Applications of four-body exponentially correlated functions

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We demonstrate the applicability of four-body exponentially correlated functions for the accurate calculations of relativistic effects in lithium-like atoms and present results for matrix elements of various operators which involve negative powers of interparticle distances.

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I. INTRODUCTION

In the accurate evaluation of atomic energy levels not only the nonrelativistic energy, but also relativistic and QED effects have to be calculated with the high precision. The only approach which consistently accounts for all corrections in small atomic systems is the one based on the expansion of the energy in the fine structure constant α

$$E = m\left[\alpha^2\,\mathcal{E}^{(2)}+\alpha^4\,\mathcal{E}^{(4)}+\alpha^5\,\mathcal{E}^{(5)}+\alpha^6\,\mathcal{E}^{(6)}+\alpha^7\,\mathcal{E}^{(7)}+\ldots\right]. \tag{1}$$

Each term in this expansion can be expressed as the expectation value of some effective Hamiltonian with the nonrelativistic wave function. Namely $\mathcal{E}^{(2)}$ is the nonrelativistic energy (in atomic units), $\mathcal{E}^{(4)}$ is the relativistic correction, which for states with the vanishing angular momentum is the expectation value of $H^{(4)}$ in Eq. (4). $\mathcal{E}^{(5)}$ and higher order corrections are expressed in terms of matrix elements of some more complicated operators. They have been calculated for low lying states of the helium atom and helium-like ions up to the order $m\,\alpha^6$ [1], and for the particularly important case of 2^3P_J splitting up to the order $m\,\alpha^7$ [2]. One of the sources of this achievement was the flexibility of the explicitly correlated exponential basis set, which due to its correct analytic properties, makes possible accurate evaluation of matrix elements with complicated and singular operators.

In the case of the lithium atom and light lithium-like ions all corrections up to $\mathcal{E}^{(5)}$ have been accurately calculated [3–5], but not that of higher orders. The principal reason for the much slower progress for three-electron atoms is the difficulty in handling integrals with explicitly correlated functions. The commonly used explicitly correlated Gaussian functions do not have right analytic properties, for example they do not satisfy the cusp condition, and therefore cannot be used for the calculation of higher order relativistic corrections, like $\mathcal{E}^{(6)}$. Hylleraas basis functions have the right analytic behavior: the accuracy in solving the Schrödinger equation is the highest among all other basis functions, but it is difficult to handle Hylleraas integrals involving quadratic negative powers of two different interparticle distances. Such integrals appear in the evaluation of $\mathcal{E}^{(6)}$ and for this reason other basis functions have been investigated in the literature.

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Zotev and Rebane in [6] were the first to apply exponentially correlated functions

$$\phi(\vec r_1,\vec r_2,\vec r_3) = e^{-\alpha_1\,r_1-\alpha_2\,r_2-\alpha_3\,r_3-\beta_1\,r_{23}-\beta_2\,r_{13}-\beta_3\,r_{12}}\,, \tag{2}$$

in variational calculations for Ps_2 and the other exotic molecules. They have found a simplified formula for matrix elements of the nonrelativistic Hamiltonian and presented numerical results of variational calculations with a few basis functions. In our recent paper [7] we presented an efficient algorithm for the evaluation of integrals involving powers of r_i and r_{ij}

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

with n_a being nonnegative integers. It is based on recursion relations which start from the master Fromm-Hill integral [8, 9], where all $n_a = 0$. We have applied this algorithm to the variational calculations of the ground state of Li and Be^+ with up to 128 functions. The comparison of nonrelativistic energies with the ones obtained with much larger number of Hylleraas functions indicates that the exponential representation of the three-electron wave function is very efficient.

The class of integrals in Eq. (3) with nonnegative n_a is sufficient for nonrelativistic energies [6, 7]. However, it is not sufficient to calculate the leading relativistic effects described by Breit-Pauli Hamiltonian, which for S-states takes the form

$$\begin{aligned} H^{(4)} \;=\; & \sum_a\biggl\{-\frac{\vec p_a^{\,4}}{8\,m^3}+\frac{\pi\,Z\,\alpha}{2\,m^2}\,\delta^3(r_a)\biggr\} \\ & +\sum_{a>b}\biggl\{\frac{\pi\,\alpha}{m^2}\,\delta^3(r_{ab})-\frac{\alpha}{2\,m^2}\,p_a^i\left(\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\right)p_b^j\biggr\}. \end{aligned} \tag{4}$$

Its matrix elements involve an extended class of integrals with exactly one of n_a equal to -1, and all others are nonnegative, while that for leading QED effects involve integrals with $n_a = -2$. This is well known from calculations with Hylleraas basis functions, where all u_a in Eq. (3) are equal to zero. Hylleraas extended integrals of that kind have been extensively studied in [10–17] using multipole-type of expansions and recently by present authors using analytical recurrence approach [18, 19].

Both methods had been successfully applied in high-precision calculations of leading relativistic and QED corrections to the energy of lithiumlike systems [3, 19, 20]. There are no similar studies for exponentially correlated integrals to the best our knowledge, and for the first time we present them in this work.

In the calculation of relativistic and QED effects beyond leading order, $\mathcal{E}^{(6)}$ for example, another class of integrals appears with two quadratic inverse powers of interparticle distances. There are only few studies in the literature for three-electron Hylleraas integrals [12, 13, 17]. The algorithm by King [17] seems to be too slow for a large scale computation, where integrals with $\Omega = \sum_a n_a$ of order 30 have to be performed. The evaluation of these integrals is quite difficult with the recursion method and have not yet been worked out so far.

