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Two-center two-electron integrals with exponential functions

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Abstract

We present an efficient approach to evaluate two-center two-electron integrals with exponential functions and with an arbitrary polynomial in electron-nucleus and electron-electron distances. We show that the master integral with the single negative power of all distances can be obtained from the second order differential equation in r, the distance between nuclei. For particular values of nonlinear parameters corresponding to the James-Coolidge basis, we find a fully analytic expression. For integrals with arbitrary powers of all distances, we construct recursion relations which starts from the master integral. The presented approach opens a window for the high precision calculations of relativistic effects in diatomic molecules.

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I. INTRODUCTION

In order to calculate accurately relativistic effects in atomic or molecular systems, the wave function should satisfy cusp conditions. Namely, at the electron-nucleus and electron-electron coalescence points the derivative of the wave function is proportional to the wave function itself, with coefficients proportional to $-Z$ or $1/2$ correspondingly. The widely used Gaussian basis set does not satisfy any of these conditions, therefore the numerical convergence of relativistic effects, is slow or sometimes even does not lead to the right result. It has been found recently [1] that inclusion of the single factor $e^{-\lambda\, r_{12}}$ on the top of Gaussian functions significantly improves convergence of the nonrelativistic energy. Even better analytic properties are satisfied by the exponential (Slater) basis set with polynomials of electron-nucleus and electron-electron distances. Moreover, the large distance asymptotics of exponential functions agrees with that obtained from quasi-classical expansion. However the usage of exponential functions in molecular calculations has been limited due to inherent difficulties in the accurate and efficient calculations of multi-center integrals. In this work we overcome this problem for the simplest case of the two-electron and two-center integral, with arbitrary nonlinear parameters and arbitrary powers of electron-nucleus and electron-electron distances. We show, that the master integral, with single negative power of all distances satisfies a second order differential equation in the nuclear distance r. This equation can be solved numerically, or in the case of James-Coolidge basis, is solved analytically in terms of Ei- the exponential integral functions. The integrals with higher powers of electron distances are obtained by analytic recursion relations which involve the master integral and elementary functions. Our approach is based on a set of integration by parts identities, and is well established in the area of multi-loop Feynman diagrams [2]. Integration by parts identities, similar to those derived here, were recently applied to three-electron one-center Hylleraas [3] and exponentially correlated [4] integrals.

Let us now define the master two-electron and two-center integral $f(r)$, where $r = r_{AB}$,

$$f(r) = \int \frac{d^3 r_1}{4\,\pi} \int \frac{d^3 r_2}{4\,\pi}\, \frac{e^{-u_3\, r_{1A}}}{r_{1A}}\, \frac{e^{-u_2\, r_{1B}}}{r_{1B}}\, \frac{e^{-w_2\, r_{2A}}}{r_{2A}}\, \frac{e^{-w_3\, r_{2B}}}{r_{2B}}\, \frac{r}{r_{12}}, \tag{1}$$

where $1, 2$ are the positions of the electrons, A, B positions of the nuclei, and the notation for nonlinear parameters will be clarified later on. For practical reasons, it is easier at first to consider another integral g defined by

$$g(u_1) = \int \frac{d^3\rho_1}{4\,\pi} \int \frac{d^3\rho_2}{4\,\pi} \int \frac{d^3\rho_3}{4\,\pi} \frac{e^{-w_1\,\rho_1 - w_2\,\rho_2 - w_3\,\rho_3 - u_1\,\rho_{23} - u_2\,\rho_{31} - u_3\,\rho_{12}}}{\rho_{23}\,\rho_{31}\,\rho_{12}\,\rho_1\,\rho_2\,\rho_3}, \tag{2}$$

with $\vec{\rho}_1 = \vec{r}_{12}$, $\vec{\rho}_2 = \vec{r}_{2A}$, $\vec{\rho}_3 = \vec{r}_{2B}$, which is related to f by a Laplace transform, namely

$$g(t)\Big|_{w_1=0} = \int \frac{d^3 r}{4\,\pi}\, f(r)\, \frac{e^{-t\,r}}{r^2} = \int_0^\infty dr\, f(r)\, e^{-t\,r}, \tag{3}$$

$$f(r) = \frac{1}{2\,\pi\,i} \int_{-i\,\infty+\epsilon}^{i\,\infty+\epsilon} dt\, e^{t\,r}\, g(t)\Big|_{w_1=0}. \tag{4}$$

The integral f_n ($f_0 = f$) with the integer power $n \geq 0$ of inter-electronic distance r_{12}

$$f_n(r) = \int \frac{d^3 r_1}{4\,\pi} \int \frac{d^3 r_2}{4\,\pi} \frac{e^{-u_3\,r_{1A}}}{r_{1A}} \frac{e^{-u_2\,r_{1B}}}{r_{1B}} \frac{e^{-w_2\,r_{2A}}}{r_{2A}} \frac{e^{-w_3\,r_{2B}}}{r_{2B}}\, r_{12}^{n-1}\, r, \tag{5}$$

can be obtained from g by differentiation over w_1, see Eq. (43). A similar situation holds for integrals with integer powers $i, j, k, l \geq 0$ of all electron-nucleus distances

$$f_n(i,j,k,l;r) = \int \frac{d^3 r_1}{4\,\pi} \int \frac{d^3 r_2}{4\,\pi} \frac{e^{-u_3\,r_{1A}}}{r_{1A}^{1-i}} \frac{e^{-u_2\,r_{1B}}}{r_{1B}^{1-j}} \frac{e^{-w_2\,r_{2A}}}{r_{2A}^{1-k}} \frac{e^{-w_3\,r_{2B}}}{r_{2B}^{1-l}} \frac{r}{r_{12}^{1-n}}. \tag{6}$$

They can be obtained by further differentiation of g in Eq. (2) over nonlinear parameters u_2, u_3, w_2, w_3. For this we derive recursion relations, which make possible in practice the evaluation of integrals with many powers of electron-electron and electron-nucleus distances. The function g will be calculated from the pertinent integral in the momentum space, namely

$$g(u_1) = G(1,1,1;1,1,1), \tag{7}$$

where

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

The topology of these integrals and the notation is presented in Fig. (1).

