Correlated exponential functions in high precision calculations for diatomic molecules

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Abstract

Various properties of the general two-center two-electron integral over the explicitly correlated exponential function are analyzed for the potential use in high precision calculations for diatomic molecules. A compact one dimensional integral representation is found, which is suited for the numerical evaluation. Together with recurrence relations, it makes possible the calculation of the two-center two-electron integral with arbitrary powers of electron distances. Alternative approach via the Taylor series in the internuclear distance is also investigated. Although numerically slower, it can be used in cases when recurrences lose stability. Separate analysis is devoted to molecular integrals with integer powers of interelectronic distances r_{12} and the vanishing corresponding nonlinear parameter. Several methods of their evaluation are proposed.

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I. INTRODUCTION

In order to achieve high accuracy for the nonrelativistic energy as well as for relativistic and quantum electrodynamics (QED) corrections in molecular systems, well optimized basis functions have to be applied. The explicitly correlated Gaussian (ECG) functions do not satisfy the cusp condition, therefore their use in the evaluation of higher order QED corrections [1] is problematic. Nevertheless, the recent calculations of the leading $O(\alpha^3)$ QED effects performed for H_2 [2] using ECG functions, lead to the most accurate to date theoretical predictions of about 10^{-3} cm^{-1} uncertainty for dissociation energies. To obtain even more accurate results and to include higher order QED effects we aim to use the basis of explicitly correlated exponential functions of the form

$$\phi = e^{-w_1 r_{12} - u_3 r_{1A} - u_2 r_{1B} - w_2 r_{2A} - w_3 r_{2B}} r_{12}^{n_1} r_{1A}^{n_2} r_{1B}^{n_3} r_{2A}^{n_4} r_{2B}^{n_5}. \tag{1}$$

The notation for interparticle distances is explained after Eq. (4). The use of such exponential functions in molecular applications is quite limited. Starting from the pioneering work of Kolos and Roothan [3], the Neumann expansion of r_{12}^{-1} (at $\omega = 0$) in spherical oblate coordinates [4] has been applied most often, see the most recent review by Harris in Ref. [5] and the collection of works in Ref. [6]. This expansion and the more general one of $e^{-\omega r_{12}} r_{12}^{-1}$ in terms of spheroidal functions [4], has been applied by several authors [7–11] in their accurate calculations for the hydrogen molecule.

An alternative approach to perform integrals with exponential function in Eq. (1) has originally been proposed in Ref. [12]. Authors have obtained an analytic, although quite complex formula for the general four-body integral with exponential functions. By taking the inverse Laplace transform [see Eq. (6)] in one of the nonlinear parameters, one can in principle obtain the general two-center two-electron integral in Eq. (2). Due to the very complicated analytic structure of the four-body formula, this inverse Laplace transform has not been applied so far. In our recent work [13], we have reformulated the problem of the calculation of the inverse Laplace transform, into the solution of some differential equations. From these differential equations satisfied by the master integral $f(r)$ (see Eq. (2) below), one derived analytic recursion relations for integrals with positive integer powers of interparticle distances, assuming that the nonlinear parameter corresponding to r_{12} vanishes, i.e. for standard molecular integrals. Using these recursions one obtained analytic results for integrals with James-Coolidge and extended Heitler-London basis functions. The application

of analytic formulas has been demonstrated by the calculation of Born-Oppenheimer energies for H_2 in Ref. [14] with accuracy of 10^{-15} au, and for HeH^+ in Ref. [15] with accuracy of about 10^{-12} au. While James-Coolidge and Heitler-London basis functions work very well for the ground states, they are not equally good for excited states, where arbitrary values of nonlinear parameters are needed. This is the main subject of this work, to develop a computational technique for general two-center two-electron integrals, which can be used for the calculation of nonrelativistic energies, and also for relativistic and QED effects in two-electron diatomic molecule. Finally we think that various properties of the general two-center two-body integral derived here, can be applied for the calculation of nonrelativistic energies of an arbitrary diatomic molecule. This subject has recently been pursued also by Lesiuk and Moszyński in Ref. [16].

The general structure of this work is the following. In Sec. II we derive the differential equation for the master integral $f(r)$ in Eq. (2). In Sec. III we find a solution in terms of one-dimensional integral over elementary functions and additionally consider few special cases. In Sec. IV the Taylor series of $f(r)$ in the internuclear distance r is derived, and this shows the general analytic properties of the master integral f. In Sec. V integrals with positive powers of interparticle distances are obtained by differentiation of the master integral with respect to the corresponding nonlinear parameter. In Sec. VI we consider standard molecular integrals, i.e., with the vanishing nonlinear parameter corresponding to r_{12}. In Sec. VII we present a summary with possible further applications.

II. THE MASTER INTEGRAL

We introduce here notation and definitions following the previous work in Ref. [13], and obtain the fourth order differential equation which is satisfied by the master integral $f(r)$. Matrix elements of the nonrelativistic Hamiltonian between functions of the type (1) can be expressed in terms of $f(r)$ and its derivatives with respect to nonlinear parameters. The master two-electron two-center integral $f(r)$ is defined by

$$f(r) = r \int \frac{d^3r_1}{4\,\pi} \int \frac{d^3r_2}{4\,\pi} \frac{e^{-w_1\,r_{12}}}{r_{12}} \frac{e^{-u_3\,r_{1A}}}{r_{1A}} \frac{e^{-u_2\,r_{1B}}}{r_{1B}} \frac{e^{-w_2\,r_{2A}}}{r_{2A}} \frac{e^{-w_3\,r_{2B}}}{r_{2B}}, \tag{2}$$

and the related class of integrals with the nonnegative integer n is

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

where $1, 2$ are indices of the electrons, A, B that of the nuclei, and $r = r_{AB}$ is the distance between the nuclei. The notation for nonlinear parameters comes from the general four-body integral g defined by

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

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

$$g(t) = \int \frac{d^3r}{4\,\pi}\, f(r)\, \frac{e^{-t\,r}}{r^2} = \int_0^\infty dr\, f(r)\, e^{-t\,r}, \tag{5}$$

and the opposite relation is the inverse Laplace transform

$$f(r) = \frac{1}{2\,\pi\,i} \int_{-i\,\infty+\epsilon}^{i\,\infty+\epsilon} dt\, e^{t\,r}\, g(t). \tag{6}$$

It was shown in Ref. [13], that the function g satisfies the first order differential equation in any of it's parameter $\alpha = u_i,\, w_i$:

$$\sigma\, \frac{\partial g}{\partial \alpha} + \frac{1}{2}\, \frac{\partial \sigma}{\partial \alpha}\, g + P_\alpha = 0\,, \tag{7}$$

or equivalently

$$\sqrt{\sigma} \frac{\partial}{\partial \alpha} (\sqrt{\sigma}\, g) + P_\alpha = 0\,, \tag{8}$$

with the inhomogeneous term P_α presented in Appendix A, and σ being the sixth order polynomial in six variables

$$\begin{aligned} \sigma \;=\; & u_1^2\,u_2^2\,w_3^2 + u_2^2\,u_3^2\,w_1^2 + u_1^2\,u_3^2\,w_2^2 + w_1^2\,w_2^2\,w_3^2 + u_1^2\,w_1^2\,(u_1^2 + w_1^2 - u_2^2 - u_3^2 - w_2^2 - w_3^2) \\ & + u_2^2\,w_2^2\,(u_2^2 + w_2^2 - u_1^2 - u_3^2 - w_1^2 - w_3^2) + u_3^2\,w_3^2\,(u_3^2 + w_3^2 - u_2^2 - u_1^2 - w_1^2 - w_2^2). \end{aligned} \tag{9}$$

For example, Eq. (7) for $\alpha = w_1$ reads

$$\sigma\, \frac{\partial g}{\partial w_1} + \frac{1}{2}\, \frac{\partial \sigma}{\partial w_1}\, g + P(w_1, u_1; w_2, u_2; w_3, u_3) = 0\,, \tag{10}$$

where the inhomogeneous term $P(w_1, u_1; w_2, u_2; w_3, u_3)$ is given by Eq. (A2). The solution of this differential equation is presented in the ingenious work of Fromm and Hill [12] by direct integration of Eq. (2) in the momentum representation. A more compact formula was obtained by Harris [17]. We do not present here their results, as its explicit form is quite long and we will not need it.

To obtain the fundamental differential equation for the master integral f, we use the differential equation (7) in variable $t = u_1$

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

and perform the inverse Laplace transform in t. This differential equation, using the following new parameters which are adapted to the symmetry of the problem

$$w_2 = w + x, \;\; w_3 = w - x, \;\; u_2 = u - y, \;\; u_3 = u + y, \tag{12}$$

takes the form

$$\left[\sigma_4 \frac{d^2}{d\,r^2}\, r \frac{d^2}{d\,r^2} + \sigma_2 \frac{d}{d\,r}\, r \frac{d}{d\,r} + \sigma_0\, r \right] f(r) = F(r), \tag{13}$$

where

$$\begin{aligned}
\sigma &= \sigma_0 + t^2\, \sigma_2 + t^4\, \sigma_4, \qquad (14)\\
\sigma_4 &= w_1^2, \\
\sigma_2 &= w_1^4 - 2\, w_1^2\, (u^2 + w^2 + x^2 + y^2) + 16\, u\, w\, x\, y \\
&= w_1^4 + w_1^2\, \sigma_{22} + \sigma_{20}, \\
\sigma_0 &= w_1^2\, (u + w - x - y)\, (u - w + x - y)\, (u - w - x + y)\, (u + w + x + y) \\
&\quad + 16\, (w\, x - u\, y)\, (u\, x - w\, y)\, (u\, w - x\, y) \\
&= w_1^2\, \sigma_{02} + \sigma_{00},
\end{aligned}$$

and $F(r) = F_{u_1}(r)$ is presented in Appendix A. The differential Eq. (13) is supplemented by the boundary conditions, namely $f(r)$ vanishes at small and large r.

