Ground state of Li and Be^+ using explicitly correlated functions

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Abstract

We compare the explicitly correlated Hylleraas and exponential basis sets in the evaluations of ground state of Li and Be^+. Calculations with Hylleraas functions are numerically stable and can be performed with the large number of basis functions. Our results for ground state energies $-7.478\,060\,323\,910\,10(32)$, $-14.324\,763\,176\,790\,43(22)$ of Li and Be^+ correspondingly, are the most accurate to date. When small basis set is considered, explicitly correlated exponential functions are much more effective. With only 128 functions we obtained about 10^{-9} relative accuracy, but the severe numerical instabilities make this basis costly in the evaluation.

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I. INTRODUCTION

In order to accurately calculate energy levels of light atomic systems, not only nonrelativistic energies, but also relativistic and QED corrections have to be obtained with the high precision. In the NRQED approach all corrections are obtained perturbatively, in powers of the fine structure constant α. Each term of this expansion is expressed as the expectation value of some effective Hamiltonian with the nonrelativistic wave function. Similarly, corrections due to the finite nuclear mass and its size can all be included perturbatively. This however requires the accurate representation of the nonrelativistic wave function.

The wave function of the ground and excited states can be obtained on the base of the Ritz variational principle. The accuracy of the upper bound for energy mainly depends on the basis set of trial functions and effectiveness of the optimization routine. There are not so many possible choices of basis functions, knowing that electron correlations have to be accurately accounted for. The most serious problem in development of explicitly correlated methods is difficulty in accurate calculations of integrals appearing in Hamiltonian matrix elements, and the complexity of these integrals grows with the increasing number of correlated electrons.

The most often in use are correlated Gaussian functions which have been applied so far to systems including up to six-electrons, and the most accurate results in comparison to other methods, have be obtained for Be atom [1–3]. Relatively simple integrals and possible generalization to systems with higher number of electrons is the main advantage of Gaussian functions. However, these functions have improper short-distance (Kato cusps) and long-rage behavior. As a result, the convergence of the variational procedure is not very fast. Quality of the globally optimized trial functions, even in a few thousand basis set is often insufficient for calculations of relativistic effects beyond the leading order. In particular, we observe poor convergence of matrix elements with singular operators i.e. Dirac δ.

Until now, the most accurate nonrelativistic wave function for lithium-like atomic systems were computed in Hylleraas basis by King in [4], by Yan and Drake in [5] and by present authors in [6]. The Hylleraas function for the three-electron system is of the form

$$\phi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = r_{23}^{n_1}\, r_{31}^{n_2}\, r_{12}^{n_3}\, r_1^{n_4}\, r_2^{n_5}\, r_3^{n_6}\, e^{-\alpha_1 r_1 - \alpha_2 r_2 - \alpha_3 r_3}\,, \tag{1}$$

with nonnegative integer values of n_i. Although, algorithms for integrals with these functions are computationally demanding, the correct long and short-range asymptotic and possibility to use a large basis set of functions ($\sim$10000) with small number of variational parameter ($\sim$15) allows one to achieve high accuracy. In a recent series of papers we formulated the analytical method for calculations of Hylleraas integrals with the help of recursion relations [7]. In this work we tuned up the optimization routine compared to our former work [6]. As a result, we significantly improved nonrelativistic energies as compared to the previously published ones in [5, 8] and achieved about 10^{-14} precision.

Even better precision can in principle be achieved with the explicitly correlated exponential function. In 1987 Fromm and Hill obtained the closed analytical formula for the related four-particle integral

$$g_0 = \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \int \frac{d^3 r_3}{4\pi} \frac{e^{-w_1 r_1 - w_2 r_2 - w_3 r_3 - u_1 r_{23} - u_2 r_{13} - u_3 r_{12}}}{r_{23}\, r_{31}\, r_{12}\, r_1\, r_2\, r_3}, \tag{2}$$

reducing the problem to the evaluation of multivalued dilogarithmic functions of complex arguments [9]. Their formula could be differentiated with respect to the w_a and u_a to introduce pre-exponential powers of the r_a and r_{ab}, thus to generate the class of integrals needed for evaluation of Hamiltonian and overlap matrix elements. The Fromm-Hill formula was modified later by Harris eliminating the necessity of branch tracking on the complex plane [10]. Zotev and Rebane presented their method for integrals with an extension to complex exponentials [11]. They demonstrated fast convergence even in small bases and high potential of this method in variational calculations of four-body systems [12]. Recently, Guevara *et al.* [13] have been able to optimize the correlated exponential function including linear terms in inter-particle distances by the six-dimensional numerical integration and obtained nonrelativistic energy with the relative precision of about 10^{-3}.

