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

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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 $-7.478\,060\,323\,910\,10(32)$ and $-14.324\,763\,176\,790\,43(22)$ 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 $\alpha$. 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 $\delta$.

Until now, the most accurate nonrelativistic wave function for lithiumlike 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 ($\sim 10\,000$) 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,

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

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] were able to optimize the correlated exponential function including linear terms in interparticle distances by the six-dimensional numerical integra-

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tion 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 follows. The master integral $g_0$ in Eq. (2) is calculated using Harris formula [10]. Integrals with higher powers of interparticle distances, are obtained using recursion relations, which are derived from differential Eq. (18). As a demonstration of this method, we performed numerical calculations of the nonrelativistic energy and of Dirac-$\delta$ 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 13 944 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 $\Psi$ is represented as a linear combination of $\psi$, the antisymmetrized product of the spatial functions $\phi$ and the spin function $\chi$,

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

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

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 $\alpha_i,\beta_i$ 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 $\alpha_1+\beta_2+\beta_3>\sqrt{2E_{\rm ion}}$, where $E_{\rm ion}$ is the ionization energy.

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

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

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

where $Ze$ 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

$$\begin{aligned}g(n_1,n_2,n_3,n_4,n_5,n_6) = \int\frac{d^3r_1}{4\pi}\int\frac{d^3r_2}{4\pi}\int\frac{d^3r_3}{4\pi} \\ \times e^{-w_1r_1-w_2r_2-w_3r_3-u_1r_{23}-u_2r_{13}-u_3r_{12}} \\ \times r_{23}^{n_1-1}r_{31}^{n_2-1}r_{12}^{n_3-1}r_1^{n_4-1}r_2^{n_5-1}r_3^{n_6-1},\end{aligned} \tag{9}$$

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 and insert thin space after:

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

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 nine corresponding integration by parts identities,

$$\begin{aligned}0 &\equiv \mathrm{id}(i,j) \\ &= \int d^3k_1\int d^3k_2\int d^3k_3\frac{\partial}{\partial\vec{k}_j} \\ &\quad\times[\vec{k}_i(k_1^2+u_1^2)^{-m_1}(k_2^2+u_2^2)^{-m_2}(k_3^2+u_3^2)^{-m_3}(k_{32}^2+w_1^2)^{-m_4} \\ &\quad\times(k_{13}^2+w_2^2)^{-m_5}(k_{21}^2+w_3^2)^{-m_6}],\end{aligned} \tag{11}$$

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:

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

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

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

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

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

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

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

where $\sigma$ is a polynomial

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

and $P$ is a the sum of two-electron integrals $\Gamma$,

$$\begin{aligned}P = {} & -u_1w_1[(u_1+w_2)^2-u_3^2]\Gamma(0,0,-1;u_1+w_2,u_3,u_2+w_1) - u_1w_1[(u_1+u_3)^2-w_2^2]\Gamma(0,0,-1;u_1+u_3,w_2,w_1+w_3)\\ & + [u_1^2w_1^2+u_2^2w_2^2-u_3^2w_3^2+w_1w_2(u_1^2+u_2^2-w_3^2)]\Gamma(0,0,-1;w_1+w_2,w_3,u_1+u_2)\\ & + [u_1^2w_1^2-u_2^2w_2^2+u_3^2w_3^2+w_1w_3(u_1^2+u_3^2-w_2^2)]\Gamma(0,0,-1;w_1+w_3,w_2,u_1+u_3)\\ & - [u_2(u_2+w_1)(u_1^2+u_3^2-w_2^2)-u_3^2(u_1^2+u_2^2-w_3^2)]\Gamma(0,0,-1;u_2+w_1,u_3,u_1+w_2)\\ & - [u_3(u_3+w_1)(u_1^2+u_2^2-w_3^2)-u_2^2(u_1^2+u_3^2-w_2^2)]\Gamma(0,0,-1;u_3+w_1,u_2,u_1+w_3)\\ & + w_1[w_2(u_1^2-u_2^2+w_3^2)+w_3(u_1^2+w_2^2-u_3^2)]\Gamma(0,0,-1;w_2+w_3,w_1,u_2+u_3)\\ & + w_1[u_2(u_1^2-w_2^2+u_3^2)+u_3(u_1^2+u_2^2-w_3^2)]\Gamma(0,0,-1;u_2+u_3,w_1,w_2+w_3).\end{aligned} \tag{16}$$

Since

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

Equation (14) takes the form of a differential equation,

$$\sigma\frac{\partial g_0}{\partial w_1} + \frac{1}{2}\frac{\partial\sigma}{\partial w_1}g_0 + P = 0 \tag{18}$$

or

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

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 formulas 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

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

where

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

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

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

where

$$\sigma\big|_{w_1=\tilde{w}_1} = 0. \tag{23}$$

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),

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

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 Eq. (19) we can deduce much more than only integral representation for $g_0$. We notice that