In Sec. II we will derive a differential equation which is satisfied by the function g. This equation can be used to obtain an analytic form of g. However, we find that it is too complicated for practical applications. In Sec. III we perform an inverse Laplace transform to obtain a differential equation for the master integral $f(r)$, which can be conveniently solved numerically. In Sec. IV and V, using this differential equation for g, we derive recursion relations for evaluation of $f_n(i,j,k,l;r)$ in Eq. (6). In Sec. VI and VII we work out special cases of direct and exchange atomic integrals. In Sec. VIII we consider symmetric integrals which are suited for the H_2 molecule, and for them we obtain a simple analytic form. Finally in Sec. IX we present a short summary.

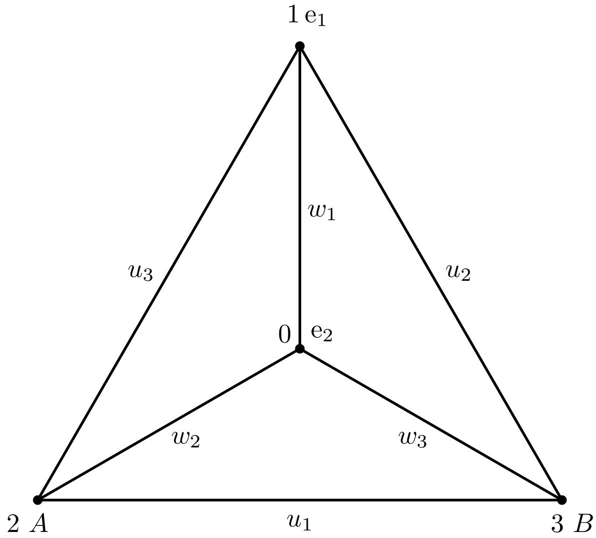

FIG. 1: The tetrahedron geometry of the master integral. The double notation is used for vertices, namely vertices $1\,(\mathrm{e}_1)$ and $0\,(\mathrm{e}_2)$ correspond to the position of the first and the second electron, vertices $2\,(A)$ and $3\,(B)$ correspond to the position of nuclei. The nonlinear parameter w_1 is related to r_{12} distance and $u_1 = t$ to $r = r_{AB}$.

II. DIFFERENTIAL EQUATION

We use the method of integration by parts identities [2], which is by now standard in the analytical calculation of Feynman diagrams. In our case, it amounts to considering the following 9 identities in the momentum space representation of the integral G, $(i,j = 1,2,3)$

$$0 \equiv \mathrm{id}(i,j) = \int d^3k_1 \int d^3k_2 \int d^3k_3 \, \frac{\partial}{\partial \vec{k}_j} \Big[\vec{k}_i \,(k_1^2 + u_1^2)^{-m_1}$$
$$(k_2^2 + u_2^2)^{-m_2} \,(k_3^2 + u_3^2)^{-m_3} (k_{32}^2 + w_1^2)^{-m_4} \,(k_{13}^2 + w_2^2)^{-m_5} \,(k_{21}^2 + w_3^2)^{-m_6}\Big], \tag{9}$$

which are trivially valid, because the integral of the derivative of a function vanishing at infinity vanishes. These identities have been first introduced in Ref. [3] for the calculation of one-center three-electron Hylleraas integrals. They group naturally into three sets. The first set consists of id(1, 1), id(2, 1), and id(3, 1). Other sets are obtained by changing the second argument from 1 into 2 or 3. The reduction of the scalar products from the numerator leads to identities between functions G of different arguments. Whenever $m_i = 0$, G becomes a known three-body integral, for example

$$G(0,1,1;1,1,1) \;=\; \frac{1}{2\,w_1}\Big[\mathrm{Li}\Big(1 - \frac{u_2+u_3+w_2+w_3}{u_2+u_3+w_1}\Big) + \mathrm{Li}\Big(1 - \frac{u_2+u_3+w_2+w_3}{w_1+w_2+w_3}\Big)$$

$$+\frac{1}{2}\,\ln^2\!\Big(\frac{w_1+w_2+w_3}{u_2+u_3+w_1}\Big)+\frac{\pi^2}{6}\Big], \tag{10}$$

where Li is the dilogarithmic function. If we assume all $m_i = 1$ in Eq. (8) and solve an arbitrary set of three equations, for example the last one, against three unknowns $G(1,1,2;1,1,1), G(1,1,1;2,1,1), G(1,1,1;1,2,1)$, then the solution for $G(1,1,1;2,1,1)$ is of the form

$$\frac{1}{2}\,\frac{\partial\sigma}{\partial w_1}\,G(1,1,1;1,1,1)-2\,w_1\,\sigma\,G(1,1,1;2,1,1)+P(w_1,u_1;w_2,u_2;w_3,u_3)=0, \tag{11}$$

where σ is a polynomial with a tetrahedral symmetry

$$\begin{aligned}\sigma \;=\;& u_1^2\,u_2^2\,w_3^2+u_2^2\,u_3^2\,w_1^2+u_1^2\,u_3^2\,w_2^2+w_1^2\,w_2^2\,w_3^2+u_1^2\,w_1^2\,(u_1^2+w_1^2-u_2^2-u_3^2-w_2^2-w_3^2)\\ &+u_2^2\,w_2^2\,(u_2^2+w_2^2-u_1^2-u_3^2-w_1^2-w_3^2)+u_3^2\,w_3^2\,(u_3^2+w_3^2-u_2^2-u_1^2-w_1^2-w_2^2),\end{aligned} \tag{12}$$

