Analytic formulas for two-center two-electron integrals with exponential functions

Magdalena Zientkiewicz and Krzysztof Pachucki*

Faculty of Physics, University of Warsaw,

Pasteura 5, 02-093 Warsaw, Poland

Abstract

We propose the use of exponential functions multiplied by the product of spherical harmonics at two centers in high precision calculations for diatomic molecules and demonstrate that all integrals can be obtained using analytic methods.

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*krp@fuw.edu.pl

I. INTRODUCTION

In spite of many advantages of exponential bases for molecular systems, it is very rarely employed due to difficulties in performing two-electron two-center integrals [1, 2]. The best-known accurate calculations with exponential functions have been performed by Kołos and coworkers for a hydrogen molecule, starting with the seminal work in [3]. They used the Neumann expansion of $1/r_{12}$ in spheroidal coordinates and its slow convergence was the main limiting factor for accurate results. This expansion has recently been improved in Ref. [4] with calculations for the Be_2 molecule. In the present work we overcome the problem of slow convergence of this expansion by direct calculation of all integrals with electronic functions of the type

$$\begin{aligned}\phi_A &= e^{-\alpha\, r_A}\, r_A^{n_A}\, Y_{lm}(\hat r_A)\, r_B^{n_B}\, Y_{l'm'}(\hat r_B),\\ \phi_B &= e^{-\beta\, r_B}\, r_B^{n_B}\, Y_{l'm'}(\hat r_B)\, r_A^{n_A}\, Y_{lm}(\hat r_A),\end{aligned} \tag{1}$$

where A, B are indices of the nuclei, r_A, r_B the electron distance from the corresponding nucleus, α and β are fixed nonlinear parameters, $n_A \geq l, n_B \geq l'$ are arbitrary non-negative integers. Matrix elements of non-relativistic Hamiltonian in this basis can all be expressed in terms of the following integrals over powers of inter-particle distances

$$f(n_0, n_1, n_2, n_3, n_4, r) = \int \frac{d^3 r_1}{4\,\pi} \int \frac{d^3 r_2}{4\,\pi}\, e^{-\alpha_1\, r_{1A}-\beta_1\, r_{1B}-\alpha_2\, r_{2A}-\beta_2\, r_{2B}}\, r_{12}^{n_0-1}\, r_{1A}^{n_1-1}\, r_{1B}^{n_2-1}\, r_{2A}^{n_3-1}\, r_{2B}^{n_4-1} \tag{2}$$

where r is the distance between nuclei. Note that products of spherical harmonics can be expressed as a polynomial in electron distances as in the above equation. Due to the choice of basis functions in Eq. (1), the nonlinear parameters may take the following values (up to $1 \leftrightarrow 2$ and $A \leftrightarrow B$ symmetries)

$$(\alpha_1,\, \beta_1,\, \alpha_2,\, \beta_2) = \begin{cases} (2\,\alpha, 0, 0, 2\,\beta) & \text{-direct} \\ (\alpha, \beta, \alpha, \beta) & \text{-exchange} \\ (2\,\alpha, 0, 2\,\alpha, 0) & \text{-ionic} \\ (2\,\alpha, 0, \alpha, \beta) & \text{-mixed} \end{cases} \tag{3}$$

We propose here to generate an explicit analytic expression for all integrals up to some $\Omega = n_0 + n_1 + n_2 + n_3 + n_4$ with the help of a computer symbolic program and the rest of this work explains how to achieve this. Due to presence of only two independent nonlinear parameters, the analytical expressions are not excessively large and can be stored in a few GB volume for Ω as large as 37.

Let us start from the integral with all $n_i = 0$, it will be called the master integral $f(r)$

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

where we changed the notation for nonlinear parameter to synchronize it with our former papers and introduced for convenience an extra factor of r. The function $f(r)$ satisfies the following differential equation [5]:

$$\left[\sigma_{20}\, \frac{d}{d\,r}\, r\, \frac{d}{d\,r} + \sigma_{00}\, r\right] f(r) = F(r), \tag{5}$$

where σ coefficients are

$$\sigma_{20} = -(u_2^2 - u_3^2)\,(w_2^2 - w_3^2) = 16\,u\,w\,x\,y \tag{6}$$

$$\sigma_{00} = (u_2^2 - u_3^2 + w_2^2 - w_3^2)\,(u_2^2\,w_2^2 - u_3^2\,w_3^2) = 16\,(w\,x - u\,y)\,(u\,x - w\,y)\,(u\,w - x\,y) \tag{7}$$

and notation for subscripts is specified below. The new parameters y, x, u, w

$$w_2 = w + x, \quad w_3 = w - x, \quad u_2 = u - y, \quad u_3 = u + y, \tag{8}$$

are adapted to the symmetry of the master integral, namely

$$f(y, x, u, w) = f(x, y, u, w) = f(y, x, w, u) = f(x, y, w, u) \tag{9}$$

The inhomogeneous term in the differential equation (5) is the following

$$\begin{aligned} F(r) &= 2\,(u\,w\,x - u\,w\,y - u\,x\,y + w\,x\,y)\,F_{1-} + 2\,(u\,w\,x - u\,w\,y + u\,x\,y - w\,x\,y)\,F_{2-} \\ &\quad -2(u\,w\,x + u\,w\,y + u\,x\,y + w\,x\,y)\,F_{3-} + 2\,(u\,w\,x + u\,w\,y - u\,x\,y - w\,x\,y)\,F_{4-}, \end{aligned} \tag{10}$$

