Ground state wave function and energy of the lithium atom

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Abstract

Highly accurate nonrelativistic ground-state wave function and energy of the lithium atom is obtained in the Hylleraas basis set. The leading relativistic corrections, as represented by Breit-Pauli Hamiltonian, are obtained in fair agreement with the former results. The calculational method is based on the analytical evaluation of Hylleraas integrals with the help of recursion relations.

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I. INTRODUCTION

Theoretical predictions for the energy levels of light few-electron atoms are much less accurate than for the hydrogenic systems. It is for two reasons. The nonrelativistic wave function has to include electron correlations to a high degree of accuracy. This can be achieved by using a Hylleraas basis set, but it is quite difficult to evaluate integrals with Hylleraas functions for three and more electrons. The second reason is the difficulty in the accurate treatment of relativistic and radiative corrections. The commonly used Dirac-Coulomb Hamiltonian for few-electron atoms does not include relativistic corrections properly as it cannot be derived from quantum electrodynamic theory and its continuous spectrum ranges from $-\infty$ to $+\infty$. One of the possible approaches is the derivation of an effective Hamiltonian [1] within the so called NRQED theory. Matrix elements of this Hamiltonian give exact correction to the energy at specified order in the fine structure constant α. However, this Hamiltonian becomes quite complicated at higher orders and for example $m\,\alpha^6$ corrections has been obtained for few low lying states of helium only [2, 3], not for lithium nor beryllium atoms.

Theoretical predictions for light hydrogen-like atoms are at present limited by uncertainty in higher-order two-loop electron self-energy corrections [4], which is a few kHz for the 1S state. For helium-like atoms predictions are approximately 10^3 times less accurate. Since, the nonrelativistic wave function was computed very accurately using Hylleraas [5] or exponential basis sets [6], the uncertainty in its levels comes mainly from the unknown $m\,\alpha^7$ terms. These corrections are currently under investigation in the context of helium 2^3P_J fine splitting. For lithium atoms, the Hylleraas functions give very accurate nonrelativistic wave function and energies [7], but the precise calculation of three-electron integrals with Hylleraas functions is very time consuming [8, 9], and so far no result for $m\,\alpha^6$ corrections have been obtained. For the beryllium atom the most accurate results have been obtained with explicitly correlated Gaussian functions [10]. Although it was possible to calculate accurately the leading relativistic and QED corrections [11], the final accuracy is limited by the nonrelativistic energy. Moreover, this basis cannot be used for higher order corrections since Gaussian wave functions do not fulfill the cusp condition.

So far the most accurate results for various states of the lithium atom were obtained by Yan and Drake in Ref. [7]. Here, we present even more accurate results for the lithium ground state, as a demonstration of an analytic method to compute the integrals with Hylleraas functions [12]. This new method is based on recursion relations between integrals with different powers of electronnucleus and inter-electron distances, which are fast and numerically stable for generating large basis sets. Our result for the ground state energy

$$E = -7.478\,060\,323\,904\,1(^{+10}_{-50})\,, \tag{1}$$

is significantly below the previous one, obtained in [7], which is $E = -7.478\,060\,323\,650\,3(71)$. As a further application of the analytic approach, we obtain the leading relativistic corrections to the binding energy by the calculation of the expectation value of Breit-Pauli Hamiltonian in Eq. (13). For this we used recursion relations for extended Hylleraas integrals with $1/r_{ij}^2$ and $1/r_i^2$ terms. They have been derived in [13] and in this work respectively.

In the next Section we construct the nonrelativistic wave function, similarly to Ref. [7] and obtain the ground state nonrelativistic energy and the wave function. In Sec. III we compute the leading relativistic correction as given by the Breit-Pauli Hamiltonian. In Sec. IV we derive recursion relations for Hylleraas integrals containing $1/r_i^2$ which among others, are necessary for relativistic matrix elements. In Sec. V we summarize our result and present prospects for calculation of higher order terms as well as the calculation of Hylleraas integrals for 4 and more electrons.

II. NONRELATIVISTIC WAVE FUNCTION AND ENERGY

In the construction of the wave function we closely follow the works of Yan and Drake in [7]. The ground state wave function Ψ is expressed as a linear combination of ψ, the antisymmetrized product of ϕ and the spin function χ

$$\psi = \mathcal{A}[\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3)\,\chi]\,, \tag{2}$$

$$\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3) = e^{-w_1\,r_1-w_2\,r_2-w_3\,r_3}\, r_{23}^{n_1}\, r_{31}^{n_2}\, r_{12}^{n_3}\, r_1^{n_4}\, r_2^{n_5}\, r_3^{n_6}\,, \tag{3}$$

