Three-electron integral in Gaussian basis set with linear terms

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Abstract

The explicitly correlated Gaussian (ECG) functions allow an accurate determination of wave functions and energies of a few electron atoms. A recently introduced new variant of these functions (LECG) involving terms linear in interparticle distances exhibits a faster convergence and correct behavior at coalescent points as shown in pilot calculations for the helium atom. Extension of this method to atoms with more than two electrons requires dealing with a new type of three-electron integrals. In this work, we study in detail a generating three-electron integral, $\int \exp\left(-\sum_{i,j=1}^{3} a_{ij}\, \boldsymbol{r}_i \boldsymbol{r}_j\right)/(r_1\, r_2\, r_3)\, d\boldsymbol{r}_1\; d\boldsymbol{r}_2\; d\boldsymbol{r}_3$, present a compact analytical form and analyze its numerical evaluation.

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The explicitly correlated basis sets are the most accurate representations of a few electron wave functions, and thus give the best nonrelativistic energies. The Hylleraas functions have been applied with great success to helium [1], lithium [2] and, to some extent, to beryllium atoms [3]. The exponential functions with random exponents exhibit a fast convergence and are very convenient for the calculation of relativistic and QED effects in the helium atom [4, 5]. It is because of simplicity of the generating integral

$$\frac{1}{16\,\pi^2}\int\frac{e^{-\alpha\,r_1-\beta\,r_2-\gamma\,r_{12}}}{r_1\,r_2\,r_{12}}d\boldsymbol{r}_1\,d\boldsymbol{r}_2=\frac{1}{(\alpha+\beta)(\alpha+\gamma)(\beta+\gamma)}\,. \tag{1}$$

However, Hamiltonian matrix elements for three electron systems, in spite of having explicit analytic expression, are so complicated [6–8] that for numerical calculations it is more convenient to use various expansions in specific angular momentum [9]. The situation is even more complicated for beryllium and heavier atoms. For this reason, explicitly correlated Gaussian (ECG) functions [10], which lead to easily integrable expressions, seem to be very convenient in applications to atoms with three or four electrons. In the ECG basis the matrix elements of the nonrelativistic Hamiltonian as well as leading relativistic and radiative corrections can easily be represented in a closed form. For example, for beryllium atom the most accurate to date results have been obtained with ECG functions [11, 12]. These functions, however, exhibit a drawback common to all Gaussian type wave functions—the cusp condition at two-particle coalescent points can never be fulfilled. For this reason, we have recently introduced a new variant of the ECG functions augmented by a linear term in interparticle distances and call them LECG [13]. The numerical investigation on a simple example of the helium atom shows that a 600-term LECG wave function fulfills the cusp condition with precision of 10^{-5}. Moreover, the convergence of energy and expectation values of one- and two-electron Dirac δ-function have been significantly improved. Encouraged by these results we study the application of LECG to atoms with more than two electrons. In such a case, however, except for the two-electron integrals considered previously [13], a new, more complicated three-electron integral appears. Analytical evaluation and basic properties of this integral are the subject of this work.

The spatial part of the n-electron LECG basis function of S symmetry is

$$\phi(\boldsymbol{r})=R\,\exp\Bigl[-\sum_{i,j}^{n}a_{ij}\,\boldsymbol{r}_i\,\boldsymbol{r}_j\Bigr], \tag{2}$$

where R equals to one of the terms $1, r_k$, or $r_{kl}=|\boldsymbol{r}_k-\boldsymbol{r}_l|$. For higher angular momentum R includes even powers of various r_k and at most one odd power of r_l or r_{kl}. The n-electron