where

$$\begin{aligned} F_{1\pm} &= \mathrm{Ei}(-2\,r\,u)\,e^{r\,(u-w-x+y)} \pm \mathrm{Ei}(-2\,r\,w)\,e^{r\,(-u+w+x-y)}, \\ F_{2\pm} &= \mathrm{Ei}(-2\,r\,w)\,e^{r\,(-u+w-x+y)} \pm \mathrm{Ei}(-2\,r\,u)\,e^{r\,(u-w+x-y)}, \\ F_{3\pm} &= \left[\mathrm{Ei}(2\,r\,x) + \mathrm{Ei}(2\,r\,y) - \mathrm{Ei}(2\,r\,(x+y)) + \ln\left(\frac{u\,w\,(x+y)}{x\,y\,(u+w)}\right)\right] e^{-r\,(u+w+x+y)} \\ &\quad \pm \mathrm{Ei}(-2\,r\,(u+w))\,e^{r\,(u+w+x+y)}, \\ F_{4\pm} &= \left[\mathrm{Ei}(-2\,r\,x) + \mathrm{Ei}(-2\,r\,y) - \mathrm{Ei}(-2\,r\,(x+y)) + \ln\left(\frac{u\,w\,(x+y)}{x\,y\,(u+w)}\right)\right] e^{-r\,(u+w-x-y)} \\ &\quad \pm \mathrm{Ei}(-2\,r\,(u+w))\,e^{r\,(u+w-x-y)}, \end{aligned} \tag{11}$$

and Ei is the exponential integral function. This differential equation is supplemented by the boundary conditions, namely $f(r)$ vanishes at small and large r.

II. INTEGRAL REPRESENTATION FOR THE MASTER INTEGRAL

Since the homogeneous differential equation (5) has solutions I_0 and K_0 modified Bessel functions, the inhomogeneous equation can be expressed as [5].

$$f(r) = -\frac{1}{\sigma_{20}} \left[I_0(p\,r) \int_r^\infty dr'\, F(r')\, K_0(p\,r') + K_0(p\,r) \int_0^r dr'\, F(r')\, I_0(p\,r') \right], \qquad (12)$$

where $p = \sqrt{-\sigma_{00}/\sigma_{20}}$, However, a more elegant integral representation for $f(r)$ is the following [6]

$$\begin{aligned} f(r) \;=\; & \int_0^{-\infty} dt\, e^{t\,r}\, \frac{1}{2\sqrt{\sigma}} \big[\theta(t_1 - t)\, \ln\beta_1 + \theta(t_2 - t)\, \ln\beta_2 \\ & \qquad -\theta(t_3 - t)\, \ln\beta_3 - \theta(t_4 - t)\, \ln\beta_4\big]. \end{aligned} \qquad (13)$$

where $\sigma = \sigma_{00} + t^2\,\sigma_{20}$ and

$$\begin{aligned} -t_1 &= u_3 + w_2 &= u + y + w + x, \\ -t_2 &= u_2 + w_3 &= u - y + w - x, \\ -t_3 &= u_3 + w_3 &= u + y + w - x, \\ -t_4 &= u_2 + w_2 &= u - y + w + x, \end{aligned} \qquad (14)$$

and where

$$\beta_i = \frac{\sqrt{\sigma} - \gamma_i}{\sqrt{\sigma} + \gamma_i}, \qquad (15)$$

with the following γ_i coefficients

$$\begin{aligned} \gamma_1 &= -4\,(u\,w\,x + u\,w\,y - u\,x\,y - w\,x\,y), \\ \gamma_2 &= 4\,(u\,w\,x + u\,w\,y + u\,x\,y + w\,x\,y), \\ \gamma_3 &= -16\,u\,w\,x\,y/(t + u + w - x + y) + 4\,(u\,w\,x - u\,w\,y + u\,x\,y + w\,x\,y), \\ \gamma_4 &= -16\,u\,w\,x\,y/(t + u + w + x - y) - 4\,(u\,w\,x - u\,w\,y - u\,x\,y - w\,x\,y), \end{aligned} \qquad (16)$$

The evaluation of the logarithms in Eq. (13) proceeds as follows [7]

$$\mathrm{Re}\left[\frac{1}{2\sqrt{\sigma}}\,\ln\left(\frac{\sqrt{\sigma}-\gamma}{\sqrt{\sigma}+\gamma}\right)\right] = \begin{cases} -\frac{1}{\gamma}\,, & \text{for } \sigma = 0\,, \\ -\frac{1}{\sqrt{\sigma}}\ \mathrm{arctanh}\left(\frac{\gamma}{\sqrt{\sigma}}\right)\,, & \text{for } \sigma > 0, |\gamma| < \sqrt{\sigma}\,, \\ -\frac{1}{\sqrt{\sigma}}\ \mathrm{arctanh}\left(\frac{\sqrt{\sigma}}{\gamma}\right)\,, & \text{for } \sigma > 0, |\gamma| > \sqrt{\sigma}\,, \\ -\frac{1}{\sqrt{-\sigma}}\left[\arctan\left(\frac{\sqrt{-\sigma}}{\gamma}\right) + k\,\pi\right]\,, & \text{for } \sigma < 0\,. \end{cases} \tag{17}$$

In the last line, the phase pre-factor $k = 0, \pm 1$ is introduced, which is determined as follows. On an integration path where σ is negative, the parameter γ may change a sign. At this point, a phase factor $\pm\pi$ is introduced so as to make the integrand continuous. Since γ changes sign twice, the correction term vanishes at the integration point where $\sigma = 0$.

