac{4}{r_i} \right] + \sum_{i=1}^{3} \sum_{j>i}^{3} \frac{1}{r_{ij}} \ . \tag{4}$$

The mass polarization contribution is not included in H; it is evaluated using first-order perturbation theory. Atomic units are employed throughout unless a statement to the contrary is made (the molar diamagnetic susceptibility and hyperfine frequency being two exceptions to the use of a.u.).

Evaluation of the matrix elements $\langle \phi_\mu | H | \phi_\nu \rangle$ is the most intensive part of the computer calculations. All matrix elements considered in this work can be reduced to the evaluation of integrals of the form[20-22]

$$I(i,j,k,l,m,n,a,b,c) = \int r_1^i r_2^j r_3^k r_{23}^l r_{31}^m r_{12}^n e^{-ar_1 - br_2 - cr_3} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \ . \tag{5}$$

The procedures involved in evaluating these integrals that have been employed in the present work can be found in several places in the literature.[21,23,24] A more recent investigation has considered the evaluation of a generalized version of the I integrals appearing in Eq. (5), which allows for the inclusion of the additional factor $e^{-\alpha_{12}r_{12} - \alpha_{31}r_{31} - \alpha_{23}r_{23}}$ in the integrand, where α_{12} α_{31}, and α_{23} are suitably chosen constants.[25] Both the nature of the analytic results obtained by Fromm and Hill[25] and the added flexibility (the constants α_{12}, α_{31}, and α_{23} could also be optimized) should allow for more efficient calculations on three-electron atomic systems to be made.

III. COMPUTATIONAL DETAILS

A. Choice of basis functions

The selection of the initial set of basis functions was made in the most unbiased manner possible. Define

$$\omega = i + j + k + l + m + n \ , \tag{6}$$

where the set (i,j,k,l,m,n) is the exponents appearing in Eq. (2). All possible choices leading to values of $\omega = 0$, 1, 2, 3, and 4 were included in the calculation. This leads to a total of 210 basis functions. Basis functions that include the second spin eigenfunction [Eq. (3b)] are included unless excluded by symmetry. Beyond $\omega = 4$, the maximum possible number of terms increases rapidly. A table of the number of basis functions as a function of ω, including the breakdown into numbers for the two spin eigenfunctions, can be found in Ref. 15.

The terms beyond 210 are show in Table I. An asterisk on an entry signifies that the spatial component is repeated with the second spin eigenfunction included. When both spin eigenfunctions occur for a particular spatial component, they are computed together as a pair, which results in a considerable reduction of computational effort. The first 115 entries in Table I represent the initial group of entries for $\omega = 5$. After term 325, entries were selected on the basis of the expected contribution to the energy expectation value. This is to some extent a matter of guess work, though past experience with the method proved to be of considerable value.

The order of the first 210 terms can be decided by examination of the early entries of Table I. All terms of a given ω are grouped together and added in order of increasing ω. For a given value of ω, the right most index of the set (n) is selected with the largest value. This is then decreased, while the next index (m) is increased. The pattern that emerges should be clear on inspection of Table I.

The orbital exponents were kept fixed during the course of the calculation, that is, $\alpha_\mu = \beta_\mu = \alpha$ and $\gamma_\mu = \gamma$. The values of α and γ were selected as follows. The 30-term Hylleraas wave function of Perkins[26] was optimized on a grid accurate to 0.01. The best energy obtained was just a few μhartree away from the energy calculated using the values $\alpha = 3.80$ and $\gamma = 1.15$ given by Perkins. Since the final choice of exponents will obviously depend on the size and selection of terms used in the test basis set, it was decided to stick with the values just cited. This choice has the advantage that it allows a segment of the present work to be tested against the 60-term calculation of Ho,[27] who also used these values.

B. Accuracy controls

Possibilities for significant figure loss occur at several stages of the calculation. The principal points for concern are (i) the integral evaluations, (ii) the matrix element calculations, (iii) the diagonalization scheme, and (iv) the evaluation of the expectation values. Each of these items is addressed below.