In the case of exponentially correlated integrals the problem seems to be even more severe, since the master integral with $u_a \neq 0$ is much more complicated. However, being able to optimize nonlinear parameters of each function independently, one does not need to use large powers of interparticle distances in the basis set. For S-states it is sufficient to use functions of the form (2). In such a case, having an analytical and thus accurate method for $g(n_1, n_2, n_3, n_4, n_5, n_6)$ with nonnegative n_a, inverse negative powers of the interparticle distance can be obtained by the numerical integration with respect to the corresponding parameter w_a or u_a. It however requires a good control of numerical accuracy of the master integral and of recursion relations in Eq. (10). The usage the higher precision arithmetic is essential in some critical areas of the integration. A key feature of our numerical integration strategy is the adapted quadrature, which allows one to get the high accuracy with a very small number of points.

We demonstrate our method on examples with expectation value of various operators on lithium ground state. Results obtained for matrix elements involving single $n_a = -1$ are compared to the most accurate ones obtained with the Hylleraas basis set. Good numerical convergence of results for matrix elements involving two negative powers, for example $1/(r_a^2 r_b^2), 1/(r_a^2 r_{ab}^2), 1/(r_{ab}^2 r_{bc}^2)$. indicate that this integration approach can be used for the calculation of higher order relativistic corrections, for example $m\,\alpha^6$ and $m\,\alpha^7$ effects in the hyperfine and fine structure of lithium-like systems.

II. CALCULATION OF INTEGRALS

A. Tetrahedral symmetry

An important property of integrals defined in Eq. (3) is the tetrahedral symmetry which is equivalent to the permutation group S_4. We can assign vertices 1,2,3 to the electrons and 0 to the nucleus as shown in Fig. (1), and to edges we assign u_a, w_a and n_a parameters of a given integral. The symmetry group S_4 corresponds to 24 renumbering of vertices 0,1,2, and 3, which means also a relevant change of parameters on the edges. The generated symmetry relations allow us to reduce the number of recurrence formulas for Slater integrals. It is necessary to derive only one recurrence scheme, and the formulas for the advancement in the other indices can then be obtained by application of the S_4 symmetry.

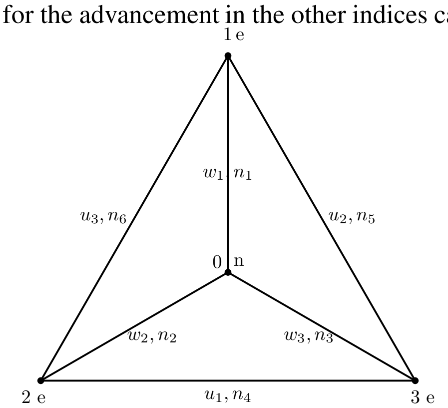

FIG. 1: Tetrahedron representing the integral from Eq. (2)

B. Basic integrals

The evaluation method for $g(n_1, n_2, n_3, n_4, n_5, n_6)$ for the basis class with all nonnegative n_a was first presented by Harris in [21] and later by us in Ref. [7]. Here we present only a short summary, which is needed for the evaluation of the extended integrals. The master integral $g_0 \equiv g(0,0,0,0,0,0)$ satisfies the following differential equation

$$\sigma\,\frac{\partial g_0}{\partial w_1} + \frac{1}{2}\,\frac{\partial \sigma}{\partial w_1}\,g_0 + P = 0\,, \tag{5}$$

where the S_4 symmetric polynomial σ is of the form

$$\begin{aligned}\sigma \;=\; & u_1^2\,u_2^2\,w_3^2 + u_2^2\,u_3^2\,w_1^2 + u_1^2\,u_3^2\,w_2^2 + w_1^2\,w_2^2\,w_3^2 \\ & + u_1^2\,w_1^2\,(u_1^2 + w_1^2 - u_2^2 - u_3^2 - w_2^2 - w_3^2) \\ & + u_2^2\,w_2^2\,(u_2^2 + w_2^2 - u_1^2 - u_3^2 - w_1^2 - w_3^2) \\ & + u_3^2\,w_3^2\,(u_3^2 + w_3^2 - u_2^2 - u_1^2 - w_1^2 - w_2^2)\,,\end{aligned} \tag{6}$$

and function P is given by

$$
\begin{aligned}
P \;=\; & -u_1\,w_1\,[(u_1+w_2)^2-u_3^2]\,\Gamma(0,0,-1;u_1+w_2,u_3,u_2+w_1)\\
& -u_1\,w_1\,[(u_1+u_3)^2-w_2^2]\,\Gamma(0,0,-1;u_1+u_3,w_2,w_1+w_3)\\
& +[u_1^2\,w_1^2+u_2^2\,w_2^2-u_3^2\,w_3^2+w_1\,w_2\,(u_1^2+u_2^2-w_3^2)]\,\Gamma(0,0,-1;w_1+w_2,w_3,u_1+u_2)\\
& +[u_1^2\,w_1^2-u_2^2\,w_2^2+u_3^2\,w_3^2+w_1\,w_3\,(u_1^2+u_3^2-w_2^2)]\,\Gamma(0,0,-1;w_1+w_3,w_2,u_1+u_3)\\
& -[u_2\,(u_2+w_1)\,(u_1^2+u_3^2-w_2^2)-u_3^2\,(u_1^2+u_2^2-w_3^2)]\,\Gamma(0,0,-1;u_2+w_1,u_3,u_1+w_2)\\
& -[u_3\,(u_3+w_1)\,(u_1^2+u_2^2-w_3^2)-u_2^2\,(u_1^2+u_3^2-w_2^2)]\,\Gamma(0,0,-1;u_3+w_1,u_2,u_1+w_3)\\
& +w_1\,[w_2\,(u_1^2-u_2^2+w_3^2)+w_3\,(u_1^2+w_2^2-u_3^2)]\,\Gamma(0,0,-1;w_2+w_3,w_1,u_2+u_3)\\
& +w_1\,[u_2\,(u_1^2-w_2^2+u_3^2)+u_3\,(u_1^2+u_2^2-w_3^2)]\,\Gamma(0,0,-1;u_2+u_3,w_1,w_2+w_3)\,, \qquad (7)
\end{aligned}
$$