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

with all n_i nonnegative integers and $w_i \in R_+$. The matrix element of the Hamiltonian H

$$H = \sum_{a=1}^{3}\left(\frac{\vec{p}_a^{\,2}}{2} - \frac{Z\,\alpha}{r_a}\right) + \sum_{a>b=1}^{3}\frac{\alpha}{r_{ab}}\,, \tag{5}$$

or of any spin independent operator can be expressed after eliminating spin variables, as

$$\langle\psi|H|\psi'\rangle = \langle 2\,\phi(1,2,3) + 2\,\phi(2,1,3) - \phi(3,1,2) - \phi(2,3,1) - \phi(1,3,2) - \phi(3,2,1)|\; H\,|\phi'(1,2,3)\rangle\,. \tag{6}$$

In this way the calculation of this matrix elements is brought to Hylleraas integrals, namely the integrals with respect to r_i of the form

$$f(n_1,n_2,n_3,n_4,n_5,n_6) = \int\frac{d^3r_1}{4\,\pi}\int\frac{d^3r_2}{4\,\pi}\int\frac{d^3r_3}{4\,\pi}\,e^{-w_1\,r_1-w_2\,r_2-w_3\,r_3}\; r_{23}^{n_1-1}\,r_{31}^{n_2-1}\,r_{12}^{n_3-1}\,r_1^{n_4-1}\,r_2^{n_5-1}\,r_3^{n_6-1}\,, \tag{7}$$

with nonnegative integers n_i. These are performed analytically for $n_1, n_2, n_3 = 0, 1$ [14] and by recursion relations for larger n_i using formulas derived in [12].

The total wave function is generated from all ϕ in Eq. (3) with n_i satisfying condition

$$\sum_{i=1}^{6} n_i \leq \Omega\,, \tag{8}$$

for Ω between 3 and 12. For each Ω we minimize energy with respect to the free parameters w_i in Eq. (3). We noticed that the use of only one set of w_i's does not lead to accurate results, therefore, following Yan and Drake [7], we divide the whole basis set into 5 sectors, each one with its own set of w_i's. This division goes as follows [7]

sector 1: all n_3, $\quad n_1 = 0$, $n_2 = 0$;
sector 2: all n_3, $\quad n_1 = 0$, $n_2 \neq 0$;
sector 3: all n_3, $\quad n_1 \neq 0$, $n_2 = 0$;
sector 4: $n_3 = 0$, $n_1 \neq 0$, $n_2 \neq 0$;
sector 5: $n_3 \neq 0$, $n_1 \neq 0$, $n_2 \neq 0$;

To avoid numerical instabilities, within each sector we drop the terms with $n_4 > n_5$ (or $n_4 < n_5$) and for $n_4 = n_5$ drop terms with $n_1 > n_2$ (or $n_1 < n_2$). This division allows for a significant improvements of nonrelativistic energies by optimization of all five sets of w_i's. These nonlinear parameters are obtained by Newton method of searching zeros using analytic derivatives

$$\frac{\partial E}{\partial w} = 2\left\langle\Psi\middle|H\middle|\frac{\partial\Psi}{\partial w}\right\rangle - 2\,E\,\left\langle\Psi\middle|\frac{\partial\Psi}{\partial w}\right\rangle\,. \tag{9}$$

In the numerical calculations, we use sextuple precision for recursion relations and quadruple precision for all other arithmetics to obtain the wave function and the energy up to $\Omega = 12$. The results obtained for ground state energies are presented in Table I. The penultimate row is a result of extrapolation to infinite length of the basis set, and the last raw are previous results of Yan and Drake [7]. The result for the nonrelativistic energy is significantly below the previous estimate [7] and indicates that extrapolation to infinite basis length does not always give the right result. In the

TABLE I: Ground state nonrelativistic energies and expectation values of Dirac δ-functions obtained using Drachman formulae [16] for various basis length.

Ω	No. of terms	$E(\Omega)$	$\sum_a \delta^3(r_a)$	$\sum_{a>b} \delta^3(r_{ab})$
3	50	-7.477 981 524 089 7	13.843 446 803 98	0.544 164 351 92
4	120	-7.478 052 334 642 2	13.842 288 641 67	0.544 331 564 16
5	256	-7.478 059 463 915 8	13.842 509 174 63	0.544 327 870 45
6	512	-7.478 060 208 663 7	13.842 637 966 67	0.544 325 260 63
7	918	-7.478 060 310 362 9	13.842 606 662 38	0.544 324 788 85
8	1589	-7.478 060 320 507 6	13.842 608 240 76	0.544 324 697 02
9	2625	-7.478 060 323 450 1	13.842 610 098 57	0.544 324 629 45
10	4172	-7.478 060 323 775 0	13.842 610 698 67	0.544 324 627 57
11	6412	-7.478 060 323 861 0	13.842 610 779 19	0.544 324 631 50
12	9576	-7.478 060 323 889 7	13.842 610 781 06	0.544 324 632 05
∞	∞	-7.478 060 323 904 1$\binom{+10}{-50}$	13.842 610 783 46(100)	0.544 324 633 96(50)
Refs. [7, 15]	∞	-7.478 060 323 650 3(71)	13.842 609 642 (55)	0.544 329 79(31)