Taking the occasion, we present here, for later use, a differential equation which is obtained from the inverse Laplace transform of Eq. (10)

$$\left(\frac{1}{2} \frac{\partial \sigma_0}{\partial w_1} + \sigma_0 \frac{\partial}{\partial w_1}\right) f(r) + \left(\frac{1}{2} \frac{\partial \sigma_2}{\partial w_1} + \sigma_2 \frac{\partial}{\partial w_1}\right) f''(r) + \left(w_1 + w_1^2 \frac{\partial}{\partial w_1}\right) f^{(4)}(r) = -F_{w_1}(r), \tag{15}$$

where $F_{w_1}(r)$ is given in Appendix A, and that for an arbitrary parameter $\alpha = u, w, x, y$

$$\left(\frac{1}{2} \frac{\partial \sigma_0}{\partial \alpha} + \sigma_0 \frac{\partial}{\partial \alpha}\right) f(r) + \left(\frac{1}{2} \frac{\partial \sigma_2}{\partial \alpha} + \sigma_2 \frac{\partial}{\partial \alpha}\right) f''(r) + w_1^2 \frac{\partial}{\partial \alpha} f^{(4)}(r) = -F_\alpha(r). \tag{16}$$

III. POISSON REPRESENTATION

We derive here the integral representation for solutions of the homogeneous and the inhomogeneous differential equation (13), which is the analog of the Poisson representation

for Bessel functions [18]. σ is a quadratic polynomial in t^2, so it has four zeros $\pm t_a$, $\pm t_b$. Assuming $t_b > t_a > 0$, the four solutions of the homogeneous equation

$$\left[\sigma_4 \frac{d^2}{d\,r^2}\, r\, \frac{d^2}{d\,r^2} + \sigma_2 \frac{d}{d\,r}\, r\, \frac{d}{d\,r} + \sigma_0\, r\right] f(r) = 0, \tag{17}$$

are

$$\int_{-\infty}^{-t_b} \frac{e^{t\,r}}{\sqrt{\sigma(t)}}\, dt, \quad \int_{-t_b}^{-t_a} \frac{e^{t\,r}}{\sqrt{\sigma(t)}}\, dt, \quad \int_{-t_a}^{t_a} \frac{e^{t\,r}}{\sqrt{\sigma(t)}}\, dt, \quad \int_{t_a}^{t_b} \frac{e^{t\,r}}{\sqrt{\sigma(t)}}\, dt\,. \tag{18}$$

Let us prove it, as an example, for the last term

$$\begin{aligned}
&\left[\sigma_4 \frac{d^2}{d\,r^2}\, r\, \frac{d^2}{d\,r^2} + \sigma_2 \frac{d}{d\,r}\, r\, \frac{d}{d\,r} + \sigma_0\, r\right] \int_{t_a}^{t_b} dt\, \frac{e^{t\,r}}{\sqrt{\sigma(t)}} \\
&= \int_{t_a}^{t_b} \frac{dt}{\sqrt{\sigma(t)}} \left[\sigma_4 \frac{d^2}{d\,r^2}\, r\, \frac{d^2}{d\,r^2} + \sigma_2 \frac{d}{d\,r}\, r\, \frac{d}{d\,r} + \sigma_0\, r\right] e^{t\,r} \\
&= \int_{t_a}^{t_b} \frac{dt}{\sqrt{\sigma(t)}} \left[\sigma_4\, t^2 \frac{d}{dt}\, t^2 + \sigma_2\, t\, \frac{d}{dt}\, t + \sigma_0 \frac{d}{dt}\right] e^{t\,r} \\
&= \frac{1}{2} \int_{t_a}^{t_b} \frac{dt}{\sqrt{\sigma(t)}} \left[\sigma(t) \frac{d}{dt} + \frac{d}{dt}\, \sigma(t)\right] e^{t\,r},
\end{aligned} \tag{19}$$

where the last equation holds because $\sigma(t) = \sigma_0 + \sigma_2\, t^2 + \sigma_4\, t^4$. One integrates by parts, boundary terms vanish because $\sigma(t_a) = \sigma(t_b) = 0$, and one obtains

$$\begin{aligned}
&= \frac{1}{2} \int_{t_a}^{t_b} dt\, e^{t\,r} \left[\frac{d}{dt}\, \sqrt{\sigma(t)} + \sigma(t)\, \frac{d}{dt}\, \frac{1}{\sqrt{\sigma(t)}}\right] \\
&= \frac{1}{2} \int_{t_a}^{t_b} dt\, e^{t\,r}\, \frac{1}{2\,\sqrt{\sigma(t)}}\, (1 - 1) = 0.
\end{aligned} \tag{20}$$

The solution of the inhomogeneous fundamental differential equation (13) is obtained by noting that the integration contour in the inverse Laplace transform can be deformed to encircle all branch cuts on the left side of the complex plain

$$f(r) = \frac{1}{2\,\pi\,i} \int_0^{-\infty} dt\, e^{t\,r} \left[g(t + i\,\epsilon) - g(t - i\,\epsilon)\right]. \tag{21}$$

The analytic properties of g have been analyzed by Fromm and Hill in [12]. The function $g(t)$ has four overlapping branch cuts, similarly to the function P, in variable t on the negative real axis starting at

$$\begin{aligned}
-t_1 &= \quad u_3 + w_2 \quad &&= u + y + w + x, \\
-t_2 &= \quad u_2 + w_3 \quad &&= u - y + w - x, \\
-t_3 &= u_3 + w_1 + w_3 \quad &&= u + y + w - x + w_1, \\
-t_4 &= u_2 + w_1 + w_2 \quad &&= u - y + w + x + w_1,
\end{aligned} \tag{22}$$

correspondingly. The fact that all t_i with $i = 1, 2, 3, 4$ are not positive comes from the requirement that the integral in Eq. (2) is finite for positive values of u_i and w_i. Fromm and Hill found the imaginary part of g for the particular ordering of t_i. Their result is generalized here to an arbitrary ordering of t_i and takes the form

$$\begin{aligned}\frac{1}{2\,\pi\,i}\left[g(t+i\,\epsilon)-g(t-i\,\epsilon)\right] \;=\; & \frac{1}{2\,\sqrt{\sigma}}\big[\theta(t_1-t)\,\ln|\beta_{0,0}|+\theta(t_2-t)\,\ln|\beta_{3,3}| \\ & -\theta(t_3-t)\,\ln|\beta_{3,1}\,\beta_{3,3}|-\theta(t_4-t)\,\ln|\beta_{0,1}\,\beta_{0,0}|\big], \end{aligned} \tag{23}$$

where

$$\beta_{i,j}=\frac{\sqrt{\sigma}-\gamma_{i,j}}{\sqrt{\sigma}+\gamma_{i,j}}, \tag{24}$$

and (cf. Ref.[12] with $a_1 = u_3, a_2 = w_2, a_3 = t, a_{23} = w_3, a_{31} = u_2, a_{12} = w_1$)

$$\begin{aligned}\gamma_{0,0} &= 2\,u_2\,w_1\,w_3+(u_2^2-u_3^2+w_1^2)\,w_3+w_1\,(-t^2+u_2^2+w_3^2)+u_2\,(w_1^2-w_2^2+w_3^2),\\ \gamma_{3,3} &= 2\,u_3\,w_1\,w_2+(-u_2^2+u_3^2+w_1^2)\,w_2+w_1\,(-t^2+u_3^2+w_2^2)+u_3\,(w_1^2+w_2^2-w_3^2),\\ \gamma_{0,1} &= -2\,t\,w_2\,w_3-(t^2-u_3^2+w_2^2)\,w_3+w_2\,(t^2-u_2^2+w_3^2)+t\,(-w_1^2+w_2^2+w_3^2),\\ \gamma_{3,1} &= -2\,t\,w_2\,w_3+(t^2-u_3^2+w_2^2)\,w_3-w_2\,(t^2-u_2^2+w_3^2)+t\,(-w_1^2+w_2^2+w_3^2). \end{aligned} \tag{25}$$

There is some arbitrariness in the form of Eq. (23) as products of β can be expressed in several ways [12, 17]

$$\begin{aligned}\beta_{\mu,\mu}\,\beta_{\mu,\nu} &= \beta_{\nu,\nu}\,\beta_{\nu,\mu}=\beta_{\rho,\rho}\,\beta_{\rho,\sigma},\\ \beta_{\mu,\sigma}\,\beta_{\nu,\sigma}\,\beta_{\rho,\sigma} &= \beta_{\sigma,\sigma}, \end{aligned} \tag{26}$$

for $\{\mu, \nu, \rho, \sigma\}$ being an arbitrary permutation of $\{0, 1, 2, 3\}$. One can verify that $\mathrm{Im}(g)$ in Eq. (23), satisfies the differential equation (11) with $\mathrm{Im}(P)$ as an inhomogeneous term. As a result, $f(r)$ can be expressed in terms of the one-dimensional integral

$$\begin{aligned}f(r) \;=\; & \int_0^{-\infty} dt\,e^{t\,r}\,\frac{1}{2\,\sqrt{\sigma}}\big[\theta(t_1-t)\,\ln|\beta_{0,0}|+\theta(t_2-t)\,\ln|\beta_{3,3}| \\ & -\theta(t_3-t)\,\ln|\beta_{3,1}\,\beta_{3,3}|-\theta(t_4-t)\,\ln|\beta_{0,1}\,\beta_{0,0}|\big]. \end{aligned} \tag{27}$$

This is a main result obtained in this work. All properties of the master integral f can in principle be obtained from this integral representation. Some of them, however, can be more easily obtained from the differential equation (13). The rest of the paper will be devoted to various properties and various ways of numerical calculation of $f(r)$ in Eq. (27) and its

derivatives with respect to nonlinear parameters. This form of Eq. (27) is suited for the direct numerical quadrature, once we know all the singularities on the integration path, and this is presented in Appendix B.