and where the two-electron integral Γ is

$$
\begin{aligned}
\Gamma(n_1,n_2,n_3,\alpha,\beta,\gamma) \;&\equiv\; \int\frac{d^3r_1}{4\,\pi}\int\frac{d^3r_2}{4\,\pi}\;r_1^{n_1-1}\,r_2^{n_2-1}\,r_{12}^{n_3-1}\\
&\quad\times e^{-\alpha\,r_1-\beta\,r_2-\gamma\,r_{12}}\,, \qquad (8)\\
\Gamma(0,0,-1,\alpha,\beta,\gamma) \;&=\; \frac{1}{(\alpha-\beta)\,(\alpha+\beta)}\,\ln\!\left(\frac{\gamma+\alpha}{\gamma+\beta}\right). \qquad (9)
\end{aligned}
$$

The recurrence relations for the integrals g result from the differential equation (5) and can be written in a compact form as

$$
\sum_{i_1\ldots i_6=0}^{n_1\ldots n_6}\binom{n_1}{i_1}_{1/2}\!\!..\binom{n_6}{i_6}_{1/2}\sigma(n_1-i_1,...,n_6-i_6)\,g(i_1,..,i_6)
= P(n_1-1,n_2,n_3,n_4,n_5,n_6), \qquad (10)
$$

where we use a Newton-like symbol notation

$$
\binom{n}{0}_{1/2}=\frac{1}{2},\quad \binom{n}{n}_{1/2}=1,
$$
$$
\binom{n}{i}_{1/2}=\binom{n-1}{i}_{1/2}+\binom{n-1}{i-1}_{1/2}, \qquad (11)
$$

and

$$
\begin{aligned}
P(n_1,n_2,n_3,n_4,n_5,n_6) \;&=\; (-1)^{n_1+\ldots+n_6}\,\frac{\partial^{n_1}}{\partial w_1^{n_1}}\cdots\frac{\partial^{n_6}}{\partial u_3^{n_6}}\,P, \qquad (12)\\
\sigma(n_1,n_2,n_3,n_4,n_5,n_6) \;&=\; (-1)^{n_1+\ldots+n_6}\,\frac{\partial^{n_1}}{\partial w_1^{n_1}}\cdots\frac{\partial^{n_6}}{\partial u_3^{n_6}}\,\sigma. \qquad (13)
\end{aligned}
$$

The relation (10) allows one to express the integral $g(n_1,..,n_6)$ with positive index n_1 through g-integrals with smaller nonnegative indices. Derivatives of polynomials in $P(n_1,n_2,n_3,n_4,n_5,n_6)$ and $\sigma(n_1,n_2,n_3,n_4,n_5,n_6)$ are calculated explicitly. The master integral $g(0,0,0,0,0,0)$ and the two-electron integrals Γ are needed to start the evaluation of $g(n_1,n_2,n_3,n_4,n_5,n_6)$ from recursion relations. For $g(0,0,0,0,0,0)$ we implemented the formula of Fromm-Hill [8] in the version improved by Harris [9]. The calculation of the two-electron Γ functions has been described in detail in Refs. [22–24]. In Eq. (10) the parameter w_1 is distinguished on the right-hand side. We can define the same recurrence relations with other variables w_a, u_a from expressions (7), (10), and (13) by applying the tetrahedral symmetry.

The proposed recurrence scheme allows us to calculate integrals from higher shells Ω very efficiently. In Table I we present values in two reference points introduced by Fromm and Hill in Ref. [8]. These are the standard reference point (SRP) $w_a=u_a=1$ where $\sigma=-2$ and the auxiliary reference point (ARP) $w_a=1, u_a=0$ with $\sigma=1$. Values for the last one can be compared to the known Hylleraas results. All presented digits are significant, which confirms the very good stability of the recursions at least at these reference points.