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

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 $\sigma$ and $P$ respectively. If $\sigma \neq 0$ then Eq. (18) takes the form

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

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 integrals (20) and (22) formulas. Now, we differentiate Eq. (26) $n_1 - 1$, $n_2$, $n_3$, $n_4$, $n_5$, $n_6$ times over $w_1$, $w_2$, $w_3$, $u_1$, $u_2$, and $u_3$, respectively,

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

where we introduced a Newton-like notation

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

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 explicitly generated as derivatives of the polynomial $\sigma$, since they become zero for large values of indices $n_i$. $P$ has a simple structure in terms of two-electron integrals $\Gamma$ multiplied by a simple polynomial. Derivatives of these polynomials can be calculated explicitly. For $\Gamma$ 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 $\sigma$ in Eq. (15) and as a remedy we used higher precision arithmetics in this particular region.

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 | $E$(Li) | $E$(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] Reference [5].
[b] Reference [8].
[c] Reference [21].
[d] Reference [22].
[e] Reference [23].

Recently, Harris obtained a family of recurrence formulas which enable construction of correlated exponential integrals with arbitrary pre-exponential powers of interparticle 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 five 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 $\Omega \equiv \max(\Sigma_i n_i) = 10$. 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 II. Nonrelativistic energies and Dirac-$\delta$ expectation values for the ground state of Li compared to results in Hylleraas basis.

| $N$ | $E$(Li) | $\delta E/E$ | $\delta(r_a)$ | $\delta(r_{ab})$ |
|---|---|---|---|---|
| 1 | −7.453 907 382 | $3.2\times10^{-3}$ | 13.631 327 | 0.614 377 |
| 2 | −7.465 318 352 | $1.7\times10^{-3}$ | 13.163 649 | 0.617 596 |
| 4 | −7.476 009 761 | $2.7\times10^{-4}$ | 13.691 905 | 0.586 670 |
| 8 | −7.476 936 884 | $1.5\times10^{-4}$ | 13.773 519 | 0.576 457 |
| 16 | −7.478 052 680 | $1.0\times10^{-6}$ | 13.840 924 | 0.545 361 |
| 32 | −7.478 059 401 | $1.2\times10^{-7}$ | 13.841 641 | 0.544 671 |
| 64 | −7.478 060 050 | $3.7\times10^{-8}$ | 13.842 162 | 0.544 526 |
| 96 | −7.478 060 272 | $7.0\times10^{-9}$ | 13.842 641 | 0.544 391 |
| 128 | −7.478 060 301 | $3.1\times10^{-9}$ | 13.842 618 | 0.544 368 |
| Hyll. ∞ | −7.478 060 323 9 | | 13.842 610 8 | 0.544 324 6 |

TABLE III. Nonrelativistic energies and Dirac-$\delta$ expectation values for the ground state of $\mathrm{Be}^+$ compared to results in Hylleraas basis.

| $N$ | $E(\mathrm{Be}^+)$ | $\delta E/E$ | $\delta(r_a)$ | $\delta(r_{ab})$ |
|---|---|---|---|---|
| 1 | −14.269 015 274 | $3.9\times10^{-3}$ | 34.584 174 | 1.726 084 |
| 2 | −14.319 868 303 | $3.4\times10^{-4}$ | 34.818 880 | 1.722 376 |
| 4 | −14.324 097 014 | $4.7\times10^{-5}$ | 35.163 138 | 1.598 315 |
| 8 | −14.324 646 319 | $8.2\times10^{-6}$ | 35.082 068 | 1.589 484 |
| 16 | −14.324 730 041 | $2.3\times10^{-6}$ | 35.118 928 | 1.583 949 |
| 32 | −14.324 760 432 | $1.9\times10^{-7}$ | 35.109 851 | 1.582 886 |
| 64 | −14.324 762 726 | $3.1\times10^{-8}$ | 35.102 872 | 1.581 131 |
| 96 | −14.324 763 106 | $4.9\times10^{-9}$ | 35.105 550 | 1.580 752 |
| 128 | −14.324 763 141 | $2.5\times10^{-9}$ | 35.105 342 | 1.580 583 |
| Hyll. ∞ | −14.324 763 768 9 | | 35.105 055 7 | 1.580 538 6 |

### 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 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 six 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 ninth 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 $\sigma$ 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 $\sigma$ 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 $\sigma$ in the denominator. This would 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 five to six significant digits for wave functions as indicated by the Dirac $\delta$ expectation values.

## V. SUMMARY

We have performed accurate calculations of the ground-state energy and the wave function of Li and $\mathrm{Be}^+$ 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 $\mathrm{Be}^+$ 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 exponential functions and even more, if numerical instabilities for small $\sigma$ 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. Equipped 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 lithiu-like systems.

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## APPENDIX: TWO-ELECTRON INTEGRALS

The two-electron integral $\Gamma$ is defined by

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

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 $\Gamma$ we use compact recurrence relations from the work of Korobov [17].

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