and

$$\begin{aligned}&P(w_1,u_1;w_2,u_2;w_3,u_3)\\ =\;& u_1\,w_1\,[(u_1+w_2)^2-u_3^2]\,\Gamma(u_2+w_1,u_3,u_1+w_2)\\ &+u_1\,w_1\,[(u_1+u_3)^2-w_2^2]\,\Gamma(w_1+w_3,w_2,u_1+u_3)\\ &-[u_1^2\,w_1^2+u_2^2\,w_2^2-u_3^2\,w_3^2+w_1\,w_2\,(u_1^2+u_2^2-w_3^2)]\,\Gamma(u_1+u_2,w_3,w_1+w_2)\\ &-[u_1^2\,w_1^2-u_2^2\,w_2^2+u_3^2\,w_3^2+w_1\,w_3\,(u_1^2+u_3^2-w_2^2)]\,\Gamma(u_1+u_3,w_2,w_1+w_3)\\ &+[u_2\,(u_2+w_1)\,(u_1^2+u_3^2-w_2^2)-u_3^2\,(u_1^2+u_2^2-w_3^2)]\,\Gamma(u_1+w_2,u_3,u_2+w_1)\\ &+[u_3\,(u_3+w_1)\,(u_1^2+u_2^2-w_3^2)-u_2^2\,(u_1^2+u_3^2-w_2^2)]\,\Gamma(u_1+w_3,u_2,u_3+w_1)\\ &-w_1\,[w_2\,(u_1^2-u_2^2+w_3^2)+w_3\,(u_1^2+w_2^2-u_3^2)]\,\Gamma(u_2+u_3,w_1,w_2+w_3)\\ &-w_1\,[u_2\,(u_1^2-w_2^2+u_3^2)+u_3\,(u_1^2+u_2^2-w_3^2)]\,\Gamma(w_2+w_3,w_1,u_2+u_3),\end{aligned} \tag{13}$$

with

$$\Gamma(\alpha_1,\alpha_2,\alpha_3)=\frac{\ln(\alpha_1+\alpha_2)-\ln(\alpha_1+\alpha_3)}{(\alpha_2-\alpha_3)\,(\alpha_2+\alpha_3)}. \tag{14}$$

Since $G(1,1,1;1,1,1)=g$ and

$$G(1,1,1;2,1,1)=-\frac{1}{2\,w_1}\,\frac{\partial g}{\partial w_1}, \tag{15}$$

Eq. (11) takes the form of a differential equation

$$\sigma\,\frac{\partial g}{\partial w_1}+\frac{1}{2}\,\frac{\partial\sigma}{\partial w_1}\,g+P(w_1,u_1;w_2,u_2;w_3,u_3)=0\,, \tag{16}$$

or

$$\sqrt{\sigma}\frac{\partial}{\partial w_1}(\sqrt{\sigma}\, g) + P(w_1, u_1; w_2, u_2; w_3, u_3) = 0\,. \tag{17}$$

Analogous differential equations with respect to other parameters can be obtained by appropriate permutation of arguments, using the tetrahedral symmetry of the function g. The solution of this differential equation is presented in the work of Fromm and Hill in [5] in the context of the analytic evaluation of the three-electron integral. However, they have not used the differential equation approach, but instead performed all integrals directly in momentum space.

III. THE MASTER INTEGRAL

Let us assume $w_1 = 0$. The differential equation in variable $t = u_1$ is

$$\sigma\,\frac{\partial g}{\partial t} + \frac{1}{2}\,\frac{\partial \sigma}{\partial t}\,g + P(t, 0; u_3, w_3; w_2, u_2) = 0\,, \tag{18}$$

where σ from Eq.(12) is now

$$\sigma = (u_2^2 - u_3^2 + w_2^2 - w_3^2)\,(u_2^2\,w_2^2 - u_3^2\,w_3^2) - t^2\,(u_2^2 - u_3^2)\,(w_2^2 - w_3^2)\,. \tag{19}$$

This differential equation takes the form

$$(t^2 - p^2)\,g' + t\,g = R(t), \tag{20}$$

where

$$p^2 = \frac{(u_2^2 - u_3^2 + w_2^2 - w_3^2)\,(u_2^2\,w_2^2 - u_3^2\,w_3^2)}{(u_2^2 - u_3^2)\,(w_2^2 - w_3^2)}, \tag{21}$$

$$\begin{aligned} R(t) &= \frac{P(t, 0; u_3, w_3; w_2, u_2)}{(u_2^2 - u_3^2)\,(w_2^2 - w_3^2)} \\ &= \frac{1}{2}\Big[a^+\,R_1(t) + b^+\,R_2(t) + a^-\,R_3(t) + b^-\,R_4(t)\Big], \end{aligned} \tag{22}$$

and

$$a^\pm = \frac{w_2}{w_2^2 - w_3^2} \pm \frac{u_3}{u_2^2 - u_3^2}, \tag{23}$$

$$b^\pm = \frac{u_2}{u_2^2 - u_3^2} \pm \frac{w_3}{w_2^2 - w_3^2}, \tag{24}$$

$$R_1(t) = \frac{1}{t + u_3 - w_2}\,\ln\!\Big(\frac{t + u_3 + w_3}{w_2 + w_3}\Big) - \frac{1}{t - u_3 + w_2}\,\ln\!\Big(\frac{t + u_2 + w_2}{u_2 + u_3}\Big), \tag{25}$$