Hamiltonian matrix elements can be reduced to a set of two- and three-electron integrals over Gaussian functions. The two-electron integrals related to the nonrelativistic Hamiltonian, using the notation $G(r_1, r_2, r_{12}) = \exp(-a_1\, r_1^2 - a_2\, r_2^2 - a_3\, r_{12}^2)/\pi^3$, $a = \sqrt{a_1\, a_2 + a_1\, a_3 + a_2\, a_3}$, are the following:

$$\int G(r_1, r_2, r_{12})\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 = \frac{1}{a^3}\,, \tag{3}$$

$$\int \frac{G(r_1, r_2, r_{12})}{r_1}\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 = \frac{2}{\sqrt{\pi}\,\sqrt{a_2 + a_3}\, a^2}\,, \tag{4}$$

$$\int \frac{G(r_1, r_2, r_{12})}{r_1\, r_2}\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 = \frac{4}{\pi\, a_3\, a}\ \arctan\left(\frac{a_3}{a}\right), \tag{5}$$

$$\int \frac{G(r_1, r_2, r_{12})}{r_1\, r_2\, r_{12}}\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 = \frac{4}{\sqrt{\pi}\,\sqrt{a_1\, a_2\, a_3}}\ \arcsin\left[\frac{2\sqrt{a_1\, a_2\, a_3}}{a\,(\sqrt{a_1 + a_2} + \sqrt{a_1 + a_3} + \sqrt{a_2 + a_3})}\right]. \tag{6}$$

The formulas with inverse powers of r can be derived from the first one, Eq. (3), with the help of the following integral representation

$$\frac{1}{r} = \frac{1}{\sqrt{\pi}} \int_0^\infty \frac{e^{-t\, r^2}}{\sqrt{t}}\, dt\,. \tag{7}$$

The integrals with positive powers of r are obtained by differentiation with respect to a corresponding parameter. Considering many-electron integrals with LECG functions, they can always be transformed by reshuffling of r_i and r_{ij} to the following three–electron integral:

$$F = \int \frac{\exp\left(-\sum_{i,j=1}^{3} a_{ij}\, \boldsymbol{r}_i \boldsymbol{r}_j\right)}{r_1\, r_2\, r_3}\, d\boldsymbol{r}_1\ d\boldsymbol{r}_2\ d\boldsymbol{r}_3\,. \tag{8}$$

Let us present one example of this reshuffling. If the coefficient is $1/(r_{12}\, r_{23}\, r_{24})$, then in terms of new variables $\boldsymbol{R}_1 = \boldsymbol{r}_{24}$, $\boldsymbol{R}_2 = \boldsymbol{r}_{23}$, $\boldsymbol{R}_3 = \boldsymbol{r}_{12}$, $\boldsymbol{R}_4 = \boldsymbol{r}_1$, this coefficient is $1/(R_3\, R_2\, R_1)$. Integration with respect to $\boldsymbol{R}_4$ can easily be performed and leads directly to Eq. (8).

The study of the integral (8) and its application is the main purpose of this work. We perform it in four steps. At the first step we calculate, with the help of Eq. (5), the integral with inverse powers of r_1 and r_2 only:

$$\int \frac{\exp\left(-\sum_{i,j=1}^{3} a_{ij}\, \boldsymbol{r}_i \boldsymbol{r}_j\right)}{r_1\, r_2}\, d\boldsymbol{r}_1\ d\boldsymbol{r}_2\ d\boldsymbol{r}_3 = \frac{4\,\pi^{7/2}}{\sqrt{\det(a)}\,(a_{33}\, a_{12} - a_{13}\, a_{23})}\ \arctan\left(\frac{a_{33}\, a_{12} - a_{13}\, a_{23}}{\sqrt{\det(a)\, a_{33}}}\right). \tag{9}$$

In the second step, $1/r_3$ is obtained by integral representation of Eq. (7), therefore one obtains F as a one dimensional integral

$$F = \int_0^\infty \frac{dt}{\sqrt{t}} \frac{4\,\pi^3}{\sqrt{\det(a')}\,(a'_{33}\,a_{12} - a_{13}\,a_{23})} \arctan\left(\frac{a'_{33}\,a_{12} - a_{13}\,a_{23}}{\sqrt{\det(a')\,a'_{33}}}\right), \tag{10}$$

where $a'_{33} = a_{33} + t$ and a' means that a_{33} is shifted by t in the matrix a. This is not a trivial integral and it requires a non-standard approach. We use, in the third step, Remiddi's method [7] to calculate not the F alone but rather a derivative of another function H defined by the following equation

$$F = \frac{8\,\pi^3}{\sqrt{(a_{11}\,a_{23} - a_{12}\,a_{13})\,(a_{22}\,a_{13} - a_{12}\,a_{23})\,(a_{33}\,a_{12} - a_{13}\,a_{23})}}\,H. \tag{11}$$

