Gaussian basis sets with the cusp condition

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Abstract

We demonstrate the applicability of correlated Gaussian functions with terms linear in the interparticle distance using the helium atom as an example. Hamiltonian matrix elements can be integrated analytically for atoms with an arbitrary number of electrons in terms of inverse trigonometric and dilogarithmic functions. This allows a full optimization of exponents through minimization of the nonrelativistic binding energy. In the new basis energy convergence is faster compared to that observed for regular correlated Gaussian functions. In addition, the cusp condition can be fulfilled to a high degree of precision.

Key words: Correlated Gaussian functions, cusp condition, variational method

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The widely used exponentially correlated Gaussian (ECG) functions [1–3] with optimized nonlinear parameters give very precise nonrelativistic binding energies of light atoms and molecules [3–7]. However, various relativistic effects, such as the hyperfine splitting, involve singular types of operators, for which the convergence in the ECG basis is much worse than for the energy. The most striking disadvantage of the Gaussian type functions is their inability to recover the cusps at both nuclear and inter-electron coalescent points. The correlated Slater [8] or Hylleraas [9,10] type basis sets have proper behavior both at small and large r, but the evaluation of matrix elements for atoms with more than two electrons is rather complicated and time consuming [11]. Only recently [12] recursion relations have been discovered for three-electron Hylleraas integrals, which can be used for lithium, and to some extent for beryllium. For a general system, the Gaussian basis set has the clear advantage of a compact analytical form for nonrelativistic Hamiltonian matrix elements, as well as for Breit-Pauli corrections. To overcome the cusp problem, we include linear terms of type r_i and $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$, and call this basis LECG. This can be considered as a first step in improving correlated Gaussian functions for getting better energies and expectation values of relativistic corrections in few electron atoms. We have not included higher powers of different r_i and r_{ij}, because integrals become not tractable. However, the linear terms alone drastically improve the behavior of the wave function near the points of coalescence.

Here we consider helium atom as an example. The necessary integrals for matrix elements of the Hamiltonian (in atomic units)

$$\hat{H} = \frac{\boldsymbol{p}_1^2}{2} + \frac{\boldsymbol{p}_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \tag{1}$$

between correlated Gaussians with and without linear terms can be derived by the appropriate differentiation with respect to a_i of a set of generating integrals. These integrals are listed below, using the following notation $G(r_1, r_2, r_{12}) = \exp(-a_1\, r_1^2 - a_2\, r_2^2 - a_3\, r_{12}^2)/\pi^3$, $a = \sqrt{a_1\, a_2 + a_1\, a_3 + a_2\, a_3}$:

$$\int G(r_1, r_2, r_{12})\, d\boldsymbol{r} = \frac{1}{a^3} \tag{2}$$
$$\int \frac{G(r_1, r_2, r_{12})}{r_1^2}\, d\boldsymbol{r} = \frac{2}{(a_2 + a_3)\, a} \tag{3}$$
$$\int \frac{G(r_1, r_2, r_{12})}{r_1^2\, r_2^2}\, d\boldsymbol{r} = \frac{4}{a_3}\, \arctan\left(\frac{a_3}{a}\right) \tag{4}$$
$$\int \frac{G(r_1, r_2, r_{12})}{r_1}\, d\boldsymbol{r} = \frac{2}{\sqrt{\pi}\, \sqrt{a_2 + a_3}\, a^2} \tag{5}$$
$$\int \frac{G(r_1, r_2, r_{12})}{r_1\, r_2}\, d\boldsymbol{r} = \frac{4}{\pi\, a_3\, a}\, \arctan\left(\frac{a_3}{a}\right) \tag{6}$$
$$\int \frac{G(r_1, r_2, r_{12})}{r_1\, r_2\, r_{12}}\, d\boldsymbol{r} = \\ = \frac{4}{\sqrt{\pi}\, \sqrt{a_1\, a_2\, a_3}}\, \arcsin\left[\frac{2\, \sqrt{a_1\, a_2\, a_3}}{a\, (\sqrt{a_1 + a_2} + \sqrt{a_1 + a_3} + \sqrt{a_2 + a_3})}\right] \tag{7}$$