same Table we present results for the Dirac δ functions, which also differs from previous results in [15]. We observe, the the number of significant digits for Dirac δ is increased by using Drachman formulae [16], namely

$$4\pi \left\langle \Psi \left|\delta^3(r_{ab})\right| \Psi \right\rangle \;=\; 2\left\langle \Psi \left|\frac{1}{r_{ab}}(E_\Psi - V)\right| \Psi \right\rangle - \sum_c \left\langle \vec{\nabla}_c\Psi \left|\frac{1}{r_{ab}}\right| \vec{\nabla}_c\Psi \right\rangle , \tag{10}$$

$$4\pi \left\langle \Psi \left|\delta^3(r_a)\right| \Psi \right\rangle \;=\; 4\left\langle \Psi \left|\frac{1}{r_a}(E_\Psi - V)\right| \Psi \right\rangle - 2\sum_c \left\langle \vec{\nabla}_c\Psi \left|\frac{1}{r_a}\right| \vec{\nabla}_c\Psi \right\rangle . \tag{11}$$

where V is a total potential energy in Eq. (5).

III. LEADING RELATIVISTIC CORRECTION TO BINDING ENERGY

The leading relativistic corrections to energy levels are given by the expectation values of the Breit-Pauli Hamiltonian $H^{(4)}$.

$$
\begin{aligned}
H^{(4)} \;=\; & \sum_a \left\{ -\frac{\vec{p}_a^{\,4}}{8\,m^3} + \frac{\pi\,Z\,\alpha}{2\,m^2}\,\delta^3(r_a) + \frac{Z\,\alpha}{4\,m^2}\,\vec{\sigma}_a\cdot\frac{\vec{r}_a}{r_a^3}\times\vec{p}_a \right\} \\
& + \sum_{a>b}\sum_b \left\{ -\frac{\pi\,\alpha}{m^2}\,\delta^3(r_{ab}) - \frac{\alpha}{2\,m^2}\,p_a^i\left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\right)p_b^j \right. \\
& -\frac{2\,\pi\,\alpha}{3\,m^2}\,\vec{\sigma}_a\cdot\vec{\sigma}_b\,\delta^3(r_{ab}) + \frac{\alpha}{4\,m^2}\frac{\sigma_a^i\,\sigma_b^j}{r_{ab}^3}\left(\delta^{ij} - 3\,\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^2}\right) + \frac{\alpha}{4\,m^2\,r_{ab}^3} \\
\times & \left.\Big[2\left(\vec{\sigma}_a\cdot\vec{r}_{ab}\times\vec{p}_b - \vec{\sigma}_b\cdot\vec{r}_{ab}\times\vec{p}_a\right) + \left(\vec{\sigma}_b\cdot\vec{r}_{ab}\times\vec{p}_b - \vec{\sigma}_a\cdot\vec{r}_{ab}\times\vec{p}_a\right)\Big]\right\}. \qquad (12)
\end{aligned}
$$

For states with vanishing angular momentum L and spin $S = 1/2$, the expectation value is simplified to the form

$$
\begin{aligned}
E^{(4)} \;=\; & \langle\Psi|H^{(4)}|\Psi\rangle = \left\langle \sum_a \left\{ -\frac{\vec{p}_a^{\,4}}{8\,m^3} + \frac{\pi\,Z\,\alpha}{2\,m^2}\,\delta^3(r_a) \right\} \right. \\
& \left. + \sum_{a>b}\sum_b \left\{ \frac{\pi\,\alpha}{m^2}\,\delta^3(r_{ab}) - \frac{\alpha}{2\,m^2}\,p_a^i\left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\right)p_b^j \right\} \right\rangle. \qquad (13)
\end{aligned}
$$

$E^{(4)}$ has already been obtained in works [15, 17]. Calculations of these matrix elements involves the usual Hylleraas integrals with all n_i nonnegative and extended integrals, namely with one parameter n_i equal to -1. The direct numerical method to calculate these integrals was presented in [8, 9]. Here we apply the analytic approach. Recursion relations for the case of n_1 or n_2 or n_3 equal to -1 have been obtained in [13]. Hylleraas integrals involving n_4 or n_5 or n_6 equal to -1 can in principle be obtained by the integration of the usual Hylleraas integral with respect to the corresponding parameter w_i [13]. However, some recursion relations may become unstable, for example in the case of $n_4 = -1$ the recursion in n_1 is numerically unstable for large w_1. To avoid this problem we derive in the next section stable recursion relations for extended Hylleraas integrals with $n_i = -1$ for $i = 4, 5, 6$. Numerical results for matrix elements of the Breit Hamiltonian using these recursion relations, has been presented in Table I and II. One observes that the lowest convergence is for the $-p^4/8$ term, and in spite of the differences for separate matrix elements, the total relativistic correction is in good agreement with the former result in [15].