The integrals $g(n_1,n_2,n_3,n_4,n_5,n_6)$ with σ is close to zero are difficult to evaluate because the recurrence relations are numerically unstable. Following Harris' studies on the master integral $g(0,0,0,0,0,0)$ in Ref. [9], we considered $w_a=1, u_a=\alpha$ close to $\alpha=3^{-1/2}$ where σ is exactly equal to zero. As an example we present in Table II values for

TABLE I: Exponentially correlated integrals in SRP and ARP reference points

	ARP : $u_a = 0,\ w_a = 1$	SRP : $u_a = w_a = 1$
$g(0,0,0,0,0,0)$	2.208 310 154 388 618 874 536 424 144 0 10^{-1}	2.173 757 633 275 034 284 081 325 213 9 10^{-2}
$g(1,0,0,0,0,0)$	2.208 310 154 388 618 874 536 424 144 0 10^{-1}	1.086 878 816 637 517 142 040 662 607 0 10^{-2}
$g(1,1,0,0,0,0)$	2.587 328 950 655 650 145 088 210 000 9 10^{-1}	7.126 296 734 072 723 436 203 022 296 4 10^{-3}
$g(2,0,0,0,0,0)$	3.658 582 716 243 175 207 969 276 574 1 10^{-1}	8.571 078 153 650 184 467 645 704 204 7 10^{-3}
$g(1,1,1,0,0,0)$	3.447 454 259 102 525 282 100 115 713 9 10^{-1}	6.027 278 683 541 261 617 671 441 399 9 10^{-3}
$g(3,0,0,0,0,0)$	8.803 723 087 040 150 596 505 448 579 7 10^{-1}	9.316 428 522 373 859 205 286 070 304 7 10^{-3}
$g(1,1,1,1,0,0)$	8.518 518 518 518 518 518 518 518 518 5 10^{0}	4.807 529 762 877 014 687 398 150 589 3 10^{-3}
$g(4,0,0,0,0,0)$	2.849 464 173 126 685 211 199 798 289 3 10^{0}	1.296 572 573 872 689 431 790 047 714 4 10^{-2}
$g(1,1,1,1,1,0)$	2.500 000 000 000 000 000 000 000 000 0 10^{0}	4.679 985 481 131 151 729 598 237 602 7 10^{-3}
$g(5,0,0,0,0,0)$	1.176 795 411 671 425 935 279 581 659 0 10^{1}	2.205 496 365 095 795 104 480 271 164 6 10^{-2}
$g(1,1,1,1,1,1)$	8.000 000 000 000 000 000 000 000 000 0 10^{0}	5.033 124 034 041 977 640 019 585 799 2 10^{-3}
$g(6,0,0,0,0,0)$	5.962 899 567 501 152 778 486 008 087 6 10^{1}	4.441 445 631 268 318 817 661 363 268 6 10^{-2}
$g(2,2,2,2,2,2)$	4.761 568 658 224 658 953 775 935 886 3 10^{4}	1.467 676 925 382 090 748 693 886 720 7 10^{-1}
$g(12,0,0,0,0,0)$	1.998 667 989 835 473 493 169 581 298 3 10^{7}	3.793 674 032 518 970 385 528 210 586 4 10^{1}
$g(3,3,3,3,3,3)$	4.595 097 600 000 000 000 000 000 000 0 10^{9}	5.979 770 415 024 714 287 528 834 619 9 10^{1}
$g(18,0,0,0,0,0)$	1.779 533 879 212 729 823 179 024 201 1 10^{14}	6.240 107 562 655 131 418 896 693 018 6 10^{5}

TABLE II: Numerical values of $g(1,1,1,1,1,1)$ around the singular point $\sigma = 0$: $w_{1,2,3} = 1$, $u_{1,2,3} = \alpha$.

α	σ	$g(1,1,1,1,1,1)$
0.577 3	1.741 3 10^{-4}	4.715 168 989 550 199 879 343 821 168 10^{-2}
0.577 350 2	2.396 798 8 10^{-7}	4.713 684 016 763 871 477 743 039 334 10^{-2}
0.577 350 269	6.568 829 17 10^{-10}	4.713 681 976 034 959 469 113 297 912 10^{-2}
0.577 350 269 189 6	8.925 087 775 552 10^{-14}	4.713 681 970 427 392 724 217 475 890 10^{-2}
0.577 350 269 189 625	2.648 337 377 078 125 10^{-15}	4.713 681 970 426 653 329 868 706 104 10^{-2}
0.577 350 269 189 625 764 5	3.169 230 531 337 161 925 10^{-20}	4.713 681 970 426 630 719 189 520 726 10^{-2}
0.577 350 269 189 625 764 509 148 7	2.788 669 608 438 596 620 038 649 3 10^{-25}	4.713 681 970 426 630 718 918 940 842 10^{-2}
$3.^{-1/2}$	0	4.713 681 970 426 630 718 918 938 462 10^{-2}
0.577 350 269 189 625 764 509 148 8	−6.754 320 066 991 579 670 162 432 10^{-26}	4.713 681 970 426 630 718 918 937 885 10^{-2}
0.577 350 269 189 625 764 6	−3.147 178 562 004 038 394 8 10^{-19}	4.713 681 970 426 630 716 231 943 331 10^{-2}
0.577 350 269 189 626	−8.157 642 380 596 28 10^{-16}	4.713 681 970 426 623 754 094 755 315 10^{-2}
0.577 350 269 189 7	−2.571 592 837 582 7 10^{-13}	4.713 681 970 424 435 146 822 397 542 10^{-2}
0.577 350 270	−2.807 218 7 10^{-9}	4.713 681 946 459 185 584 378 695 888; 10^{-2}
0.577 350 3	−1.067 302 7 10^{-7}	4.713 681 059 186 068 003 930 086 238 10^{-2}
0.577 4	−1.722 8 10^{-4}	4.712 211 406 354 297 107 821 210 234 10^{-2}

$g(1,1,1,1,1,1)$ which needs six evaluations of recursions (10). Close to the critical point $\sigma = 0$, we used Bailey's multiprecision library [25]. We control the number of significant digits by dynamical estimating and adjusting the appropriate precision of the arithmetic. As presented in Table II, we can approach the critical point $\sigma = 0$ as close as we need for practical purposes. This strategy of course slows down the algorithm significantly, but in practical applications the parameters close to the critical point $\sigma = 0$ are very rare. This strategy of controlling precision in the region of instabilities allows one to cross $\sigma = 0$ points in the minimization of the nonrelativistic energy. In Table III we present results for nonrelativistic energies for the ground state of Li obtained with global minimization of all nonlinear parameters in the basis length of $N = 128$, 256, 512 respectively. The achieved precision is much higher than that from similar number of Hylleraas functions.

