Compact wave functions for the beryllium isoelectronic series, Li^- to Ne^{6+}: A standard Hylleraas approach

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Variational calculations have been carried out for the ground states of several members of the beryllium isoelectronic series using a standard Hylleraas approach involving Slater-type basis functions. The species examined are Li^-, Be, B^+, C^{2+}, N^{3+}, O^{4+}, F^{5+}, and Ne^{6+}. For each species, the nonrelativistic energy, the electronic density at the nucleus, the expectation value $\langle \nabla_i \cdot \nabla_j \rangle$, the moments $\langle r_i^n \rangle$ for $n = -1$, 1, 2, and 3, and $\langle r_{ij}^n \rangle$ for $n = -1$, 1, and 2, are reported. With relatively compact basis sets, the ground state energies are obtained with uncertainties ranging from 50 parts per million to just under 4 parts per million. © *2011 American Institute of Physics*. [doi:10.1063/1.3569565]

I. INTRODUCTION

Over approximately the past 40 years, there has been extensive interest in computation of the ground state energy of the beryllium atom and members of its isoelectronic series.[1–59] A wide variety of computational techniques have been employed, including configuration interaction (CI),[3,10,13,22,25,27,32] Hylleraas-CI,[4,7–9,29,34,59] Hylleraas,[2,5] explicitly correlated Gaussian-based Hylleraas-type calculations,[24,31,37–39,43–45,52,57,58] multiconfiguration Hartree–Fock,[6,26] coupled-cluster,[12,15,16,23,30] many-body perturbation theory,[11,18] Monte Carlo,[33,35,41,42,46] and other methods.

In this study, our objective is to obtain relatively compact wave functions for several members of the beryllium isoelectronic series by employing a standard Hylleraas approach using Slater-type orbital (STO) basis functions. Because of the significant mathematical problems that arise in the evaluation of the required four-electron correlated integrals, very little progress has been reported using the Hylleraas approach with a STO basis set. For several members of the series, we report a number of expectation values that are currently known only with limited accuracy.

The Hylleraas approach has a long history in calculations on atomic two- and three-electron systems, and has been particularly successful in producing results of high accuracy.[60–68] For the four-electron case, two pioneering calculations using a standard Hylleraas calculation employing Slater-type basis functions have been reported for the ground state of the beryllium atom.[2,5] Gentner and Burke[2] employed a 25 term wave function, with the restriction that each term in the expansion of the wave function had at most one r_{ij}^n term, with n restricted to the values 0, 1, and 2, and r_{ij} is the interelectron separation distance between electrons i and j. This yielded a ground state energy $\sim 9.4 \times 10^3$ microhartree above the best calculated value.[52] Later, Perkins[5] used a more compact wave function with 18 basis functions, also restricted so that each term in the expansion of the wave function had at most one r_{ij}^n term, with n restricted to the values 0, 1, and 2, and obtained a ground state energy $\sim 5.2 \times 10^3$ microhartree above the most accurate result.

Another approach that has employed basis functions with explicit r_{ij} factors is the hybrid Hylleraas-CI technique.[4,7–9,29,34,59] The most accurate result available using this approach, but with restrictions on how many r_{ij} factors can be employed for each term, yields a ground state energy accurate to better than 1 microhartree.[59]

The most accurate results for the ground state energy of the beryllium atom have been obtained using explicitly correlated Gaussian functions.[24,31,37–39,43–45,47,48,52,57,58] The best result currently available gives a ground state energy converged to approximately the nanohartree level.[52] These works demonstrate how effective explicitly correlated Gaussian basis sets can be for treating few-electron problems. For the beryllium ground state, and also for the ground states of other members of the Be isoelectronic series that have been studied, the correlated Gaussian basis sets show the best convergence for the energy and a number of expectation values, in comparison with other computational techniques. A principal advantage of the explicitly correlated Gaussian basis sets is that the underlying integration problem is manageable. The main drawback is that Gaussian basis functions have unsuitable asymptotic behavior—they decay too quickly as the radial coordinate approaches infinity, relative to Slater-type functions. They also have problems describing the cusp conditions. However, the latter two difficulties can be overcome if one is willing to employ very large basis set expansions. The size of three of the most accurate variational calculations for the ground state energy of the beryllium atom employ 6000, 6500, and 10 000 terms, respectively.[47,48,52] By comparison with these large basis set expansions, the wave functions of the present study are relatively compact.

It is to be noted that the Hylleraas approach that has been so successful with few-electron atomic systems, can also be readily adapted to carry out high precision non-Born–Oppenheimer (BO) calculations on small 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

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the molecular systems that can be currently attacked is limited primarily by the ability to resolve the mathematical problems associated with 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 using correlated Gaussian functions has been particularly successful using this atomiclike approach. For a recent example see Ref. 69 and the references therein.