The I integrals defined in Eq. (5) can be reduced to integrals of the form

$$W(i,j,k,a,b,c) = \int_0^\infty x^i e^{-ax} dx \int_x^\infty y^j e^{-by} dy \int_y^\infty z^k e^{-cz} dz \ . \tag{7}$$

For special cases, both the W integrals and the I integrals are evaluated by truncation of an infinite series. All other W integrals and I integrals are evaluated to essentially machine tolerance. For wave functions of the size reported in this study, it is not possible to determine the effect of small errors in the W integrals and I integrals (arising from inappropriate cutoff conditions in the evaluation of the infinite series), on the final expectation values. In connection with our previous work on Li I, such studies have been carried out for some small-term wave functions.[15] The cutoff parameters for evaluation of the infinite series were set at 10^{-18}. It is expected at this limit that the accuracy of the integral evaluations has no impact on the number of significant figures reported for

each expectation value. The W integrals and I integrals are expected to have approximately 18 significant figures for those evaluated by series expansion, and approximately 28 significant figures for all other integrals.

The individual matrix elements are constructed from terms that typically have differing signs, which leads to the possibilities of significant figure loss on combining the positive and negative contributions to each matrix ele-

TABLE I. Terms 211 to 401 employed in the basis set. An asterisk indicates that the same *ijklmn* function was employed with both spin functions.

Number of terms	i	j	k	l	m	n	Number of terms	i	j	k	l	m	n
211	0	0	0	0	0	5	303*	0	2	1	0	0	2
212*	0	0	0	0	1	4	305	1	1	1	0	0	2
214*	0	0	0	0	2	3	306*	0	3	1	0	1	0
216*	0	0	0	0	3	2	308*	1	2	1	0	1	0
218*	0	0	0	0	4	1	310*	0	2	1	0	2	0
220*	0	0	0	0	5	0	312*	1	1	1	0	2	0
222	0	0	0	1	1	3	314*	0	1	1	0	3	0
223*	0	0	0	1	2	2	316*	0	3	1	1	0	0
225*	0	0	0	1	3	1	318*	1	2	1	1	0	0
227*	0	0	0	1	4	0	320*	0	2	1	2	0	0
229	0	0	0	2	2	1	322*	0	1	1	3	0	0
230*	0	0	0	2	3	0	324*	0	1	1	0	0	3
232	0	0	1	0	0	4	326*	1	4	1	0	0	0
233*	0	0	1	0	1	3	328*	0	5	1	0	0	0
235*	0	0	1	0	2	2	330*	0	4	1	0	0	1
237*	0	0	1	0	3	1	332*	2	3	1	0	0	0
239*	0	0	1	0	4	0	334*	1	3	1	0	0	1
241	0	0	1	1	1	2	336*	0	3	1	0	0	2
242*	0	0	1	1	2	1	338*	0	1	5	0	0	0
244*	0	0	1	1	3	0	340	0	0	1	0	0	5
246	0	0	1	2	2	0	341	2	2	1	0	0	1
247	0	0	2	0	0	3	342*	0	2	1	0	0	3
248*	0	0	2	0	1	2	344*	0	1	1	0	0	4
250*	0	0	2	0	2	1	346*	0	0	1	0	5	0
252*	0	0	2	0	3	0	348*	1	2	1	0	0	2
254	0	0	2	1	1	1	350*	0	1	1	4	0	0
255*	0	0	2	1	2	0	352	0	0	6	0	0	0
257	0	0	3	0	0	2	353*	0	2	1	3	0	0
258*	0	0	3	0	1	1	355	0	0	1	0	0	6
260*	0	0	3	0	2	0	356*	0	0	1	0	6	0
262	0	0	3	1	1	0	358*	0	1	1	0	0	5
263	0	0	4	0	0	1	360*	0	2	1	0	0	4
264*	0	0	4	0	1	0	362*	0	6	1	0	0	0
266	0	0	5	0	0	0	364*	0	5	1	0	0	1
267*	0	1	0	0	0	4	366*	0	4	1	0	0	2
269*	0	1	0	0	1	3	368*	0	6	1	0	0	1
271*	0	1	0	0	2	2	370	0	0	1	0	0	7
273*	0	1	0	0	3	1	371*	0	2	1	0	0	5
275*	0	1	0	0	4	0	373*	0	1	1	0	0	6
277*	0	1	0	1	0	3	375*	0	3	1	0	0	5
279*	0	1	0	1	1	2	377	0	0	1	0	0	8
281*	0	1	0	1	2	1	378*	0	1	1	0	0	7
283*	0	4	1	0	0	0	380*	1	2	1	0	0	3
285*	1	3	1	0	0	0	382*	1	2	1	0	0	4
287	2	2	1	0	0	0	384*	1	5	1	0	0	0
288*	0	1	4	0	0	0	386*	0	5	1	0	0	2
290*	0	2	3	0	0	0	388*	0	7	1	0	0	0
292*	0	3	2	0	0	0	390*	1	6	1	0	0	0
294*	0	5	0	0	0	0	392*	1	3	1	0	0	2
296	1	1	3	0	0	0	394*	0	0	1	0	7	0
297*	1	2	2	0	0	0	396*	0	2	1	0	2	2
299*	0	3	1	0	0	1	398*	0	1	1	0	5	0
301*	1	2	1	0	0	1	400*	0	1	1	0	6	0

