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 \(\alpha\)

\[
E = m \left[ \alpha^2 \mathcal{E}^{(2)} + \alpha^4 \mathcal{E}^{(4)} + \alpha^6 \mathcal{E}^{(5)} + \alpha^8 \mathcal{E}^{(7)} + \ldots \right].
\]

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.

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

\[
\phi(r_1, r_2, r_3) = e^{-\alpha r_1 - \alpha r_2 - \alpha r_3 - \beta_1 r_2 - \beta_2 r_3} - \beta_3 r_1 r_2 r_3,
\]

in variational calculations for \(\text{Ps}_2\) 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 \(r_{ij}\)

\[
g(n_1, n_2, n_3, n_4, n_5, n_6) = \int \frac{d^3r_1}{4\pi} \int \frac{d^3r_2}{4\pi} \int \frac{d^3r_3}{4\pi} \rho^{n_1-1}(r_1) \rho^{n_2-1}(r_2) \rho^{n_3-1}(r_3) \delta(r_{12}) \delta(r_{31}) \delta(r_{23}) e^{-w_1 r_1 - w_2 r_2 - w_3 r_3 - w_1 w_2 - w_1 w_3 - w_2 w_3 r_1 r_2 r_3}
\]

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 \(\text{Be}^+\) 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

\[
H^{(4)} = \sum_a \left\{ -\frac{p_a^4}{8 m_3} + \frac{\pi Z \alpha}{2 m^2} \delta^3(r_a) \right\} + \sum_{a>b} \left\{ \frac{\pi \alpha}{2 m^2} \delta^3(r_{ab}) - \frac{\alpha}{2 m^2} p_a^2 \left( \frac{\delta^{ij}}{r_{ab}} + \frac{r_a^i r_b^j}{r_{ab}^3} \right) p_b^j \right\}.
\]

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 of our knowledge, and for the first time we present them in this work.

In the calculation of relativistic and QED effects beyond leading order, \( E^{(6)} \) 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 Hylleras integrals [12,13,17]. The algorithm by King [17] seems to be too slow for a large scale computation, where integrals with \( \Omega = \sum_n n_a \) 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 \( 1/(r_a^2 r_b^2), 1/(r_a^2 r_{ab}^2), 1/(r_{ab}^2 r_c^2) \), indicates that this integration approach can be used for the calculation of higher order relativistic corrections, for example \( m a^b \) and \( m \alpha^b \) 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.

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 \( g_0 = g(0,0,0,0,0,0) \) 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 \( \sigma \) is of the form

\[
\begin{align*}
\sigma &= u_1^2 u_2^2 w_3^2 + u_2^2 u_3^2 w_1^2 + u_3^2 u_1^2 w_2^2 + w_1^2 w_2^2 w_3^2 \\
&+ u_1^2 w_1^2 (u_2^2 + w_1^2 - u_2^2 - w_3^2 - w_2^2 - w_3^2) \\
&+ u_2^2 w_2^2 (u_3^2 + w_3^2 - u_3^2 - u_1^2 - w_1^2 - w_3^2) \\
&+ u_3^2 w_3^2 (u_1^2 + w_1^2 - u_1^2 - u_2^2 - w_2^2 - w_2^2), \tag{6}
\end{align*}
\]

and function \( P \) is given by

![FIG. 1: Tetrahedron representing the integral from Eq. (2)](image)
\[ P = -u_1 w_1 [(u_1 + w_2)^2 - u_3^2] \Gamma(0, 0, -1; u_1 + w_2, u_3, u_2 + w_1)
- u_1 w_1 [(u_1 + u_3)^2 - u_2^2] \Gamma(0, 0, -1; u_1 + u_3, w_2, u_1 + w_3)
+ [u_1^2 w_2^2 + u_2^2 w_3^2 - u_3^2 w_1^2 + u_1 w_1 (u_1^2 + u_2^2 - u_3^2)] \Gamma(0, 0, -1; w_1 + w_2, w_3, u_1 + u_2)
+ [u_1^2 w_2^2 - u_2^2 w_3^2 + u_3^2 w_1^2 + w_1 w_3 (u_1^2 + u_2^2 - u_3^2)] \Gamma(0, 0, -1; w_1 + w_3, u_2, u_1 + u_3)
- [u_2 (u_2 + w_1) (u_1^2 + u_2^2 - u_3^2) - u_3^2 (u_1^2 + u_2^2 - u_3^2)] \Gamma(0, 0, -1; u_2 + w_1, u_3, u_1 + w_2)
- [u_3 (u_3 + w_1) (u_1^2 + u_3^2 - u_2^2) - u_2^2 (u_1^2 + u_3^2 - u_2^2)] \Gamma(0, 0, -1; u_3 + w_1, u_2, u_1 + w_3)
+ w_1 [w_2 (u_2^2 - u_2^2 + u_3^2) + w_3 (u_1^2 + u_2^2 - u_3^2)] \Gamma(0, 0, -1; w_2 + w_3, w_1, u_1 + u_3)
+ w_1 [u_2 (u_1^2 - w_2^2 + u_3^2) + u_3 (u_1^2 + w_2^2 - u_3^2)] \Gamma(0, 0, -1; u_2 + u_3, w_1, w_2 + w_3), \tag{7} \]