It would be interesting to investigate various expansions of $f(r)$ in Eq. (27), in particular the expansion around $w_1 = 0$ is studied in Sec. VI. Here, we obtain the master integral f at $w_1 = 0$ in a simple form which is convenient for the numerical evaluation. The σ polynomial reads

$$\begin{aligned}\sigma|_{w_1=0} &= (u_2^2 - u_3^2 + w_2^2 - w_3^2)\,(u_2^2\,w_2^2 - u_3^2\,w_3^2) - t^2\,(u_2^2 - u_3^2)\,(w_2^2 - w_3^2) \\ &= 16\,(w\,x - u\,y)(u\,x - w\,y)(u\,w - x\,y) + 16\,t^2\,u\,w\,x\,y, \end{aligned} \tag{28}$$

and the differential equation becomes [13]

$$\left[16\,u\,w\,x\,y\,\frac{d}{d\,r}\,r\,\frac{d}{d\,r} + 16\,r\,(w\,x - u\,y)\,(u\,x - w\,y)\,(u\,w - x\,y)\right] f(r) = F(r)\big|_{w_1=0}, \tag{29}$$

where the inhomogeneous term $F(r)$ using Eq.(A5) is

$$\begin{aligned} F(r)\big|_{w_1=0} &= 2\,(u\,w\,x - u\,w\,y - u\,x\,y + w\,x\,y)\,F_{1-} + 2\,(u\,w\,x - u\,w\,y + u\,x\,y - w\,x\,y)\,F_{2-} \\ &\quad -2(u\,w\,x + u\,w\,y + u\,x\,y + w\,x\,y)\,F_{3-} + 2\,(u\,w\,x + u\,w\,y - u\,x\,y - w\,x\,y)\,F_{4-}, \end{aligned} \tag{30}$$

and where

$$\begin{aligned} F_{1\pm} &= \mathrm{Ei}(-2\,r\,u)\,e^{r\,(u-w-x+y)} \pm \mathrm{Ei}(-2\,r\,w)\,e^{r\,(-u+w+x-y)}, \\ F_{2\pm} &= \mathrm{Ei}(-2\,r\,w)\,e^{r\,(-u+w-x+y)} \pm \mathrm{Ei}(-2\,r\,u)\,e^{r\,(u-w+x-y)}, \\ F_{3\pm} &= \left[\mathrm{Ei}(2\,r\,x) + \mathrm{Ei}(2\,r\,y) - \mathrm{Ei}(2\,r\,(x+y)) + \ln\left(\frac{u\,w\,(x+y)}{x\,y\,(u+w)}\right)\right] e^{-r\,(u+w+x+y)} \\ &\quad \pm\mathrm{Ei}(-2\,r\,(u+w))\,e^{r\,(u+w+x+y)}, \\ F_{4\pm} &= \left[\mathrm{Ei}(-2\,r\,x) + \mathrm{Ei}(-2\,r\,y) - \mathrm{Ei}(-2\,r\,(x+y)) + \ln\left(\frac{u\,w\,(x+y)}{x\,y\,(u+w)}\right)\right] e^{-r\,(u+w-x-y)} \\ &\quad \pm\mathrm{Ei}(-2\,r\,(u+w))\,e^{r\,(u+w-x-y)}, \end{aligned} \tag{31}$$

with Ei being the exponential integral function. The solution of this differential equation (assuming $p^2 > 0$) in terms of solutions of the homogeneous equation was presented in Ref. [13].

$$f(r) = -\frac{1}{16\,u\,w\,x\,y}\left[I_0(p\,r)\int_r^\infty dr'\,F(r')\,K_0(p\,r') + K_0(p\,r)\int_0^r dr'\,F(r')\,I_0(p\,r')\right], \tag{32}$$

where

$$p^2 = \frac{(w\,x - u\,y)\,(w\,y - u\,x)\,(u\,w - x\,y)}{u\,w\,x\,y}, \tag{33}$$

and I_0, K_0 are modified Bessel functions. A more convenient, however is the integral form of Eq. (27)

$$\begin{aligned} f(r) \;=\; & \left(\int_{-u-w-x-y}^{-\infty} \ln|\beta_{0,0}| + \int_{-u-w+x+y}^{-\infty} \ln|\beta_{3,3}| \right. \\ & \left. - \int_{-u-w+x-y}^{-\infty} \ln|\beta_{3,1}\,\beta_{3,3}| - \int_{-u-w-x+y}^{-\infty} \ln|\beta_{0,1}\,\beta_{0,0}| \right) \frac{e^{t\,r}}{2\,\sqrt{\sigma}}\,dt, \end{aligned} \tag{34}$$

with the following $\gamma_{i,j}$ coefficients

$$\begin{aligned} \gamma_{0,0} \;&=\; -4\,(u\,w\,x + u\,w\,y - u\,x\,y - w\,x\,y), \\ \gamma_{3,3} \;&=\; 4\,(u\,w\,x + u\,w\,y + u\,x\,y + w\,x\,y), \\ \Gamma(\beta_{3,1}\,\beta_{3,3}) \;&=\; -16\,u\,w\,x\,y/(t + u + w - x + y) + 4\,(u\,w\,x - u\,w\,y + u\,x\,y + w\,x\,y), \\ \Gamma(\beta_{0,1}\,\beta_{0,0}) \;&=\; -16\,u\,w\,x\,y/(t + u + w + x - y) - 4\,(u\,w\,x - u\,w\,y - u\,x\,y - w\,x\,y), \end{aligned} \tag{35}$$

where Γ is defined in Eq. (B3). In the particular case of exchange integral $w = u$, $x = y$, σ_{00} vanishes and the master integral becomes

$$\begin{aligned} f(r) \;=\; & \frac{1}{8\,w\,x} \left(\int_{-2\,(w+x)}^{-\infty} dt\, \ln\left|\frac{t + 2\,(w - x)}{t - 2\,(w - x)}\right| \frac{e^{t\,r}}{t} \right. \\ & + \int_{-2\,(w-x)}^{-\infty} dt\, \ln\left|\frac{t - 2\,(w + x)}{t + 2\,(w + x)}\right| \frac{e^{t\,r}}{t} \\ & \left. -2 \int_{-2\,w}^{-\infty} dt\, \ln\left|\frac{t + 2\,(w - x)}{t + 2\,(w + x)}\right| \frac{e^{t\,r}}{t} \right). \end{aligned} \tag{36}$$

An equivalent integral representation, obtained from the differential equation (29) was presented in Ref. [13], but this form is more convenient for the numerical evaluation.

IV. TAYLOR EXPANSION IN r

Here, we find the Taylor expansion in the internuclear distance r of the master integral f. As it was noticed by Fromm and Hill in [12] this expansion is absolutely convergent, therefore it is another way to calculate the master integral as well as its derivatives with respect to u_i and w_i. Following Ref. [12], we find the initial terms and the recurrence relation for subsequent terms of the Taylor series.

The expansion in small r of the master integral has the form

$$f(r) = \sum_{k=1}^{\infty} r^k \left[f_k^{(1)} \ln(r) + f_k^{(2)} \right]. \tag{37}$$

The leading term, can be obtained by noting that the limit $r \to 0$ corresponds to the one-center integral [12]

$$\begin{aligned} &\frac{1}{16\,\pi^2} \int d^3 r_1 \int d^3 r_2 \frac{e^{-\alpha\, r_1 - \beta\, r_2 - \gamma\, r_{12}}}{r_1^2\, r_2^2\, r_{12}} \\ =&\frac{1}{2\,\gamma} \left[\frac{\pi^2}{6} + \frac{1}{2} \ln^2\!\left(\frac{\alpha+\gamma}{\beta+\gamma} \right) + \mathrm{L}_2\!\left(1 - \frac{\alpha+\beta}{\alpha+\gamma} \right) + \mathrm{L}_2\!\left(1 - \frac{\beta+\alpha}{\beta+\gamma} \right) \right], \end{aligned} \tag{38}$$

where L_2 is the dilogarthmic function [18]. Let us introduce for the later use the following X_i symbols

$$\begin{aligned} X_0 &= \frac{1}{2\,w_1} \left[\frac{\pi^2}{6} + \frac{1}{2} \ln^2\!\left(\frac{2\,u + w_1}{2\,w + w_1} \right) + \mathrm{L}_2\!\left(1 - \frac{2\,(u+w)}{2\,u + w_1} \right) + \mathrm{L}_2\!\left(1 - \frac{2\,(u+w)}{2\,w + w_1} \right) \right], \\ X_1 &= \ln\!\left(\frac{2\,u + w_1}{2\,(u+w)} \right), \\ X_2 &= \ln\!\left(\frac{2\,w + w_1}{2\,(u+w)} \right), \\ X_r &= \frac{1}{2} \ln[r^2\,(2\,u + w_1)(2\,w + w_1)] + \gamma_{\mathrm{E}}. \end{aligned} \tag{39}$$

where γ_{E} is the Euler constant. The leading terms in small r expansion using Eq. (38) are

$$\begin{aligned} f_1^{(1)} &= 0, \\ f_1^{(2)} &= X_0. \end{aligned} \tag{40}$$

and $f_0^{(i)} = f_{-1}^{(i)} = 0$. The next terms of this expansion $f_2^{(1)}, f_2^{(2)}$ are obtained from the large t asymptotics of the function g

$$g = \frac{X_0}{t^2} + \frac{g^{(1)} \ln t + g^{(2)}}{t^3} + o\big(t^{-4}\big). \tag{41}$$

Since $g(t)$ satisfies the differential equation (11) with the inhomogenous term $P(t) = P(t, w_1, u_3, w_3, w_2, u_2)$

$$P(t) = w_1^2 \left[2 + \ln(u_2 + u_3 + w_1) + \ln(w_1 + w_2 + w_3) - 2 \ln(t) \right] + o\big(t^{-1}\big), \tag{42}$$

the $1/t^3$ coefficients are

$$\begin{aligned} g^{(1)} &= -2, \\ g^{(2)} &= \ln(u_2 + u_3 + w_1) + \ln(w_1 + w_2 + w_3). \end{aligned} \tag{43}$$

As noticed by Fromm and Hill [12], they are related to $f_2^{(i)}$ coefficients by

$$\begin{aligned} f_2^{(1)} &= -\frac{g^{(1)}}{2}, \\ f_2^{(2)} &= \frac{\psi(3)\, g^{(1)} + g^{(2)}}{2}, \end{aligned} \tag{44}$$

where ψ is the Euler ψ-function [18] and $\psi(3) = -\gamma_{\rm E}+1+1/2$. The next terms in r expansion can be obtained from the fundamental differential equation (13). As the inhomogeneous term $F(r)$ has a similar expansion

$$F(r) = \sum_{k=-1}^{\infty} r^k \left(F_k^{(1)}\, \ln(r) + F_k^{(2)}\right), \tag{45}$$

the recurrence relations are the following

$$\begin{aligned} f_{k+1}^{(1)} &= \frac{F_{k-2}^{(1)} - \sigma_0\, f_{k-3}^{(1)} - \sigma_2\, (k-1)^2\, f_{k-1}^{(1)}}{\sigma_4\, (k+1)\, k^2\, (k-1)}, \\ f_{k+1}^{(2)} &= \frac{F_{k-2}^{(2)} - \sigma_0\, f_{k-3}^{(2)} - \sigma_2\, (k-1)^2\, f_{k-1}^{(2)} - \sigma_2\, 2\, (k-1)\, f_{k-1}^{(1)} - \sigma_4\, 2\, k\, [2\, (k+1)\, (k-1)+1]\, f_{k+1}^{(1)}}{\sigma_4\, (k+1)\, k^2\, (k-1)}, \end{aligned} \tag{46}$$