ment. As part of a major rewrite on the software involved in this work, approximately 20 000 matrix elements for each of several expectation values were recalculated and checked against prior calculations. Both calculations were done on a machine with 18 decimal digits of precision. One matrix element was found to differ from its previously calculated value by 1 in the 12th significant figure. This difference was traced to a loss of six significant figures in forming the matrix element from its component contributions. Typically, the loss in significant figures amounted to two to three in forming the individual matrix elements in the test run.

In the present investigation, the specific mass shift (mass polarization) matrix elements were computed along the lines described in Ref. 22. Part of each specific mass shift matrix element is computed at the same stage as the kinetic energy; the second part is computed independently. Since the two parts of a particular matrix element in many cases have opposite signs, a check for loss of significant figures was explicitly made in the evaluation of each specific mass shift matrix element. Of the 80 601 matrix elements, one case was found where seven significant figures were lost, and three examples where six significant figures were lost. The impact of this loss in precision for a few matrix elements, on the final expectation value, depends, of course, on the size of the appropriate variationally determined coefficients that multiply these matrix elements.

The accuracy of the matrix elements is dependent on what I integrals are required in the evaluation. For matrix elements not dependent on I integrals evaluated by truncation of an infinite series, approximately 24 or better significant figures are obtained. This estimate allows for a generous though realistic estimate of the significant figure loss that occurs in combining the positive and negative contributions of a matrix element. For those matrix elements dependent on the I integrals with series cutoff, approximately 15–16 significant figures are expected, though exceptions could certainly arise. For the specific mass shift matrix elements, approximately 99.991% of them are expected to be accurate to approximately 13 significant figures, with just a couple being restricted to 12 significant figures.

Since it is not practically possible to carry out a propagation of errors analysis from individual matrix elements to the final expectation values, a more realistic assessment of the reliability of the number of significant figures in the reported expectation values can be found by deliberate truncation of the number of significant figures for *all* matrix elements. Separate diagonalizations and expectation value evaluations were carried out using 18, 16, 14, and 13 significant figures for each matrix element. None of the final expectation values derived from the final 401-term wave function are changed in the first seven significant figures, on dropping from matrix elements with 18 significant figures to matrix elements with 13 significant figures. The biggest changes observed were approximately an increase of 2 in the eighth significant figure for the Fermi contact term and 7 in the ninth significant figure for the electronic density evaluated at the nucleus. With appropriate round up to the next digit, a change of 1 in the last reported significant figure for both of these expectation values is obtained. For this same reduction in significant figures for the matrix elements, the energy expectation value is found to change by 1 in the 12th significant figure.

The matrix diagonalization routine employed is based on Nesbet's procedure.[28] This routine has been extensively tested in the past and found to be reliable in comparison with known results. The cutoff tolerance was tested sufficiently that we expect the digits reported for the final expectation values are all significant.

Each final expectation value was evaluated by combining the sum of all positive and the sum of all the negative contributions. This gives an indication of the possible loss of significant figures in the final expectation values. Typically, 3–4 significant figures are lost when the two contributions of opposite sign are combined. Tests for linear independence in the basis set have not been made for the present wave function calculation. In previous calculations deliberate introduction of linear dependence has been studied. The resulting numerical problems led to program abort. The same behavior would be expected in the present calculation.