$$
\begin{aligned}
R_2(t) &= \frac{1}{t-u_2+w_3}\,\ln\Big(\frac{t+u_3+w_3}{u_2+u_3}\Big)-\frac{1}{t+u_2-w_3}\,\ln\Big(\frac{t+u_2+w_2}{w_2+w_3}\Big), && (26)\\
R_3(t) &= \frac{1}{t-u_3-w_2}\,\ln\Big(\frac{t+u_2+w_3}{u_2+u_3+w_2+w_3}\Big)\\
&\quad -\frac{1}{t+u_3+w_2}\,\ln\Big[\frac{(t+u_2+w_2)\,(t+u_3+w_3)\,(u_2+u_3+w_2+w_3)}{(t+u_2+w_3)(u_2+u_3)\,(w_2+w_3)}\Big], && (27)\\
R_4(t) &= \frac{1}{t-u_2-w_3}\,\ln\Big(\frac{t+u_3+w_2}{u_2+u_3+w_2+w_3}\Big)\\
&\quad -\frac{1}{t+u_2+w_3}\,\ln\Big[\frac{(t+u_2+w_2)\,(t+u_3+w_3)\,(u_2+u_3+w_2+w_3)}{(t+u_3+w_2)(u_2+u_3)\,(w_2+w_3)}\Big]. && (28)
\end{aligned}
$$

One performs the inverse Laplace transform of Eq. (20) and obtains the differential equation for the function f

$$
r\,f''(r)+f'(r)-p^2\,r f(r)+F(r)=0\,, \tag{29}
$$

where

$$
\begin{aligned}
F(r) &= \frac{1}{2\,\pi\,i}\int_{-i\,\infty+\epsilon}^{i\,\infty+\epsilon} dt\,e^{t\,r}\,R(t) && (30)\\
&= \frac{1}{2}\Big[a^+\,F_1^-(r)+b^+\,F_2^-(r)+a^-\,F_3^-(r)+b^-\,F_4^-(r)\Big], && (31)
\end{aligned}
$$

and F_i^- are the inverse Laplace transform of R_i,

$$
\begin{aligned}
F_1^{\pm}(r) &= e^{r\,(u_3-w_2)}\,\mathrm{Ei}[-r(u_2+u_3)]\pm e^{r\,(w_2-u_3)}\,\mathrm{Ei}[-r(w_2+w_3)], && (32)\\
F_2^{\pm}(r) &= e^{r\,(w_3-u_2)}\,\mathrm{Ei}[-r(w_2+w_3)]\pm e^{r\,(u_2-w_3)}\,\mathrm{Ei}[-r(u_2+u_3)], && (33)\\
F_3^{\pm}(r) &= e^{-r\,(u_3+w_2)}\,\Big\{\ln\Big|\frac{(u_2+w_3-u_3-w_2)(u_2+u_3)\,(w_2+w_3)}{(u_2+u_3+w_2+w_3)(u_2-u_3)(w_2-w_3)}\Big|-\mathrm{Ei}[r(u_3+w_2-u_2-w_3)]\\
&\quad +\mathrm{Ei}[r(w_2-w_3)]+\mathrm{Ei}[r(u_3-u_2)]\Big\}\pm e^{r\,(u_3+w_2)}\,\mathrm{Ei}[-r(u_2+u_3+w_2+w_3)], && (34)\\
F_4^{\pm}(r) &= e^{-r\,(u_2+w_3)}\Big\{\ln\Big|\frac{(u_2+w_3-u_3-w_2)(u_2+u_3)\,(w_2+w_3)}{(u_2+u_3+w_2+w_3)(u_2-u_3)(w_2-w_3)}\Big|-\mathrm{Ei}[r(u_2+w_3-u_3-w_2)]\\
&\quad +\mathrm{Ei}[r(w_3-w_2)]+\mathrm{Ei}[r(u_2-u_3)]\Big\}\pm e^{r\,(u_2+w_3)}\,\mathrm{Ei}[-r(u_2+u_3+w_2+w_3)]. && (35)
\end{aligned}
$$

The solution of the differential equation (29) is

$$
f(r)=I_0(p\,r)\int_r^{\infty} dr'\,F(r')\,K_0(p\,r')+K_0(p\,r)\int_0^r dr'\,F(r')\,I_0(p\,r')\,, \tag{36}
$$

where I_0 and K_0 are modified Bessel functions. This is our principal result for the master integral f. In this work we do not present any numerical examples for validation of Eq. (36), but nevertheless verify, that in the limit of small r the function $f(r)$

$$
f(r)=-r\,F(0)+O(r^2), \tag{37}
$$

where

$$F(0) = \frac{1}{w_2+w_3}\,\ln\Bigl(\frac{u_2+u_3}{u_2+u_3+w_2+w_3}\Bigr) + \frac{1}{u_2+u_3}\,\ln\Bigl(\frac{w_2+w_3}{u_2+u_3+w_2+w_3}\Bigr) \tag{38}$$

coincides with the corresponding helium integral.

We will show in next sections that all the two-electron two-center integrals can be expressed in terms of f, the first derivative f'

$$f'(r) = p\,\Bigl[I_1(p\,r)\int_r^\infty dr'\,F(r')\,K_0(p\,r') - K_1(p\,r)\int_0^r dr'\,F(r')\,I_0(p\,r')\Bigr], \tag{39}$$

the exponential integral Ei, and exponential functions. In the derivation of integrals with powers of r_{12}, we will need higher order derivatives $f^{(n)}$ and they can be obtained directly from the differential equation (29),

$$f^{(n)}(r) = (n-2)\,\frac{p^2}{r}\,f^{(n-3)}(r) + p^2\,f^{(n-2)}(r) - (n-1)\,\frac{1}{r}\,f^{(n-1)}(r) - \frac{1}{r}\,F^{(n-2)}(r). \tag{40}$$