The resulting first terms in the expansion of the master integral f in powers of r are

$$\begin{aligned} f(r) &= r\, X_0 + r^2 \left(X_r - \frac{3}{2}\right) \\ &\quad + r^3 \left[-\frac{w_1^2\, X_0}{12} - \frac{w_1}{4} + \frac{(u^2+w^2+x^2+y^2)\, X_0 - w\, X_1 - u\, X_2 - 2\, (u+w)}{6} \right. \\ &\qquad \left. + \frac{x\, y}{3\, w_1} - \frac{2\, x\, y\, (2\, u\, w\, X_0 + u\, X_1 + w\, X_2)}{3\, w_1^2}\right] \\ &\quad + r^4 \left[\frac{7}{54}\, w_1^2 + \frac{w_1\, (u+w)}{12} + \frac{3\, u\, w - 3\, x\, y - 11\, u^2 - 11\, w^2 - 9\, x^2 - 9\, y^2}{36} \right. \\ &\qquad \left. + X_r \left(-\frac{w_1^2}{18} + \frac{u^2+w^2+x^2+y^2}{6}\right)\right] + O(r^5). \end{aligned} \tag{47}$$

Let's consider now the special case of $w_1 = 0$. The recurrence relation takes the form:

$$\begin{aligned} f_{k+1}^{(1)} &= \frac{F_k^{(1)} - \sigma_{00}\, f_{k-1}^{(1)}}{\sigma_{20}\, (k+1)^2}, \\ f_{k+1}^{(2)} &= \frac{F_k^{(2)} - \sigma_{00}\, f_{k-1}^{(2)}}{\sigma_{20}\, (k+1)^2} - \frac{2}{k+1}\, f_{k+1}^{(1)}, \end{aligned} \tag{48}$$

and the first terms in r-expansion are

$$
\begin{aligned}
f(r)|_{w_1=0} \;=\; & r\left[\frac{1}{2\,u}\,\ln\!\Big(1+\frac{u}{w}\Big)+\frac{1}{2\,w}\,\ln\!\Big(1+\frac{w}{u}\Big)\right]+r^2\left[-\frac{3}{2}+\gamma+\frac{1}{2}\,\ln(4\,r^2\,u\,w)\right]\\
& +r^3\left[-\frac{u}{3}-\frac{w}{3}+\frac{x\,y}{18\,u}+\frac{x\,y}{18\,w}+\left(\frac{u}{4}+\frac{w^2+x^2+y^2}{12\,u}-\frac{w\,x\,y}{18\,u^2}\right)\ln\!\Big(1+\frac{u}{w}\Big)\right.\\
& \quad \left.+\left(\frac{w}{4}+\frac{u^2+x^2+y^2}{12\,w}-\frac{u\,x\,y}{18\,w^2}\right)\ln\!\Big(1+\frac{w}{u}\Big)\right]\\
& +r^4\left[\frac{u\,w-x\,y}{12}-\frac{w^2+u^2}{18}+\frac{1}{6}\,(u^2+w^2+x^2+y^2)\left(-\frac{3}{2}+\gamma+\frac{1}{2}\,\ln(4\,r^2\,u\,w)\right)\right]\\
& +O(r^5). \qquad (49)
\end{aligned}
$$

In order to obtain the Taylor expansion of $f(r,n)$

$$
f(r,n)=\sum_{k=1}^{\infty} r^k\,\big[f_k^{(1)}(n)\,\ln(r)+f_k^{(2)}(n)\big], \qquad (50)
$$

one expands Eq. (15) in power series in r and obtains the following recursions for coefficients

$$
\begin{aligned}
f_{k+2}^{(1)}(n) \;=\; & \frac{-1}{\sigma_{20}\,(k+2)\,(k+1)}\left[\sigma_{00}\,f_k^{(1)}(n)+\sigma_{02}\,(n-1)^2\,f_k^{(1)}(n-2)\right.\\
& +\sigma_{22}\,(n-1)^2\,(k+2)\,(k+1)\,f_{k+2}^{(1)}(n-2)\\
& +(n-1)^2\,(k+4)\,(k+3)\,(k+2)\,(k+1)\,f_{k+4}^{(1)}(n-2)\\
& \left.+(n-3)\,(n-2)^2\,(n-1)\,(k+2)\,(k+1)\,f_{k+2}^{(1)}(n-4)\right], \qquad (51)\\
f_{k+2}^{(2)}(n) \;=\; & \frac{1}{\sigma_{20}\,(k+2)\,(k+1)}\left[F_{w_1,k}(n-1)-\sigma_{20}\,(2\,k+3)\,f_{k+2}^{(1)}(n)\right.\\
& -\sigma_{00}\,f_k^{(2)}(n)-\sigma_{02}\,(n-1)^2\,f_k^{(2)}(n-2)\\
& -\sigma_{22}\,(n-1)^2\left[(k+2)\,(k+1)\,f_{k+2}^{(2)}(n-2)+(2\,k+3)\,f_{k+2}^{(1)}(n-2)\right]\\
& -(n-3)\,(n-2)^2\,(n-1)\left[(k+2)\,(k+1)\,f_{k+2}^{(2)}(n-4)+(2\,k+3)\,f_{k+2}^{(1)}(n-4)\right]\\
& -(n-1)^2\left[(k+4)\,(k+3)\,(k+2)\,(k+1)\,f_{k+4}^{(2)}(n-2)\right.\\
& \qquad \left.\left.+2\,(2\,k+5)\,(k^2+5\,k+5)\,f_{k+4}^{(1)}(n-2)\right]\right], \qquad (52)
\end{aligned}
$$

where $f_k^{(i)}(0)=f_k^{(i)}$. The usefulness of the calculation of $f(r)$ and $f(r,n)$ via Taylor series in r and the above recursions needs to be verified numerically. Nevertheless, the expansion terms say a lot about analytic properties of f, as a function of w_1, x, y, u and w. In particular, the expansion in Eq. (47) suggests that f is an entire function in x, y at fixed r, u, w, w_1.

V. GENERAL RECURSION RELATIONS

In order to use the exponentially correlated basis in molecular calculations, one has to be able to calculate derivatives of the master integral f with respect to nonlinear parameters. Differential equations (13,15) and (16) are used below, to express the derivative of $f(r)$ with respect to an arbitrary parameter $\alpha = w_1, x, y, u, w$ in terms of $f(r)$, $f'(r)$, $f''(r)$, and $f'''(r)$. This is done as follows. From Eq. (13), the fourth derivative $f^{(4)}(r)$ can be expressed in terms of lower derivatives of $f(r)$ and we use this in Eqs. (15) and (16) to eliminate fourthth derivative. Next, differentiate these equations with respect to r and again eliminate fourth derivative. Doing this differentiation and elimination three times, one obtains four equations for four unknowns: the derivative of f with respect to w_1, and its three further derivatives with respect to r. The solution of these linear equations for $\alpha = w_1$ is

$$2\,\delta\,\sigma_0\,\frac{\partial f(r)}{\partial w_1} = r\,\delta\,\frac{\partial \sigma_0}{\partial w_1}\,f'(r) + w_1\left(-2\,\sigma_0\,\sigma_2 - w_1\,\sigma_2\,\frac{\partial \sigma_0}{\partial w_1} + 2\,w_1\,\sigma_0\,\frac{\partial \sigma_2}{\partial w_1}\right)[f''(r) + r\,f'''(r)]$$
$$- \sigma_0\left(4\,w_1\,\sigma_0 + 2\,w_1^2\,\frac{\partial \sigma_0}{\partial w_1} - \sigma_2\,\frac{\partial \sigma_2}{\partial w_1}\right)[f(r) + r\,f'(r)] + \dots\,, \tag{53}$$

and for $\alpha = u, w, x, y$

$$2\,\delta\,\sigma_0\,\frac{\partial f(r)}{\partial \alpha} = r\,\delta\,\frac{\partial \sigma_0}{\partial \alpha}\,f'(r) - w_1^2\left(\sigma_2\,\frac{\partial \sigma_0}{\partial \alpha} - 2\,\sigma_0\,\frac{\partial \sigma_2}{\partial \alpha}\right)[f''(r) + r\,f'''(r)]$$
$$- \sigma_0\left(2\,w_1^2\,\frac{\partial \sigma_0}{\partial \alpha} - \sigma_2\,\frac{\partial \sigma_2}{\partial \alpha}\right)[f(r) + r\,f'(r)] + \dots\,, \tag{54}$$

where $\dots$ denotes inhomogeneous terms presented in Eqs. (C3,C5), and where

$$\delta = 4\,w_1^2\,\sigma_0 - \sigma_2^2 = -(w_1^2 - 4\,u^2)\,(w_1^2 - 4\,w^2)\,(w_1^2 - 4\,x^2)\,(w_1^2 - 4\,y^2). \tag{55}$$

The solution for higher order derivatives with respect to r can be represented in the matrix form. Let us introduce a symbol $\vec{f}$ to denote

$$\vec{f}(r) = \begin{pmatrix} f(r) \\ f'(r) \\ f''(r) \\ f'''(r) \end{pmatrix}. \tag{56}$$

Then

$$\frac{\partial \vec{f}}{\partial \alpha} = \hat{A}_\alpha\,\vec{f} + \vec{F}_\alpha, \tag{57}$$

where $\hat{A}_\alpha$ and F_α are presented in Appendix C. These vector differential equations with respect to the nonlinear parameter α can be used as recursion relations to express the integral with any powers of electron distances in terms of the master integral $f(r)$ and it's first three derivatives with respect to r. These recursions become unstable when $w_1 \approx 0$, $\delta \approx 0$ or $\sigma_0 \approx 0$. These cases require a separate analysis. In the next Section we consider recursion relations for $w_1 = 0$ which has applications for standard molecular integrals.

The particular case of $\sigma_0 = 0$ happens for an exchange integral where $w = u$ and $x = y$. Here, one can use recurrence only for $f'(r)$ to generate the analytic expressions for derivatives with respect to $w - u$ and $x - y$. They are quite compact as there will be only three independent parameters, and can be expressed in terms of $f(r)$ and $f'(r)$. The derivatives with respect to remaining nonlinear parameters can be calculated afterwards, by setting $w = u, x = y$.

VI. RECURSIONS FOR STANDARD MOLECULAR INTEGRALS

We describe in this Section the evaluation of standard molecular integrals, where $w_1 = 0$. Recursion relations for the integral $f(r, n)$ in Eq. (3) have been presented in Ref. [13]. Here we rederive them using a more compact notation. In particular cases, close to spurious singularities, we propose to use these recursions to derive an analytical expression for individual integrals, which are then implemented in the numerical codes.