The calculations of the matrix elements were carried out on a Cray 1S at Cray Research, Inc. using double precision (approximately 29 decimal digits of precision). Calculation of the matrix elements in double precision certainly minimizes significant figure loss, but adds greatly to the computational overhead. The two parts of the specific mass shift matrix elements were put together on the Honeywell DPS8/49 at the University of Wisconsin–Eau Claire (UWEC). The matrix diagonalizations and expectation values were also evaluated at UWEC. This work was all in double precision (18 decimal digits of precision).

IV. RESULTS

The principal results of the calculations are assembled in Tables II and III. The shorthand notation for expectation values is employed:

$$\langle \mathcal{O}_i \rangle \equiv \left\langle \psi \left| \sum_{i=1}^{3} \mathcal{O}_i \right| \psi \right\rangle , \tag{8a}$$

$$\langle \mathcal{O}_{ij} \rangle \equiv \left\langle \psi \left| \sum_{i=1}^{3} \sum_{j>i}^{3} \mathcal{O}_{ij} \right| \psi \right\rangle , \tag{8b}$$

and ψ is normalized. Besides the energy components, and moments of r_i^n and r_{ij}^n, Table II also gives the electron density at the nucleus:

$$\rho(0) = \langle \delta(\mathbf{r}_i) \rangle , \tag{9}$$

the Fermi contact interaction

$$f = 4\pi \langle \delta(\mathbf{r}_i)\sigma_{zi} \rangle , \tag{10}$$

and the expectation value required in the evaluation of the specific mass shift, $\langle \nabla_i \cdot \nabla_j \rangle$.

TABLE II. Expectation values for the ^2S ground state of Be II $\langle \mathcal{O}_i \rangle = \langle \sum_{i=1}^{3} \mathcal{O}_i \rangle$ and $\langle \mathcal{O}_{ij} \rangle = \langle \sum_{i=1}^{3} \sum_{j>i}^{3} \mathcal{O}_{ij} \rangle$. The numbers in square brackets denote powers of ten.

Expectation value	Number of terms 100	160	220	280	340	401
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	1.432 461[1]	1.432 465[1]	1.432 472[1]	1.432 473[1]	1.432 475[1]	1.432 476[1]
$\left\langle -\frac{4}{r_i} \right\rangle$	−3.189 540[1]	−3.189 548[1]	−3.189 554[1]	−3.189 555[1]	−3.189 555[1]	−3.189 555[1]
$\left\langle \frac{1}{r_{ij}} \right\rangle$	3.246 182	3.246 178	3.246 094	3.246 088	3.246 053	3.246 032
$\langle r_i \rangle$	3.102 028	3.101 768	3.101 401	3.101 394	3.101 407	3.101 401
$\langle r_i^2 \rangle$	6.512 158	6.510 665	6.507 878	6.507 892	6.508 023	6.507 998
$\langle r_i^3 \rangle$	1.871 059[1]	1.870 449[1]	1.868 592[1]	1.868 636[1]	1.868 733[1]	1.868 715[1]
$\langle r_{ij} \rangle$	5.268 290	5.267 768	5.267 065	5.267 052	5.267 075	5.267 062
$\langle r_{ij}^2 \rangle$	1.308 225[1]	1.307 931[1]	1.307 386[1]	1.307 390[1]	1.307 415[1]	1.307 410[1]
$\langle \delta(\mathbf{r}_i) \rangle$	3.506 333[1]	3.508 223[1]	3.508 991[1]	3.509 186[1]	3.510 117[1]	3.510 357[1]
$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	1.253 346[1]	1.245 895[1]	1.250 985[1]	1.249 595[1]	1.250 215[1]	1.249 795[1]
$\langle \nabla_i \cdot \nabla_j \rangle$	−4.542 612[−1]	−4.539 694[−1]	−4.532 346[−1]	−4.531 845[−1]	−4.530 534[−1]	−4.529 361[−1]

TABLE III. Ground-state energy for ^2S Be II and scale factor for wave functions of different size.

Number of terms	Energy	Scale factor η
20	−14.315 676	0.999 804 2
60	−14.323 719	0.999 918 0
100	−14.324 607	1.000 041 6
160	−14.324 653	1.000 029 3
220	−14.324 723	1.000 009 4
280	−14.324 729	1.000 008 1
340	−14.324 747	1.000 004 3
401	−14.324 760	1.000 000 9

Table III lists the ground-state energy and the scale factor η defined by

$$\eta = -\frac{\frac{1}{2}\langle V \rangle}{\langle T \rangle} , \tag{11}$$

where $\langle V \rangle$ and $\langle T \rangle$ are the potential energy and kinetic energy, respectively. All reported expectation values have been appropriately scaled using the values of η tabulated in Table III.