IV. POWERS OF r_{12}

We now pass to the calculation of $f_n(r)$, the integral with r_{12}^{n-1}. For this we use two differential equations with respect to w_1 and u_1

$$\mathrm{eq}_1 \;\equiv\; \sigma\,\frac{\partial g}{\partial u_1} + \frac{1}{2}\,\frac{\partial \sigma}{\partial u_1}\,g + P(u_1,w_1;u_3,w_3;w_2,u_2) = 0\,, \tag{41}$$

$$\mathrm{eq}_2 \;\equiv\; \sigma\,\frac{\partial g}{\partial w_1} + \frac{1}{2}\,\frac{\partial \sigma}{\partial w_1}\,g + P(w_1,u_1;w_2,u_2;w_3,u_3) = 0\,. \tag{42}$$

In the first step the first equation is differentiated $n+1$ times with respect to w_1 and the second equation n times, at $w_1 = 0$. In the second step, an inverse Laplace transform is performed of both equations. According to Eq. (6)

$$f_n(r) = (-1)^n\,\frac{\partial^n}{\partial w_1^n}\Big|_{w_1=0}\,\frac{1}{2\,\pi\,i}\int_{-i\,\infty+\epsilon}^{i\,\infty+\epsilon} dt\,e^{t\,r}\,g(t)\,, \tag{43}$$

and let us introduce analogous notation

$$U_n(r) \;=\; (-1)^n\,\frac{\partial^n}{\partial w_1^n}\Big|_{w_1=0}\,\frac{1}{2\,\pi\,i}\int_{-i\,\infty+\epsilon}^{i\,\infty+\epsilon} dt\,e^{t\,r}\,P(t,w_1;u_3,w_3;w_2,u_2), \tag{44}$$

$$W_n(r) \;=\; (-1)^n\,\frac{\partial^n}{\partial w_1^n}\Big|_{w_1=0}\,\frac{1}{2\,\pi\,i}\int_{-i\,\infty+\epsilon}^{i\,\infty+\epsilon} dt\,e^{t\,r}\,P(w_1,t;w_2,u_2;w_3,u_3), \tag{45}$$

$$V_n(r) \;=\; (-1)^n\,\frac{\partial^n}{\partial w_1^n}\Big|_{w_1=0}\,\frac{1}{2\,\pi\,i}\int_{-i\,\infty+\epsilon}^{i\,\infty+\epsilon} dt\,e^{t\,r}\,P(w_3,u_3;w_2,u_2;w_1,t). \tag{46}$$

In the third step the combination

$$\frac{\partial}{\partial r}(\mathrm{eq}_1 + r\,\mathrm{eq}_2) + \mathrm{eq}_2 \tag{47}$$

is formed, where all derivatives of $f_{n+1}(r)$ cancel out, and the resulting equation is solved against $f_{n+1}(r)$

$$\begin{aligned} f_{n+1}(r) \;=\; & \frac{1}{(u_2^2-u_3^2+w_2^2-w_3^2)\,(u_2^2\,w_2^2-u_3^2\,w_3^2)}\Big\{2\,W_n(r)+r\,W_n'(r)-U_{n+1}'(r) \\ & +n\,(u_3^2-w_2^2)\,(u_2^2-w_3^2)\,[r\,f_{n-1}'(r)-(n-1)\,f_{n-1}(r)] \\ & -n\,(u_2^2+u_3^2+w_2^2+w_3^2)\,[r\,f_{n-1}^{(3)}(r)+2\,f_{n-1}^{(2)}(r)] \\ & +n\,[r\,f_{n-1}^{(5)}(r)+(n+3)\,f_{n-1}^{(4)}(r)] \\ & +2\,(n-2)\,(n-1)\,n\,[r\,f_{n-3}^{(3)}(r)+2\,f_{n-3}^{(2)}(r)]\Big\}. \end{aligned} \tag{48}$$

This recursion relation allows one to obtain integral with an arbitrary power n of r_{12}, knowing integrals with $n-2, n-4$ and its derivatives with respect to r, for example

$$\begin{aligned} f_2(r) \;=\; & \frac{(u_2^2-u_3^2+w_3^2-w_2^2)\,(u_2^2\,w_3^2-u_3^2\,w_2^2)\,f(r)}{q^2} - \frac{a^-\,a^+\,b^-\,b^+\,q\,r\,f'(r)}{p^2} + \frac{f''(r)}{q} \\ & +\left(r+\frac{u_2}{u_2^2-u_3^2}+\frac{w_2}{w_2^2-w_3^2}\right)\frac{e^{-r\,(u_2+w_2)}}{q\,r} + \left(r-\frac{u_3}{u_2^2-u_3^2}-\frac{w_3}{w_2^2-w_3^2}\right)\frac{e^{-r\,(u_3+w_3)}}{q\,r} \\ & -b^-\,\frac{e^{-r\,(u_3+w_2)}}{q\,r} - a^-\,\frac{e^{-r\,(u_2+w_3)}}{q\,r} - \frac{a^+\,a^-\,b^+\,b^-}{2\,p^2}\left[\frac{(w_2-u_3)}{a^+}\,F_1^+(r)\right. \\ & \left.+\frac{(u_2-w_3)}{b^+}\,F_2^+(r)+\frac{(w_2+u_3)}{a^-}\,F_3^+(r)+\frac{(u_2+w_3)}{b^-}\,F_4^+(r)\right], \end{aligned} \tag{49}$$

where

$$q \;=\; (u_2^2-u_3^2)\,(w_2^2-w_3^2). \tag{50}$$

V. POWERS OF r_{1A}, r_{1B}, r_{2A}, AND r_{2B}

Finally we pass to integrals with powers of r_{1A}, r_{1B}, r_{2A}, and r_{2B}. These are obtained by differentiation of $f_n(r)$ with respect to corresponding parameters u_3, u_2, w_2, and w_3. Let us consider differentiation of f with respect to w_3. We again use differential equations to derive corresponding recursion relations, namely

$$\mathrm{eq}_1 \;\equiv\; \sigma\,\frac{\partial g}{\partial u_1}+\frac{1}{2}\,\frac{\partial\sigma}{\partial u_1}\,g+P(u_1,w_1;u_3,w_3;w_2,u_2)=0\,, \tag{51}$$

$$\mathrm{eq}_3 \;\equiv\; \sigma\,\frac{\partial g}{\partial w_3}+\frac{1}{2}\,\frac{\partial\sigma}{\partial w_3}\,g+P(w_3,u_3;w_2,u_2;w_1,u_1)=0\,. \tag{52}$$