TABLE II: Matrix elements of the Breit-Pauli Hamiltonian $H^{(4)}$ in atomic units.

Ω	$\sum_a -\frac{1}{8}\nabla_a^4$	$\sum_{a>b} \frac{1}{2}\nabla_a^i \big(\frac{\delta^{ij}}{r_{ab}} + \frac{r^i_{ab}\, r^j_{ab}}{r^3_{ab}}\big)\nabla_b^j$	$H^{(4)}$
3	-78.587 286 690 90	-0.438 632 545 84	-12.080 670 336 80
4	-78.557 331 859 61	-0.436 096 586 40	-12.053 111 944 61
5	-78.556 355 905 97	-0.435 697 344 91	-12.050 709 116 55
6	-78.556 714 503 43	-0.435 616 426 50	-12.050 388 076 38
7	-78.556 195 780 85	-0.435 602 362 02	-12.050 004 294 51
8	-78.556 162 642 13	-0.435 599 523 90	-12.049 961 162 16
9	-78.556 137 477 61	-0.435 598 217 44	-12.049 926 149 76
10	-78.556 135 734 01	-0.435 598 047 58	-12.049 921 414 27
11	-78.556 131 596 34	-0.435 597 963 57	-12.049 916 800 81
12	-78.556 128 632 10	-0.435 597 910 50	-12.049 913 772 96
∞	-78.556 112 88(200)	-0.435 597 765(50)	-12.049 897 86(200)
Ref. [15]	-78.556 135 55(148)	-0.435 598 001 (137)	-12.049 909 94(180)

IV. RECURSION RELATIONS FOR THREE-ELECTRON EXTENDED HYLLERAAS INTEGRAL WITH $1/r_1^2$

In the former section we calculated relativistic corrections. For this we needed various extended Hylleraas integrals, among them, integrals with $1/r_i^2$, which are being derived here. To obtain recursion relations for three-electron Hylleraas integral in Eq. (7), one first considers the integral G

$$\begin{aligned} G(m_1,m_2,m_3;m_4,m_5,m_6) \;=\; & \frac{1}{8\,\pi^6}\int d^3k_1\int d^3k_2\int d^3k_3\,(k_1^2+u_1^2)^{-m_1}\,(k_2^2+u_2^2)^{-m_2} \\ & (k_3^2+u_3^2)^{-m_3}\,(k_{32}^2+w_1^2)^{-m_4}\,(k_{13}^2+w_2^2)^{-m_5}\,(k_{21}^2+w_3^2)^{-m_6}, \end{aligned} \tag{14}$$

which is related to f by: $f(0,0,0,0,0,0) = G(1,1,1,1,1,1)|_{u_1=u_2=u_3=0}$. The following 9 integration by part identities are valid because the integral of the derivative of a function vanishing at infinity vanishes,

$$\begin{aligned} 0 \equiv \mathrm{id}(i,j) = & \int d^3k_1\int d^3k_2\int d^3k_3\,\frac{\partial}{\partial\,\vec k_i}\Big[\vec k_j\,(k_1^2+u_1^2)^{-1} \\ & (k_2^2+u_2^2)^{-1}\,(k_3^2+u_3^2)^{-1}(k_{32}^2+w_1^2)^{-1}\,(k_{13}^2+w_2^2)^{-1}\,(k_{21}^2+w_3^2)^{-1}\Big], \end{aligned} \tag{15}$$

where $i, j = 1, 2, 3$. The reduction of the scalar products from the numerator leads to the identities for the linear combination of the G functions. If any of the arguments is equal to 0, then G becomes a known two-electron Hylleraas type integral. These identities are used to derive various recursion relations. Here, we derive a set of recursions for the case when n_4, n_5 or n_6 is equal to -1. Let us assume that $n_4 = -1$. The analytic expression for $f(0, 0, 0, -1, n_5, n_6)$ involves powers of $w_2 - w_3$ in the denominator which is not very convenient in high precision numerical calculations. Instead, we use recursions for $f(0, 0, 0, 0, n_5, n_6)$ and numerically integrate with respect to w_1, namely

$$f(0,0,0,-1,n_5,n_6) = \int_{w_1}^{\infty} d\,w_1\, f(0,0,0,0,n_5,n_6)\,. \tag{16}$$