Let us take Eqs. (13) and (15), and differentiate them with respect to w_1, n and $n-1$ times respectively at $w_1 = 0$

$$
\begin{aligned}
& r\,\sigma_{00}\,f(r,n) + \sigma_{20}\,f'(r,n) + r\,\sigma_{20}\,f''(r,n) + (n-1)\,n\,r\,\sigma_{02}\,f(r,n-2) \\
& + (n-1)\,n\,\sigma_{22}\,f'(r,n-2) + (n-1)\,n\,r\,\sigma_{22}\,f''(r,n-2) + 2\,(n-1)\,n\,f^{(3)}(r,n-2) \\
& + (n-1)\,n\,r\,f^{(4)}(r,n-2) + (n-3)\,(n-2)\,(n-1)\,n\,f'(r,n-4) \\
& + (n-3)\,(n-2)\,(n-1)\,n\,r\,f''(r,n-4) = F_{u_1}(r,n)\,, \qquad (58)
\end{aligned}
$$

$$
\begin{aligned}
& \sigma_{00}\,f(r,n) + \sigma_{20}\,f''(r,n) + (n-1)^2\,\sigma_{02}\,f(r,n-2) + (n-1)^2\,\sigma_{22}\,f''(r,n-2) \\
& + (n-1)^2\,f^{(4)}(r,n-2) + (n-3)\,(n-2)^2\,(n-1)\,f''(r,n-4) = F_{w_1}(r,n-1)\,. \qquad (59)
\end{aligned}
$$

These are two linear equations for three unknowns $f(r,n), f'(r,n), f''(r,n)$. The third equation is obtained by elimination of $f''(r,n)$ and further differentiation with respect to r. The

solution of these three equations for $f(r,n)$ and $f'(r,n)$ are

$$\begin{aligned}
f(r,n) &= \frac{1}{\sigma_{00}}\big[-(n-2)\,(n-1)\,\sigma_{02}\,f(r,n-2)+(n-1)\,r\,\sigma_{02}\,f'(r,n-2)\\
&\quad +2\,(n-1)\,\sigma_{22}\,f''(r,n-2)+(n-1)\,r\,\sigma_{22}\,f^{(3)}(r,n-2)\\
&\quad +(n-1)\,(n+2)\,f^{(4)}(r,n-2)+(n-1)\,r\,f^{(5)}(r,n-2)\\
&\quad +4\,(n-3)\,(n-2)\,(n-1)\,f''(r,n-4)+2\,(n-3)\,(n-2)\,(n-1)\,r\,f^{(3)}(r,n-4)\\
&\quad +2\,F_{w_1}(r,n-1)+r\,F'_{w_1}(r,n-1)-F'_{u_1}(r,n)\big]\,, \qquad (60)\\
f'(r,n) &= -\frac{1}{\sigma_{20}}\big[(n-1)\,r\,\sigma_{02}\,f(r,n-2)+(n-3)\,(n-2)\,(n-1)\,n\,f'(r,n-4)\\
&\quad +(n-1)\,n\,\sigma_{22}\,f'(r,n-2)+2\,(n-3)\,(n-2)\,(n-1)\,r\,f''(r,n-4)\\
&\quad +(n-1)\,r\,\sigma_{22}\,f''(r,n-2)+2\,(n-1)\,n\,f^{(3)}(r,n-2)+(n-1)\,r\,f^{(4)}(r,n-2)\\
&\quad +r\,F_{w_1}(r,n-1)-F_{u_1}(r,n)\big], \qquad (61)
\end{aligned}$$

where

$$F_X(r,n)=(-1)^n\,\frac{\partial^n}{\partial w_1^n}\bigg|_{w_1=0}F_X(r), \qquad (62)$$

for $X=w_1,u_1$. Equation (60) allows one to obtain integral $f(r,n)$ with an arbitrary power $n-1$ of r_{12} in terms of $f(r)$, for example

$$\begin{aligned}
f(r,0) &= f(r),\\
f(r,1) &= \frac{r^3}{4}\,h_0(r\,u)\,h_0(r\,w)\,j_0(r\,x)\,j_0(r\,y),\\
f(r,2) &= \frac{1}{\sigma_{00}}\big[r\,\sigma_{02}\,f'(r)+2\,\sigma_{22}\,f''(r)+r\,\sigma_{22}\,f^{(3)}(r)+4\,f^{(4)}(r)+r\,f^{(5)}(r)\\
&\quad +2\,F_{w_1}(r,1)+r\,F'_{w_1}(r,1)-F'_{u_1}(r,2)\big],\\
f(r,3) &= \frac{r^5}{24}\bigg[-3\,h_1(r\,u)\,h_1(r\,w)\,j_1(r\,x)\,j_1(r\,y)-h_0(r\,u)\,h_0(r\,w)\,j_0(r\,x)\,j_0(r\,y)\\
&\quad +h_0(r\,w)\,h_2(r\,u)\,j_0(r\,x)\,j_0(r\,y)+h_0(r\,u)\,h_2(r\,w)\,j_0(r\,x)\,j_0(r\,y)\\
&\quad +h_0(r\,u)\,h_0(r\,w)\,j_2(r\,x)\,j_0(r\,y)+h_0(r\,u)\,h_0(r\,w)\,j_0(r\,x)\,j_2(r\,y)\bigg], \qquad (63)
\end{aligned}$$

where j_n and h_n are modified spherical Bessel functions

$$\begin{aligned}
j_n(x) &= x^n\left(\frac{1}{x}\,\frac{d}{dx}\right)^n\frac{\sinh(x)}{x},\\
h_n(x) &= x^n\left(\frac{1}{x}\,\frac{d}{dx}\right)^n\frac{\exp(-x)}{x}. \qquad (64)
\end{aligned}$$

One notices, that $f(r,n)$ for odd n can be expressed in terms of j_n and h_n only, and their numerical evaluation is straightforward. In contrast, numerical evaluation of the formulas

for even n is much more difficult. If σ_{20} is not small, then derivatives of $f(r)$ can be reduced to $f(r)$ and $f'(r)$ using

$$f^{(n)}(r) = -\frac{1}{r\,\sigma_{20}}\left[\sigma_{00}\left[(n-2)\,f^{(n-3)}(r)+r\,f^{(n-2)}(r)\right]+\sigma_{20}\,(n-1)\,f^{(n-1)}(r)-F_{u_1}^{(n-2)}(r)\right] \quad (65)$$

If σ_{20} is small, then the inverse recursion

$$f^{(n)}(r) = -\frac{1}{(n+1)\,\sigma_{00}}\left[r\,\sigma_{00}\,f^{(n+1)}(r) + (n+2)\,\sigma_{20}\,f^{(n+2)}(r) + r\,\sigma_{20}\,f^{(n+3)}(r) - F_{u_1}^{(n+1)}(r)\right] \quad (66)$$

is stable and can be used to obtain all the derivatives including the function $f(r)$ itself. Alternatively $f^{(n)}(r)$ can be obtained directly, using the integral form of Eq. (34). If σ_{00} is small but not σ_{20}, then these formulas can be rewritten using Eq. (61) to the form without σ_{00} in the denominator, for example

$$f(r,2) = \frac{1}{\sigma_{20}}\left[\sigma_{02}\,f^{(-2)}(r)-r\,\sigma_{02}\,f^{(-1)}(r)-\sigma_{22}\,f(r)-r\,\sigma_{22}\,f'(r)-3\,f''(r)-r\,f'''(r)\right]+\ldots \quad (67)$$

where $f^{(-n)}(r)$ is defined by

$$f^{(-n)}(r) = \int_0^r f^{(-n+1)}(r)\,dr\,, \quad (68)$$

and can be obtained from Eqs. (34) or (66). It may lead however to other type of numerical instabilities, if the branch point starts at 0, see Eq. (22), and in this case one can build the explicit table of integrals, as in Ref. [14, 15]. When both $\sigma_{20} \approx 0$ and $\sigma_{00} \approx 0$, then parameters x, y are small and in this case the Neumann expansion [5] can be applied.

What remains are the derivative of f with respect to $\alpha = u, w, x, y$ at $w_1 = 0$. We adapt here the derivation of corresponding formulas from Ref. [13]. One takes fundamental differential equations in u_1 and α at $w_1 = 0$

$$r\,\sigma_{00}\,f(r) + \sigma_{20}\,f'(r) + r\,\sigma_{20}\,f''(r) = F_{u_1}(r) \quad (69)$$

$$\frac{1}{2}\,\frac{\partial\sigma_{00}}{\partial\alpha}\,f(r) + \sigma_{00}\,\frac{\partial f(r)}{\partial\alpha} + \frac{1}{2}\,\frac{\partial\sigma_{20}}{\partial\alpha}f''(r) + \sigma_{20}\,\frac{\partial f''(r)}{\partial\alpha} = -F_\alpha(r) \quad (70)$$

differentiates the first equation with respect to α, eliminates $\partial f''(r)/\partial\alpha$ and differentiate resulting equation again with respect to r. The obtained equation for the derivative of f, using $\partial\sigma_{20}/\partial\alpha = \sigma_{20}/\alpha$ is

$$\frac{\partial f}{\partial\alpha} = -\frac{1}{2\,\alpha}\,f(r) + \frac{r}{2}\left(\frac{1}{\sigma_{00}}\,\frac{\partial\sigma_{00}}{\partial\alpha} - \frac{1}{\alpha}\right)f'(r) + \frac{G_\alpha(r)}{\sigma_{00}}\,, \quad (71)$$

where

$$G_\alpha(r) = \Big[\Big(\frac{1}{2\,\alpha} - \frac{\partial}{\partial\alpha}\Big)\,F'_{u_1}(r) - \Big(2 + r\,\frac{d}{dr}\Big)\,F_\alpha(r)\Big]_{w_1=0} \tag{72}$$

and

$$\begin{aligned}
G_w(r) &= \frac{1}{w}\Big[(u\,y - w\,x)\,(u\,x - w\,y)\,(-F_{1+} - F_{2+} + F_{3+} + F_{4+}) \\
&\quad +(u+w)\,(x-y)\,(u\,w - x\,y)\,(-F_{1+} + F_{2+}) \\
&\quad +(u-w)\,(x+y)\,(u\,w - x\,y)\,(-F_{3+} + F_{4+})\Big] \\
G_u(r) &= \frac{1}{u}\Big[(u\,y - w\,x)\,(u\,x - w\,y)\,(-F_{1+} - F_{2+} + F_{3+} + F_{4+}) \\
&\quad +(u+w)\,(x-y)\,(u\,w - x\,y)\,(F_{1+} - F_{2+}) \\
&\quad +(u-w)\,(x+y)\,(u\,w - x\,y)\,(-F_{3+} + F_{4+})\Big] \\
G_x(r) &= \frac{1}{x}\Big[(u\,y - w\,x)\,(u\,x - w\,y)\,(F_{1+} + F_{2+} - F_{3+} - F_{4+}) \\
&\quad +(u+w)\,(x-y)\,(u\,w - x\,y)\,(-F_{3+} + F_{4+}) \\
&\quad +(u-w)\,(x+y)\,(u\,w - x\,y)\,(-F_{1+} + F_{2+})\Big] \\
G_y(r) &= \frac{1}{y}\Big[(u\,y - w\,x)\,(u\,x - w\,y)\,(F_{1+} + F_{2+} - F_{3+} - F_{4+}) \\
&\quad +(u+w)\,(x-y)\,(u\,w - x\,y)\,(F_{3+} - F_{4+}) \\
&\quad +(u-w)\,(x+y)\,(u\,w - x\,y)\,(F_{1+} - F_{2+})\Big]\,.
\end{aligned} \tag{73}$$