In the special case of the direct integral

$$\begin{aligned} u_3 &= \alpha \\ w_3 &= \beta \\ u_2 &= w_2 = 0 \end{aligned} \tag{18}$$

the integral representation becomes

$$f(r) = \int_0^{-\infty} dt\,\frac{e^{t\,r}}{2\sqrt{\sigma}}\big[\theta(-\alpha-t)\,\ln\beta_1 + \theta(-\beta-t)\,\ln\beta_2 - \theta(-\alpha-\beta-t)\,\ln\beta_3 - \ln\beta_4\big]. \tag{19}$$

with

$$\begin{aligned} \sigma &= \alpha^2\,\beta^2\,(\alpha^2+\beta^2-t^2) \\ \gamma_1 &= -\alpha^2\,\beta \\ \gamma_2 &= -\alpha\,\beta^2 \\ \gamma_3 &= -\alpha\,\beta\,(\alpha+\beta) + \frac{\alpha^2\,\beta^2}{t+\alpha+\beta} \\ \gamma_4 &= \frac{\alpha^2\,\beta^2}{t} \end{aligned} \tag{20}$$

In the case of an exchange integral $w = u$, $x = y$, σ_{00} vanishes and the master integral becomes

$$\begin{aligned} f(r) &= \frac{1}{8\,w\,x}\left(\int_{-2\,(w+x)}^{-\infty} dt\,\ln\left|\frac{t+2\,(w-x)}{t-2\,(w-x)}\right|\,\frac{e^{t\,r}}{t}\right. \\ &\quad + \int_{-2\,(w-x)}^{-\infty} dt\,\ln\left|\frac{t-2\,(w+x)}{t+2\,(w+x)}\right|\,\frac{e^{t\,r}}{t} \\ &\quad \left. -2\int_{-2\,w}^{-\infty} dt\,\ln\left|\frac{t+2\,(w-x)}{t+2\,(w+x)}\right|\,\frac{e^{t\,r}}{t}\right). \end{aligned} \tag{21}$$

This integral cannot be expressed in terms of standard functions but its derivative can, namely

$$
\begin{aligned}
f'(r) \;=\; & \frac{1}{2\,r\,(u^2-w^2)}\biggl[\mathrm{Ei}[-2\,r\,(u+w)]\,\bigl[\exp(2\,r\,u)-\exp(2\,r\,w)\bigr] \\
& +\biggl(\mathrm{Ei}[2\,r\,(w-u)]-2\,\mathrm{Ei}[r\,(w-u)]+\ln\biggl|\frac{u-w}{u+w}\biggr|\biggr)\,\exp(-2\,r\,w) \\
& -\biggl(\mathrm{Ei}[2\,r\,(u-w)]-2\,\mathrm{Ei}[r\,(u-w)]+\ln\biggl|\frac{u-w}{u+w}\biggr|\biggr)\,\exp(-2\,r\,u)\biggr]
\end{aligned} \tag{22}
$$

Two other cases of Eq. (3) are similar, so the master integral can be calculated as accurately as the one-dimensional integral and we found that Gaussian integrations adapted to the logarithmic singularity at the end point [8] converge very quickly.

III. RECURENCE RELATIONS FOR THE GENERAL INTEGRAL WITH $\sigma_{00} \neq 0$

In order to obtain the molecular integrals with higher powers of r_{12},

$$
f(r,n) = r\int\frac{d^3r_1}{4\,\pi}\int\frac{d^3r_2}{4\,\pi}\,r_{12}^{n-1}\,\frac{e^{-u_3\,r_{1A}}}{r_{1A}}\,\frac{e^{-u_2\,r_{1B}}}{r_{1B}}\,\frac{e^{-w_2\,r_{2A}}}{r_{2A}}\,\frac{e^{-w_3\,r_{2B}}}{r_{2B}} \tag{23}
$$

we consider a more general function $\tilde f(r)$, which includes $\exp(-w_1\,r_{12})$, see Eq. (A1). Its properties are very similar to that of $f(r)$. In particular it satisfies the master differential equation Eq. (A2) [6, 9], several other differential equations (A10,A11), and it can also be represented as a one-dimensional integral [6]. The recurrence relations for $f(r,n)$ have already been presented in Refs. [5, 6]. Here we re-derive them in a compact way, namely let us take Eqs. (13) and (15), and differentiate them with respect to w_1, n and $n-1$ times respectively at $w_1=0$

$$
\begin{aligned}
& r\,\sigma_{00}\,f(r,n)+\sigma_{20}\,f'(r,n)+r\,\sigma_{20}\,f''(r,n)+(n-1)\,n\,r\,\sigma_{02}\,f(r,n-2) \\
& +(n-1)\,n\,\sigma_{22}\,f'(r,n-2)+(n-1)\,n\,r\,\sigma_{22}\,f''(r,n-2)+2\,(n-1)\,n\,f^{(3)}(r,n-2) \\
& +(n-1)\,n\,r\,f^{(4)}(r,n-2)+(n-3)\,(n-2)\,(n-1)\,n\,f'(r,n-4) \\
& +(n-3)\,(n-2)\,(n-1)\,n\,r\,f''(r,n-4)=F_{u_1}(r,n)\,,
\end{aligned} \tag{24}
$$

$$
\begin{aligned}
& \sigma_{00}\,f(r,n)+\sigma_{20}\,f''(r,n)+(n-1)^2\,\sigma_{02}\,f(r,n-2)+(n-1)^2\,\sigma_{22}\,f''(r,n-2) \\
& +(n-1)^2\,f^{(4)}(r,n-2)+(n-3)\,(n-2)^2\,(n-1)\,f''(r,n-4)=F_{w_1}(r,n-1)\,.
\end{aligned} \tag{25}
$$