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 \( g(0, 0, 0, 0, 0, 0) \) implemented the formula of Fromm-Hill in the version improved by Harris. The calculation of the two-electron \( \Gamma \)-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 \( w_\sigma, u_\sigma \) from expressions (7), (10), and (13) by applying the tetrahedral symmetry.

The proposed recurrence scheme allows us to calculate integrals from higher shells \( \Omega \) 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) \( w_\alpha = u_\alpha = 1 \) where \( \sigma = -2 \) and the auxiliary reference point (ARP) \( w_\alpha = 1, u_\alpha = 0 \) 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 \( \sigma \) 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 \( w_\sigma = 1, u_\sigma = \alpha \) close to \( \alpha = 3^{1/2} \) where \( \sigma \) is exactly equal to zero. As an example we present in Table II values for
equal to controlling precision in the region of instabilities allows one much higher than that from similar number of Hylleraas functions. As presented in Table II, we can approach the critical point 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 II 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.

### C. Extended integrals

In this section we present an algorithm for calculations of extended integrals with $1/r_a^2$ or $1/r_{ab}$ 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. (5) gives the opportunity to obtain extended integrals by using either a single integration over $u_a$ or $u_a$ i.e.

$$g(n_1, n_2, n_3, -1, n_5, n_6) = \int_{u_1}^{\infty} du_1 g(n_1, n_2, n_3, 0, n_5, n_6),$$

(14)
TABLE IV: Examples of extended integrals with $1/r^2_{23}$ in SRP and ARP reference points calculated using numerical integration with $N = 30.$

|                | ARP: $w_a = 0, w_b = 1$                | SRP: $w_a = w_b = 1$ |
|----------------|----------------------------------------|----------------------|
| $g(0, 0, 0, −1, 0, 0)$ | $3.852 610 933 069 379 240 110 048 369 9 10^{-4}$ | $9.496 501 144 497 432 180 784 237 909 6 10^{-2}$ |
| $g(1, 0, 0, −1, 0, 0)$ | $3.027 449 106 575 050 367 308 702 234 4 10^{-1}$ | $3.729 972 160 750 497 052 308 263 021 7 10^{-2}$ |
| $g(1, 1, 0, −1, 0, 0)$ | $2.360 709 002 552 231 395 696 277 796 4 10^{-4}$ | $1.895 953 170 412 559 215 217 374 496 4 10^{-2}$ |
| $g(2, 0, 0, −1, 0, 0)$ | $4.360 947 194 620 688 310 533 551 110 5 10^{-1}$ | $2.519 224 983 963 737 154 014 628 472 2 10^{-2}$ |
| $g(1, 1, 1, −1, 0, 0)$ | $2.503 315 976 630 860 793 316 473 181 3 10^{-1}$ | $1.453 670 463 091 034 929 350 269 890 4 10^{-2}$ |
| $g(3, 0, 0, −1, 0, 0)$ | $9.678 534 014 755 149 691 745 602 065 7 10^{-4}$ | $2.452 489 069 429 084 805 380 219 451 1 10^{-2}$ |
| $g(1, 1, 1, −1, 1, 0)$ | $4.965 970 761 362 395 801 363 888 667 7 10^{-4}$ | $8.929 779 730 282 261 688 941 298 690 9 10^{-3}$ |
| $g(4, 0, 0, −1, 0, 0)$ | $2.994 734 857 888 708 511 724 418 787 7 10^{-6}$ | $3.140 438 234 282 031 347 870 179 278 8 10^{-2}$ |
| $g(1, 1, 1, −1, 1, 1)$ | $1.333 333 333 333 333 333 333 333 3 10^{-3}$ | $7.833 365 875 543 837 545 344 094 254 1 10^{-3}$ |
| $g(5, 0, 0, −1, 0, 0)$ | $1.207 413 986 734 661 793 622 502 357 9 10^{-4}$ | $5.003 447 967 255 362 321 317 326 509 6 10^{-2}$ |
| $g(2, 2, 2, −1, 2, 2)$ | $5.436 536 048 634 697 021 345 813 276 4 10^{-1}$ | $6.776 488 986 538 662 624 450 203 053 8 10^{-2}$ |
| $g(10, 0, 0, −1, 0, 0)$ | $1.820 037 338 296 110 774 925 172 748 9 10^{5}$ | $4.998 826 524 680 257 565 021 055 520 2 10^{0}$ |
| $g(3, 3, 3, −1, 3, 3)$ | $2.636 015 376 623 376 623 376 623 376 6 10^{0}$ | $6.615 220 449 456 842 761 016 682 847 7 10^{0}$ |
| $g(15, 0, 0, −1, 0, 0)$ | $4.363 311 343 749 328 364 240 301 511 7 10^{15}$ | $6.183 347 201 330 971 024 067 326 468 8 10^{5}$ |

or a double integration i.e.