Effectiveness of correlated exponential functions gives opportunity to reduce significantly the size of the basis set as compared to Gaussian and Hylleraas functions. However, the evaluation of corresponding integrals is the most time consuming part of the variational method. This fact suggests to use rather short basis with carefully optimized parameters. In this work these integrals are calculated as folows. The master integral g_0 in Eq. (2) is calculated using Harris formula [10]. Integrals with higher powers of inter-particle distances, are obtained using recursion relations, which are derived from the differential equation (18). As a demonstration of this method, we performed numerical calculations of the nonrelativistic energy and of Dirac-δ for the ground state of Li and Be^+. With 128 well optimized correlated exponential functions with real parameters we have obtained nonrelativistic energies with relative precision of about 10^{-9}. This precision is not impressive in comparison to the value extrapolated from 13944 Hylleraas functions. However, the result for lithium is comparable to six times bigger set of Hylleraas functions or 1500 optimized Gaussians. The highly accurate wave function in a small basis set gives a flexibility in development of numerical methods for evaluation of more complicated integrals. It is expected to be especially valuable for evaluation of matrix elements of $m\,\alpha^6$ operators, which involves integrals very difficult to deal with Hylleraas functions.

II. NONRELATIVISTIC WAVE FUNCTION

The ground state wave function Ψ is represented as a linear combination of ψ, the antisymmetrized product of the spatial functions ϕ and the spin function χ

$$\psi = \mathcal{A}[\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3)\,\chi]\,, \tag{3}$$

$$\chi = \alpha(1)\,\beta(2)\,\alpha(3) - \beta(1)\,\alpha(2)\,\alpha(3)\,. \tag{4}$$

In the case of correlated exponential functions, $\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3)$ is

$$\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3) = e^{-\alpha_1\,r_1-\alpha_2\,r_2-\alpha_3\,r_3-\beta_1\,r_{23}-\beta_2\,r_{13}-\beta_3\,r_{12}}\,, \tag{5}$$

and we assume that α_i,β_i are real numbers. These nonlinear parameters are subject of additional conditions. Namely, when one of the electrons goes to infinity, the wave function shall decay exponentially sufficiently fast, so for example $\alpha_1+\beta_2+\beta_3 > \sqrt{2\,E_{\rm ion}}$, where $E_{\rm ion}$ is the ionization energy.

The expansion coefficients and nonlinear parameter are obtained by minimization of energy with the Hamiltonian H

$$H = T+V\,, \tag{6}$$

$$T = \sum_{a=1}^{3}\frac{\vec{p}_a^{\,2}}{2}, \qquad V = \sum_{a=1}^{3} -\frac{Z}{r_a} + \sum_{a>b=1}^{3}\frac{1}{r_{ab}}\,, \tag{7}$$

where $Z\,e$ is the nuclear charge and atomic units are used elsewhere. After elimination of spin variables, the matrix element of H can be expressed as

$$\begin{aligned}\langle\psi^L|H|\psi^R\rangle = {} & \langle 2\,\phi^L(1,2,3) + 2\,\phi^L(2,1,3) - \phi^L(3,1,2) - \phi^L(2,3,1) - \phi^L(1,3,2)\\ & -\phi^L(3,2,1)|H\,|\phi^R(1,2,3)\rangle\,.\end{aligned} \tag{8}$$