These recursions are derived as follows. We take $\mathrm{id}(i, i)$ with $i = 1, 2, 3$ and put $u_i = 0$. Resulting three equations are solved against three unknowns: $G(1, 1, 1, 2, 1, 1)$, $G(1, 1, 1, 1, 2, 1)$, and $G(1, 1, 1, 1, 1, 2)$. The solution for the last two G functions is the following

$$\begin{aligned} G(1,1,1,1,2,1) &= \frac{1}{w_2^2}\big[G(0,1,1,1,1,2) - G(1,0,1,1,1,2) - G(1,0,1,2,1,1) \\ &\quad +G(1,1,0,2,1,1) + G(1,1,1,1,1,1)/2\big]\,, \qquad (17) \\ G(1,1,1,1,1,2) &= \frac{1}{w_3^2}\big[G(0,1,1,1,2,1) + G(1,0,1,2,1,1) - G(1,1,0,1,2,1) \\ &\quad -G(1,1,0,2,1,1) + G(1,1,1,1,1,1)/2\big]\,. \qquad (18) \end{aligned}$$

By differentiation with respect to w_2 and w_3 one obtains the following recursion relations

$$\begin{aligned} f(0,0,0,0,n_5+1,n_6) &= \frac{1}{w_1\,w_2\,w_3}\big[(n_5+1)\,f(0,0,0,0,n_5,n_6)\,w_1\,w_3 \\ &\quad -(n_5+1)\,n_6\,f(0,0,0,0,n_5,n_6-1)\,w_1 \\ &\quad +n_6\,f(0,0,0,0,n_5+1,n_6-1)\,w_1\,w_2 \\ &\quad -n_6\,\Gamma(n_5,n_6-1,-1,w_1+w_2,w_3,0) \\ &\quad +n_6\,\Gamma(n_6-1,n_5,-1,w_1+w_3,w_2,0) \\ &\quad -\Gamma(n_6,n_5,-1,w_1+w_3,w_2,0)\,w_1 \\ &\quad +\Gamma(n_5+n_6,0,-1,w_2+w_3,w_1,0)\,w_1 \\ &\quad +\Gamma(n_5,n_6,-1,w_1+w_2,w_3,0)\,w_3 \\ &\quad -\Gamma(n_6,n_5,-1,w_1+w_3,w_2,0)\,w_3\big]\,, \end{aligned} \tag{19}$$

$$
\begin{aligned}
f(0,0,0,0,n_5,n_6+1) \;=\; & \frac{1}{w_1\,w_2\,w_3}\big[(n_6+1)\,f(0,0,0,0,n_5,n_6)\,w_1\,w_2 \\
& -n_5\,(n_6+1)\,f(0,0,0,0,n_5-1,n_6)\,w_1 \\
& +n_5\,f(0,0,0,0,n_5-1,n_6+1)\,w_1\,w_3 \\
& +n_5\,\Gamma(n_5-1,n_6,-1,w_1+w_2,w_3,0) \\
& -n_5\,\Gamma(n_6,n_5-1,-1,w_1+w_3,w_2,0) \\
& -\Gamma(n_5,n_6,-1,w_1+w_2,w_3,0)\,w_1 \\
& +\Gamma(n_5+n_6,0,-1,w_2+w_3,w_1,0)\,w_1 \\
& -\Gamma(n_5,n_6,-1,w_1+w_2,w_3,0)\,w_2 \\
& +\Gamma(n_6,n_5,-1,w_1+w_3,w_2,0)\,w_2\big]\,. \qquad (20)
\end{aligned}
$$

where Γ is a known [18–20] two-electron integral

$$\Gamma(n_1,n_2,n_3,\alpha_1,\alpha_2,\alpha_3) = \int\frac{d^3\,r_1}{4\,\pi}\int\frac{d^3\,r_2}{4\,\pi}\,e^{-\alpha_1\,r_1-\alpha_2\,r_2-\alpha_3\,r_{12}}\,r_1^{n_1-1}\,r_2^{n_2-1}\,r_{12}^{n_3-1}\,. \qquad (21)$$