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 $f(r,n)$ is

$$\begin{aligned} f(r,n) &= \frac{1}{\sigma_{00}}\left[-(n-2)\,(n-1)\,\sigma_{02}\,f(r,n-2)+(n-1)\,r\,\sigma_{02}\,f'(r,n-2)\right. \\ &+2\,(n-1)\,\sigma_{22}\,f''(r,n-2)+(n-1)\,r\,\sigma_{22}\,f^{(3)}(r,n-2) \\ &+(n-1)\,(n+2)\,f^{(4)}(r,n-2)+(n-1)\,r\,f^{(5)}(r,n-2) \\ &+4\,(n-3)\,(n-2)\,(n-1)\,f''(r,n-4)+2\,(n-3)\,(n-2)\,(n-1)\,r\,f^{(3)}(r,n-4) \\ &\left.+2\,F_{w_1}(r,n-1)+r\,F'_{w_1}(r,n-1)-F'_{u_1}(r,n)\right], \end{aligned} \tag{26}$$

where

$$F_X(r,n) = (-1)^n \left.\frac{\partial^n}{\partial w_1^n}\right|_{w_1=0} \tilde{F}_X(r), \tag{27}$$

for $X = w_1, u_1$. Equation (26) allows one to obtain $f(r,n)$ in terms of $f(r)$, exponential and exponential integral functions, for example

$$\begin{aligned} f(r,0) &= f(r), \\ f(r,1) &= \frac{r^3}{4}\,h_0(r\,u)\,h_0(r\,w)\,j_0(r\,x)\,j_0(r\,y), \\ f(r,2) &= \frac{1}{\sigma_{00}}\left[r\,\sigma_{02}\,f'(r)+2\,\sigma_{22}\,f''(r)+r\,\sigma_{22}\,f^{(3)}(r)+4\,f^{(4)}(r)+r\,f^{(5)}(r)\right. \\ &\left.+2\,F_{w_1}(r,1)+r\,F'_{w_1}(r,1)-F'_{u_1}(r,2)\right], \\ f(r,3) &= \frac{r^5}{24}\left[-3\,h_1(r\,u)\,h_1(r\,w)\,j_1(r\,x)\,j_1(r\,y)-h_0(r\,u)\,h_0(r\,w)\,j_0(r\,x)\,j_0(r\,y)\right. \\ &+h_0(r\,w)\,h_2(r\,u)\,j_0(r\,x)\,j_0(r\,y)+h_0(r\,u)\,h_2(r\,w)\,j_0(r\,x)\,j_0(r\,y) \\ &\left.+h_0(r\,u)\,h_0(r\,w)\,j_2(r\,x)\,j_0(r\,y)+h_0(r\,u)\,h_0(r\,w)\,j_0(r\,x)\,j_2(r\,y)\right], \end{aligned} \tag{28}$$

where j_n and h_n are (up to the sign) the modified spherical Bessel functions [10]

$$\begin{aligned} j_n(x) &= x^n \left(\frac{1}{x}\frac{d}{dx}\right)^n \frac{\sinh(x)}{x}, \\ h_n(x) &= x^n \left(\frac{1}{x}\frac{d}{dx}\right)^n \frac{\exp(-x)}{x}. \end{aligned} \tag{29}$$

Note that $f(r,n)$ for odd n can be expressed in terms of j_n and h_n only, so their numerical evaluation is straightforward.

What remains are the derivatives of f with respect to $\alpha = u, w, x, y$ at $w_1 = 0$. We adapt here the derivation of the corresponding formulas from Ref. [5]. One takes fundamental differential equations in u_1 and α

$$r\,\sigma_{00}\,f(r) + \sigma_{20}\,f'(r) + r\,\sigma_{20}\,f''(r) = F_{u_1}(r) \tag{30}$$

$$\frac{1}{2}\,\frac{\partial\sigma_{00}}{\partial\alpha}\,f(r) + \sigma_{00}\,\frac{\partial f(r)}{\partial\alpha} + \frac{1}{2}\,\frac{\partial\sigma_{20}}{\partial\alpha}f''(r) + \sigma_{20}\,\frac{\partial f''(r)}{\partial\alpha} = -F_\alpha(r) \tag{31}$$

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

$$\frac{\partial f}{\partial\alpha} = -\frac{1}{2\,\alpha}\,f(r) + \frac{r}{2}\left(\frac{1}{\sigma_{00}}\,\frac{\partial\sigma_{00}}{\partial\alpha} - \frac{1}{\alpha}\right) f'(r) + \frac{G_\alpha(r)}{\sigma_{00}}\,, \tag{32}$$

where

$$\begin{aligned}
\frac{G_w}{\sigma_{00}} &= \frac{1}{16\,w}\left(\frac{H_1}{w\,x - u\,y} + \frac{H_2}{w\,y - u\,x} + \frac{H_3}{u\,w - x\,y}\right)\\
\frac{G_u}{\sigma_{00}} &= \frac{1}{16\,u}\left(\frac{H_1}{u\,y - w\,x} + \frac{H_2}{u\,x - w\,y} + \frac{H_3}{u\,w - x\,y}\right)\\
\frac{G_x}{\sigma_{00}} &= \frac{1}{16\,x}\left(\frac{H_1}{w\,x - u\,y} + \frac{H_2}{u\,x - w\,y} + \frac{H_3}{x\,y - u\,w}\right)\\
\frac{G_y}{\sigma_{00}} &= \frac{1}{16\,y}\left(\frac{H_1}{u\,y - w\,x} + \frac{H_2}{w\,y - u\,x} + \frac{H_3}{x\,y - u\,w}\right)
\end{aligned} \tag{33}$$

and where

$$\begin{aligned}
H_1 &= -F_{1+} + F_{2+} - F_{3+} + F_{4+}\\
H_2 &= F_{1+} - F_{2+} - F_{3+} + F_{4+}\\
H_3 &= F_{1+} + F_{2+} - F_{3+} - F_{4+}
\end{aligned} \tag{34}$$

The formula (32) allows one to obtain integrals with arbitrary powers of electronic distances, but it requires that $\sigma_{00} \neq 0$

IV. RECURRENCE RELATIONS AT $\sigma_{00} = 0$

When $\sigma_{00} = 0$, as it is for an exchange integral, one derives recurrence relations not for $f(r)$, but for $f'(r)$, and afterwards integrates analytically the expression. This analytic integration is possible, since $r\,f'(r)$ is a simple combination of exponential and exponential integral functions, see Eq. (22).