Here σ_0 from the denominator can be removed, when necessary, as in the case of $f(r,n)$ by introducing $f^{(-n)}(r)$. The formula (71) allows one to obtain integrals with arbitrary powers of electronic distances. It requires however, further investigations of various numerical instabilities when the denominator approaches 0. In particular, σ_{00} vanishes for exchange integrals. In this case $w = u, x = y$ and one can generate a table of integrals avoiding recursions, by Taylor expansion of the fundamental solution in Eq. (27) in w_1, $w - u$, and $x - y$. Alternatively, one can take recursion relations presented in Eq. (61) and integrate it once over r.

VII. SUMMARY

The evaluation of two-center two-electron integrals is a difficult task. Depending on a physical problem different approaches are employed. For the calculation of nonrelativistic energies of a two-electron diatomic molecule the best way is by the use of Kolos-Wolniewicz

basis functions, namely $w_1 = 0$ and arbitrary nonlinear parameters u, w, x, y. The master integral can be calculated numerically using Eqs. (34) and (37). Integrals with powers of interparticle distances can be obtained by using analytic recursions Eq. (60), (65), and 71) followed by numerical evaluation of obtained formulas.

For the calculation of QED effects in a two-electron diatomic molecule, the best way is to use the most general basis functions with nonvanishing w_1, u, w, x, y. The master integral can be evaluated according to Eq. (27), and integrals with additional positive powers of interparticle distance can be obtained through recursion relations Eq. (57). Integrals with negative powers can be obtained by numerical integration with respect to the corresponding nonlinear parameter. In order to demonstrate correctness of obtained formulas for two-center two-electron integrals, Table I presents a simple, examplary calculations of the ground electronic Σ_g^+ state of the H_2 molecule.

TABLE I: Examplary calculations of the Born-Oppenheimer energy at the equilibrium distance $R = 1.4$ of the ground Σ_g^+ state of H_2 molecule, obtained using functions of the form Eq. (1), with parameters $w_1 = -0.5, u = 1, w = 1, y = 0.125, x = -0.125$ defined in Eqs. (12), N is a number of basis functions, and $n_1 + n_2 + n_3 + n_4 + n_5 \leq \Omega$. The result with ∞ is accurate to all digits and was obtained in [7–11, 14]

Ω	N	$E_{\rm BO}(a.u.)$
0	1	−1.038 401 456
1	4	−1.157 108 377
2	13	−1.172 368 483
3	32	−1.174 254 201
∞		−1.174 475 714

An additional approach to evaluate two-center integrals is by the Taylor expansion in small internuclear distance r. Its applicability has to be verified numerically. Nevertheless, it serves at present as a simple check of various formulas for recursion relations and the master integral. The advantage of calculations by Taylor series, is that expansion terms are quite simple. They are related to the known one-center (helium-like) integrals and can be obtained recursively (46, 51, 52). A similar Taylor expansion can in principle be obtained for many-body three-linked integrals (at most three odd powers of interparticle integrals).

This would open a window for high precision results in many electron diatomic molecules.

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Appendix A: Inhomogeneous terms

The first order differential equation (8), satisfied by the general four body integral, defined by Eq. (3), involves the inhomogeneous term P_α for $\alpha = u_i, w_i$. They are related to each other by

$$\begin{aligned}
P_{w_1} &= P(w_1,u_1;w_2,u_2;w_3,u_3) \\
&= P(w_1,u_1;w_3,u_3;w_2,u_2) \\
P_{u_1} &= P(u_1,w_1;w_2,u_2;u_3,w_3) \\
P_{w_2} &= P(w_2,u_2;w_3,u_3;w_1,u_1) \\
P_{u_2} &= P(u_2,w_2;w_3,u_3;u_1,w_1) \\
P_{w_3} &= P(w_3,u_3;w_1,u_1;w_2,u_2) \\
P_{u_3} &= P(u_3,w_3;u_1,w_1;w_2,u_2)
\end{aligned} \tag{A1}$$

The expression for P was obtained in [13] and is the following

$$\begin{aligned}
&P(w_1,u_1;w_2,u_2;w_3,u_3) \\
=\ & \frac{u_1\,w_1\,[(u_1+w_2)^2-u_3^2]}{(-u_1+u_3-w_2)\,(u_1+u_3+w_2)}\,\ln\left[\frac{u_2+u_3+w_1}{u_1+u_2+w_1+w_2}\right] \\
&+\frac{u_1\,w_1\,[(u_1+u_3)^2-w_2^2]}{(-u_1-u_3+w_2)\,(u_1+u_3+w_2)}\,\ln\left[\frac{w_1+w_2+w_3}{u_1+u_3+w_1+w_3}\right] \\
&-\frac{u_1^2\,w_1^2+u_2^2\,w_2^2-u_3^2\,w_3^2+w_1\,w_2\,(u_1^2+u_2^2-w_3^2)}{(-w_1-w_2+w_3)\,(w_1+w_2+w_3)}\,\ln\left[\frac{u_1+u_2+w_3}{u_1+u_2+w_1+w_2}\right] \\
&-\frac{u_1^2\,w_1^2-u_2^2\,w_2^2+u_3^2\,w_3^2+w_1\,w_3\,(u_1^2+u_3^2-w_2^2)}{(-w_1+w_2-w_3)\,(w_1+w_2+w_3)}\,\ln\left[\frac{u_1+u_3+w_2}{u_1+u_3+w_1+w_3}\right] \\
&+\frac{u_2\,(u_2+w_1)\,(u_1^2+u_3^2-w_2^2)-u_3^2\,(u_1^2+u_2^2-w_3^2)}{(-u_2+u_3-w_1)\,(u_2+u_3+w_1)}\,\ln\left[\frac{u_1+u_3+w_2}{u_1+u_2+w_1+w_2}\right] \\
&+\frac{u_3\,(u_3+w_1)\,(u_1^2+u_2^2-w_3^2)-u_2^2\,(u_1^2+u_3^2-w_2^2)}{(u_2-u_3-w_1)\,(u_2+u_3+w_1)}\,\ln\left[\frac{u_1+u_2+w_3}{u_1+u_3+w_1+w_3}\right] \\
&-\frac{w_1\,[w_2\,(u_1^2-u_2^2+w_3^2)+w_3\,(u_1^2-u_3^2+w_2^2)]}{(w_1-w_2-w_3)\,(w_1+w_2+w_3)}\,\ln\left[\frac{u_2+u_3+w_1}{u_2+u_3+w_2+w_3}\right] \\
&-\frac{w_1\,[u_2\,(u_1^2+u_3^2-w_2^2)+u_3\,(u_1^2+u_2^2-w_3^2)]}{(-u_2-u_3+w_1)\,(u_2+u_3+w_1)}\,\ln\left[\frac{w_1+w_2+w_3}{u_2+u_3+w_2+w_3}\right]
\end{aligned} \tag{A2}$$

In the case the nonlinear parameter α is the combination of w_i, u_i as in Eq. (12), then P_α is given by

$$\begin{aligned} P_w &= P_{w_2} + P_{w_3} \\ P_x &= P_{w_2} - P_{w_3} \\ P_u &= P_{u_2} + P_{u_3} \\ P_y &= P_{u_3} - P_{u_2} \end{aligned} \tag{A3}$$

The inhomogeneous term in the fundamental differential equation (13) is the inverse Laplace transform of P

$$F_\alpha = \frac{1}{2\,\pi\,i}\,\int_{-i\,\infty+\epsilon}^{i\,\infty+\epsilon} dt\, e^{t\,r}\, P_\alpha\Big|_{u_1=t} \tag{A4}$$

In particular, F_{u_1} is given by

$$\begin{aligned} F_{u_1}(r) \;=\; & \left\{ w_1 \left(\frac{1}{r^2} + \frac{2\,w_1 + u + w - x + y}{r} \right) e^{-r\,(u+w+w_1-x+y)} \right. \\ & - w_1 \left(\frac{1}{r^2} + \frac{u + w + x + y}{r} \right) e^{-r\,(u+w+x+y)} \\ & + \left[\frac{w_1^2}{2}\,(u - w - x + y) + 2\,u\,w\,(x - y) + 2\,x\,y\,(w - u) \right] \\ & \times \left[\mathrm{Ei}(-r\,(2\,u + w_1))\, e^{r\,(u-w-x+y)} - \mathrm{Ei}(-r\,(2\,w + w_1))\, e^{-r\,(u-w-x+y)} \right] \\ & + \left[\frac{w_1^2}{2}\,(u + w + x + y) + 2\,u\,w\,(x + y) + 2\,x\,y\,(u + w) \right] \\ & \times \left[\left(\mathrm{Ei}(2\,r\,(x + y)) - \mathrm{Ei}(-r\,(w_1 - 2\,x)) - \mathrm{Ei}(-r\,(w_1 - 2\,y)) \right.\right. \\ & \left.\left. - \ln\left[\frac{(x + y)\,(w_1 + 2\,u)\,(w_1 + 2\,w)}{(u + w)\,(w_1 - 2\,x)\,(w_1 - 2\,y)} \right] \right) e^{-r\,(u+w+x+y)} + \mathrm{Ei}(-2\,r\,(u + w))\, e^{r\,(u+w+x+y)} \right] \Bigg\} \\ & + \Big\{ x \to -x, y \to -y \Big\} \end{aligned} \tag{A5}$$