Calculations were also carried out with only the single spin eigenfunction given by Eq. (3a) included in the basis set. The basis set for this calculation was ordered in exactly the same manner discussed above. The results obtained for the various expectation values are presented in Table IV.

The standard bracket notation is employed (except in Tables II and IV) to denote the uncertainty in the preceding digit or pair of digits. For experimentally determined quantities employed in this work, the errors are one standard deviation estimates, though in some cases, no statements are made concerning this matter. The uncertainties associated with computed expectation values are based on rough evaluations of the convergence of the particular expectation value. This is complicated by the nonsmooth convergence exhibited by several of the expectation values.

A. Nuclear magnetic shielding constant

The nuclear magnetic shielding constant (diamagnetic shielding factor) is determined from the formula

$$\sigma = \tfrac{1}{3}\alpha^2 \left\langle \psi \left| \sum_{i=1}^{3} \frac{1}{r_i} \right| \psi \right\rangle , \tag{12}$$

where α is the fine-structure constant. Using the value[29] $\alpha = 7.297\,353\,08 \times 10^{-3}$, the shielding constant for Be^+ is determined to be $1.415\,401(1) \times 10^{-4}$ a.u.

B. Diamagnetic susceptibility

The molar diamagnetic susceptibility is defined by

$$\chi = -\tfrac{1}{6} N_A \alpha^2 a_0^3 \left\langle \psi \left| \sum_{i=1}^{3} r_i^2 \right| \psi \right\rangle , \tag{13}$$

TABLE IV. Expectation values for the ^2S ground state of Be II, for wave functions involving only one spin eigenfunction. Numbers in square brackets denote powers of ten.

Expectation value	Number of terms 50	100	150	200	226
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	1.432 446[1]	1.432 467[1]	1.432 471[1]	1.432 474[1]	1.432 476[1]
$\left\langle -\frac{4}{r_i} \right\rangle$	−3.189 520[1]	−3.189 545[1]	−3.189 555[1]	−3.189 554[1]	−3.189 555[1]
$\left\langle \frac{1}{r_{ij}} \right\rangle$	3.246 280	3.246 122	3.246 129	3.246 051	3.246 033
$\langle r_i \rangle$	3.102 832	3.101 629	3.101 331	3.101 418	3.101 411
$\langle r_i^2 \rangle$	6.518 845	6.508 857	6.507 348	6.508 085	6.508 061
$\langle r_i^3 \rangle$	1.875 480[1]	1.868 888[1]	1.868 261[1]	1.868 771[1]	1.868 760[1]
$\langle r_{ij} \rangle$	5.269 911	5.267 508	5.266 931	5.267 099	5.267 082
$\langle r_{ij}^2 \rangle$	1.309 582[1]	1.307 580[1]	1.307 282[1]	1.307 427[1]	1.307 423[1]
$\langle \delta(\mathbf{r}_i) \rangle$	3.504 830[1]	3.510 272[1]	3.508 290[1]	3.509 457[1]	3.510 330[1]
$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \rangle$	1.256 194[1]	1.290 184[1]	1.264 491[1]	1.253 995[1]	1.255 862[1]
$\langle \nabla_i \cdot \nabla_j \rangle$	−4.557 627[−1]	−4.536 006[−1]	−4.533 594[−1]	−4.530 783[−1]	−4.529 540[−1]
Energy	−14.324 458	−14.324 666	−14.324 709	−14.324 745	−14.324 758

where N_A is Avogadro's constant and a_0 is the Bohr radius. Using the value $N_A = 6.022\,136\,7 \times 10^{23}$ mol^{-1} and $a_0 = 0.529\,177\,249 \times 10^{-8}$ cm leads to χ in units of cm^{3}mol^{-1} as

$$\chi = -0.792\,015\,3(4) \times 10^{-6} \left\langle \psi \left| \sum_{i=1}^{3} r_i^2 \right| \psi \right\rangle \tag{14}$$

and the expectation value is expressed in atomic units. For the ^2S ground state of Be^+ the molar diamagnetic susceptibility is determined to be $\chi = -5.154\,43(4) \times 10^{-6}$ cm^{3}mol^{-1}.