TABLE III: Nonrelativistic energy of the Li ground state using exponentially correlated basis set with the number of functions N, ∞ is the extrapolated value from Ref. [5] using Hylleraas basis functions.

N	$\mathcal{E}^{(2)}$
32	−7.478 059 40
64	−7.478 060 050
128	−7.478 060 304 6
256	−7.478 060 321 31
512	−7.478 060 323 427
∞	−7.478 060 323 910 1(3)

C. Extended integrals

In this section we present an algorithm for calculations of extended integrals with $1/r_a^2$ or $1/r_{ab}^2$ factors in Eq (3). This means that some of indices in $g(n_1, n_2, n_3, n_4, n_5, n_6)$ are equal to -1. Fully correlated exponent in Eq. (3) gives the opportunity to obtain extended integrals by using either a single integration over w_a or u_a i.e.

$$g(n_1, n_2, n_3, -1, n_5, n_6) = \int_{u_1}^{\infty} \mathrm{d}u_1\, g(n_1, n_2, n_3, 0, n_5, n_6)\,, \tag{14}$$

TABLE IV: Examples of extended integrals with $1/r_{23}^2$ in SRP and ARP reference points calculated using numerical integration with $N = 30$.

	$\mathrm{ARP}:\ u_a = 0,\ w_a = 1$	$\mathrm{SRP}:\ u_a = w_a = 1$
$g(0,0,0,-1,0,0)$	$3.852\,610\,933\,969\,379\,240\,110\,048\,369\,9\ 10^{-1}$	$9.496\,501\,144\,947\,432\,180\,784\,237\,909\,6\ 10^{-2}$
$g(1,0,0,-1,0,0)$	$3.027\,449\,106\,575\,050\,367\,308\,702\,234\,4\ 10^{-1}$	$3.729\,972\,160\,750\,497\,052\,308\,263\,021\,7\ 10^{-2}$
$g(1,1,0,-1,0,0)$	$2.360\,700\,062\,552\,231\,395\,696\,277\,796\,4\ 10^{-1}$	$1.895\,953\,170\,412\,559\,215\,217\,374\,496\,4\ 10^{-2}$
$g(2,0,0,-1,0,0)$	$4.360\,947\,194\,620\,688\,310\,533\,551\,110\,5\ 10^{-1}$	$2.519\,224\,983\,963\,737\,154\,014\,628\,472\,2\ 10^{-2}$
$g(1,1,1,-1,0,0)$	$2.503\,315\,976\,630\,860\,793\,316\,473\,181\,3\ 10^{-1}$	$1.453\,670\,463\,091\,034\,929\,350\,269\,890\,4\ 10^{-2}$
$g(3,0,0,-1,0,0)$	$9.678\,534\,014\,755\,149\,691\,745\,602\,065\,7\ 10^{-1}$	$2.452\,489\,069\,429\,084\,805\,380\,219\,451\,1\ 10^{-2}$
$g(1,1,1,-1,1,0)$	$4.965\,970\,761\,362\,395\,801\,363\,888\,667\,7\ 10^{-1}$	$8.929\,779\,730\,282\,261\,688\,941\,298\,690\,9\ 10^{-3}$
$g(4,0,0,-1,0,0)$	$2.994\,734\,857\,888\,708\,511\,724\,418\,787\,7\ 10^{0}$	$3.140\,438\,234\,282\,031\,347\,870\,179\,278\,8\ 10^{-2}$
$g(1,1,1,-1,1,1)$	$1.333\,333\,333\,333\,333\,333\,333\,333\,333\,3\ 10^{0}$	$7.833\,365\,875\,543\,837\,545\,344\,094\,254\,1\ 10^{-3}$
$g(5,0,0,-1,0,0)$	$1.207\,413\,986\,734\,661\,793\,622\,502\,357\,9\ 10^{1}$	$5.003\,447\,967\,255\,362\,321\,317\,326\,500\,6\ 10^{-2}$
$g(2,2,2,-1,2,2)$	$5.436\,536\,048\,634\,697\,021\,325\,813\,246\,7\ 10^{2}$	$6.776\,488\,986\,538\,662\,624\,450\,203\,053\,8\ 10^{-2}$
$g(10,0,0,-1,0,0)$	$1.820\,037\,338\,296\,110\,774\,925\,172\,748\,9\ 10^{5}$	$4.998\,826\,524\,680\,257\,565\,021\,055\,520\,2\ 10^{0}$
$g(3,3,3,-1,3,3)$	$2.636\,015\,376\,623\,376\,623\,376\,623\,376\,6\ 10^{6}$	$6.615\,220\,449\,456\,842\,761\,016\,682\,847\,5\ 10^{0}$
$g(15,0,0,-1,0,0)$	$4.364\,311\,343\,749\,328\,364\,240\,301\,511\,7\ 10^{10}$	$6.183\,347\,201\,330\,971\,024\,067\,326\,468\,8\ 10^{3}$

or a double integration i.e.