The individual matrix element $\langle\phi^L|H|\phi^R\rangle$ is represented as a linear combination of 34 Slater integrals defined as

$$g(n_1,n_2,n_3,n_4,n_5,n_6) = \int\frac{d^3r_1}{4\,\pi}\int\frac{d^3r_2}{4\,\pi}\int\frac{d^3r_3}{4\,\pi}\,e^{-w_1\,r_1-w_2\,r_2-w_3\,r_3-u_1\,r_{23}-u_2\,r_{13}-u_3\,r_{12}}\, r_{23}^{n_1-1}\,r_{31}^{n_2-1}\,r_{12}^{n_3-1}\,r_1^{n_4-1}\,r_2^{n_5-1}\,r_3^{n_6-1}\,, \tag{9}$$

where n_i are nonnegative integers and $w_a=\alpha_a^L+\alpha_a^R$, $u_a=\beta_a^L+\beta_a^R$. The number of necessary integrals for the matrix element of H can be significantly reduced. Rebane and Zotev [14] derived the formula which includes only seven integrals: the overlap integral $\langle\phi^L|\phi^R\rangle$ and six Coulomb integrals $\langle\phi^L|r^{-1}|\phi^R\rangle$, which we have found very useful. It reduces significantly the computational costs in most of cases except for small w_a,u_a, where it becomes numerically unstable. In this case we use the numerically stable standard form of the kinetic energy operator obtained by direct differentiation of the left and the right wave function over the electron coordinates.

III. CALCULATION OF SLATER INTEGRALS

A. Integration by parts method

The evaluation method of $g(n_1,n_2,n_3,n_4,n_5,n_6)$ in Eq. (9) is based on the integration by parts identities, which are widely used for the analytical calculation of Feynman diagrams [15]. Let us consider the following integral in the momentum space

$$G(m_1,m_2,m_3;m_4,m_5,m_6) = \frac{1}{8\,\pi^6}\int d^3k_1\int d^3k_2\int d^3k_3\,(k_1^2+u_1^2)^{-m_1}\,(k_2^2+u_2^2)^{-m_2}\,(k_3^2+u_3^2)^{-m_3}\,(k_{32}^2+w_1^2)^{-m_4}\,(k_{13}^2+w_2^2)^{-m_5}\,(k_{21}^2+w_3^2)^{-m_6} \tag{10}$$

which is related to g function by $g_0\equiv g(0,0,0,0,0,0)=G(1,1,1,1,1,1)$. There are 9 corresponding integration by parts identities

$$0\equiv\mathrm{id}(i,j)=\int d^3k_1\int d^3k_2\int d^3k_3\,\frac{\partial}{\partial\,\vec k_j}\Big[\vec k_i\,(k_1^2+u_1^2)^{-m_1}\,(k_2^2+u_2^2)^{-m_2}\,(k_3^2+u_3^2)^{-m_3}(k_{32}^2+w_1^2)^{-m_4}\,(k_{13}^2+w_2^2)^{-m_5}\,(k_{21}^2+w_3^2)^{-m_6}\Big], \tag{11}$$

where $i,j=1,2,3$. The reduction of the scalar products from the numerator leads to the relations between functions G of different arguments. These identities group naturally into three sets with respect to j. For example for $j=3$ and $m_i=1$ we have the following system of three equations

$$
\begin{aligned}
0 \;=\; & G(0,1,1,1,2,1) - G(0,1,2,1,1,1) + G(1,0,1,2,1,1) - G(1,1,0,1,2,1) \\
& - G(1,1,0,2,1,1) + G(1,1,1,2,0,1) - G(1,1,1,2,1,0) + G(1,1,2,1,0,1) \\
& + G(1,1,1,1,2,1)\,(-u_1^2+u_3^2-w_2^2) + G(1,1,2,1,1,1)\,(u_1^2+u_3^2-w_2^2) \\
& + G(1,1,1,2,1,1)\,(-u_2^2+u_3^2-w_2^2+w_3^2). \\
0 \;=\; & G(0,1,1,1,2,1) + G(1,0,1,2,1,1) - G(1,0,2,1,1,1) - G(1,1,0,1,2,1) \\
& - G(1,1,0,2,1,1) + G(1,1,1,0,2,1) - G(1,1,1,1,2,0) + G(1,1,2,0,1,1) \\
& + G(1,1,1,2,1,1)\,(-u_2^2+u_3^2-w_1^2) + G(1,1,2,1,1,1)\,(u_2^2+u_3^2-w_1^2) \\
& + G(1,1,1,1,2,1)\,(-u_1^2+u_3^2-w_1^2+w_3^2), \\
0 \;=\; & G(0,1,1,1,2,1) + G(1,0,1,2,1,1) - G(1,1,0,1,2,1) - G(1,1,0,2,1,1) \\
& - G(1,1,1,1,1,1) + 2\,G(1,1,2,1,1,1)\,u_3^2 + G(1,1,1,2,1,1)\,(-u_2^2+u_3^2+w_1^2) \\
& + G(1,1,1,1,2,1)\,(-u_1^2+u_3^2+w_2^2),
\end{aligned}
\tag{12}
$$