C. Specific mass shift

The nonrelativistic form of the specific mass shift is given by

$$\Delta E_{\mathrm{SMS}} = -\frac{\mu}{M_{^9\mathrm{Be}}} \left\langle \psi \left| \sum_{i<j}^{3} \nabla_i \cdot \nabla_j \right| \psi \right\rangle , \tag{15}$$

where μ is the reduced electron mass $m_e M_{^9\mathrm{Be}}/(m_e + M_{^9\mathrm{Be}})$ and $M_{^9\mathrm{Be}}$ is the nuclear mass. The value of $M_{^9\mathrm{Be}} = 9.009\,9879u$ is taken from the most recent atomic mass tables of Wapstra and Audi[30] and has been corrected for the mass of four electrons. The specific mass shift is given in Table V along with some previous theoretical evaluations for this quantity.

Beryllium has only one stable isotope. As a consequence, no experimental transition isotopes shifts have been measured for Be II.[31] This is unfortunate, since the latter property is a very sensitive test of how well electron correlation is accounted for in a trial wave function.

The value of ΔE_{SMS}, like the transition isotope shift, is a sensitive measure of electron correlation. The value of ΔE_{SMS} reported in Table V (based on the 401-term wave function) should be the most accurate estimate available for this quantity for the ^2S Be^+ ground state.

V. DISCUSSION

A. Nonrelativistic energy

Table VI gives a summary of some of the more accurate calculations of the nonrelativistic energy, E_{NR}, of the ^2S ground state of Be^+. The present result for E_{NR} is the lowest upper bound reported to date. Two empirical estimates of the nonrelativistic ground-state energy are available in the literature (see Table VI). The present calculation yields an energy of ~ 30–47 μhartree above the respective literature estimates. The lack of accurate values for the relativistic contributions and uncertainties associated with estimating the Lamb shift make it impossible to assess the accuracy of either of the empirical estimates for E_{NR}.

The Hartree-Fock energy for the ^2S Be^+ ground state has been evaluated to be $-14.277\,39$ a.u. (Ref. 37). The present calculation therefore accounts for 99.9% of the correlation energy.

TABLE V. Specific mass shift, ΔE_{SMS}, for the ^2S ground state of Be^+.

Wave function	Type	Number of terms	ΔE_{SMS}
Flannery and Stewart[a]	Open shell	4	5.038×10^{-5}
Prasad and Stewart[b]	CI	45	2.760×10^{-5}
Davis and Chung[c]	CI		2.738×10^{-5}
Present work	Hylleraas (single spin eigenfunction)	226	$2.758(7)\times10^{-5}$
Present work	Hylleraas (both spin eigenfunctions)	401	$2.758(7)\times10^{-5}$

[a]Reference 32. An alternative mathematical form for ΔE_{SMS} is evaluated in this work.
[b]Reference 33.
[c]Reference 34. The explicit number of terms used for the ^2S ground state of Be^+ is not reported, but it is indicated that at least 52 (and less than 110) terms are used. CI denotes configuration interaction.

B. Convergence characteristics

Inspection of Table III reveals the relatively slow convergence of the calculation. This result is not totally unexpected, and has been noted elsewhere for similar calculations involving basis sets of Hylleraas-type functions of moderate size.[15,21,27,36,37] For systems with three (or more) electrons, exceedingly few Hylleraas-type wave functions of the size reported herein are available in the literature. Hence there are relatively few comparisons that can be made as to what extent the convergence might be tied to the form of the basis functions versus the size of the basis set.

The present basis set is more biased toward the short-range nuclear region—the region important for calculating an accurate E_{NR}. At the point that the calculation terminates, it is the electron-electron potential energy and the kinetic energy that are changing most significantly. From terms 360 to 380, the following changes (in μhartree) are obtained: -5.7, 2.9, and ~0.1, for the electron-electron potential energy, the kinetic energy, and the electron-nuclear potential energy, respectively. The corresponding changes for terms 380–401 are -1.6, 1, and 0.4. If the empirical estimates of E_{NR} are

TABLE VI. Upper bounds to the nonrelativistic ground-state energy of ^2S Be II.