$$g(n_1,-1,n_3,-1,n_5,n_6) = \int_{u_1}^{\infty} \mathrm{d}\,u_1 \int_{w_2}^{\infty} \mathrm{d}w_2\, g(n_1,0,n_3,0,n_5,n_6). \tag{15}$$

The adaptive increase of the arithmetic precision close to critical points $\sigma = 0$ is necessary here for the precise evaluation of $g(n_1,n_2,n_3,n_4,n_5,n_6)$. Moreover, one is able to perform accurately this integration by using N-point generalized Gaussian quadrature with logarithmic end-point singularity [26]

$$\begin{aligned} I &= \int_0^1 dx\, \big[W_1(x) + \ln(x)\, W_2(x)\big] \\ &\approx \sum_{i=1}^{N} w_i\, \big[W_1(x_i) + \ln(x_i)\, W_2(x_i)\big]\,, \end{aligned} \tag{16}$$

where W_i are regular functions on the interval $(0,1)$. This quadrature becomes exact for W_i being polynomials of maximal degree $N-1$, and the example of 30 point quadrature, which is used through out this paper for calculation of mean values, is presented in Appendix A.

If integration variable u in Eq. (14) is mapped into the interval $(0,1)$ by the following change of variable

$$\int_0^{\infty} du\, f(u) = \int_0^1 dx\, \frac{1}{x^2}\, f\left(\frac{1}{x} - 1\right) \tag{17}$$

then the quadrature with logarithmic end-point singularity is sufficient for one-dimensional integrals in Eq. (14), where $N = 30$ quadrature allows one to obtain about 30 significant digits as shown in Table IV.

The presented values for integrals are obtained at ARP and SRP points. Some of them can be found in the literature, for example $g(2,2,2,-1,2,2)$ at ARP point [17, 18], which corresponds to a Hylleraas type of integral. Perfect agreement with those results, demonstrates high accuracy is achieved for the extended integrals. The proposed evaluation method fully relies on properties of the recurrence algorithm for basis integrals, which must be very stable on the integration path over the corresponding parameter.

In comparison to the one-dimensional integral in Eq. (14), the convergence of two-dimensional integral Eq. (15) with respect to the number of integration points is much worse. For this reason we use a slightly different mapping into $(0,1)$ intervals, which is

$$\int_0^{\infty} du \int_0^{\infty} dw\, f(u,w) = \int_0^1 dx \int_0^1 dy\, \frac{4}{x^3\, y^3}\, f\left(\frac{1}{x^2} - 1, \frac{1}{y^2} - 1\right). \tag{18}$$

The numerical convergence of the integral in Eq. (15) is the worst for the case $n_3 = 0$, where the leading asymptotics includes a square of the logarithm. For $n_3 > 0$ convergence improves significantly. The use of Gaussian quadrature adapted to logarithmic end-point singularity with 30 points is enough for practical applications. In Table V we presented numerical values for $g(n_1,-1,n_3,-1,n_5,n_6)$ in ARP and SRP reference points with the accuracy of 10^{-16}. In the case of $n_3 = 0$ they have been obtained with 60 point quadrature. It is possible to obtain even higher accuracy for $n_3 > 0$, but further improvement for $n_3 = 0$ requires a more sophisticated integration strategy. There are no such problems with integration involving parameters which are attached to opposite edges of the tetrahedron, i.e. $g(-1,n_2,n_3,-1,n_5,n_6)$, see Fig. 1, so this case of integral in Eq. (14) with $n_3 = 0$ is the one which limits accuracy of mean values.

TABLE VI: Expectation value for Breit-Pauli operators for the ground state involving integrals with one $n_i = -1$. Implicit summation over a, or over pairs $a > b$ is assumed. Last entries are extrapolated results obtained in Hylleraas basis set

N	r_a^{-2}	r_{ab}^{-2}	$\delta^3(r_a)$	$\delta^3(r_{ab})$	p_a^4	$p_a^i\, r_{ab}^{-3}(\delta^{ij} r_{ab}^2 + r_{ab}^i r_{ab}^j) p_b^j$
1	30.082 797 986 7	4.506 456 504 1	13.764 569 952 4	0.536 449 208 3	625.582 840 9	0.936 654 826
2	29.747 608 655 0	4.576 769 565 1	13.585 859 628 1	0.561 647 862 3	611.553 996 7	1.138 521 450
4	30.130 068 846 4	4.443 919 421 0	13.787 803 129 0	0.543 639 175 1	625.468 724 2	0.914 892 317
8	30.187 481 732 0	4.421 446 718 9	13.815 726 640 6	0.543 582 099 9	627.407 849 4	0.903 179 423
16	30.241 078 773 0	4.381 681 063 4	13.842 637 278 6	0.544 318 958 8	628.479 718 2	0.871 711 023
32	30.240 966 286 8	4.381 283 593 8	13.842 598 063 3	0.544 325 804 3	628.457 736 5	0.871 331 224
64	30.240 892 554 9	4.381 232 031 6	13.842 567 782 2	0.544 325 359 5	628.451 398 8	0.871 268 418
128	30.240 987 196 9	4.381 186 567 3	13.842 617 080 2	0.544 324 836 8	628.450 904 8	0.871 208 043
256	30.240 973 605 8	4.381 176 947 3	13.842 611 088 3	0.544 324 684 9	628.449 069 5	0.871 196 220
Hyll.	30.240 972 72(3)	4.381 176 64(4)	13.842 610 86(3)	0.544 324 632 5(7)	628.448 985(12)	0.871 195 62(14)