Whenever $m_i=0$, G becomes a known two-electron integral Γ as defined in Appendix A. For example

$$
\begin{aligned}
G(0,1,1;1,1,1) \;=\; & \Gamma(-1,0,-1;w_2+w_3,w_1,u_2+u_3) \\
=\; & \frac{1}{2\,w_1}\left[\mathrm{Li}\left(1-\frac{u_2+u_3+w_2+w_3}{u_2+u_3+w_1}\right) + \mathrm{Li}\left(1-\frac{u_2+u_3+w_2+w_3}{w_1+w_2+w_3}\right)\right. \\
& \left. + \frac{1}{2}\,\ln^2\left(\frac{w_1+w_2+w_3}{u_2+u_3+w_1}\right) + \frac{\pi^2}{6}\right].
\end{aligned}
\tag{13}
$$

We solve the system of equation (12), for example against $G(1,1,1;2,1,1)$, and obtain

$$
\frac{1}{2}\,\frac{\partial\sigma}{\partial w_1}\,G(1,1,1;1,1,1) - 2\,w_1\,\sigma\,G(1,1,1;2,1,1) + P = 0\,,
\tag{14}
$$

where σ is a polynomial

$$
\begin{aligned}
\sigma \;=\; & u_1^2\,u_2^2\,w_3^2 + u_2^2\,u_3^2\,w_1^2 + u_1^2\,u_3^2\,w_2^2 + w_1^2\,w_2^2\,w_3^2 + u_1^2\,w_1^2\,(u_1^2+w_1^2-u_2^2-u_3^2-w_2^2-w_3^2) \\
& + u_2^2\,w_2^2\,(u_2^2+w_2^2-u_1^2-u_3^2-w_1^2-w_3^2) + u_3^2\,w_3^2\,(u_3^2+w_3^2-u_2^2-u_1^2-w_1^2-w_2^2)\,,
\end{aligned}
\tag{15}
$$

and P is a the sum of two-electron integrals Γ

$$
\begin{aligned}
P \;=\; & -u_1\,w_1\,[(u_1+w_2)^2-u_3^2]\,\Gamma(0,0,-1;u_1+w_2,u_3,u_2+w_1)\\
& -u_1\,w_1\,[(u_1+u_3)^2-w_2^2]\,\Gamma(0,0,-1;u_1+u_3,w_2,w_1+w_3)\\
& +[u_1^2\,w_1^2+u_2^2\,w_2^2-u_3^2\,w_3^2+w_1\,w_2\,(u_1^2+u_2^2-w_3^2)]\,\Gamma(0,0,-1;w_1+w_2,w_3,u_1+u_2)\\
& +[u_1^2\,w_1^2-u_2^2\,w_2^2+u_3^2\,w_3^2+w_1\,w_3\,(u_1^2+u_3^2-w_2^2)]\,\Gamma(0,0,-1;w_1+w_3,w_2,u_1+u_3)\\
& -[u_2\,(u_2+w_1)\,(u_1^2+u_3^2-w_2^2)-u_3^2\,(u_1^2+u_2^2-w_3^2)]\,\Gamma(0,0,-1;u_2+w_1,u_3,u_1+w_2)\\
& -[u_3\,(u_3+w_1)\,(u_1^2+u_2^2-w_3^2)-u_2^2\,(u_1^2+u_3^2-w_2^2)]\,\Gamma(0,0,-1;u_3+w_1,u_2,u_1+w_3)\\
& +w_1\,[w_2\,(u_1^2-u_2^2+w_3^2)+w_3\,(u_1^2+w_2^2-u_3^2)]\,\Gamma(0,0,-1;w_2+w_3,w_1,u_2+u_3)\\
& +w_1\,[u_2\,(u_1^2-w_2^2+u_3^2)+u_3\,(u_1^2+u_2^2-w_3^2)]\,\Gamma(0,0,-1;u_2+u_3,w_1,w_2+w_3)\,. \qquad (16)
\end{aligned}
$$