II. THEORY

The nonrelativistic Hamiltonian for a four-electron atomic system can be written in the following form,

$$H = -\sum_{i=1}^{4} \frac{1}{2\mu_i}\nabla_i^2 - \frac{1}{M}\sum_{i=1}^{4}\sum_{j>i}^{4} \nabla_i \cdot \nabla_j - Z\sum_{i=1}^{4}\frac{1}{r_i} + \sum_{i=1}^{4}\sum_{j>i}^{4}\frac{1}{r_{ij}}. \quad (1)$$

In Eq. (1), r_i designates the electron-nuclear separation distance for electron i, M and Z are the mass and charge of the nucleus, respectively, the reduced mass is $\mu_i = M/(1+M)$, and atomic units are employed. Adopting the infinite nuclear mass approximation, the Hamiltonian for the S states of an atomic four-electron system can be written as

$$\begin{aligned} H = &-\sum_{i=1}^{4}\left(\frac{1}{2}\frac{\partial^2}{\partial r_i^2} + \frac{1}{r_i}\frac{\partial}{\partial r_i} + \frac{Z}{r_i}\right) \\ &-\sum_{i=1}^{4}\sum_{j>i}^{4}\left(\frac{\partial^2}{\partial r_{ij}^2} + \frac{2}{r_{ij}}\frac{\partial}{\partial r_{ij}} - \frac{1}{r_{ij}}\right) \\ &-\sum_{i=1}^{4}\sum_{\substack{j=1\\(j\neq i)}}^{4}\frac{r_i^2 - r_j^2 + r_{ij}^2}{2r_i r_{ij}}\frac{\partial^2}{\partial r_{ij}\partial r_i} \\ &-\sum_{i=1}^{4}\sum_{\substack{j=1\\(j\neq i)}}^{4}\sum_{\substack{k>j\\(k\neq i)}}^{4}\frac{r_{ij}^2 + r_{ik}^2 - r_{jk}^2}{2r_{ij}r_{ik}}\frac{\partial^2}{\partial r_{ij}\partial r_{ik}}. \end{aligned} \quad (2)$$

This form of the Hamiltonian is particularly convenient when working with basis functions depending explicitly on the interelectron separation distance, that is, a Hylleraas expansion is assumed. The contribution of the mass polarization term, the factor involving the double sum over $\nabla_i \cdot \nabla_j$ in Eq. (1), can be treated as a perturbation, and evaluated by first-order perturbation theory. Alternately, this term can be retained in the Hamiltonian, leading to wave functions and expectation values depending explicitly on the finite nuclear mass.

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

$$\psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4) = A\sum_{\mu=1}^{N} C_\mu r_1^{i_\mu} r_2^{j_\mu} r_3^{k_\mu} r_4^{l_\mu} r_{12}^{m_\mu} r_{13}^{n_\mu} r_{14}^{p_\mu} r_{23}^{q_\mu} r_{24}^{s_\mu} r_{34}^{t_\mu} \times e^{-a_\mu r_1 - b_\mu r_2 - c_\mu r_3 - d_\mu r_4}\chi_\mu, \quad (3)$$

where A is the four-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, c_μ, and d_μ are >0, and the integer indices $\{i_\mu,\ j_\mu,\ k_\mu,\ l_\mu,\ m_\mu, n_\mu\}$ are each ≥ 0.

III. COMPUTATIONAL DETAILS

The basis functions were selected with the principal objective of keeping the underlying integration problem manageable. With the Hamiltonian given in the form of Eq. (2), the evaluation of the energy expectation value and the other expectation values reported in this work for the atomic S states, reduces to four-electron correlated integrals that take the form:

$$\begin{aligned} &I_4(i,j,k,l,m,n,p,q,s,t,\alpha,\beta,\gamma,\delta) \\ &= \int r_1^i r_2^j r_3^k r_4^l r_{12}^m r_{13}^n r_{14}^p r_{23}^q r_{24}^s r_{34}^t e^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4} \\ &\quad \times d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4, \end{aligned} \quad (4)$$

where $\alpha > 0$, $\beta > 0$, $\gamma > 0$, and $\delta > 0$. The individual integer indices i through t must be ≥ -2 for the integral to be convergent. For an energy evaluation, only integrals having m, n, p, q, s, t each ≥ -1 are required. Various cases of the integral in Eq. (4) have been discussed in the literature for the situation where m, n, p, q, s, t are each ≥ -1.[1,2,34,70–78] A survey on the approaches to treat single center correlated integrals based on Slater-type functions, including special cases of Eq. (4), can be found in Ref. 79. For an energy evaluation, the most difficult cases of the integral in Eq. (4) to evaluate occur when the indices $\{m, n, p, q, s, t\}$ are odd integers. At present, computationally viable methods are not available to handle the cases where five or six members of the set of indices $\{m, n, p, q, s, t\}$ are odd.