TABLE V: Examples of extended integrals $g(n_1, -1, n_3, -1, n_5, n_6)$ in SRP and ARP reference points, numerical quadrature with $N = 60$ points, all digits are significant

	ARP : $u_a = 0,\ w_a = 1$	SRP : $u_a = w_a = 1$
$g(0,-1,0,-1,0,0)$	$1.884\,392\,088\,158\,216\ 10^{0}$	$8.424\,892\,130\,134\,382\ 10^{-1}$
$g(1,-1,0,-1,0,0)$	$9.485\,660\,506\,739\,961\ 10^{-1}$	$1.797\,709\,314\,546\,008\ 10^{-1}$
$g(1,-1,1,-1,0,0)$	$4.284\,596\,512\,743\,028\ 10^{-1}$	$4.614\,367\,395\,977\,269\ 10^{-2}$
$g(2,-1,0,-1,0,0)$	$1.165\,927\,539\,416\,184\ 10^{0}$	$8.712\,176\,344\,048\,701\ 10^{-2}$
$g(1,-1,1,-1,1,0)$	$6.829\,291\,358\,121\,588\ 10^{-1}$	$2.470\,684\,625\,918\,397\ 10^{-2}$
$g(3,-1,0,-1,0,0)$	$2.440\,178\,087\,422\,623\ 10^{0}$	$6.789\,663\,816\,285\,613\ 10^{-2}$
$g(1,-1,1,-1,1,1)$	$1.467\,401\,100\,272\,340\ 10^{0}$	$1.868\,910\,909\,646\,633\ 10^{-2}$
$g(4,-1,0,-1,0,0)$	$7.400\,703\,871\,489\,098\ 10^{0}$	$7.375\,782\,376\,091\,605\ 10^{-2}$
$g(2,-1,2,-1,2,2)$	$1.325\,932\,535\,285\,045\ 10^{2}$	$3.788\,534\,374\,425\,215\ 10^{-2}$
$g(7,-1,0,-1,0,0)$	$8.898\,402\,193\,692\,669\ 10^{2}$	$3.628\,968\,910\,010\,360\ 10^{-1}$

D. Expectation values

The basis class of integrals ($n_i \geq 0$) and the class with the one index equal to -1 is sufficient for all mean values of operators like those in the Breit-Pauli Hamiltonian, Eq. (4). As an example we demonstrate their evaluation for the lithium ground state. In Table VI we present results for the Dirac δ functions using the Drachman formulae [27]

$$\langle 4\pi\delta^3(r_a)\rangle = \left\langle \frac{4}{r_a}(E_0 - V)\right\rangle - \sum_c \left\langle \vec{\nabla}_c\phi \left| \frac{2}{r_a} \right| \vec{\nabla}_c\phi \right\rangle , \tag{19}$$

$$\langle 4\pi\delta^3(r_{ab})\rangle = \left\langle \frac{2}{r_{ab}}(E_0 - V)\right\rangle - \sum_c \left\langle \vec{\nabla}_c\phi \left| \frac{1}{r_{ab}} \right| \vec{\nabla}_c\phi \right\rangle , \tag{20}$$

where V is a total interaction potential. The similar prescriptions can be used for p_a^4 operator

$$\left\langle \sum_a p_a^4 \right\rangle = 4\langle (E_0 - V)^2\rangle - \sum_{b>c} \langle \nabla_b^2\phi|\nabla_c^2\phi\rangle. \tag{21}$$

These forms significantly improve accuracy of numerical results in comparison to direct calculations, like those presented in our previous paper [7], see Table VI. Nevertheless, with 256 functions they are about two digits less accurate than the most precise results obtained from 9564 Hylleraas basis functions. These Hyleraas results are slightly more accurate than those in [19] due to better optimization of the nonrelativistic wave function.

As we have noticed, for the nonrelativistic energy one needs approximately six times smaller basis set of exponentially correlated functions as compared to Hylleraas functions to obtain similar accuracy, and the same is confirmed for the mean values of operators. The achieved accuracy is limited only by the number of basis functions, which nevertheless should be well optimized. In practice it demands more computing power than we used up to now and a parallel version of the algorithm would be necessary for optimization of a large number of Slater functions.

In Table VII we present numerical values for typical operators in higher order perturbation theory i.e. $m\alpha^6$ correction to the energy. For these operators we need to use all the discussed classes of integrals. $g(n_1, n_2, n_3, n_4, n_5, n_6)$ integrals

TABLE VII: Expectation value for operators for operators involving extended class of integrals.

N	$\sum_{a>b} r_a^{-2} r_b^{-2}$	$\sum_{a\neq b} r_a^{-2} r_{ab}^{-2}$	$\sum_{a>b>c} r_{ab}^{-2} r_{bc}^{-2}$	$\sum_{a\neq b} \vec{r}_a \cdot \vec{r}_{ab} r_a^{-3} r_{ab}^{-3}$	$\sum_a \sum_{b>c} p_b^2 r_a^{-1} p_c^2$
1	204.916 879	289.283 997	1.177 470 80	45.945 338 1	842.720 739
2	211.038 011	297.213 636	1.112 887 76	48.080 149 7	891.514 656
4	202.558 151	284.360 921	1.071 904 15	45.386 279 3	840.040 129
8	202.665 783	283.643 499	1.066 132 65	45.443 462 5	844.843 155
16	202.840 737	282.053 625	1.064 131 54	45.240 730 3	853.983 531
32	202.852 464	282.008 017	1.064 188 66	45.236 709 9	854.271 406
64	202.862 382	282.005 597	1.064 179 55	45.236 342 7	854.374 209
128	202.883 252	282.002 183	1.064 178 17	45.236 047 4	854.554 104

with two parameters equal to -1 are obtained with double integration with 30×30 points and all the presented digits in Table VII are accurate for the corresponding approximate wave function.