Since

$$G(1,1,1;2,1,1) = -\frac{1}{2\,w_1}\,\frac{\partial g_0}{\partial w_1} \qquad (17)$$

Eq. (14) takes the form of a differential equation

$$\sigma\,\frac{\partial g_0}{\partial w_1}+\frac{1}{2}\,\frac{\partial \sigma}{\partial w_1}\,g_0+P=0\,, \qquad (18)$$

or

$$\sqrt{\sigma}\frac{\partial}{\partial w_1}(\sqrt{\sigma}\,g_0)+P=0\,. \qquad (19)$$

Analogous differential equation with respect to other parameters w_i and u_i can be obtain by appropriate permutation of arguments, using the tetrahedral symmetry of the function g_0. This differential equation has been previously derived in Ref. [16].

B. Calculation of g_0

g_0 was obtained in analytical form by Fromm and Hill in [9] in terms of combination of multivalued dilogarithmic function of complex arguments. Their formula was later simplified by Harris [10], who was able to eliminate the ambiguity of choosing the right branch of dilogarithmic function. In this work we use directly his formulae and allowed ourselves to verify its correctness. For this we used the solution of the differential equation in terms of one-dimensional integral. Namely, for $\sigma > 0$ we find

$$g_0 = \frac{1}{\sqrt{\sigma}}\biggl(\int_{w_1}^{\infty} dw_1'\,\frac{P(w_1')}{\sqrt{\sigma(w_1')}}+g_0\,\sqrt{\sigma}\big|_{w_1=\infty}\biggr), \qquad (20)$$

where

$$g_0\,\sqrt{\sigma}\big|_{w_1=\infty} \;=\; \frac{\mathrm{sgn}(u_1)}{2}\left[\frac{\pi^2}{6}+\frac{1}{2}\ln^2\!\left(\frac{u_1+u_3+w_2}{u_1+u_2+w_3}\right)+\mathrm{Li}_2\!\left(1-\frac{u_2+u_3+w_2+w_3}{u_1+u_3+w_2}\right)\right.$$
$$\left.+\mathrm{Li}_2\!\left(1-\frac{u_2+u_3+w_2+w_3}{u_1+u_2+w_3}\right)\right]. \qquad (21)$$

The above integration over w_1 is performed numerically using adapted Gaussian points for the logarithmic singularity at $w_1=\infty$, see Appendix of [8].

For $\sigma<0$ we find

$$g_0=\frac{1}{\sqrt{-\sigma}}\int_{\tilde{w}_1}^{w_1}dw_1'\frac{P(w_1')}{\sqrt{\sigma(w_1')}}, \qquad (22)$$

where

$$\sigma|_{w_1=\tilde{w}_1}=0\,. \qquad (23)$$

This integral is performed numerically using Gauss-Legendre quadrature in variable $t=\sqrt{w_1-\tilde{w}_1}$. In the simplest case when $\sigma=0$, g_0 can be readily obtained from Eq. (18)

$$g_0=-2\,P\left(\frac{\partial\sigma}{\partial\,w_1}\right)^{-1}. \qquad (24)$$

In almost all the cases, we achieved 28 digits accuracy using quadruple precision arithmetic with about 100 integration points.