The preceding limitation restricts the choice of basis functions to those having multiple r_{ij}^n factors with no more than one of those r_{ij} factors having an odd power. That is, the set $\{m_\mu, n_\mu, p_\mu, q_\mu, s_\mu, t_\mu\}$ in Eq. (3) contains at most one odd integer per basis function. A basis function containing a term $r_{ij}^m r_{kl}^n$ with m and n both odd, leads to a five-odd case for the set $\{m, n, p, q, s, t\}$ in Eq. (4) because of the antisymmetrizer operation present in Eq. (3). Lifting this restriction has been an ongoing research topic for some time.

The exponential parameters were optimized separately for each member of the BeI series using a stochastic optimization approach. This was done as each basis function was added to the expansion. This is the most computer time intensive phase of the calculations.

In Table I, the following shorthand notation is employed for one-electron and two-electron expectation values:

$$\langle O_i \rangle = \langle \psi | \sum_{i=1}^{4} O_i | \psi \rangle, \quad (5)$$

$$\langle O_{ij} \rangle = \langle \psi | \sum_{i=1}^{4}\sum_{j>i}^{4} O_{ij} | \psi \rangle. \quad (6)$$

IV. RESULTS

In Table I, we report the results for the ground state energies and several expectation values for selected members of the beryllium isoelectronic series. A comparison of the present results with what are the best available literature values is also presented. There are highly accurate benchmark results available for comparison for the ground state energies and for $\langle \nabla_i \cdot \nabla_j \rangle$. For the other expectation values, there are accurate values available for Be, and just a few isolated

TABLE I. Expectation values (in a.u.) for the BeI series for 100 and 200 term Hylleraas wave functions.

	Li^-		Be		B^+		C^{2+}	
Expectation				Number of terms				
value	100	200	100	200	100	200	100	200
Energy	−7.49979	−7.50040	−14.66627	−14.66702	−24.34781	−24.34861	−36.53404	−36.53458
Literature[a]	−7.5007766134 [Ref. 53]		−14.667356486 [Ref. 52]		−24.348884446(35) [Ref. 57]		−36.534852338(35) [Ref. 58]	
$\left\langle -\frac{Z}{r_i} \right\rangle$	−17.6927	−17.6916(50)	−33.70917	−33.70895(50)	−54.6690	−54.6724(50)	−80.62245	−80.62266(60)
Literature			−33.709400(8) [Ref. 52]		−54.650(10) [Ref. 35]		−80.580(18) [Ref. 35]	
$\left\langle \frac{1}{r_{ij}} \right\rangle$	2.69208	2.69054(80)	4.37652	4.37523(80)	5.97570	5.97500(80)	7.55437	7.55362(80)
Literature			4.37467(5) [Ref. 31]		5.9643(6) [Ref. 35]		7.548(1) [Ref. 35]	
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	7.50077	7.50069	14.66638	14.66671	24.34545	24.34878	36.53403	36.53446
$\langle r_i \rangle$	11.634	11.671(60)	5.9688	5.9716(30)	4.1760	4.1765(30)	3.2358	3.2360(20)
Literature	11.727484 [Ref. 53]		5.97256(8) [Ref. 31]		4.1978(6) [Ref. 35]		3.2468(4) [Ref. 35]	
$\langle r_i^2 \rangle$	70.3	71.1(20)	16.203	16.235(20)	7.6178	7.6239(60)	4.4807	4.4821(30)
Literature	72.439132 [Ref. 53]		16.248(8) [Ref. 31]		7.690(3) [Ref. 35]		4.506(1) [Ref. 35]	
$\langle r_i^3 \rangle$	565	578(20)	56.42	56.66(20)	17.690	17.727(60)	7.8718	7.8776(90)
Literature			56.772(8) [Ref. 31]		17.88(1) [Ref. 35]		7.919(4) [Ref. 35]	
$\langle r_{ij} \rangle$	30.71	30.88(30)	15.253	15.267(20)	10.527	10.533(30)	8.0967	8.0982(50)
Literature	31.046450 [Ref. 53]		15.2721(12) [Ref. 31]		10.581(2) [Ref. 35]		8.118(1) [Ref. 35]	
$\langle r_{ij}^2 \rangle$	227.9	231.5(60)	52.660	52.798(60)	24.623	24.666(60)	14.441	14.447(60)
Literature	235.61777 [Ref. 53]		52.854(18) [Ref. 31]		24.857(9) [Ref. 35]		14.502(5) [Ref. 5]	
$\langle \delta(\mathbf{r}_i) \rangle$	13.8399	13.8376(20)	35.339	35.386(30)	72.451	72.517(30)	129.627	129.490(30)
Literature	13.83700 [Ref. 53]		35.36892(4) [Ref. 44]		71.9(2) [Ref. 35]		128.5(5) [Ref. 35]	
	13.83808(20) [Ref. 45]							
$\langle \nabla_i \cdot \nabla_j \rangle$	−0.31489	−0.30879(70)	−0.46025	−0.45991(40)	−0.59555	−0.59554(40)	−0.71384	−0.71314(50)
Literature	−0.308344 [Ref. 38]		−0.460205(3) [Ref. 31]		−0.595140 [Ref. 38]		−0.713671 [Ref. 38]	
	−0.308104(3) [Ref. 45]		−0.460224(4) [Ref. 44]					