III. SUMMARY

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 applied it for the accurate numerical calculation of expectation values of some operators corresponding to higher order relativistic and QED effects. They involve integrals with quadratic inverse powers of at least two interparticle distances, which are the most difficult in the evaluation. Using this compact and very flexible correlated exponential basis set, we are aiming to determine $m\,\alpha^6$ and $m\,\alpha^7$ effects in the hyperfine and fine structure of lithium-like systems, which have not been investigated so far.

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Appendix A: Weights and nodes of generalized Gaussian quadrature with logarithmic end-point singularity

We present here a set of 30 nodes and corresponding weights for generalized Gaussian quadrature with logarithmic end-point singularity [26], which was obtained using the algorithm described in Appendix A of Ref. [19]. We used these quadrature points for numerical integration of extended integrals in Tables IV, VI, and VII.

TABLE VIII: Weights and nodes of generalized Gaussian quadrature with logarithmic end-point singularity

N	nodes	weights
1	$7.323\,797\,44272605707927651215334608\,10^{-6}$	$2.79892154309547416710987828334736\,10^{-5}$
2	$1.100\,447\,00457774879623368108247943\,10^{-4}$	$2.17365526502541548589108155033626\,10^{-4}$
3	$5.469\,183\,26183967432457719790539051\,10^{-4}$	$7.20703586534389568501488362593518\,10^{-4}$
4	$1.701\,857\,51910164118701225273639596\,10^{-3}$	$1.67446096505498972978224436308689\,10^{-3}$
5	$4.083\,863\,60971437462932298732108869\,10^{-3}$	$3.19128240641146524350794278296664\,10^{-3}$
6	$8.300\,041\,17688233905931162736411746\,10^{-3}$	$5.35378831352933564469099803155786\,10^{-3}$
7	$1.502\,297\,81560799959114892646895942\,10^{-2}$	$8.20962136808195567645775658689256\,10^{-3}$
8	$2.495\,392\,36157545503008513656313159\,10^{-2}$	$1.17680292130848124961801044296255\,10^{-2}$
9	$3.878\,338\,61710629356474590553368630\,10^{-2}$	$1.59981435048914024332333704241883\,10^{-2}$
10	$5.715\,089\,84811763898261154101387036\,10^{-2}$	$2.08290410936242947283573768810863\,10^{-2}$
11	$8.060\,574\,14726551690255082886279043\,10^{-2}$	$2.61515976613093133103470957985343\,10^{-2}$
12	$1.095\,703\,94234517942760556318344690\,10^{-1}$	$3.18220682694563815827694187138199\,10^{-2}$
13	$1.443\,083\,73001500812672361144038109\,10^{-1}$	$3.76672559998067174250314484868819\,10^{-2}$
14	$1.848\,979\,49427531958876501649047717\,10^{-1}$	$4.34910622632233969988331688489985\,10^{-2}$
15	$2.312\,130\,01548255181588787651651928\,10^{-1}$	$4.90821532284030403760822595772833\,10^{-2}$
16	$2.829\,119\,60197207748156616199457019\,10^{-1}$	$5.42224286612626157484616606008227\,10^{-2}$
17	$3.394\,354\,81190852660583946762696458\,10^{-1}$	$5.86959442909769135605447275253662\,10^{-2}$
18	$4.000\,131\,13109450190847537317246366\,10^{-1}$	$6.22979181149364796169604799658096\,10^{-2}$
19	$4.636\,788\,56939306293165441422602120\,10^{-1}$	$6.48434457072330546001338183346875\,10^{-2}$
20	$5.292\,951\,42741036253816689241764505\,10^{-1}$	$6.61755598512543778100952715354295\,10^{-2}$
21	$5.955\,843\,95325645009469243558808251\,10^{-1}$	$6.61722952772004782470943263263082\,10^{-2}$
22	$6.611\,670\,40396915198682135573185723\,10^{-1}$	$6.47524589229209230876914855177978\,10^{-2}$
23	$7.246\,045\,28176032770586180257340226\,10^{-1}$	$6.18798583499546375301194127428597\,10^{-2}$
24	$7.844\,457\,34734941543894377419518002\,10^{-1}$	$5.75658036634420432925717153926242\,10^{-2}$
25	$8.392\,749\,51478663018317278487334798\,10^{-1}$	$5.18697691924656775668123741331021\,10^{-2}$
26	$8.877\,595\,97617343115537224494301863\,10^{-1}$	$4.48981784955672218807632566389701\,10^{-2}$
27	$9.286\,957\,95963227580314671288014994\,10^{-1}$	$3.68013625003694933496657925550436\,10^{-2}$
28	$9.610\,500\,59187409711054297148665964\,10^{-1}$	$2.77688703774135920873618253138605\,10^{-2}$
29	$9.839\,957\,03521288981120560285698734\,10^{-1}$	$1.80238737841607431150476240903211\,10^{-2}$
30	$9.969\,459\,58679763051044061968242492\,10^{-1}$	$7.82767019549675700264134910161448\,10^{-3}$