C. Recurrence scheme

Since the direct evaluation of $g(n_1,n_2,n_3,n_4,n_5,n_6)$ in Eq. (9) is very time consuming, it is desirable to derive recurrence relations permitting integrals of larger index values to be expressed in terms of those with smaller indices. From differential equation (19) we can deduce much more than only integral representation for g_0. We notice that

$$g(n_1,n_2,n_3,n_4,n_5,n_6)=(-1)^{n_1+\ldots+n_6}\frac{\partial^{n_1}}{\partial w_1^{n_1}}\ldots\frac{\partial^{n_6}}{\partial u_3^{n_6}}\,g_0. \qquad (25)$$

Analogously, we introduce $\sigma(n_1,n_2,n_3,n_4,n_5,n_6)$ and $P(n_1,n_2,n_3,n_4,n_5,n_6)$ derived form σ and P respectively. If $\sigma\neq 0$ then equation (18) takes the form

$$\frac{1}{2}\,\sigma(1,0,0,0,0,0)\,g(0,0,0,0,0,0)+\sigma(0,0,0,0,0,0)\,g(1,0,0,0,0,0)=P(0,0,0,0,0,0)\,. \qquad (26)$$

Clearly this algebraic equation can be used to obtain $g(1,0,0,0,0,0)$ once $g(0,0,0,0,0,0)$ is evaluated from the direct Ref. [10] or integral (20,22) formulae. Now, we differentiate equation

(26) n_1-1, n_2, n_3, n_4, n_5, n_6 times over w_1,w_2, w_3, u_1, u_2, u_3 respectively

$$\sum_{i_1\ldots i_6=0}^{n_1\ldots n_6} \binom{n_1}{i_1}_{1/2} .. \binom{n_6}{i_6}_{1/2} \sigma(n_1-i_1,...,n_6-i_6)\, g(i_1,..,i_6) = P(n_1-1,n_2,n_3,n_4,n_5,n_6), \quad (27)$$

where we introduced a Newton-like notation

$$\binom{n}{0}_{1/2} = \frac{1}{2}, \quad \binom{n}{n}_{1/2} = 1, \quad \binom{n}{i}_{1/2} = \binom{n-1}{i}_{1/2} + \binom{n-1}{i-1}_{1/2}. \quad (28)$$

The above formula allows to express the integral $g(n_1,..,n_6)$ with nonzero n_1 through g-integrals with smaller index values. The expression for $\sigma(n_1,n_2,n_3,n_4,n_5,n_6)$ can be explicitely generated as derivatives of the polynomial σ, since they become zero for large values of indices n_i. P has a simple structure in terms of two-electron integrals Γ multiplied by a simple polynomial. Derivatives of these polynomials can be calculated explicitly. For Γ we use the recurrence scheme proposed by Korobov in [17].

Similar recurrence relations can be obtained from the differential equation like that in Eq. (18), but with respect to a different variable. We use them for the missing integrals with $n_1 = 0$ in the above w_1 scheme, thus completing the algorithm for all g-integrals starting from the master one g_0. We use them also to check the numerical stability of the recurrence scheme, as $g(1,1,1,1,1,1)$ can be obtained from the differential equation in any of these nonlinear parameters. As the result of this checking, we found out, that these recursions become unstable for small values of σ in Eq. (15) and as a remedy we used higher precision arithmetics in this particular region.

Recently, Harris obtained a family of recurrence formulas which enable construction of correlated exponential integrals with arbitrary pre-exponential powers of inter-particle distances [18]. In comparison to them, our recurrences are not equivalent. Harris's recurrences in the denominator involve additional powers of u_i and thus may become numerically unstable in the limit of small u_i. This however, requires numerical verification.

IV. OPTIMIZATION AND RESULTS

A. Hylleraas basis set

In Table I we present results obtained with Hylleraas functions for ground states of Li and Be$^+$, as they are much more accurate than previous ones in [5, 6]. In comparison to these former works, we used slightly different division into 5 sectors with its own set of nonlinear parameters as proposed in Ref. [5], and enhanced the optimization process by replacement of the minimization routine with CG Polak-Ribberie [19] with modifications of the line search algorithm [20]. In Ref. [6] we performed optimization in quadruple precision arithmetics. Here we observe that this precision is sufficient for determination of the nonrelativistic energy, but it is at the edge of numerical stability for analytical calculation of gradients in a basis set corresponding to $\Omega \equiv \max(\sum_i n_i) = 10$. Therefore, in this work we used sextuple precision arithmetics for the whole calculation. Obviously, optimization process in higher precision arithmetics takes more time, in this case it is about 5 times longer, but the accuracy is improved by at least an order of magnitude. The results presented in Table I are better than the former ones in 50 percent bigger basis set. Especially important is the numerical result for maximum set of 13944 carefully optimized functions, as this guarantees good quality of extrapolation to ∞ and estimation of an uncertainty.