The integration in Eq. (16) is performed numerically using adapted points and weights to the function which has logarithmic end-point singularity, namely

$$\int_0^1 dx\,\big[W_1(x)+W_2(x)\,\ln(x)\big]\,, \qquad (22)$$

where W_i are functions without any singularities. The method to obtain n adapted points and weights is presented in Appendix A, and this integral is exact for W_i being polynomials up to the order $n-1$. In the actual calculations we achieved at least 48 digits precision with only 100 points. Having obtained $f(0,0,0,-1,n_5,n_6)$ we construct recursion relations in n_1, n_2, and n_3. This is achieved in two steps. In the first step we use integration by parts in momentum representation Eq. (15), to form the following linear combination

$$
\begin{aligned}
\mathrm{id}(2,2)+\mathrm{id}(3,3)-\mathrm{id}(1,1) \;=\; & 2\,\big[G(0,1,1,1,1,2)+G(0,1,1,1,2,1)-G(1,0,1,1,1,2) \\
& -G(1,1,0,1,2,1)-G(1,1,1,1,1,1)/2-G(2,1,1,1,1,1)\,u_1^2 \\
& -G(1,1,1,1,1,2)\,(u_1^2-u_2^2)+G(1,2,1,1,1,1)\,u_2^2 \\
& -G(1,1,1,1,2,1)\,(u_1^2-u_3^2)+G(1,1,2,1,1,1)\,u_3^2 \\
& +G(1,1,1,2,1,1)\,w_1^2\big]=0\,. \qquad (23)
\end{aligned}
$$

We integrate with respect to w_1 and differentiate over u_1, u_2, u_3, w_2, and w_3 to obtain the main formula

$$
\begin{aligned}
f(n_1, n_2, n_3, -1, n_5, n_6) \;=\; & \frac{1}{(n_2+n_3-n_1)\, w_2\, w_3} \Big[\\
& (n_1-1)\, n_1\, n_5\, f(n_1-2, n_2, n_3, -1, n_5-1, n_6+1) \\
& +(n_1-1)\, n_1\, n_6\, f(n_1-2, n_2, n_3, -1, n_5+1, n_6-1) \\
& -(n_2-1)\, n_2\, n_5\, f(n_1, n_2-2, n_3, -1, n_5-1, n_6+1) \\
& -(n_3-1)\, n_3\, n_6\, f(n_1, n_2, n_3-2, -1, n_5+1, n_6-1) \\
& +(n_1-n_2-n_3)\, n_5\, n_6\, f(n_1, n_2, n_3, -1, n_5-1, n_6-1) \\
& +n_5\, n_6\, f(n_1, n_2, n_3, 0, n_5-1, n_6-1)\, w_1 \\
& -(n_1-1)\, n_1\, f(n_1-2, n_2, n_3, -1, n_5, n_6+1)\, w_2 \\
& +(n_2-1)\, n_2\, f(n_1, n_2-2, n_3, -1, n_5, n_6+1)\, w_2 \\
& -(n_1-n_2-n_3)\, n_6\, f(n_1, n_2, n_3, -1, n_5, n_6-1)\, w_2 \\
& -n_6\, f(n_1, n_2, n_3, 0, n_5, n_6-1)\, w_1\, w_2 \\
& -(n_1-1)\, n_1\, f(n_1-2, n_2, n_3, -1, n_5+1, n_6)\, w_3 \\
& +(n_3-1)\, n_3\, f(n_1, n_2, n_3-2, -1, n_5+1, n_6)\, w_3 \\
& -(n_1-n_2-n_3)\, n_5\, f(n_1, n_2, n_3, -1, n_5-1, n_6)\, w_3 \\
& -n_5\, f(n_1, n_2, n_3, 0, n_5-1, n_6)\, w_1\, w_3 \\
& +f(n_1, n_2, n_3, 0, n_5, n_6)\, w_1\, w_2\, w_3 \\
& +n_6\, \delta(n_3)\, \Gamma(n_5-1, n_6-1, n_1+n_2-1, w_1+w_2, w_3, 0) \\
& +n_5\, \delta(n_2)\, \Gamma(n_6-1, n_5-1, n_1+n_3-1, w_1+w_3, w_2, 0) \\
& -n_5\, \delta(n_1)\, \Gamma(n_5+n_6-1, -1, n_2+n_3-1, w_2+w_3, w_1, 0) \\
& -n_6\, \delta(n_1)\, \Gamma(n_5+n_6-1, -1, n_2+n_3-1, w_2+w_3, w_1, 0) \\
& -\delta(n_2)\, \Gamma(n_6, n_5-1, n_1+n_3-1, w_1+w_3, w_2, 0)\, w_2 \\
& +\delta(n_1)\, \Gamma(n_5+n_6, -1, n_2+n_3-1, w_2+w_3, w_1, 0)\, w_2 \\
& -\delta(n_3)\, \Gamma(n_5, n_6-1, n_1+n_2-1, w_1+w_2, w_3, 0)\, w_3 \\
& +\delta(n_1)\, \Gamma(n_5+n_6, -1, n_2+n_3-1, w_2+w_3, w_1, 0)\, w_3 \Big]\,. \qquad (24)
\end{aligned}
$$