In the first step we differentiate both equations n times with respect to w_1 and set $w_1 = 0$. In the second step we perform an inverse Laplace transform. In the third step we form the expression

$$\frac{\partial}{\partial r}\left(\frac{\partial \mathrm{eq}_1}{\partial w_3} + r\,\mathrm{eq}_3\right) + \mathrm{eq}_3\,, \tag{53}$$

which cancels out derivatives of f_n with respect to t, and solve the corresponding equation against $f_n(0,0,0,1;r)$

$$\begin{aligned} f_n(0,0,0,1;r) \;&\equiv\; -\frac{\partial f_n}{\partial w_3} \\ &= \frac{1}{(u_2^2-u_3^2+w_2^2-w_3^2)\,(u_2^2\,w_2^2-u_3^2\,w_3^2)}\Big[2\,V_n(r)+r\,V_n'(r)+\frac{\partial U_n(r)}{\partial w_3} \\ &\quad +w_3\,(u_2^2\,u_3^2-u_3^4+u_2^2\,w_2^2+u_3^2\,w_2^2-2\,u_3^2\,w_3^2)\,r\,f_n'(r) \\ &\quad -w_3\,(u_2^2-u_3^2)\,[2\,f_n^{(2)}(r)+r\,f_n^{(3)}(r)] \\ &\quad +(n-1)\,n\,\Big[(u_3^2-w_2^2)\,(u_2^2-w_3^2)\,\frac{\partial f_{n-2}(r)}{\partial w_3}-\frac{\partial f_{n-2}^{(4)}(r)}{\partial w_3} \\ &\quad +r\,(u_3^2-w_2^2)\,w_3\,f_{n-2}'(r)+2\,w_3\,f_{n-2}^{(2)}(r)+r\,w_3\,f_{n-2}^{(3)}(r)\Big]\Big]. \end{aligned} \tag{54}$$

In the particular case of $n = 0$ it takes the form

$$\begin{aligned} f(0,0,0,1;r) \;&=\; -\frac{\partial f}{\partial w_3} \\ &= -\frac{w_3}{w_2^2-w_3^2}\,f(r)-\frac{a^-\,a^+\,w_3\,(u_2^2-u_3^2)}{p^2}\,r\,f'(r) \\ &\quad +\frac{1}{2\,p^2\,(w_2^2-w_3^2)}\Big\{a^-\,(u_3-w_2)\,w_3\,F_1^+-a^+\,(u_3+w_2)\,w_3\,F_3^+ \\ &\quad -\frac{1}{q}\,[u_2\,w_2^2\,(u_2^2-u_3^2+w_2^2-w_3^2)-w_3\,(u_2^2\,w_2^2-u_3^2\,w_3^2)]\,F_2^+ \\ &\quad +\frac{1}{q}\,[u_2\,w_2^2\,(u_2^2-u_3^2+w_2^2-w_3^2)+w_3\,(u_2^2\,w_2^2-u_3^2\,w_3^2)]\,F_4^+\Big\}. \end{aligned} \tag{55}$$

The other single powers of the electron distances can be obtained from the above by appropriate exchange of u_2, u_3, w_2, and w_3. The general recursion can be obtained by further differentiation of Eq. (54) (after multiplying by the common denominator) with respect to w_2, u_2, w_3, u_3, or by recursive application of this single differentiation formulae.

VI. SPECIAL CASE: ATOMIC ORBITALS

The explicit form of $f_n(i,j,k,l;r)$ in the general case becomes very lengthy for increasing values of i, j, k, and l. Therefore it is worth while to consider special cases which may find practical realization in quantum chemistry codes. When in Eq. (6) atomic orbitals are used, then two nonlinear parameters in the direct (no exchange) integral are $u_2 = w_2 = 0$. We thus assume here vanishing of u_2 and w_2, but allow for an arbitrary polynomial in electron-nucleus and electron-electron distances. If we introduce the notation $u_3 = u$, and $w_3 = w$, then $p = \sqrt{u^2 + w^2}$, and

$$
\begin{aligned}
f(r) &= \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-u\, r_{1A}}}{r_{1A}} \frac{e^{-w\, r_{2B}}}{r_{2B}} \frac{1}{r_{1B}} \frac{1}{r_{2A}} \frac{r}{r_{12}} && (56)\\
&= I_0(p\, r) \int_r^\infty dr'\, F(r')\, K_0(p\, r') + K_0(p\, r) \int_0^r dr'\, F(r')\, I_0(p\, r')\,, && (57)
\end{aligned}
$$

and F becomes

$$
\begin{aligned}
F(r) = &-\frac{e^{u\, r}}{2\, u}\Big[\mathrm{Ei}(-r\,(u+w)) + \mathrm{Ei}(-r\, u)\Big] - \frac{e^{w\, r}}{2\, w}\Big[\mathrm{Ei}(-r\,(u+w)) + \mathrm{Ei}(-r\, w)\Big]\\
&+\frac{e^{-u\, r}}{2\, u}\left[\ln\left|\frac{w-u}{w+u}\right| - \mathrm{Ei}(r(u-w)) + \mathrm{Ei}(r\, u) + 2\,\mathrm{Ei}(-r\, w)\right]\\
&+\frac{e^{-w\, r}}{2\, w}\left[\ln\left|\frac{w-u}{w+u}\right| - \mathrm{Ei}(r(w-u)) + \mathrm{Ei}(r\, w) + 2\,\mathrm{Ei}(-r\, u)\right]. \qquad (58)
\end{aligned}
$$

All recursion formulae for higher powers of electron distances can be obtained directly from the general case considered in the previous section by setting $u_2 = w_2 = 0$, and they take here a much simpler form.