The formulas with inverse powers of r can be derived from the first one, Eq. (2), with the help of the following integral representations

$$\frac{1}{r^2} = \int_0^\infty e^{-t\, r^2} dt, \tag{8}$$
$$\frac{1}{r} = \frac{1}{\sqrt{\pi}} \int_0^\infty \frac{e^{-t\, r^2}}{\sqrt{t}}\, dt. \tag{9}$$

The more difficult integral of Eq. (7) is at first expressed as a one-dimensional integral with the help of Eqs. (6) and (9) and then integrated using a method due to Remiddi [13] (see Eqs. (20) and (21) of that work). Matrix elements of the nonrelativistic Hamiltonian, as derived with the help of Eqs. (2)–(7) are too long to be written here, but they have a simple structure without numerical instabilities.

Matrix elements for states with nonzero angular momentum can always be expressed in terms of integral over powers of r_i^2 and $\boldsymbol{r}_i\boldsymbol{r}_j$, and therefore can also be obtained from Eqs. (2)-(7) by a differentiation over the corresponding parameter. However, large angular momentum ($l > 3$) may lead to the numerically unstable expression. For this reason one may consider Hylleraas type of basis set, namely uncorrelated Gaussian functions times polynomial of r_i and r_{ij}. The simplicity of Eqs. (2)-(7) at $a_3 = 0$ indicates that it might be possible to derive recursion relations for large powers of r_i and r_{ij}.

For atoms with larger than 2 number of electrons a different type of integrals will appear in LECG basis set. It turns out, that by reshuffling r_i and r_{ij}, the matrix elements can always be expressed in terms of two-electron integrals listed above and only one type of the three electron integral

$$F = \int \frac{\exp\left(-\sum_{i,j=1}^{3} a_{ij}\, \boldsymbol{r}_i\boldsymbol{r}_j\right)}{r_1\, r_2\, r_3}\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2\, d\boldsymbol{r}_3. \tag{10}$$

Its evaluation is little cumbersome. With the help of integral representation Eq. (9) and Remiddi's method [13] it can be transformed to the following one-dimensional integral

$$\begin{aligned} F = {} & -\frac{4\,\pi^3}{x_1} \int_{a_{11}}^{\infty} \frac{1}{\det(a)} \left[\frac{x_2^2}{y_3\, x_1}\ \arctan\left(\frac{a_{12}}{y_3}\right)\right. \\ & \left. + \frac{x_3^2}{y_2\, x_1}\ \arctan\left(\frac{a_{13}}{y_2}\right) - \frac{y_1}{x_1}\ \arctan\left(\frac{a_{23}}{y_1}\right)\right] da_{11}\,, \end{aligned} \tag{11}$$

where

$$x_1 = \sqrt{a_{11}\, a_{23} - a_{12}\, a_{13}} \qquad y_1 = \sqrt{a_{22}\, a_{33} - a_{23}^2} \tag{12}$$

$$x_2 = \sqrt{a_{22}\, a_{13} - a_{12}\, a_{23}} \qquad y_2 = \sqrt{a_{11}\, a_{33} - a_{13}^2} \tag{13}$$

$$x_3 = \sqrt{a_{33}\, a_{12} - a_{13}\, a_{23}} \qquad y_3 = \sqrt{a_{11}\, a_{22} - a_{12}^2} \tag{14}$$

A simple compact expression for this integral has not yet been achieved, although it can be integrated analytically. However, the brute force integration method leads to a quite large number of dilogarithmic functions.