TABLE I: Ground state nonrelativistic energies for the ground state of Li and Be^+ for various basis length with Hylleraas functions with comparison to earlier results including correlated Gaussian functions.

No. of terms	$E(\mathrm{Li})$	$E(\mathrm{Be}^+)$
2625	-7.478 060 323 570 509	-14.324 763 176 517 134
4172	-7.478 060 323 845 785	-14.324 763 176 746 865
6412	-7.478 060 323 898 268	-14.324 763 176 783 625
9576	-7.478 060 323 907 743	-14.324 763 176 789 144
13944	-7.478 060 323 909 560	-14.324 763 176 790 150
∞	-7.478 060 323 910 10(32)	-14.324 763 176 790 43(22)
9577[a]	-7.478 060 323 892 4	-14.324 763 176 766 8
∞[b]	-7.478 060 323 906(8)	-14.324 763 176 784(11)
10000[c]	-7.478 060 323 81	
8000[d]		-14.324 763 176 4
16764[e]	-7.478 060 323 451 9	

a - Ref. [5], b - Ref. [8], c - Ref. [21], d - Ref. [22], e - Ref. [23].

B. Correlated exponential basis set

We optimized the correlated exponential basis set incrementally starting from 1 up to 128 functions as shown in Tables II and III. At the starting point, the bigger basis was composed of

TABLE II: Nonrelativistic energies and Dirac-δ expectation values for the ground state of Li compared to results in Hylleraas basis

N	$E(\text{Li})$	$\delta E/E$	$\delta(r_a)$	$\delta(r_{ab})$
1	-7.453 907 382	$3.2\,10^{-3}$	13.631 327	0.614 377
2	-7.465 318 352	$1.7\,10^{-3}$	13.163 649	0.617 596
4	-7.476 009 761	$2.7\,10^{-4}$	13.691 905	0.586 670
8	-7.476 936 884	$1.5\,10^{-4}$	13.773 519	0.576 457
16	-7.478 052 680	$1.0\,10^{-6}$	13.840 924	0.545 361
32	-7.478 059 401	$1.2\,10^{-7}$	13.841 641	0.544 671
64	-7.478 060 050	$3.7\,10^{-8}$	13.842 162	0.544 526
96	-7.478 060 272	$7.0\,10^{-9}$	13.842 641	0.544 391
128	-7.478 060 301	$3.1\,10^{-9}$	13.842 618	0.544 368
Hyll. ∞	-7.478 060 323 9		13.842 610 8	0.544 324 6

previously optimized smaller basis and functions with randomly chosen nonlinear parameters under constraints resulting from interparticle separation conditions. Due to the presence of many nonlinear parameters, each function has its own set of 6 parameters, the optimization process was divided into steps. In a single step nonlinear parameters of only one function were optimized using Powell method without gradient. In one cycle all functions were optimized separately. For small basis several cycles were needed to achieve convergence at the 9th digit after the decimal point, and for larger set of functions number of cycles increases. Implementation is done in Fortran 95 in the quadruple precision arithmetics. In the region of typical values of w_a and u_a, we observe very good numerical stability of recurrence relations. However, in some particular cases during the minimization process, where σ in Eq. (15) becomes small and changes its sign, the sextuple precision arithmetics was needed, as the recurrence relations lose numerical precision. The region of small σ is numerically unstable and we have not found yet an alternative way of evaluation of $g(n_1, n_2, n_3, n_4, n_5, n_6)$ functions, by avoiding the presence of σ in the denominator. This would

TABLE III: Nonrelativistic energies and Dirac-δ expectation values for the ground state of Be^+ compared to results in Hylleraas basis