The recurrence relations for $f'(r)$ in powers of r_{12} is obtained from Eqs (24,25), in analogous way as for $f(r)$, and the result is

$$\begin{aligned} f'(r,n) &= -\frac{1}{\sigma_{20}}\Big[(n-1)\,r\,\sigma_{02}\,f(r,n-2)+(n-3)\,(n-2)\,(n-1)\,n\,f'(r,n-4)\\ &\quad +(n-1)\,n\,\sigma_{22}\,f'(r,n-2)+2\,(n-3)\,(n-2)\,(n-1)\,r\,f''(r,n-4)\\ &\quad +(n-1)\,r\,\sigma_{22}\,f''(r,n-2)+2\,(n-1)\,n\,f^{(3)}(r,n-2)+(n-1)\,r\,f^{(4)}(r,n-2)\\ &\quad +r\,F_{w_1}(r,n-1)-F_{u_1}(r,n)\Big], \end{aligned} \tag{35}$$

The derivatives of $f'(r)$ with respect to nonlinear parameters, can be obtained from Eq.(32), by taking the derivative over r and using the master equation (5). Alternatively, one can use general equations (A12) and set $w_1=0$ there. The result is

$$\begin{aligned} 4\,w^2\,\frac{\partial f'(r)}{\partial w} &= \frac{r\,f(r)}{2}\,\frac{\partial\sigma_{02}}{\partial w}+2\,r\,w\,f''(r)-\frac{-F_{1-}+F_{2-}-F_{3-}-F_{4-}}{2}\,,\\ 4\,u^2\,\frac{\partial f'(r)}{\partial u} &= \frac{r\,f(r)}{2}\,\frac{\partial\sigma_{02}}{\partial u}+2\,r\,u\,f''(r)-\frac{F_{1-}-F_{2-}-F_{3-}-F_{4-}}{2}\,,\\ 4\,x^2\,\frac{\partial f'(r)}{\partial x} &= \frac{r\,f(r)}{2}\,\frac{\partial\sigma_{02}}{\partial x}+2\,r\,x\,f''(r)-\frac{F_{1-}+F_{2-}-F_{3-}+F_{4-}}{2}\,,\\ 4\,y^2\,\frac{\partial f'(r)}{\partial y} &= \frac{r\,f(r)}{2}\,\frac{\partial\sigma_{02}}{\partial y}+2\,r\,y\,f''(r)-\frac{-F_{1-}-F_{2-}-F_{3-}+F_{4-}}{2}\,, \end{aligned} \tag{36}$$

where σ_{02} is defined in Eq. (A7) and F_{i-} in Eqs. (11).

V. JAMES-COOLIDGE INTEGRALS $\sigma_{20}=0$

This is the simplest case where all f's can be obtained explicitly [11, 12]. It is related to the fact that the Neumann expansion of $1/r_{12}$ in spheroidal coordinates is finite when $x=0$ or $y=0$, what corresponds to $\sigma_{20}=0$ [3]. Let us use one of Eqs. (A12) from the Appendix

$$(w_1^2-4\,x^2)\,\frac{\partial\tilde f'(r)}{\partial x} = -\frac{r\,\tilde f(r)}{2}\,\frac{\partial\sigma_{02}}{\partial x}-2\,r\,x\,\tilde f''(r)+\frac{\tilde F_{1-}+\tilde F_{2-}-\tilde F_{3-}+\tilde F_{4-}}{2}\,. \tag{37}$$

If we set $w_1=x=0$ it becomes an algebraic equation for $f(r)$, namely

$$\begin{aligned} f(r)|_{x=0} &= \frac{\sinh(r\,y)}{4\,r\,y\,u\,w}\Big\{-\mathrm{Ei}[-2\,r\,u]\,\exp[r\,(u-w)]-\mathrm{Ei}[-2\,r\,w]\,\exp[r\,(w-u)]\\ &\quad +\mathrm{Ei}[-2\,r\,(u+w)]\,\exp[r\,(u+w)]+\Big(\gamma+\ln\Big[\frac{2\,r\,u\,w}{u+w}\Big]\Big)\,\exp[-r\,(u+w)]\Big\} \end{aligned} \tag{38}$$

To obtain $f(n_0,n_1,r)$ defined as

$$f(n_0,n_2,r) = \Big(-\frac{\partial}{\partial w_1}\Big)^{n_0}\Big(-\frac{\partial}{\partial x}\Big)^{n_2}\,\tilde f(r)|_{w_1=x=0} \tag{39}$$

one takes derivatives of the above differential equation, and remaining derivatives can be taken directly on $f(n_0, n_2, r)$.

VI. CONCLUSION

We have presented an approach to perform calculations for diatomic systems in the exponential basis. Assuming the nonlinear parameter is fixed for any center, all integrals can be explicitly derived from differential equations using any computer symbolic program and stored on the hard disk. Such calculations have already been performed for H_2 [11] and HeH^+ molecules [13], demonstrating the computational applicability and high accuracy.