We now turn back to the helium atom and study numerically the effectiveness of LECG. We consider for simplicity the ground state helium and use basis with approximately equal number of functions for each linear term, namely

$$\phi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{k=1}^{K} c_k \left[R_k \exp(-a_{1k}\, r_1^2 - a_{2k}\, r_2^2 - a_{3k}\, r_{12}^2) + (r_1 \leftrightarrow r_2)\right], \tag{15}$$

where

$$R_k = \begin{cases} 1, & \mathrm{mod}(k,4) = 1 \\ r_1, & \mathrm{mod}(k,4) = 2 \\ r_2, & \mathrm{mod}(k,4) = 3 \\ r_{12}, & \mathrm{mod}(k,4) = 0 \end{cases} . \tag{16}$$

The linear coefficients c_k were obtained by solving the generalized eigenvalue equation

$$H\, c = E\, S\, c\,, \tag{17}$$

where H and S are the Hamiltonian and overlap matrix, respectively. All coefficients in the exponent were obtained by extensive minimization of the energy E for 4 subsequently doubled expansion lengths. Using the wave functions obtained this way we calculated energies, the expectation values of Dirac $\delta(\boldsymbol{r}_i)$, and the ratios

$$\mathrm{cusp}(\boldsymbol{r}) = \frac{\langle\phi|\delta(\boldsymbol{r})\,\frac{\partial}{\partial r}|\phi\rangle}{\langle\phi|\delta(\boldsymbol{r})|\phi\rangle}, \tag{18}$$

which should be equal to -2 for $r = r_i$ and $1/2$ for $r = r_{12}$, for the exact wave function.

Table 1

Comparison of the convergence in ECG [14] and in LECG basis for the helium ground state energy and Dirac δ expectation values.

K	E		$\langle\delta(\boldsymbol{r}_1)\rangle$		$\langle\delta(\boldsymbol{r}_{12})\rangle$	
	LECG	ECG	LECG	ECG	LECG	ECG
75	$-2.903\,724\,301\,929$	$-2.903\,723\,935\,937$	1.810 034	1.804 108	0.106 388	0.106 952
150	$-2.903\,724\,374\,715$	$-2.903\,724\,371\,954$	1.810 336	1.808 891	0.106 360	0.106 466
300	$-2.903\,724\,377\,002$	$-2.903\,724\,376\,737$	1.810 411	1.809 798	0.106 347	0.106 378
600	$-2.903\,724\,377\,033$	$-2.903\,724\,377\,022$	1.810 427	1.810 306	0.106 346	0.106 358
exact [15]	$-2.903\,724\,377\,034$	$-2.903\,724\,377\,034$	1.810 429	1.810 429	0.106 345	0.106 345

The convergence of energy computed in LECG basis is better when compared to regular ECG functions and is significantly improved in the case of the expectation value of $\delta(\boldsymbol{r})$ (see Table 1). Moreover, we observe a fast $1/K^2$ convergence for $\mathrm{cusp}(\boldsymbol{r}_1)$ and a slower one $1/K$ for $\mathrm{cusp}(\boldsymbol{r}_{12})$. Both converge to expected values at $K \to \infty$, with accuracy of 10^{-4}, see Table 2. Based on these observations we expect that LECG basis can be used effectively in calculations of expectation values of other singular operators.

In summary, we have shown two things. First, it is possible to integrate analytically few electron ECG functions with terms linear in the interparticle distance. Second, the inclusion of linear terms significantly improves the incorrect behavior of ECG at coalescent points, which is important in the calculation of various relativistic effects. In particular, Kato's cusp relations, which in an ECG basis can never be fulfilled, can be recovered with high accuracy using LECG functions.

Table 2

Convergence of $\mathrm{cusp}(\boldsymbol{r}_i)$ with growing size of LECG expansion.

K	$\mathrm{cusp}(\boldsymbol{r}_1)$	$\mathrm{cusp}(\boldsymbol{r}_{12})$
75	$-1.959\,17$	$0.494\,307$
150	$-1.986\,80$	$0.497\,217$
300	$-1.996\,05$	$0.499\,349$
600	$-1.999\,60$	$0.499\,714$
∞	$-2.000\,0(1)$	$0.500\,0(1)$

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