N	$E(\mathrm{Be}^+)$	$\delta E/E$	$\delta(r_a)$	$\delta(r_{ab})$
1	-14.269 015 274	$3.9\,10^{-3}$	34.584 174	1.726 084
2	-14.319 868 303	$3.4\,10^{-4}$	34.818 880	1.722 376
4	-14.324 097 014	$4.7\,10^{-5}$	35.163 138	1.598 315
8	-14.324 646 319	$8.2\,10^{-6}$	35.082 068	1.589 484
16	-14.324 730 041	$2.3\,10^{-6}$	35.118 928	1.583 949
32	-14.324 760 432	$1.9\,10^{-7}$	35.109 851	1.582 886
64	-14.324 762 726	$3.1\,10^{-8}$	35.102 872	1.581 131
96	-14.324 763 106	$4.9\,10^{-9}$	35.105 550	1.580 752
128	-14.324 763 141	$2.5\,10^{-9}$	35.105 342	1.580 583
Hyll. ∞	-14.324 763 176 8		35.105 055 7	1.580 538 6

be necessary for larger basis set and for states with the higher angular momentum. The quadruple precision arithmetics for the maximum basis of 128 functions guarantees high quality of the total wave function and the energy. We observe by comparison with Hylleraas results, that the relative accuracy of about 10^{-9} is achieved for energies, and about 5-6 significant digits for wave functions as indicated by the Dirac δ expectation values.

V. SUMMARY

We have performed accurate calculations of the ground state energy and the wave function of Li and Be^+ using explicitly correlated Hylleraas and exponential basis sets. Obtained results with Hylleraas basis are the most accurate to date, due to the use of large number of functions and efficient optimization. Results with correlated exponential functions are much less accurate, but they are the most efficient for the limited number of functions. The relative accuracy of about 10^{-9} for the nonrelativistic energy of the ground state of Li and Be^+ with only 128 functions confirms high effectiveness of this basis. Compared to both the Hylleraas and the Gaussians functions, it allows to reduce significantly the size of basis set. Using the computational method based on recurrence relations, we are able for the first time to perform optimization process with as much as 128 correlated exppnential functions and even more, if numerical instabilities for small σ are eliminated, probably by a different type of recurrences.

Our primary motivation for developing explicitly correlated exponential basis set is the efficient representation of the wave function in a small number of basis functions. We aim to apply them for numerical calculations of expectation values of operators corresponding to higher order relativistic and QED effects. They involve integrals with quadratic inverse powers of at least two interparticle distances. That kind of integrals are very complicated in the evaluation in the Hylleraas basis set and have not yet been worked out by the recursion method of the authors. However, there is a know algorithm by King [4], but his method is much too slow for a large scale computation. In the case of Slater integrals the problem would even much more complicated, but we think, one shall be able to perform this class of integrals numerically. Equiped with the large and accurately optimized Hylleraas basis [24], and with the short and flexible correlated exponential basis functions, we are aiming to determine $m\,\alpha^6$ and $m\,\alpha^7$ effects in the hyperfine and fine structure of lithium-like systems.

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Appendix A: Two-electron integrals

The two-electron integral Γ is defined by

$$\Gamma(n_1, n_2, n_3, \alpha, \beta, \gamma) \equiv \int \frac{d^3r_1}{4\,\pi} \int \frac{d^3r_2}{4\,\pi}\, e^{-\alpha\, r_1 - \beta\, r_2 - \gamma\, r_{12}}\, r_1^{n_1-1}\, r_2^{n_2-1}\, r_{12}^{n_3-1}. \tag{A1}$$

This integral takes very simple form when all $n_i = 0$

$$\Gamma(0,0,0,\alpha,\beta,\gamma) = \frac{1}{(\alpha+\beta)\,(\alpha+\gamma)\,(\beta+\gamma)}. \tag{A2}$$

The explicit form for $n_i > 0$ can be obtained by differentiation with respect to the corresponding nonlinear parameter, the result for negative n_i is obtained by an integration, for example

$$\Gamma(0,0,-1,\alpha,\beta,\gamma) = \frac{1}{(\alpha-\beta)\,(\alpha+\beta)}\ln\left(\frac{\gamma+\alpha}{\gamma+\beta}\right). \tag{A3}$$

For the actual evaluation of Γ we use compact reccurence relations from the work of Korobov [17].