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Appendix A: Master integral

The master integral $\tilde f$ is defined by

$$\tilde f(r) = r \int \frac{d^3 r_1}{4\,\pi} \int \frac{d^3 r_2}{4\,\pi}\,\frac{e^{-w_1\,r_{12}}}{r_{12}}\,\frac{e^{-u_3\,r_{1A}}}{r_{1A}}\,\frac{e^{-u_2\,r_{1B}}}{r_{1B}}\,\frac{e^{-w_2\,r_{2A}}}{r_{2A}}\,\frac{e^{-w_3\,r_{2B}}}{r_{2B}}, \tag{A1}$$

where $r = r_{AB}$ is the distance between the nuclei. $\tilde f(r)$ satisfies several differential equations. The master differential equation is [6, 9]

$$\left[\sigma_4\,\frac{d^2}{d\,r^2}\,r\,\frac{d^2}{d\,r^2} + \sigma_2\,\frac{d}{d\,r}\,r\,\frac{d}{d\,r} + \sigma_0\,r\right]\tilde f(r) = \tilde F(r), \tag{A2}$$

where $\sigma = \sigma_0 + u_1^2\,\sigma_2 + u_1^4\,\sigma_4$ and σ being the sixth order polynomial

$$\begin{aligned}\sigma \;=\;& u_1^2\,u_2^2\,w_3^2 + u_2^2\,u_3^2\,w_1^2 + u_1^2\,u_3^2\,w_2^2 + w_1^2\,w_2^2\,w_3^2 + u_1^2\,w_1^2\,(u_1^2 + w_1^2 - u_2^2 - u_3^2 - w_2^2 - w_3^2)\\ &+u_2^2\,w_2^2\,(u_2^2 + w_2^2 - u_1^2 - u_3^2 - w_1^2 - w_3^2) + u_3^2\,w_3^2\,(u_3^2 + w_3^2 - u_2^2 - u_1^2 - w_1^2 - w_2^2).\end{aligned} \tag{A3}$$

Using the following new parameters which reflect symmetries of $\tilde f$

$$w_2 = w + x,\quad w_3 = w - x,\quad u_2 = u - y,\quad u_3 = u + y, \tag{A4}$$

σ polynomials are

$$\sigma_4 \;=\; w_1^2, \tag{A5}$$

$$\begin{aligned}\sigma_2 \;&=\; w_1^4\; - 2\,w_1^2\,(u^2 + w^2 + x^2 + y^2) + 16\,u\,w\,x\,y\\ &=\; w_1^4 + w_1^2\,\sigma_{22} + \sigma_{20},\end{aligned} \tag{A6}$$

$$\begin{aligned}\sigma_0 \;&=\; w_1^2\,(u + w - x - y)\,(u - w + x - y)\,(u - w - x + y)\,(u + w + x + y)\\ &\quad +16\,(w\,x - u\,y)\,(u\,x - w\,y)\,(u\,w - x\,y)\\ &=\; w_1^2\,\sigma_{02} + \sigma_{00},\end{aligned} \tag{A7}$$

and the inhomogeneous term is

$$
\begin{aligned}
\tilde{F}(r) \;=\;& w_1 \left(\frac{1}{r^2} + \frac{2\,w_1 + u + w + x - y}{r} \right) e^{-r\,(u+w+w_1+x-y)} \\
&+ w_1 \left(\frac{1}{r^2} + \frac{2\,w_1 + u + w - x + y}{r} \right) e^{-r\,(u+w+w_1-x+y)} \\
&- w_1 \left(\frac{1}{r^2} + \frac{u + w - x - y}{r} \right) e^{-r\,(u+w-x-y)} \\
&- w_1 \left(\frac{1}{r^2} + \frac{u + w + x + y}{r} \right) e^{-r\,(u+w+x+y)} \\
&+ \left[\frac{w_1^2}{2}\,(u - w + x - y) + 2\,u\,w\,(y - x) + 2\,x\,y\,(w - u) \right] \tilde{F}_{1-} \\
&+ \left[\frac{w_1^2}{2}\,(w - u + x - y) + 2\,u\,w\,(y - x) + 2\,x\,y\,(u - w) \right] \tilde{F}_{2-} \\
&- \left[\frac{w_1^2}{2}\,(u + w + x + y) + 2\,u\,w\,(x + y) + 2\,x\,y\,(u + w) \right] \tilde{F}_{3-} \\
&- \left[\frac{w_1^2}{2}\,(u + w - x - y) - 2\,u\,w\,(x + y) + 2\,x\,y\,(u + w) \right] \tilde{F}_{4-}\,, \qquad \text{(A8)}
\end{aligned}
$$