Wave function	Type	Number of terms	Energy
Weiss[a]	CI	45	−14.323 50
Davis and Chung[b]	CI		−14.323 557
Perkins[c]	Hylleraas	30	−14.324 57
Ho[d]	Hylleraas	60	−14.324 696
Muszynska *et al.*[e]	Combined CI-Hylleraas	100	−14.324 714
Pipin and Woznicki[f]	Combined CI-Hylleraas	170	−14.324 72
Present work	Hylleraas (single spin function)	226	−14.324 758
Present work	Hylleraas (both doublet spin functions)	401	−14.324 760
Empirical estimates for the nonrelativistic ground-state energy			−14.324 79[a] −14.324 807[e]

[a]Reference 35.
[b]Reference 34. For the number of terms employed, see footnote c in Table V.
[c]Reference 26.
[d]Reference 27.
[e]Reference 36.
[f]Reference 37.

accepted, it is clear from the numbers just cited that the convergence of the energy expectation value has slowed considerably. Two other factors should, however, be considered. The restriction to fixed exponents may unduly slow the convergence, particularly as s orbitals with more diffuse character are included as the size of the basis set increases. While this undoubtedly influences the rate of convergence of the calculation, it is probably not the critical factor. This remark is based on observations from a Hylleraas-type calculation with optimization of exponents in progress on the ^2S ground state of Li I. In this study, slow convergence is also observed. The second factor to consider is the relatively modest number of basis functions to account for the tail region of the electron cloud. The rate of convergence of the molar diamagnetic susceptibility and of the moment $\langle r_i^3 \rangle$ will in part reflect how well the outer region of the electronic charge cloud is described by the basis set.

The charge cloud in the near nuclear region is not fully described, as reflected in the rate of convergence for the electronic density at the nucleus $\rho(0)$ (see Table II). Basis functions that include a logarithmic functional dependence on electronic coordinates and more accurately describe the electronic density in the near nuclear region,[38] as have been employed with great success for two-electron systems,[39–41] certainly merit attention. Unfortunately, considerable technical difficulties arise in the evaluation of the integrals that are required with the use of such basis functions.

A general observation is that all the expectation values shown in Tables II and IV do not converge monotonically. This is true in several cases even after a large number of basis functions have been added. Such behavior makes attempts at determining extrapolated estimates for the expectation values of limited value.

C. One-spin versus two-spin eigenfunctions

Table IV lists the expectation values evaluated using only one spin eigenfunction [Eq. (3a)]. There are a total of 226 such terms in the overall wave function. A comparison of the results in the final columns of Tables II and IV shows that the expectation values are fairly insensitive to the second spin eigenfunction, the one exception being the Fermi contact interaction. For the latter case, a decrease of approximately 0.061 a.u. (0.5%) is observed, which brings the calculated value into much closer agreement with the experimental result (see below). These results are not totally unexpected and support observations made elsewhere in the literature.[15,21]

D. Fermi contact interaction—comparison with experiment

As indicated in the Introduction, an accurate calculation of the Fermi contact interaction is a principal goal of the present investigation. The Fermi contact operator evaluated in this work is

$$H_F = \tfrac{2}{3}\mu_0 g_e g_I \mu_B \mu_N \mathbf{I} \cdot \sum_{i=1}^{3} \delta(\mathbf{r}_i)\mathbf{S}_i \ , \tag{16}$$

which can be rewritten as an effective operator:

$$H_F \equiv h A_J \mathbf{I} \cdot \mathbf{J} \ , \tag{17}$$

where μ_0 is the vacuum permeability, g_e is the electronic g factor (incorporating bound state corrections), 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, $\delta(\mathbf{r}_i)$ is the Dirac δ function, h is Planck's constant, $\mathbf{J}$ is the total electronic angular momentum operator, and A_J is the hyperfine coupling constant. The energy splitting for the ^2S state occurs between the $(I+\frac{1}{2})$ and $(I-\frac{1}{2})$ levels $(J=\frac{1}{2})$. For ^{9}Be, $I=\frac{3}{2}$ and the total angular momentum $F=2$ and so