The derivative of H with respect to any parameter is a much simpler function than H itself. In fact, what will become clear later, H is a sum of dilogarithmic functions. Function H depends effectively on three arguments

$$H = H\Big(\frac{a_{11}\,a_{23}}{a_{12}\,a_{13}}, \frac{a_{22}\,a_{13}}{a_{12}\,a_{23}}, \frac{a_{33}\,a_{12}}{a_{13}\,a_{23}}\Big) \equiv H(A_1, A_2, A_3), \tag{12}$$

where the last equation is a definition of A_1, A_2, A_3. The derivative of H with respect to the first argument is

$$\frac{\partial H}{\partial A_1} = \frac{x_2\,x_3}{2\,x_1\,(x_1^2\,y_1^2 + x_2^2\,x_3^2)} \left[\frac{x_2^2}{y_3} \arctan\left(\frac{1}{y_3}\right) + \frac{x_3^2}{y_2} \arctan\left(\frac{1}{y_2}\right) - y_1 \arctan\left(\frac{1}{y_1}\right)\right], \tag{13}$$

where

$$\begin{aligned} x_1 &= \sqrt{A_1 - 1}\,, & y_1 &= \sqrt{A_2\,A_3 - 1}\,, \\ x_2 &= \sqrt{A_2 - 1}\,, & y_2 &= \sqrt{A_1\,A_3 - 1}\,, \\ x_3 &= \sqrt{A_3 - 1}\,, & y_3 &= \sqrt{A_1\,A_2 - 1}\,. \end{aligned} \tag{14}$$

Because H is a symmetric function of its arguments A_1, A_2, A_3, the derivatives with respect to A_2 and A_3 can also be obtained from Eq. (13) by an exchange of indices.

Before going to the fourth step, let us note that the derivatives of H can be rewritten in a compact form as

$$\begin{aligned} dH = {} & \arctan\left(\frac{1}{y_1}\right) d\left[\arctan\left(\frac{1}{z_1}\right)\right] + \\ & \arctan\left(\frac{1}{y_2}\right) d\left[\arctan\left(\frac{1}{z_2}\right)\right] + \\ & \arctan\left(\frac{1}{y_3}\right) d\left[\arctan\left(\frac{1}{z_3}\right)\right], \end{aligned} \tag{15}$$

where

$$z_1 = \frac{x_1\,y_1}{x_2\,x_3}; \quad z_2 = \frac{x_2\,y_2}{x_1\,x_3}; \quad z_3 = \frac{x_3\,y_3}{x_1\,x_2}. \tag{16}$$

Such a differential form has already been considered in literature in the context of a volume of the tetrahedron in a space of the constant curvature and has the name of Schläfli‘s differential formula (see [14]). The differential (15) differs from that of Schläfli‘s merely in the argument of arctan. Instead of $1/y_i$ Schläfli has y_i which leads to a trivial change $\arctan(1/y) = \pi/2 - \arctan(y)$.

In the fourth and the last step of performing three-electron integral we apply a recent, compact and symmetric result of Murakami, Ushijima and Yano which has been reported in Refs. [14–16]. The identification of our integral to the volume of the tetrahedron is the following. Its 6 edges have the lengths x_i and y_i with $i = 1, 2, 3$. Three dihedral angles with edges x_i coming from the same vertex are equal to $\pi/2$, three other dihedral angles are equal to $\alpha_i = \arctan(z_i)$ and correspond to edges y_i. The relation between the tetrahedron angles and edge lengths corresponds exactly to dependence of x_i and y_i on α_i, namely

$$y_1 = \frac{\sin\alpha_1}{\cos\alpha_2\,\cos\alpha_3}\sqrt{1-\cos^2(\alpha_1)-\cos^2(\alpha_2)-\cos^2(\alpha_3)}\,, \tag{17}$$

$$x_1 = \frac{1}{\cos\alpha_1}\sqrt{1-\cos^2(\alpha_1)-\cos^2(\alpha_2)-\cos^2(\alpha_3)}\,. \tag{18}$$