This general formula does not work in the case $n_1 = n_2+n_3$. In the second step we use integration by part identities in the coordinate space to fill this hole. We limit ourselves only to a special case of these identities in the form

$$0 = \mathrm{id}(i) \equiv \int d^3 r_1 \int d^3 r_2 \int d^3 r_3 \left(g\, \nabla_i^2 h - h\, \nabla_i^2 g\right), \tag{25}$$

where

$$\begin{aligned} g &= e^{-w_1 r_1 - w_2 r_2 - w_3 r_3}\, r_1^{n_4-1}\, r_2^{n_5-1}\, r_3^{n_6-1}, \\ h &= r_{23}^{n_1-1}\, r_{31}^{n_2-1}\, r_{12}^{n_3-1}. \end{aligned} \tag{26}$$

The identities $\mathrm{id}(2)$ and $\mathrm{id}(3)$

$$\begin{aligned} f(n_1,n_2,n_3,-1,n_5,n_6) &= \big[(n_1-1)\,(n_1+n_3-1)\,f(n_1-2,n_2,n_3,-1,n_5,n_6) \\ &\quad -(n_1-1)\,(n_3-1)\,f(n_1-2,n_2+2,n_3-2,-1,n_5,n_6) \\ &\quad +(n_3-1)\,(n_1+n_3-1)\,f(n_1,n_2,n_3-2,-1,n_5,n_6) \\ &\quad -(n_5-1)\,n_5\,f(n_1,n_2,n_3,-1,n_5-2,n_6) \\ &\quad +2\,n_5\,f(n_1,n_2,n_3,-1,n_5-1,n_6)\,w_2 \\ &\quad +\delta(n_5)\,\Gamma(n_1+n_6-1,n_3-2,n_2,w_3,w_1,0)\big]/w_2^2, \qquad (27) \\ f(n_1,n_2,n_3,-1,n_5,n_6) &= \big[-(n_1-1)\,(n_2-1)\,f(n_1-2,n_2-2,n_3+2,-1,n_5,n_6) \\ &\quad +(n_1-1)\,(n_1+n_2-1)\,f(n_1-2,n_2,n_3,-1,n_5,n_6) \\ &\quad +(n_2-1)\,(n_1+n_2-1)\,f(n_1,n_2-2,n_3,-1,n_5,n_6) \\ &\quad -(n_6-1)\,n_6\,f(n_1,n_2,n_3,-1,n_5,n_6-2) \\ &\quad +2\,n_6\,f(n_1,n_2,n_3,-1,n_5,n_6-1)\,w_3 \\ &\quad +\delta(n_6)\,\Gamma(n_2-2,n_1+n_5-1,n_3,w_1,w_2,0)\big]/w_3^2, \qquad (28) \end{aligned}$$

replace the main recursion in Eq. (24) for the case $n_1 = n_2 + n_3$ and can be used also for all other n_i under conditions that $n_1 > 0$, $n_3 > 0$ or $n_1 > 0$, $n_2 > 0$, respectively.

V. SUMMARY

We have demonstrated the advantages of the analytic approach to three-electron Hylleraas integrals by the calculation of nonrelativistic energy of the ground state lithium atom and the leading relativistic corrections. The achieved accuracy is the best to date and this is mainly due to the use of much larger basis sets. In fact it is possible to perform calculation with $\Omega > 12$ by using sextuple precision arithmetics. The typical evaluation time in sextuple precision for $\Omega = 12$ is 24 hours on 2.4 GHz Opteron, and most of the time is devoted to LU decomposition.

Having precise wave functions, we have calculated leading relativistic corrections and the results only partially agree with that of Yan and Drake [15] and of King [17]. We are now in position to calculate higher order, namely $m\,\alpha^6$ relativistic and QED corrections, for example to the lithium ground state hyperfine splitting [21]. However, this involves more complicated Hylleraas integrals containing two factors among $1/r_i^2$ and $1/r_{ij}^2$, which have not yet been worked out by the recursion methods of the authors.

Even more interesting is the possible extension of this analytic method to beryllium and beryllium-like ions, the 4-electron systems. The use of large Hylleraas basis set will allow for a high precision calculation of the wave function, energies and transition rates. For example, knowing the isotope shifts, one can obtain charge radii as for the lithium isotope [22]. General Hylleraas integrals for 4-electron systems has not yet been worked out [23, 24]. The so called double linked basis set, the functions with at most two odd powers of r_{ij} have been used by Büsse *et al* in [25] to obtain an accurate nonrelativistic energy, but still less accurate than the result of Komasa in [10]. It has not yet been attempted to calculate relativistic corrections with Hylleraas functions as they involve even more difficult integrals. We think, the integration by part technique, should allow for the derivation of compact formulas for all 4-electron Hylleraas integrals.