$$h\Delta\nu = E(F=1) - E(F=2) = -2hA_{1/2} \tag{18}$$

and

$$A_{1/2} = -\tfrac{1}{2}\Delta\nu \ . \tag{19}$$

Two accurate measurements of $\Delta\nu$ are available. For the ^2S ground state of Be^+ Vetter and co-workers[42] have determined using optical pumping techniques that

$$\Delta\nu = 1250.018(5) \text{ MHz}$$

giving $A_{1/2} = -625.009(3)$ MHz. A most recent investigation using electromagnetic trapping techniques yields the value[9]

$$A_{1/2} = -625.008\,837\,048(10) \text{ MHz} \ .$$

The connection between the coupling constant (expressed in MHz) and the expectation value f is (using a conventional grouping of terms)

$$A_{1/2} = \left[\frac{\mu_0 \mu_B \mu_N}{2\pi h a_0^3}\right] \frac{g_e \mu_I f}{3I} \ , \tag{20}$$

where f is defined in Eq. (10). Using the most recent[29] values of μ_B, μ_N, h, and a_0 Eq. (20) simplifies to

$$A_{1/2} = 95.410\,67(7) \left[\frac{g_e \mu_I}{3I}\right] f \ . \tag{21}$$

The electronic g factor for $^9Be^+$ has recently been determined[9] to be 2.002 262 06(42) and the unshielded magnetic moment, μ_{Be}^0, has been evaluated[43] to be $\mu_{Be}^0 = -1.177\,432(3)\mu_N$. Employing these values in Eq. (21), leads to

$$A_{1/2} = -49.985\,2(2) f \ . \tag{22}$$

Table VII compares some accurate evaluations of f for the ^2S Be^+ ground state. The $A_{1/2}$ value reported by Das[46] and by Heully *et al.*[47] has been converted to f using Eq. (22). The experimental f value has also been evaluated using this equation. An earlier comparison of calculations of f values for Be^+ may be found in Ref. 48. The finite nuclear mass can be incorporated by multiplication of the reported f values by the factor $(1+m_e/M_{^9Be})^{-3} \approx 0.999\,817\,4$. This reduces the f value evaluated from the 401-term wave function to 12.495 7 a.u. The agreement between theory and experiment is

TABLE VII. Fermi contact interaction, Eq. (10), for the ^2S ground state of Be^+.

Wave function	Type	Number of terms	$\langle 4\pi\delta(\mathbf{r}_i)\sigma_{zi}\rangle$
Martin and Weiss[a]	CI	45	11.93
Garpman *et al.*[b]	MBPT		12.56
Das[c]	MBPT		12.32(12)[d]
Heully and Martensson-Pendrill[e]	MBPT		12.2[d]
Present work	Hylleraas (single spin eigenfunction)	226	12.559
Present work	Hylleraas (both spin eigenfunctions)	401	12.498 0(40)
Experimental value			12.503 88(5)[f]

[a]Reference 44.
[b]Reference 45.
[c]Reference 46.
[d]See text for the evaluation of this value.
[e]Reference 47.
[f]Determined using Eq. (22) and the experimental result from Ref. 9. MBPT denotes many-body perturbation theoric approach.

gratifying, the absolute percent error being $\sim 0.07\%$. Part of the difference between the present theoretical value and the experimental result is expected to be a fairly small relativistic correction. A rough estimate of the relativistic correction to f has been given by Garpman *et al.* as $\sim +0.02$.[45] It is to be noted that the very close agreement between theory and experiment requires the inclusion of the second spin eigenfunction in the calculations.

VI. CONCLUSIONS

The principal result of this study is the lowest upper-bound estimate for the nonrelativistic ground-state energy of Be II. The Fermi contact interaction, a property generally known to reflect in a sensitive manner the quality of the wave function in the region at the nucleus is calculated to within an error of 0.07% of the experimental result. The importance of including the second spin eigenfunction to achieve the aforementioned accuracy for the Fermi contact interaction is established. It is possible that for much larger basis sets, accurate calculations of f can be made with a single spin eigenfunction. A study is in progress on Li I to attempt to resolve this question.

The general rate of convergence of the energy expectation is observed to be rather slow. It would appear that probably another couple of hundred terms in the basis set would be needed to approach a 1-μhartree uncertainty for E_{NR}. Efforts are in progress to test out this assertion.

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