$$g(n_1, −1, n_3, −1, n_5, n_6) = \int_{u_1}^{\infty} du_1 \int_{w_2}^{\infty} dw_2 g(n_1, 0, n_3, 0, n_5, n_6).$$

(15)

The adaptive increase of the arithmetic precision close to critical points $\sigma = 0$ is necessary here for the precise evaluation of $g(n_{i1}, n_2, n_3, n_4, n_5, n_6)$. Moreover, one is able to perform accurately this integration by using $N$-point generalized Gaussian quadrature with logarithmic end-point singularity [26]

$$I = \int_0^1 dx \left[ W_1(x) + \ln(x) W_2(x) \right]$$

$$\approx \sum_{i=1}^{N} w_i \left[ W_1(x_i) + \ln(x_i) W_2(x_i) \right],$$

(16)

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 Huylersas 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

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

(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 IV we presented numerical values for $g(n_{i1}, −1, n_3, −1, n_5, n_6)$ in ARP and SRP reference points with the accuracy of $10^{-10}$. 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 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

| \(N\) | \(r_x^{-2}\) | \(r_y^{-2}\) | \(\delta^3(r_x)\) | \(\delta^3(r_{ab})\) | \(p^4\) | \(p_a^4 \epsilon_a^2 (\delta^3 r_x + r_{ab}^2 r_{ab}^4) p_x\) |
|------|------|------|----------------|----------------|-------|-----------------------------------------------|
| 1    | 30.082 798 967 | 4.506 456 504 | 13.764 569 962 | 0.536 449 208 | 625.582 840 | 0.936 654 826 |
| 2    | 29.747 608 650 | 4.576 706 561 | 13.585 859 628 | 0.561 647 862 | 611.533 996 | 1.138 521 450 |
| 4    | 30.130 068 846 | 4.443 919 421 | 13.787 803 129 | 0.543 639 175 | 625.486 724 | 0.914 892 317 |
| 8    | 30.187 441 732 | 4.421 446 719 | 13.815 726 640 | 0.543 582 099 | 627.407 840 | 0.903 179 423 |
| 16   | 30.241 078 773 | 4.381 681 063 | 13.842 637 278 | 0.544 318 958 | 628.479 718 | 0.871 711 023 |
| 32   | 30.240 966 286 | 4.381 283 593 | 13.842 598 063 | 0.544 325 804 | 628.457 736 | 0.871 332 224 |
| 64   | 30.240 892 554 | 4.381 232 031 | 13.842 567 782 | 0.544 325 359 | 628.451 398 | 0.871 268 418 |
| 128  | 30.240 987 196 | 4.381 186 567 | 13.842 617 080 | 0.544 324 836 | 628.450 904 | 0.871 208 043 |
| 256  | 30.240 973 605 | 4.381 176 947 | 13.842 611 083 | 0.544 324 684 | 628.449 069 | 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 10^7 | 1.884 392 088 158 216 10^7 |
| \(g(1, -1, 0, -1, 0, 0)\) | 9.485 660 506 739 961 10^-1 | 9.485 660 506 739 961 10^-1 |
| \(g(1, -1, -1, -1, 0, 0)\) | 4.284 596 512 743 028 10^-1 | 4.284 596 512 743 028 10^-1 |
| \(g(2, -1, 0, -1, 0, 0)\) | 1.165 927 539 416 184 10^0 | 1.165 927 539 416 184 10^0 |
| \(g(1, -1, -1, -1, 0, 0)\) | 6.829 291 358 121 588 10^-1 | 6.829 291 358 121 588 10^-1 |
| \(g(3, -1, 0, -1, 0, 0)\) | 2.440 178 087 422 623 10^0 | 2.440 178 087 422 623 10^0 |
| \(g(1, -1, -1, -1, 1, 1)\) | 1.467 401 100 272 340 10^0 | 1.467 401 100 272 340 10^0 |
| \(g(4, -1, -1, -1, 0, 0)\) | 7.400 703 871 480 008 10^0 | 7.400 703 871 480 008 10^0 |
| \(g(2, -1, 2, -1, 2, 2)\) | 1.325 932 535 285 045 10^2 | 1.325 932 535 285 045 10^2 |
| \(g(7, -1, 0, -1, 0, 0)\) | 8.898 402 193 692 669 10^2 | 8.898 402 193 692 669 10^2 |