It allows us to quickly obtain a compact analytic form for H. First, we assume that x_i, y_i, z_i are real and other cases are considered subsequently. The result is

$$H = H_1 = v - \frac{\pi^2}{4} - \frac{\pi}{2}\,(\alpha_1+\alpha_2+\alpha_3) - 2\,\pi\,\beta_1 + \pi\,\beta_2\,, \tag{19}$$

where

$$v = \frac{u(\beta_1)-u(\beta_2)}{2}\,, \tag{20}$$

$$\begin{aligned} u(\beta) = {} & \mathrm{Li}_2\left[-e^{i\,(\beta-\pi/4)}\right] - \mathrm{Li}_2\left[-e^{i\,(\beta+\pi/4)}\right] + \\ & \mathrm{Li}_2\left[e^{i\,(\alpha_1+\alpha_2+\beta-\pi/4)}\right] - \mathrm{Li}_2\left[e^{i\,(\alpha_1+\alpha_2+\beta+\pi/4)}\right] + \\ & \mathrm{Li}_2\left[e^{i\,(\alpha_1+\alpha_3+\beta-\pi/4)}\right] - \mathrm{Li}_2\left[e^{i\,(\alpha_1+\alpha_3+\beta+\pi/4)}\right] + \\ & \mathrm{Li}_2\left[e^{i\,(\alpha_2+\alpha_3+\beta-\pi/4)}\right] - \mathrm{Li}_2\left[e^{i\,(\alpha_2+\alpha_3+\beta+\pi/4)}\right]\,, \end{aligned} \tag{21}$$

$$\beta_1 = -i\,\ln\left[\frac{\sqrt{2}}{q}\left(\sin(\alpha_1)+\sin(\alpha_2)+\sin(\alpha_3)+\sqrt{d}\right)\right] - \pi\,, \tag{22}$$

$$\beta_2 = -i\,\ln\left[\frac{\sqrt{2}}{q}\left(\sin(\alpha_1)+\sin(\alpha_2)+\sin(\alpha_3)-\sqrt{d}\right)\right] - \pi\,, \tag{23}$$

$$q = -i\left[e^{i\,\alpha_1} + e^{i\,\alpha_2} + e^{i\,\alpha_3} - e^{i\,(\alpha_1+\alpha_2+\alpha_3)}\right], \tag{24}$$

$$d = 1 - \cos^2(\alpha_1) - \cos^2(\alpha_2) - \cos^2(\alpha_3)\,. \tag{25}$$

Dilogarithm, Li_2, is a multiple-valued function, therefore, when assuming a principal Riemann sheet, additional terms had to be added in Eq. (19) to ensure the correctness of the obtained result. These additional terms are different when x_i and z_i become imaginary. Note, that y_i are always real and by definition positive which is a consequence of the positive definiteness of the a_{ij} matrix. If any of A_i is less than 1, the corresponding x_i is purely imaginary. For this reason we have to consider three different possibilities. Firstly, all three x_i are real, and this case has already been described above. The second case is when all x_i are imaginary, and the third case corresponds to just one imaginary x_i. The case of two imaginary x_i is excluded due again to positive definiteness of a_{ij} matrix. We follow here a convention that a square root of any negative number c is by definition equal to $+i\sqrt{-c}$.

Thus, if all x_i are imaginary, from positive definiteness of a_{ij} matrix, one has $\Im(z_1) < -1$, $\Im(z_2) < -1$, $\Im(z_3) < -1$, and function H reads

$$H_2 = v - \frac{\pi^2}{4} - \frac{\pi}{2}\,(\alpha_1 + \alpha_2 + \alpha_3) - 2\,\pi\,\beta_1 + \pi\,\beta_2\,, \tag{26}$$

with

$$\begin{aligned} \alpha_1 &= \frac{\pi}{2} + i\,\mathrm{arccoth}(i\,z_1)\,, \\ \alpha_2 &= \frac{\pi}{2} + i\,\mathrm{arccoth}(i\,z_2)\,, \\ \alpha_3 &= \frac{\pi}{2} + i\,\mathrm{arccoth}(i\,z_3)\,. \end{aligned} \tag{27}$$