VII. SPECIAL CASE: EXCHANGED ATOMIC ORBITALS

For the exchange integral with atomic orbitals, the relation $u_3 = w_2 \equiv u, u_2 = w_3 \equiv w$ holds, then $p = 0$ and using the small x limit of Bessel functions,

$$
\begin{aligned}
\mathrm{I}_0(x) &= 1 + O(x)\,, && (59)\\
\mathrm{K}_0(x) &= -\Big(\gamma + \ln\frac{x}{2}\Big) + O(x)\,. && (60)
\end{aligned}
$$

the master integral becomes

$$
\begin{aligned}
f(r) &= \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-u\,(r_{1A}+r_{2A})}}{r_{1A}\, r_{2A}} \frac{e^{-w\,(r_{1B}+r_{2B})}}{r_{1B}\, r_{2B}} \frac{r}{r_{12}} && (61)\\
&= \int_r^\infty dr'\, F(r')\, \ln\frac{r}{r'} = \int_r^\infty dr'\, F^{(-1)}(r')\, \frac{1}{r'}\,, && (62)
\end{aligned}
$$

where

$$
F^{(-1)}(r) = \frac{1}{2\,(u^2 - w^2)} \Big\{(e^{2\, r\, w} - e^{2\, r\, u})\, \mathrm{Ei}(-2\, r\,(u+w)) \qquad (63)
$$

$$
\begin{aligned}
&-e^{-2\,r\,w}\left[\mathrm{Ei}(2\,r\,(w-u)) - 2\,\mathrm{Ei}(r\,(w-u)) + \ln\left|\frac{w-u}{w+u}\right|\right] \\
&+e^{-2\,r\,u}\left[\mathrm{Ei}(2\,r\,(u-w)) - 2\,\mathrm{Ei}(r\,(u-w)) + \ln\left|\frac{w-u}{w+u}\right|\right]\Biggr\},
\end{aligned}
$$

and the superscript $^{(-1)}$ denotes not the differentiation, but the integration over r with the boundary condition $F^{(-1)}(\infty) = 0$, so $dF^{(-1)}(r)/dr = F(r)$.

The recurrence relations for powers of r_{12} is obtained from the differential equation in w_1, Eq. (42). One divides it by t^2, differentiates over w_1 n-times, performs the inverse Laplace transform, and obtains

$$
\begin{aligned}
f_{n+1}(r) &= \frac{1}{(u^2-w^2)^2}\,[2\,n^2\,(u^2+w^2)\,f_{n-1}(r) - n^2\,f^{(2)}_{n-1}(r) - (n-2)\,(n-1)^2\,n\,f_{n-3}(r) \\
&\quad +W_n^{(-2)}(r)]\,,
\end{aligned} \tag{64}
$$

where

$$
W_n^{(-2)}(r) = (-1)^n\,\frac{\partial^n}{\partial w_1^n}\bigg|_{w_1=0} W^{(-2)}(r)\,, \tag{65}
$$

$$
\begin{aligned}
W^{(-2)}(r) &= \frac{e^{-2\,r\,u}}{r}\left(1-\frac{w_1}{w_1-u+w}-\frac{w_1}{w_1+u+w}\right) \\
&\quad +\frac{e^{-2\,r\,w}}{r}\left(1-\frac{w_1}{w_1+u-w}-\frac{w_1}{w_1+u+w}\right) \\
&\quad +\frac{e^{-r\,(w_1+u+w)}}{r}\left(-2+\frac{w_1}{w_1-u+w}+\frac{w_1}{w_1+u-w}+\frac{2\,w_1}{w_1+u+w}\right) \\
&\quad -2\,w_1\,\mathrm{Ei}(-r\,(u+w+w_1))\,.
\end{aligned} \tag{66}
$$

Similarly differentiation of the master integral with respect to nonlinear parameter, for example w_3 is obtained from the differential equation in this nonlinear parameter

$$
\begin{aligned}
f(0,0,0,1;r) &= \frac{w}{u^2-w^2}\,f(r) + \frac{1}{4\,w\,(u^2-w^2)}\Bigl\{2\,\mathrm{Ei}(-r\,(u+w)) - e^{2\,r\,w}\,\mathrm{Ei}(-2\,r\,(u+w)) \\
&\quad +e^{-2\,r\,w}\left[\mathrm{Ei}(2\,r\,(w-u)) - 2\,\mathrm{Ei}(r\,(w-u)) + \ln\left|\frac{w-u}{w+u}\right|\right]\Bigr\}
\end{aligned} \tag{67}
$$

The appearance of $u-w$ in the denominator affects numerical stability of these recursions when $u \approx w$. This problem can be probably solved by employing sufficiently lengthy Taylor expansions around $u = w$, and in this special case f is known analytically, as will be discussed in the next section.