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 almost 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 \(\delta\) functions using the Drachman formulae [27]

\[
\langle 4\pi\delta^3(r_a) \rangle = \frac{4}{r_a} (E_0 - V) - \sum_c \left| \nabla_c \phi \right| \frac{2}{r_a} \left| \nabla_c \phi \right| ,
\]

(19)

\[
\langle 4\pi\delta^3(r_{ab}) \rangle = \frac{2}{r_{ab}} (E_0 - V) - \sum_c \left| \nabla_c \phi \right| \frac{1}{r_{ab}} \left| \nabla_c \phi \right| ,
\]

(20)

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

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

(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 Hylleraas 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
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 with two parameters equal to \(-1\) are obtained with double integration with \(30 \times 30\) 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.
| N  | nodes            | weights                           |
|----|-----------------|-----------------------------------|
| 1  | 7.323797 4427260570972651215334608 10^-6 | 2.79892154309547416710987828334736 10^-3 |
| 2  | 1.100 447 0045577487962336108247943 10^-4 | 2.17365265025041548589108155033626 10^-4 |
| 3  | 5.469 183 26183967432457719790539051 10^-4 | 7.20735865343995685014886262593518 10^-4 |
| 4  | 1.701 857 51910161418701225273639596 10^-3 | 1.674460650549897972824244369869 10^-3 |
| 5  | 4.083 863 66971047346322987632188869 10^-3 | 3.191282406411662435079427827664 10^-3 |
| 6  | 8.300 041 17688233905951162736411746 10^-3 | 5.353788315293564649099803155786 10^-3 |
| 7  | 1.502 297 815607995911489266895942 10^-2 | 8.206213680819556764575658697956 10^-2 |
| 8  | 2.495 392 361575455030851365631359 10^-2 | 1.17689292130848124961801044292655 10^-2 |
| 9  | 3.878 339 617062935647549055338630 10^-2 | 1.599814350489140243333704241883 10^-2 |
| 10 | 5.715 089 884117638982611541038706 10^-2 | 2.082940109624294728357468810661 10^-2 |
| 11 | 8.060 574 14726551690255082886279043 10^-2 | 2.6151976613093313047057985343 10^-2 |
| 12 | 1.095 703 9423435179276556318344690 10^-1 | 3.18220682694563815827694187131899 10^-1 |
| 13 | 1.443 083 7300150812672361144038109 10^-1 | 3.766725599806712453031448468819 10^-1 |
| 14 | 1.848 979 4942735195887650169407717 10^-1 | 4.349106226332396988833168848995 10^-1 |
| 15 | 2.312 130 015482558115887651651928 10^-1 | 4.908215329840304375088229577283 10^-1 |
| 16 | 2.829 119 601972077481566199457019 10^-1 | 5.4222428661262615748461600860827 10^-2 |
| 17 | 3.394 354 81190852660583946762696458 10^-1 | 5.869544290976135605447275253662 10^-2 |
| 18 | 4.000 131 13010945019084753731724636 10^-1 | 6.229798111490347961604799658906 10^-2 |
| 19 | 4.636 788 569393062931644122662120 10^-1 | 6.8444547072330546000133818348675 10^-2 |
| 20 | 5.292 953 427410362538166989241764505 10^-1 | 6.61755598512543778109052715354295 10^-2 |
| 21 | 5.955 843 953256450904964924358808251 10^-1 | 6.617292557200472470943262362082 10^-2 |
| 22 | 6.611 670 40396915198682135573185723 10^-2 | 6.4752458922920923087691485517797 10^-2 |
| 23 | 7.246 045 28176032770568180255340226 10^-2 | 6.187985834995637510419127428597 10^-2 |
| 24 | 7.844 457 34734941543894377419518002 10^-2 | 5.756580866344204329257115392624 10^-2 |
| 25 | 8.392 749 5147666018317278487343798 10^-2 | 5.1869761922465775568123741331021 10^-2 |
| 26 | 8.877 595 9743473411533722449301863 10^-2 | 4.4981784195572218807632566889701 10^-2 |
| 27 | 9.286 957 9596322758013461728801499 10^-1 | 3.68013625003694394366675972555436 10^-2 |
| 28 | 9.610 500 59187409711054297144865964 10^-1 | 2.77688703741539520873618253138605 10^-2 |
| 29 | 9.839 957 03521288911205602565897834 10^-1 | 1.8023877734160743110457624093211 10^-2 |
| 30 | 9.969 459 5867976.01510440196982424292 10^-1 | 7.827670194567576026413491016448 10^-3 |