	N^{3+}		O^{4+}		F^{5+}		Ne^{6+}	
Expectation				Number of terms				
value	100	200	100	200	100	200	100	200
Energy	−51.22163	−51.22230	−68.41041	−68.41115	−88.09982	−88.10057	−110.28888	−110.29018
Literature	−51.2227083 [Ref. 38]		−68.4115353 [Ref. 38]		−88.1009188 [Ref. 38]		−110.2906495 [Ref. 38]	
$\left\langle -\frac{Z}{r_i} \right\rangle$	−111.5650	−111.5688(40)	−147.5120	−147.5129(40)	−188.4528	−188.4558(50)	−234.3878	−234.3960(80)
Literature	−111.50(3) [Ref. 35]		−147.56(8) [Ref. 35]		−188.33(5) [Ref. 35]		−234.26(6) [Ref. 35]	
$\left\langle \frac{1}{r_{ij}} \right\rangle$	9.12482	9.12431(60)	10.6926	10.6909(30)	12.2562	12.2551(30)	13.8193	13.8178(30)
Literature	9.129(1) [Ref. 35]		10.694(1) [Ref. 35]		12.236(1) [Ref. 35]		13.807(2) [Ref. 35]	
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	51.21858	51.22221	68.40903	68.41085	88.09678	88.10012	110.2796	110.2881
$\langle r_i \rangle$	2.6478	2.6479(10)	2.2424	2.2431(10)	1.9465	1.9468(10)	1.72016	1.72023(20)
Literature	2.6486(3) [Ref. 35]		2.2410(3) [Ref. 35]		1.9535(3) [Ref. 35]		1.7255(2) [Ref. 35]	
$\langle r_i^2 \rangle$	2.9617	2.9627(30)	2.1055	2.1075(30)	1.5768	1.5775(30)	1.2253	1.2258(20)
Literature	2.959(1) [Ref. 35]		2.0983(7) [Ref. 35]		1.5907(5) [Ref. 35]		1.2331(4) [Ref. 35]	
$\langle r_i^3 \rangle$	4.1933	4.1961(90)	2.4982	2.5026(90)	1.6122	1.6136(90)	1.1006	1.1017(90)
Literature	4.178(2) [Ref. 35]		2.474(1) [Ref. 35]		1.637(1) [Ref. 35]		1.110(6) [Ref. 35]	
$\langle r_{ij} \rangle$	6.5919	6.5931(50)	5.5629	5.5651(50)	4.8160	4.8171(50)	4.2466	4.2476(50)
Literature	6.5898(8) [Ref. 35]		5.5706(8) [Ref. 35]		4.8414(6) [Ref. 35]		4.2540(5) [Ref. 35]	
$\langle r_{ij}^2 \rangle$	9.518	9.523(50)	6.7527	6.7594(60)	5.0482	5.0509(60)	3.9172	3.9194(60)
Literature	9.504(3) [Ref. 35]		6.769(2) [Ref. 35]		5.113(1) [Ref. 35]		3.929(1) [Ref. 35]	
$\langle \delta(\mathbf{r}_i) \rangle$	210.743	210.715(40)	320.148	320.212(40)	462.64	462.46(40)	642.51	642.10(50)
Literature	211(1) [Ref. 35]		318(1) [Ref. 35]		460(1) [Ref. 35]		639(3) [Ref. 35]	
$\langle \nabla_i \cdot \nabla_j \rangle$	−0.81342	−0.81569(50)	−0.91535	−0.90194(50)	−0.97424	−0.97224(50)	−1.0422	−1.0247(40)
Literature	−0.816044 [Ref. 38]		−0.902377 [Ref. 38]		−0.972739 [Ref. 38]		−1.027164 [Ref. 38]	

[a]Literature references indicates by [ ].

results for other members of the BeI series. In particular, for the species N^{3+}, O^{4+}, F^{5+}, and Ne^{6+}, only Monte Carlo results are available for most of the expectation values, and these results have modest accuracy.