VIII. SPECIAL CASE: SYMMETRIC

This is the case when nonlinear parameters are the same for nuclei A and B, namely $w_2 = w_3 = w, u_2 = u_3 = u$, and then $p = \infty$. It is the James-Coolidge basis for H_2 molecule, and was recently used by Sims and Hagstrom [6] for the very accurate calculation of BO potential for small nuclear distances. Here we show that all integrals can be expressed in terms of Ei and exponential functions. It is convenient in this case to consider a slightly different form of the integral, namely

$$\begin{aligned} f(n_1, n_2, n_3, n_4, n_5; r) \;=\; & \int \frac{d^3 r_1}{4\,\pi} \int \frac{d^3 r_2}{4\,\pi}\, \frac{e^{-u\, r_{1A}}}{r_{1A}}\, \frac{e^{-u\, r_{1B}}}{r_{1B}}\, \frac{e^{-w\, r_{2A}}}{r_{2A}}\, \frac{e^{-w\, r_{2B}}}{r_{2B}}\, \frac{r}{r_{12}^{1-n_1}} \\ & (r_{1A} - r_{1B})^{n_2}\, (r_{2A} - r_{2B})^{n_3}\, (r_{1A} + r_{1B})^{n_4}\, (r_{2A} + r_{2B})^{n_5}. \end{aligned} \tag{68}$$

f for all values of parameters n_i can be obtained from one differential equation in variable $u_1 \equiv t$

$$\sigma\, \frac{\partial g}{\partial t} + \frac{1}{2}\, \frac{\partial \sigma}{\partial t}\, g + P(t, w_1; u_3, w_3; w_2, u_2) = 0 \tag{69}$$

by the inverse Laplace transform in t and differentiation with respect to w_1, $(w_2-w_3)/2$, $(u_2-u_3)/2$, $(w_2+w_3)/2$, and $(u_2+u_3)/2$, at $w_1 = w_2 - w_3 = u_2 - u_3 = 0$. This differential equation becomes then an algebraic equation, which relates values of f for different arguments, and can easily be solved. For example, the master integral is

$$\begin{aligned} f(0,0,0,0,0;r) \;=\; & \frac{1}{4\,u\,w}\Big[e^{r\,(u+w)}\,\mathrm{Ei}(-2\,r\,(u+w)) + e^{-r(u+w)}\Big(\gamma + \ln\frac{2\,r\,u\,w}{u+w}\Big) \\ & - e^{r(u-w)}\,\mathrm{Ei}(-2\,r\,u) - e^{r(w-u)}\,\mathrm{Ei}(-2\,r\,w)\Big]. \end{aligned} \tag{70}$$

Other examples include

$$\begin{aligned} f(2,0,0,0,0;r) \;=\; & \frac{(u^2+w^2)}{6\,u^2\,w^2}\, f(0,0,0,0,0;r) + \frac{e^{-r\,(u+w)}\, r^2}{12\,u\,w} \\ & + \frac{r}{24\,u^2\,w^2}\Big[(u+w)\,e^{-r\,(u+w)} - (u-w)\,e^{r\,(u-w)}\,\mathrm{Ei}(-2\,r\,u) \\ & - (w-u)\,e^{r\,(w-u)}\,\mathrm{Ei}(-2\,r\,w) - (u+w)\,e^{r\,(u+w)}\,\mathrm{Ei}(-2\,r\,(u+w)) \\ & + (u+w)\,e^{-r\,(u+w)}\Big(\gamma + \ln\frac{2\,r\,u\,w}{u+w}\Big)\Big], \end{aligned} \tag{71}$$

$$f(0,2,0,0,0;r) \;=\; \frac{r^2}{3}\, f(0,0,0,0,0;r)\,. \tag{72}$$

Since all other integrals can also be expressed in terms of the Ei and exponential functions, matrix elements of the nonrelativistic Hamiltonian can all be obtained analytically. This should allow one to obtain highly accurate nonrelativistic wave functions, and thus precisely calculate various relativistic effects to rovibrational energies, shielding and spin-rotational constants in the H_2 molecule.

IX. SUMMARY

We have presented an approach to evaluate two-center two-electron integrals with exponential functions and with the arbitrary polynomial in electron-nucleus and electron-electron distances. All integrals are expressed in terms of the master integral f, the derivative f', Ei and exponential functions. The master integral satisfies the second order differential equation (29) in variable $r = r_{AB}$, and can be accurately solved. This approach certainly finds an application in the H_2 molecule, for example the present theoretical predictions for the dissociation energy [7, 8] are limited by unknown higher order $m\,\alpha^6$ corrections and the finite nuclear mass effects in the leading relativistic corrections $m\,\alpha^4$. Both of these corrections are difficult (if not impossible) to calculate using Gaussian functions. Apart from H_2, this approach may find applications in arbitrary few electron diatomic molecules. The special cases of integrals with direct and exchange atomic functions were considered for this purpose. We do not know however, how well relativistic effects can be calculated in this aproach. This would require numerical experiments. But the message is that the integrals with exponential functions can now be precisely calculated.

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[1] W. Klopper, F.R. Manby, S. Ten-no and E.F. Valeev, Int. Rev. Phys. Chem. 25, 427 (2006).
[2] F.V. Tkachov, Phys. Lett. **B100**, 65 (1981); K.G. Chetyrkin and F.V. Tkachov, Nucl. Phys. **B192**, 159 (1981).
[3] K. Pachucki, M. Puchalski, and E. Remiddi, Phys. Rev. A. **70**, 032502 (2004).
[4] F.E. Harris, Phys. Rev. A **79**, 032517 (2009).

[5] D. M. Fromm and R. N. Hill, Phys. Rev. A **36**, 1013 (1987).

[6] J. S. Sims and S. A. Hagstrom, J. Chem. Phys. **124**, 094101 (2006).

[7] L. Wolniewicz, J. Chem. Phys. **103**, 1792 (1995).

[8] K. Piszczatowski, G. Łach, B. Jeziorski, M. Przybytek, J. Komasa, and K. Pachucki, *submitted to* Journal of Chemical Theory And Computation (2009).