where Ei is the exponential integral function, and F_{w_1} is

$$
\begin{aligned}
F_{w_1}(r) \;=\; & \left\{ \left[\frac{r\,(u+w+x+y)+1}{r^3} \left(2 - \frac{w_1}{2\,u+w_1} - \frac{w_1}{2\,w+w_1} - \frac{w_1}{w_1-2\,x} - \frac{w_1}{w_1-2\,y} \right) \right.\right. \\
& + \frac{2}{r} \left(\frac{(u+w)\,(u+x)\,(u+y)}{2\,u+w_1} + \frac{(u+w)\,(w+x)\,(w+y)}{2\,w+w_1} \right. \\
& \left.\left. - \frac{(u+x)\,(w+x)\,(x+y)}{w_1-2\,x} - \frac{(u+y)\,(w+y)\,(x+y)}{w_1-2\,y} - \frac{(u+w+x+y)^2}{2} \right) \right] \\
& \times e^{-r\,(u+w+x+y)} \\
& + \left[\frac{r\,(u+w+w_1-x+y)+1}{r^3} \left(-2 + \frac{w_1}{2\,u+w_1} + \frac{w_1}{2\,w+w_1} + \frac{w_1}{w_1-2\,x} + \frac{w_1}{w_1+2\,y} \right) \right. \\
& + \frac{w_1}{r^2} + \frac{1}{r} \left(w_1^2 + 4\,(x\,y + u\,x + w\,x - u\,y - w\,y - u\,w) + (w_1+u+w-x+y)^2 \right. \\
& - \frac{2\,(u-w)\,(u+x)\,(u-y)}{2\,u+w_1} + \frac{2\,(u-w)\,(w+x)\,(w-y)}{2\,w+w_1} \\
& \left.\left. + \frac{2\,(u+x)\,(w+x)\,(x+y)}{w_1-2\,x} + \frac{2\,(u-y)\,(w-y)\,(-x-y)}{w_1+2\,y} \right) \right] e^{-r\,(u+w+w_1-x+y)} \Bigg\} \\
& + \Big\{ x \to -x, y \to -y \Big\}
\end{aligned}
\tag{A6}
$$

One notes, that F_{w_1} involves only the exponential and rational functions.

Appendix B: Numerical evaluation of the master integral

For the numerical evaluation of the master integral in Eq. (27), one should find all singularities on the integration path [12]. For this one decomposes $\sigma - \gamma_{i,j}^2$ into products

$$
\begin{aligned}
\sigma - \gamma_{0,0}^2 \;=\; & (u_2 - u_3 + w_1)\,(u_2 + u_3 + w_1)\,(t - u_2 - w_3) \\
& (t + u_2 + w_3)\,(w_1 - w_2 + w_3)\,(w_1 + w_2 + w_3) \\
\sigma - \gamma_{3,3}^2 \;=\; & (u_2 - u_3 - w_1)\,(u_2 + u_3 + w_1)\,(-t + u_3 + w_2) \\
& (t + u_3 + w_2)\,(w_1 + w_2 - w_3)\,(w_1 + w_2 + w_3) \\
\sigma - \gamma_{3,1}^2 \;=\; & (t + u_3 - w_2)\,(-t + u_3 + w_2)\,(-t + u_2 - w_3) \\
& (w_1 + w_2 - w_3)\,(t + u_2 + w_3)\,(w_1 - w_2 + w_3) \\
\sigma - \gamma_{0,1}^2 \;=\; & (-t + u_3 - w_2)\,(t + u_3 + w_2)\,(t + u_2 - w_3) \\
& (w_1 + w_2 - w_3)\,(-t + u_2 + w_3)\,(w_1 - w_2 + w_3)
\end{aligned}
\tag{B1}
$$

and observes that $\beta_{0,0}$ vanishes on the negative axis at $t = t_2$, $\beta_{3,3}$ at $t = t_1$, $\beta_{3,1}$ at $t = t_2$, and $\beta_{0,1}$ at $t = t_1$. All singularities at other points $t - u_i - w_j$, $t + u_i - w_j$ and $t - u_i + w_j$ cancel

out among various $\ln\beta$'s, because the original integral Eq. (2) is finite at these points and g is analytic. The cancellation can be achieved explicitly, by combining the corresponding β's under the common logarithm. For this one has to consider all possible orderings of t_i. Because of the symmetries $1 \leftrightarrow 2$ and $A \leftrightarrow B$ one can assume, without loosing generality, that $t_1 > t_2$ and $t_3 > t_4$. We remain with six possible orderings of t_i, $t_1 \geq t_2 \geq t_3 \geq t_4$, $t_1 \geq t_3 \geq t_2 \geq t_4$, $t_1 \geq t_3 \geq t_4 \geq t_2$, $t_3 \geq t_1 \geq t_2 \geq t_4$, $t_3 \geq t_1 \geq t_4 \geq t_2$, $t_3 \geq t_4 \geq t_1 \geq t_2$, and six corresponding representations of the master integral f

$$\begin{aligned}
f(r) &= \left(\int_{t_1}^{t_2} \ln|\beta_{0,0}| + \int_{t_2}^{t_3} \ln|\beta_{0,0}\,\beta_{3,3}| + \int_{t_3}^{t_4} \ln|\beta_{0,0}/\beta_{3,1}| - \int_{t_4}^{-\infty} \ln|\beta_{0,1}\,\beta_{3,1}|\right) \frac{e^{t\,r}}{\sqrt{\sigma}}\,dt \\
&= \left(\int_{t_1}^{t_3} \ln|\beta_{0,0}| - \int_{t_3}^{t_2} \ln|\beta_{0,2}| + \int_{t_2}^{t_4} \ln|\beta_{0,0}/\beta_{3,1}| - \int_{t_4}^{-\infty} \ln|\beta_{0,1}\,\beta_{3,1}|\right) \frac{e^{t\,r}}{\sqrt{\sigma}}\,dt \\
&= \left(\int_{t_1}^{t_3} \ln|\beta_{0,0}| - \int_{t_3}^{t_4} \ln|\beta_{0,2}| - \int_{t_4}^{t_2} \ln|\beta_{0,0}\,\beta_{0,1}\,\beta_{0,2}| - \int_{t_2}^{-\infty} \ln|\beta_{0,1}\,\beta_{3,1}|\right) \frac{e^{t\,r}}{\sqrt{\sigma}}\,dt \\
&= \left(-\int_{t_3}^{t_1} \ln|\beta_{0,0}\,\beta_{0,2}| - \int_{t_1}^{t_2} \ln|\beta_{0,2}| + \int_{t_2}^{t_4} \ln|\beta_{0,0}/\beta_{3,1}| - \int_{t_4}^{-\infty} \ln|\beta_{0,1}\,\beta_{3,1}|\right) \frac{e^{t\,r}}{\sqrt{\sigma}}\,dt \\
&= \left(-\int_{t_3}^{t_1} \ln|\beta_{0,0}\,\beta_{0,2}| - \int_{t_1}^{t_4} \ln|\beta_{0,2}| - \int_{t_4}^{t_2} \ln|\beta_{0,0}\,\beta_{0,1}\,\beta_{0,2}| - \int_{t_2}^{-\infty} \ln|\beta_{0,1}\,\beta_{3,1}|\right) \frac{e^{t\,r}}{\sqrt{\sigma}}\,dt \\
&= \left(-\int_{t_3}^{t_4} \ln|\beta_{0,0}\,\beta_{0,2}| - \int_{t_4}^{t_1} \ln|\beta_{0,0}^2\,\beta_{0,1}\,\beta_{0,2}| - \int_{t_1}^{t_2} \ln|\beta_{0,0}\,\beta_{0,1}\,\beta_{0,2}| - \int_{t_2}^{-\infty} \ln|\beta_{0,1}\,\beta_{3,1}|\right) \frac{e^{t\,r}}{\sqrt{\sigma}}\,dt
\end{aligned} \tag{B2}$$

In order to eliminate singularities algebraically, the products and ratios of β can be combined together [17]

$$\frac{\sqrt{\sigma}-\gamma}{\sqrt{\sigma}+\gamma}\,\frac{\gamma'-\sqrt{\sigma}}{\gamma'+\sqrt{\sigma}} = \frac{\sqrt{\sigma}-\Gamma}{\sqrt{\sigma}+\Gamma} \tag{B3}$$

where

$$\Gamma = \frac{\sigma+\gamma\,\gamma'}{\gamma+\gamma'} \tag{B4}$$

As a result, no singularity appears on the integration path, which is demonstrated by the following decompositions

$$\begin{aligned}
\sigma - \Gamma^2(\beta_{0,1}\,\beta_{3,1}) &= -(t-u_3-w_2)\,(t+u_3-w_2)\,(t-u_3+w_2)\,(t+u_3+w_2) \\
&\quad (t-u_2-w_3)\,(t+u_2-w_3)\,(t-u_2+w_3)\,(t+u_2+w_3)/(4\,t^2) \\
\sigma - \Gamma^2(\beta_{0,0}/\beta_{3,1}) &= -(u_2-u_3+w_1)\,(u_2+u_3+w_1)\,(t-u_3-w_2)\,(t+u_3-w_2)\,(t-u_2-w_3) \\
&\quad (w_1+w_2-w_3)\,(t-u_2+w_3)\,(w_1+w_2+w_3)/(t-u_2-w_1-w_2)^2 \\
\sigma - \Gamma^2(\beta_{0,0}\,\beta_{0,2}) &= -(-u_2+u_3+w_1)\,(u_2+u_3+w_1)\,(t+u_3-w_2)\,(t+u_3+w_2)\,(t-u_2+w_3) \\
&\quad (t+u_2+w_3)\,(w_1-w_2+w_3)\,(w_1+w_2+w_3)/(t+u_3+w_1+w_3)^2 \\
\sigma - \Gamma^2(\beta_{0,0}\,\beta_{0,1}) &= -(u_2-u_3+w_1)\,(u_2+u_3+w_1)\,(t-u_3+w_2)\,(t+u_3+w_2)\,(t+u_2-w_3) \\
&\quad (w_1+w_2-w_3)\,(t+u_2+w_3)\,(w_1+w_2+w_3)/(t+u_2+w_1+w_2)^2 \qquad \text{(B5)}
\end{aligned}$$

Table II presents numerical results for f for several internuclear distances r and nonlinear parameters w_1, x, y, u and w. For $r < 0.01$ f is evaluated from the Taylor series up to r^8, and for $r > 0.01$ from the integral representation in Eq. (B2).