In Table I, only the most accurate value available was used for comparison. Additional values can be found for the energy and some expectation values for Li^- in Refs. 8, 22, 26, 30, 38, 45, 49, 50, and 53. For the ground state of Be additional values for various expectation values can be found in Refs. 13, 25, 26, 29–31, 33–35, 37–39, 41–44, 46–48, 50, 52, 54, and 55.

The virial scale factor, η, defined by

$$\eta = -\frac{\langle V \rangle}{2\langle T \rangle}, \tag{7}$$

where $\langle V \rangle$ and $\langle T \rangle$ are the potential energy and the kinetic energy expectation values, respectively, should be 1 for the exact wave function. For the 200 term wave functions the following values were obtained: Li^- 0.999981, Be 1.000011, B^+ 0.9999966, C^{2+} 1.000002, N^{3+} 1.0000008, O^{4+} 1.000002, F^{5+} 1.000003, and Ne^{6+} 1.000009. The expectation values reported in Table I have not been scaled using these values of η.

V. DISCUSSION

The ground state energies reported in Table I have uncertainties that are 50 parts per million (ppm) for Li^-, 23 ppm for Be, 11 ppm for B^+, 7.5 ppm for C^{2+}, 3.9 ppm for N^{3+}, 5.6 ppm for O^{4+}, 4.0 ppm for F^{5+}, and 4.3 ppm for Ne^{6+}, in comparison with the results from large scale calculations involving correlated Gaussian basis sets.[38,52,53,56,58] Approximate estimates for the errors for several of the expectation values, based in part on the convergence rate of the calculations, and in part on comparison with the results from large scale correlated Gaussian-based calculations, are given in Table I in parenthesis.

The values of $\langle \nabla_i \cdot \nabla_j \rangle$ given in Table I, which lead to the mass polarization correction to the energy, have errors ranging from 2 to 5 in the fourth significant digit reported, by comparison with the results available from large scale correlated Gaussian basis set calculations.[38,43–45]

For several members of the Be isoelectronic series the only literature values available for the moments $\langle r_i^n \rangle$ for $n = -1$, 1, 2, and 3, and $\langle r_{ij}^n \rangle$ for $n = -1$, 1, and 2, come from Monte Carlo calculations. Inspection of Table I indicates that a number of Monte Carlo results are in satisfactory agreement for several of the expectation values calculated in the present study. We expect the present results to be more accurate than the corresponding Monte Carlo results. As justification of the preceding statement, a comparison of the results from the present work and the corresponding Monte Carlo results, with more accurate values for the beryllium atom, indicates that the present results are more accurate than the Monte Carlo calculations, with one exception. The expectation value $\langle r_i^3 \rangle$ is the one exception. We also note the overall accuracy of our calculations improves slightly for the more highly charged ions of the BeI series.

The nuclear magnetic shielding constant and the diamagnetic susceptibility can be obtained directly for each of the members of the BeI series from the moments $\langle r_i^{-1} \rangle$ and $\langle r_i^2 \rangle$, respectively.[61] The specific mass shift is obtained directly from $\langle \nabla_i \cdot \nabla_j \rangle$ and the electron density at the nucleus is given by $\langle \delta(r_i) \rangle$. A key quantity of interest is the ionization potential, which affords a direct comparison with experimental work. The calculation of this quantity requires an accurate determination of relativistic corrections, and higher accuracy for the nonrelativistic energy. Both of these projects are in progress.

For the Li^- ion, a relatively slow convergence of the moments $\langle r_i^n \rangle$ for $n = 2$ and 3, and of $\langle r_{ij}^n \rangle$ for $n = 2$, is noted, as judged by the relatively large jumps observed between the expectation values calculated using the 100 term and 200 term wave functions. This indicates the basis sets employed are not doing an adequate job of describing the more diffuse region of configuration space for this species.

VI. SUMMARY

In this work, we have reported the results from variational calculations on selected members of the BeI isoelectronic series using relatively compact Hylleraas-type expansions with a Slater-type basis. For several members of the series, a number of the expectation values reported are more accurate than existing values in the literature. Efforts to improve upon the present approach are in progress, including refined parameter optimization, and enhanced methods to attack the four-electron correlated integrals that arise.

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