where

$$
\begin{aligned}
\tilde{F}_{1-} \;=\;& \mathrm{Ei}[-r\,(w_1 + 2\,u)]\;\exp[r\,(u - w + x - y)] - \mathrm{Ei}[-r\,(w_1 + 2\,w)]\;\exp[r\,(w - u - x + y)]\,, \\
\tilde{F}_{2-} \;=\;& \mathrm{Ei}[-r\,(w_1 + 2\,w)]\;\exp[r\,(w - u + x - y)] - \mathrm{Ei}[-r\,(w_1 + 2\,u)]\;\exp[r\,(u - w - x + y)]\,, \\
\tilde{F}_{3-} \;=\;& -\mathrm{Ei}[-2\,r\,(u + w)]\;\exp[r\,(u + w + x + y)] + \Big\{ -\mathrm{Ei}[2\,r\,(x + y)] + \mathrm{Ei}[-r\,(w_1 - 2\,x)] \\
& + \mathrm{Ei}[-r\,(w_1 - 2\,y)] + \ln\left[\frac{(w_1 + 2\,u)\,(w_1 + 2\,w)\,(x + y)}{(u + w)\,(w_1 - 2\,x)\,(w_1 - 2\,y)} \right] \Big\}\;\exp[-r\,(u + w + x + y)]\,, \\
\tilde{F}_{4-} \;=\;& -\mathrm{Ei}[-2\,r\,(u + w)]\;\exp[r\,(u + w - x - y)] + \Big\{ -\mathrm{Ei}[-2\,r\,(x + y)] + \mathrm{Ei}[-r\,(w_1 + 2\,x)] \\
& + \mathrm{Ei}[-r\,(w_1 + 2\,y)] + \ln\left[\frac{(w_1 + 2\,u)\,(w_1 + 2\,w)\,(x + y)}{(u + w)\,(w_1 + 2\,x)\,(w_1 + 2\,y)} \right] \Big\}\;\exp[-r\,(u + w - x - y)]\,, \\
& \qquad \text{(A9)}
\end{aligned}
$$

and Ei is the exponential integral function.

The complementary differential equations are [6]

$$
\Big(\frac{1}{2}\,\frac{\partial \sigma_0}{\partial w_1} + \sigma_0\,\frac{\partial}{\partial w_1} \Big)\, f(r) + \Big(\frac{1}{2}\,\frac{\partial \sigma_2}{\partial w_1} + \sigma_2\,\frac{\partial}{\partial w_1} \Big)\, f''(r) + \Big(w_1 + w_1^2\,\frac{\partial}{\partial w_1} \Big)\, f^{(4)}(r) = -F_{w_1}(r), \quad \text{(A10)}
$$

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

$$
\Big(\frac{1}{2}\,\frac{\partial \sigma_0}{\partial \alpha} + \sigma_0\,\frac{\partial}{\partial \alpha} \Big)\, f(r) + \Big(\frac{1}{2}\,\frac{\partial \sigma_2}{\partial \alpha} + \sigma_2\,\frac{\partial}{\partial \alpha} \Big)\, f''(r) + w_1^2\,\frac{\partial}{\partial \alpha}\, f^{(4)}(r) = -F_\alpha(r). \qquad \text{(A11)}
$$

From the master differential equation (A2) and from Eq. (A11) one derives [7] the following simple formulas for derivatives with respect to nonlinear parameters

$$
\begin{aligned}
(w_1^2 - 4\,w^2)\,\frac{\partial f'(r)}{\partial w} &= -\frac{r\,f(r)}{2}\,\frac{\partial\sigma_{02}}{\partial w} - 2\,r\,w\,f''(r) + \frac{-F_{1-} + F_{2-} - F_{3-} - F_{4-}}{2}\,,\\
(w_1^2 - 4\,u^2)\,\frac{\partial f'(r)}{\partial u} &= -\frac{r\,f(r)}{2}\,\frac{\partial\sigma_{02}}{\partial u} - 2\,r\,u\,f''(r) + \frac{F_{1-} - F_{2-} - F_{3-} - F_{4-}}{2}\,,\\
(w_1^2 - 4\,x^2)\,\frac{\partial f'(r)}{\partial x} &= -\frac{r\,f(r)}{2}\,\frac{\partial\sigma_{02}}{\partial x} - 2\,r\,x\,f''(r) + \frac{F_{1-} + F_{2-} - F_{3-} + F_{4-}}{2}\,,\\
(w_1^2 - 4\,y^2)\,\frac{\partial f'(r)}{\partial y} &= -\frac{r\,f(r)}{2}\,\frac{\partial\sigma_{02}}{\partial y} - 2\,r\,y\,f''(r) + \frac{-F_{1-} - F_{2-} - F_{3-} + F_{4-}}{2}\,, \quad \text{(A12)}
\end{aligned}
$$

where σ_{02} is defined in Eq. (A7), the inhomogeneous F_i terms are given by Eq. (A9) and prime in $f'(r)$ means derivative with respect to r.

Appendix B: Inhomogeneous terms

The inhomogeneous terms in the master differential equation (A2) and in the supplementary differential equations (A10,A11) are the inverse Laplace transform of P_α for $\alpha = u_i, w_i$.

$$
F_\alpha = \frac{1}{2\,\pi\,i}\int_{-i\,\infty+\epsilon}^{i\,\infty+\epsilon} dt\, e^{t\,r}\, P_\alpha\Big|_{u_1=t} \qquad \text{(B1)}
$$

P_α are related to each other by

$$
\begin{aligned}
P_{w_1} &= P(w_1, u_1; w_2, u_2; w_3, u_3)\\
&= P(w_1, u_1; w_3, u_3; w_2, u_2)\\
P_{u_1} &= P(u_1, w_1; w_2, u_2; u_3, w_3)\\
P_{w_2} &= P(w_2, u_2; w_3, u_3; w_1, u_1)\\
P_{u_2} &= P(u_2, w_2; w_3, u_3; u_1, w_1)\\
P_{w_3} &= P(w_3, u_3; w_1, u_1; w_2, u_2)\\
P_{u_3} &= P(u_3, w_3; u_1, w_1; w_2, u_2) \qquad \text{(B2)}
\end{aligned}
$$