In the last, third case, let us take x_1 imaginary, and x_2, x_3 real. Then $0 < \Im(z_1) < 1$, $\Im(z_2) < -1$, $\Im(z_3) < -1$, and one has

$$H_3 = v - \frac{\pi^2}{4} - \frac{\pi}{2}\,(3\,\alpha_1 + \alpha_2 + \alpha_3) - \pi\,\beta_1\,, \tag{28}$$

and

$$\begin{aligned} \alpha_1 &= i\,\mathrm{arctanh}(i\,z_1)\,, \\ \alpha_2 &= \frac{\pi}{2} + i\,\mathrm{arccoth}(i\,z_2)\,, \\ \alpha_3 &= \frac{\pi}{2} + i\,\mathrm{arccoth}(i\,z_3)\,. \end{aligned} \tag{29}$$

The obtained formulas can now be used for the evaluation of the three-electron integral F, Eq. (11). Dilogarithmic functions in Eqs. (19,26,28) are assumed to lie on a principal Riemann sheet with the discontinuity on real axis with $x > 1$. However, these formulas become numerically unstable when off-diagonal terms a_{ij} are very small or equal to 0. In this case H has to be rewritten to such a form that the limit of $a_{ij} \to 0$ can be performed safely.

To summarize this part of the work, let us present numerical values at some chosen points for all three cases, with the notation $F = F(a_{11}, a_{22}, a_{33}, a_{23}, a_{13}, a_{12})$

$$\begin{aligned} F(3,3,3,1,1,1) &= 11.350\,156\,185\,314\,221\,719\,, \\ F(3,3,3,-1,-1,-1) &= 12.492\,829\,944\,019\,484\,168\,, \\ F(1,8,8,2,2,2) &= 10.906\,347\,222\,455\,437\,808\,. \end{aligned} \tag{30}$$

In the calculation of Hamiltonian matrix elements in LECG basis set the actual integral involves $r_1 r_2/r_3$. It can be obtained from F by a differentiation with respect to a_{11} and a_{22}. With the help of Eq. (13) one obtains

$$\begin{aligned} &\int \exp\left(-\sum_{i,j=1}^{3} a_{ij}\,\boldsymbol{r}_i \boldsymbol{r}_j\right) \frac{r_1\,r_2}{r_3}\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2\, d\boldsymbol{r}_3 = \frac{F}{4\,a_{12}^2\,x_1^2\,x_2^2} + \\ &\frac{2\,\pi^3}{a_{12}^3\,a_{23}\,a_{13}} \left\{ \frac{1}{\delta\,y_3^2} + \frac{(\delta - 2\,x_1^2\,x_3^2)}{\delta^2\,x_1^2\,x_2^2}\, y_1 \arctan\left(\frac{1}{y_1}\right) + \frac{(\delta - 2\,x_2^2\,x_3^2)}{\delta^2\,x_1^2\,x_2^2}\, y_2 \arctan\left(\frac{1}{y_2}\right) \right. \\ &\left. + \left[\frac{3\,\delta - 2\,x_1^2\,x_2^2}{\delta^2\,y_3^3} - \frac{x_1^2 + x_2^2}{\delta\,x_1^2\,x_2^2\,y_3}\right] \arctan\left(\frac{1}{y_3}\right) \right\}, \end{aligned} \tag{31}$$

where

$$\delta = x_1^2\,x_2^2\,x_3^2 + x_1^2\,x_2^2 + x_2^2\,x_3^2 + x_1^2\,x_3^2 = x_1^2\,y_1^2 + x_2^2\,x_3^2. \tag{32}$$

The obtained formula completes the analytical evaluation of the three electron integrals with LECG functions.

Hopefully, this basis set will allow obtaining significantly improved energies of a few electron atoms such as lithium and beryllium. Our expectations are based on the fact that with LECG functions the cusp condition at two-particle coalescent points can be fulfilled to a high accuracy, which overcomes the main problem of the ordinary ECG functions. This feature is responsible for the acceleration of the convergence observed already in the two-electron case [13]. The price one pays is, however, more complicated analytical expression for the Hamiltonian matrix elements. It would be interesting to perform similar integral for molecular systems. Although it can be expressed as a one-dimensional integral similar to the inverse Laplace transform, we have not yet been able to obtain an analytic form.

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