TABLE II: Master integral f for selected values of internuclear distances r and nonlinear parameters

w_1	u_2	w_2	u_3	w_3	$f(0.1)\,10^2$	$f(1.0)\,10^3$	$f(10)\,10^{13}$
2.5	2.0	1.5	1.0	0.5	1.539 488 720 658 182	3.811 561 883 331 994	2.916 697 700 943 504
2.0	2.5	1.5	1.0	0.5	1.575 469 059 882 717	3.538 642 196 033 083	1.056 827 512 869 080
1.5	2.0	2.5	1.0	0.5	1.592 898 118 308 067	3.359 218 711 378 032	0.983 486 526 526 378
1.0	2.0	1.5	2.5	0.5	1.687 851 128 764 463	3.142 086 593 091 502	0.648 185 277 118 373
0.5	2.0	1.5	1.0	2.5	1.687 626 825 828 684	2.985 309 587 884 137	0.621 477 317 148 430
−0.5	2.0	1.5	1.0	2.5	2.285 510 252 707 772	5.843 903 698 492 676	2.026 400 131 640 827

Appendix C: Exact form of general recursion relations

The recursion relations for the general master integral, as given by Eq. (57) involves the 4 by 4 matrix A_α. For $\alpha = x, y, u, w$, A is the following

$$A_\alpha = \frac{1}{\delta}\begin{pmatrix} -\frac{1}{4}\frac{\partial\delta}{\partial\alpha}, & -\frac{r}{4}\left(\frac{\partial\delta}{\partial\alpha} - \frac{2\,\delta}{\sigma_0}\frac{\partial\sigma_0}{\partial\alpha}\right), & -\frac{w_1^2\,\sigma_\alpha}{2\,\sigma_0}, & -\frac{r\,w_1^2\,\sigma_\alpha}{2\,\sigma_0} \\ \frac{r\,\sigma_\alpha}{2}, & , & \frac{r}{4}\frac{\partial\delta}{\partial\alpha}, & \\ \frac{\sigma_\alpha}{2}, & \frac{r\,\sigma_\alpha}{2}, & \frac{1}{4}\frac{\partial\delta}{\partial\alpha}, & \frac{r}{4}\frac{\partial\delta}{\partial\alpha} \\ -\frac{r\,\sigma_0}{4\,w_1^2}\frac{\partial\delta}{\partial\alpha}, & -\frac{\delta}{2\,w_1^2}\frac{\partial\sigma_2}{\partial\alpha}, & -\frac{r\,\delta}{2\,w_1^2}\frac{\partial\sigma_2}{\partial\alpha} - \frac{r\,\sigma_\alpha}{2}, & \end{pmatrix} \tag{C1}$$

where

$$\sigma_\alpha = \frac{\sigma_2}{w_1^2}\frac{\partial\left(w_1^2\,\sigma_0\right)}{\partial\alpha} - 2\,\sigma_0\frac{\partial\sigma_2}{\partial\alpha} \tag{C2}$$

and the inhomogeneous term $\vec{F}_\alpha$ is

$$\begin{aligned}\vec{F}_\alpha \;=\; & \frac{1}{\delta}\begin{pmatrix} -\frac{\sigma_2}{2\,\sigma_0}\frac{\partial\sigma_2}{\partial\alpha}\frac{\partial}{\partial r} + \left(2\,w_1^2 - \frac{\delta}{\sigma_0}\right)\frac{\partial^2}{\partial r\partial\alpha} + w_1^2\,\frac{\sigma_2}{\sigma_0}\frac{\partial^3}{\partial r^3} \\ \frac{\partial\sigma_2}{\partial\alpha} - \sigma_2\frac{\partial}{\partial\alpha} - 2\,w_1^2\frac{\partial^3}{\partial r^2\,\partial\alpha} \\ \frac{\partial\sigma_2}{\partial\alpha}\frac{\partial}{\partial r} - \sigma_2\frac{\partial^2}{\partial r\partial\alpha} - 2\,w_1^2\frac{\partial^4}{\partial r^3\partial\alpha} \\ -\frac{\sigma_2}{2\,w_1^2}\frac{\partial\sigma_2}{\partial\alpha} + 2\,\sigma_0\frac{\partial}{\partial\alpha} + \sigma_2\frac{\partial^3}{\partial r^2\,\partial\alpha} \end{pmatrix} F_{u_1}(r) \\ & + \frac{1}{\delta}\begin{pmatrix} 2\left(w_1^2 - \frac{\delta}{\sigma_0}\right) + r\left(2\,w_1^2 - \frac{\delta}{\sigma_0}\right)\frac{\partial}{\partial r} + \frac{5\,w_1^2\,\sigma_2}{\sigma_0}\frac{\partial^2}{\partial r^2} + \frac{r\,w_1^2\,\sigma_2}{\sigma_0}\frac{\partial^3}{\partial r^3} \\ -r\,\sigma_2 - 8\,w_1^2\frac{\partial}{\partial r} - 2\,r\,w_1^2\frac{\partial^2}{\partial r^2} \\ -\sigma_2 - r\,\sigma_2\frac{\partial}{\partial r} - 10\,w_1^2\frac{\partial^2}{\partial r^2} - 2\,r\,w_1^2\frac{\partial^3}{\partial r^3} \\ 2\,r\,\sigma_0 + 4\,\sigma_2\frac{\partial}{\partial r} + r\,\sigma_2\frac{\partial^2}{\partial r^2} \end{pmatrix} F_\alpha(r) \end{aligned} \tag{C3}$$

For $\alpha = w_1$ matrix A is

$$A_{w_1} = \frac{1}{\delta}\begin{pmatrix} -\frac{1}{4}\frac{\partial\delta}{\partial w_1}, & -\frac{r}{4}\left(\frac{\partial\delta}{\partial w_1} - \frac{2\,\delta}{\sigma_0}\frac{\partial\sigma_0}{\partial w_1}\right), & -\frac{w_1^2\,\sigma_{w_1}}{2\,\sigma_0}, & -\frac{r\,w_1^2\,\sigma_{w_1}}{2\,\sigma_0} \\ \frac{r\,\sigma_{w_1}}{2}, & -\frac{\delta}{w_1}, & \frac{r}{4}\frac{\partial\delta}{\partial w_1} - \frac{r\,\delta}{w_1}, & \\ \frac{\sigma_{w_1}}{2}, & \frac{r\,\sigma_{w_1}}{2}, & \frac{1}{4}\frac{\partial\delta}{\partial w_1} - \frac{2\,\delta}{w_1}, & \frac{r}{4}\frac{\partial\delta}{\partial w_1} - \frac{r\,\delta}{w_1} \\ \frac{r\,\sigma_0\,\delta}{w_1^3} - \frac{r\,\sigma_0}{4\,w_1^2}\frac{\partial\delta}{\partial w_1}, & \frac{\delta\,\sigma_2}{w_1^3} - \frac{\delta}{2\,w_1^2}\frac{\partial\sigma_2}{\partial w_1}, & \frac{r\,\delta\,\sigma_2}{w_1^3} - \frac{r\,\delta}{2\,w_1^2}\frac{\partial\sigma_2}{\partial w_1} - \frac{r\,\sigma_{w_1}}{2}, & -\frac{\delta}{w_1} \end{pmatrix} \tag{C4}$$

and the inhomogeneous term

$$\vec{F}_{w_1} = \frac{1}{\delta}\begin{pmatrix} \frac{1}{4\,\sigma_0}\left(\frac{\partial\delta}{\partial w_1} - 4\,w_1^2\,\frac{\partial\sigma_0}{\partial w_1}\right) + \left(2\,w_1^2 - \frac{\delta}{\sigma_0}\right)\frac{\partial^2}{\partial r\partial w_1} - w_1\,\frac{\sigma_2}{\sigma_0}\,\frac{\partial^3}{\partial r^3} + w_1^2\,\frac{\sigma_2}{\sigma_0}\,\frac{\partial^4}{\partial r^3\partial w_1} \\ \left(\frac{\partial\sigma_2}{\partial w_1} - \frac{\sigma_2}{w_1}\right) - \sigma_2\,\frac{\partial}{\partial w_1} + 2\,w_1\,\frac{\partial^2}{\partial r^2} - 2\,w_1^2\,\frac{\partial^3}{\partial r^2\partial w_1} \\ \left(\frac{\partial\sigma_2}{\partial w_1} - \frac{\sigma_2}{w_1}\right)\frac{\partial}{\partial r} - \sigma_2\,\frac{\partial^2}{\partial r\partial w_1} + 2\,w_1\,\frac{\partial^3}{\partial r^3} - 2\,w_1^2\,\frac{\partial^4}{\partial r^3\partial w_1} \\ -\frac{\delta}{w_1^3} + \frac{1}{4\,w_1^2}\,\frac{\partial\delta}{\partial w_1} - \frac{\partial\sigma_0}{\partial w_1} + 2\,\sigma_0\,\frac{\partial}{\partial w_1} - \frac{\sigma_2}{w_1}\,\frac{\partial^2}{\partial r^2} + \sigma_2\,\frac{\partial^3}{\partial r^2\partial w_1} \end{pmatrix} F_{u_1}(r)$$

$$+\frac{1}{\delta}\begin{pmatrix} 2\left(w_1^2 - \frac{\delta}{\sigma_0}\right) + r\left(2\,w_1^2 - \frac{\delta}{\sigma_0}\right)\frac{\partial}{\partial r} + 5\,w_1^2\,\frac{\sigma_2}{\sigma_0}\,\frac{\partial^2}{\partial r^2} + r\,w_1^2\,\frac{\sigma_2}{\sigma_0}\,\frac{\partial^3}{\partial r^3} \\ -r\,\sigma_2 - 8\,w_1^2\,\frac{\partial}{\partial r} - 2\,r\,w_1^2\,\frac{\partial^2}{\partial r^2} \\ -\sigma_2 - r\,\sigma_2\,\frac{\partial}{\partial r} - 10\,w_1^2\,\frac{\partial^2}{\partial r^2} - 2\,r\,w_1^2\,\frac{\partial^3}{\partial r^3} \\ 2\,r\,\sigma_0 + 4\,\sigma_2\,\frac{\partial}{\partial r} + r\,\sigma_2\,\frac{\partial^2}{\partial r^2} \end{pmatrix} F_{w_1}(r) \qquad \text{(C5)}$$