The expression for P was obtained in [5] and is the following

$$
\begin{aligned}
& P(w_1, u_1; w_2, u_2; w_3, u_3) \\
= \; & \frac{u_1\, w_1\, [(u_1 + w_2)^2 - u_3^2]}{(-u_1 + u_3 - w_2)\,(u_1 + u_3 + w_2)} \ln\left[\frac{u_2 + u_3 + w_1}{u_1 + u_2 + w_1 + w_2}\right] \\
& + \frac{u_1\, w_1\, [(u_1 + u_3)^2 - w_2^2]}{(-u_1 - u_3 + w_2)\,(u_1 + u_3 + w_2)} \ln\left[\frac{w_1 + w_2 + w_3}{u_1 + u_3 + w_1 + w_3}\right] \\
& - \frac{u_1^2\, w_1^2 + u_2^2\, w_2^2 - u_3^2\, w_3^2 + w_1\, w_2\, (u_1^2 + u_2^2 - w_3^2)}{(-w_1 - w_2 + w_3)\,(w_1 + w_2 + w_3)} \ln\left[\frac{u_1 + u_2 + w_3}{u_1 + u_2 + w_1 + w_2}\right] \\
& - \frac{u_1^2\, w_1^2 - u_2^2\, w_2^2 + u_3^2\, w_3^2 + w_1\, w_3\, (u_1^2 + u_3^2 - w_2^2)}{(-w_1 + w_2 - w_3)\,(w_1 + w_2 + w_3)} \ln\left[\frac{u_1 + u_3 + w_2}{u_1 + u_3 + w_1 + w_3}\right] \\
& + \frac{u_2\,(u_2 + w_1)\,(u_1^2 + u_3^2 - w_2^2) - u_3^2\,(u_1^2 + u_2^2 - w_3^2)}{(-u_2 + u_3 - w_1)\,(u_2 + u_3 + w_1)} \ln\left[\frac{u_1 + u_3 + w_2}{u_1 + u_2 + w_1 + w_2}\right] \\
& + \frac{u_3\,(u_3 + w_1)\,(u_1^2 + u_2^2 - w_3^2) - u_2^2\,(u_1^2 + u_3^2 - w_2^2)}{(u_2 - u_3 - w_1)\,(u_2 + u_3 + w_1)} \ln\left[\frac{u_1 + u_2 + w_3}{u_1 + u_3 + w_1 + w_3}\right] \\
& - \frac{w_1\,[w_2\,(u_1^2 - u_2^2 + w_3^2) + w_3\,(u_1^2 - u_3^2 + w_2^2)]}{(w_1 - w_2 - w_3)\,(w_1 + w_2 + w_3)} \ln\left[\frac{u_2 + u_3 + w_1}{u_2 + u_3 + w_2 + w_3}\right] \\
& - \frac{w_1\,[u_2\,(u_1^2 + u_3^2 - w_2^2) + u_3\,(u_1^2 + u_2^2 - w_3^2)]}{(-u_2 - u_3 + w_1)\,(u_2 + u_3 + w_1)} \ln\left[\frac{w_1 + w_2 + w_3}{u_2 + u_3 + w_2 + w_3}\right]
\end{aligned}
\tag{B3}
$$

In the case the nonlinear parameter α is the combination of w_i, u_i as in Eq. (8), P_α is given by

$$
\begin{aligned}
P_w &= P_{w_2} + P_{w_3} \\
P_x &= P_{w_2} - P_{w_3} \\
P_u &= P_{u_2} + P_{u_3} \\
P_y &= P_{u_3} - P_{u_2}
\end{aligned}
\tag{B4}
$$

In particular, $F_{u_1} = F(r)$ is given by Eq. (A8), and F_{w_1} is

$$\begin{aligned}
F_{w_1}(r) \;=\; & \Bigg\{ \Bigg[\frac{r\,(u+w+x+y)+1}{r^3} \left(2 - \frac{w_1}{2\,u+w_1} - \frac{w_1}{2\,w+w_1} - \frac{w_1}{w_1-2\,x} - \frac{w_1}{w_1-2\,y}\right) \\
& + \frac{2}{r} \left(\frac{(u+w)\,(u+x)\,(u+y)}{2\,u+w_1} + \frac{(u+w)\,(w+x)\,(w+y)}{2\,w+w_1} \right. \\
& \left. - \frac{(u+x)\,(w+x)\,(x+y)}{w_1-2\,x} - \frac{(u+y)\,(w+y)\,(x+y)}{w_1-2\,y} - \frac{(u+w+x+y)^2}{2} \right) \Bigg] \\
& \times e^{-r\,(u+w+x+y)} \\
& + \Bigg[\frac{r\,(u+w+w_1-x+y)+1}{r^3} \left(-2 + \frac{w_1}{2\,u+w_1} + \frac{w_1}{2\,w+w_1} + \frac{w_1}{w_1-2\,x} + \frac{w_1}{w_1+2\,y} \right) \\
& + \frac{w_1}{r^2} + \frac{1}{r} \left(w_1^2 + 4\,(x\,y + u\,x + w\,x - u\,y - w\,y - u\,w) + (w_1+u+w-x+y)^2 \right. \\
& - \frac{2\,(u-w)\,(u+x)\,(u-y)}{2\,u+w_1} + \frac{2\,(u-w)\,(w+x)\,(w-y)}{2\,w+w_1} \\
& \left. + \frac{2\,(u+x)\,(w+x)\,(x+y)}{w_1-2\,x} + \frac{2\,(u-y)\,(w-y)\,(-x-y)}{w_1+2\,y} \right) \Bigg] \, e^{-r\,(u+w+w_1-x+y)} \Bigg\} \\
& + \Big\{ x \to -x, y \to -y \Big\} \qquad \text{(B5)}
\end{aligned}$$

Note that F_{w_1} involves only the exponential and rational functions.