Our primary motivation for developing Hylleraas basis set is the calculation of higher order relativistic and QED effects, and to demonstrate that standard techniques used in relativistic quantum chemistry, which are based on the multi-electron Dirac-Coulomb Hamiltonian are not correct for principal reasons. This Hamiltonian does not not include properly negative energy states. The correct treatment has to be based on quantum electrodynamics and several very accurate results for few electron ions have already been obtained within the so called $1/Z$ expansion [26–28]. Nevertheless, there is no yet formalism which allows for systematic inclusion of negative energy states and QED effects for many electron atoms.

VI. ACKNOWLEDGMENTS

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APPENDIX A: QUADRATURE WITH LOGARITHMIC END-POINT SINGULARITY

Consider the integral

$$I = \int_0^1 dx \left[W_1(x) + \ln(x)\, W_2(x)\right], \tag{A1}$$

where W_i are arbitrary polynomials of maximal degree $n-1$. We would like to find n nodes x_i and n weights w_i such that

$$I = \sum_{i=1}^{n} w_i \left[W_1(x_i) + \ln(x_i)\, W_2(x_i)\right]. \tag{A2}$$

In general it is a difficult numerical problem to find a solution of corresponding $2\,n$ nonlinear equations with $j = 1, n$

$$\int_0^1 dx\, x^{j-1} = \frac{1}{j} \;=\; \sum_{i=1}^{n} w_i\, x_i^j\,, \tag{A3}$$

$$\int_0^1 dx\, x^{j-1}\, \ln x = -\frac{1}{j^2} \;=\; \sum_{i=1}^{n} w_i\, x_i^j\, \ln x_j\,. \tag{A4}$$

The work [29] solves this problem and proves that w_i are all positive. The solution is as follows.

One defines $2\,n$ functions ϕ_i

$$\phi_k(x) \;=\; x^{k-1}, \text{ for } k = 1, n \tag{A5}$$

$$\phi_k(x) \;=\; x^{k-1}\, \ln x, \text{ for } k = n+1, 2\,n\,. \tag{A6}$$

Consider n points x_i which are not necessarily the solution of Equations (A3,A4) but are close to them, and construct another set of functions σ_i, η_i, for $i = 1, n$

$$\sigma_i(x) = \sum_{j=1}^{2\,n} \alpha_{ij}\, \phi_j(x)\,, \tag{A7}$$

$$\eta_i(x) = \sum_{j=1}^{2\,n} \beta_{ij}\, \phi_j(x)\,, \tag{A8}$$

such that

$$\begin{aligned}
\sigma_i(x_k) &= 0\,, \\
\sigma_i'(x_k) &= \delta_{ik}\,, \\
\eta_i(x_k) &= \delta_{ik}\,, \\
\eta_i'(x_k) &= 0\,.
\end{aligned} \tag{A9}$$

The set of conditions (A9) uniquely determines the matrices α_{ij} and β_{ij}. If x_k are nodes, then

$$\begin{aligned}
\int_0^1 dx\,\sigma_i(x) &= 0\,, \\
\int_0^1 dx\,\eta_i(x) &= w_i\,.
\end{aligned} \tag{A10}$$

If x_k are not exactly the nodes, but are sufficiently close, then according to work [29], the iteration $x_i \to \tilde{x}_i$

$$\tilde{x}_i = x_i + \frac{\int_0^1 dx\,\sigma_i(x)}{\int_0^1 dx\,\eta_i(x)}\,, \tag{A11}$$

converges to nodes, the solution of Eqs. (A3,A4). The only problem now, is to find a sufficiently good initial values for x_i. For this one constructs a homotopy $\phi_k(x,t)$ such that

$$\begin{aligned}
\phi_k(x,t) &= x^{k-1} \text{ for } k = 1, n\,, \\
\phi_k(x,t) &= (1-t)\sqrt{x} + t\,x^{k-1-n}\,\ln(x) \text{ for } k = n+1, 2\,n\,.
\end{aligned} \tag{A12}$$

At $t = 0$, $\phi(x,0)$ are polynomials in $\sqrt{x}$, therefore one obtains $x_i = y_i^2$ where y_i are nodes for Gauss-Legendre quadrature. By slowly changing t from 0 one finds the solution at $t = 1$. In the actual numerical calculations we found that the steps $t_i = i/100$ were sufficiently small for the above iteration to converge. This generalized Gaussian quadrature can also be constructed for other types of functions including various, even nonintegrable singularities.