Efficient approach to two-centre exponential integrals with applications to excited states of molecular hydrogen

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Abstract

A general approach to evaluation of two-centre two-electron exponential integrals with arbitrary parameters is presented. The results for the Born-Oppenheimer potential for various excited states of molecular hydrogen with Kołos-Wolniewicz functions are obtained with precision exceeding previous values by about 3 orders of magnitude.

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I. INTRODUCTION

The hydrogen molecule was a test of quantum mechanics since its early beginnings. The calculations of the H_2 dissociation energy by Kołos and Wolniewicz [1, 2] were more accurate than experiments at that time [3] and led to the verification of experimental values [4, 5]. At present theoretical predictions for the dissociation energy [6] are in perfect agreement with the most recent experiments [7–9] and test the validity of quantum electrodynamic theory (QED) in molecular systems. Moreover, assuming that QED theory is correct, the comparison with experimental spectra puts strong bounds on the unknown long-range interaction between hadrons [10]. In this work we intend to extend the high-precision results obtained for the ground electronic state of H_2 to excited states, where accurate measurements have recently became feasible [11]. The principal problem is the accurate solution of the Schrödinger equation. It is surprising that the calculations by Wolniewicz *et al.* years ago [12, 13] have been surpassed only for the lowest lying states of H_2 [14–17] by calculations based on explicitly correlated Gaussian functions (ECG).

The aim of this work is to present a computational approach to the nonrelativistic energies of the H_2 molecule using an explicitly correlated basis of the form

$$\begin{aligned}\phi =& e^{-y\,(r_{1A}-r_{1B})-x\,(r_{2A}-r_{2B})-u\,(r_{1A}+r_{1B})-w\,(r_{2A}+r_{2B})} \\ & \times r_{12}^{n_0}\,(r_{1A}-r_{1B})^{n_1}\,(r_{2A}-r_{2B})^{n_2}\,(r_{1A}+r_{1B})^{n_3}\,(r_{2A}+r_{2B})^{n_4}\,, \end{aligned} \tag{1}$$

where u, w, x and y are real nonlinear parameters, the subscripts 1 and 2 numerate the electrons, and A and B numerate the nuclei. Thus, r_{12} is the interelectronic distance, whereas r_{1A} is the distance between the first electron and the nuclei A. This basis was introduced by Kołos and Wolniewicz [1] to obtain the first accurate results for ground and excited states of two-electron diatomic molecules. Integrals with these functions were performed by using the Neumann expansion of $1/r_{12}$ in spherical oblate coordinates, see the most recent review by Harris [18]. In the approach developed here, these integrals are calculated by the Taylor expansion in $r = r_{AB}$, the internuclear distance. Since this expansion is absolutely convergent for all positive values of r, and all terms of expansion are simple algebraic and logarithmic functions of nonlinear parameters, with the help of a multiprecision floating-point library [20] one can obtain all the integrals in Eq. (4) with arbitrary powers of the electron distances.

II. MASTER INTEGRAL

According to this approach, one considers in the first step the so-called master two-electron two-centre integral $f(r)$,

$$f(r) = r \int \frac{d^3 r_1}{4\,\pi} \int \frac{d^3 r_2}{4\,\pi} \frac{e^{-w_1\,r_{12} - u\,(r_{1A}+r_{1B}) - w\,(r_{2A}+r_{2B}) - y\,(r_{1A}-r_{1B}) - x\,(r_{2A}-r_{2B})}}{r_{12}\,r_{1A}\,r_{1B}\,r_{2A}\,r_{2B}}. \tag{2}$$

Any additional power of electronic distances in the above integral,

$$\begin{aligned} f(r, n_0, n_1, n_2, n_3, n_4) = {} & \frac{r}{n_0!\,n_1!\,n_2!\,n_3!\,n_4!} \int \frac{d^3 r_1}{4\,\pi} \int \frac{d^3 r_2}{4\,\pi}\, r_{12}^{n_0}\,(r_{1A} - r_{1B})^{n_1}\,(r_{2A} - r_{2B})^{n_2} \\ & \times (r_{1A} + r_{1B})^{n_3}\,(r_{2A} + r_{2B})^{n_4} \frac{e^{-w_1\,r_{12} - u\,(r_{1A}+r_{1B}) - w\,(r_{2A}+r_{2B}) - y\,(r_{1A}-r_{1B}) - x\,(r_{2A}-r_{2B})}}{r_{12}\,r_{1A}\,r_{1B}\,r_{2A}\,r_{2B}}\,, \end{aligned} \tag{3}$$

can be obtained from $f(r)$ by differentiation with respect to the corresponding nonlinear parameter,

$$\begin{aligned} & f(r, n_0, n_1, n_2, n_3, n_4) \\ & = \frac{1}{n_0!\,n_1!\,n_2!\,n_3!\,n_4!} \left(-\frac{\partial}{\partial w_1}\right)^{n_0} \Bigg|_{w_1=0} \left(-\frac{\partial}{\partial y}\right)^{n_1} \left(-\frac{\partial}{\partial x}\right)^{n_2} \left(-\frac{\partial}{\partial u}\right)^{n_3} \left(-\frac{\partial}{\partial w}\right)^{n_4} f(r)\,, \end{aligned} \tag{4}$$

where we include additional factorials in the denominator for simplicity of recursion relations in the next section. The master integral $f(r)$ is not known in a closed analytical form, but it can be expressed in terms of a one-dimensional integral representation, see Refs. [22, 23] for details. Moreover, it can be shown [23, 24] that $f(r)$ satisfies the following differential equation

$$\left[\sigma_4 \frac{d^2}{d\,r^2}\,r\,\frac{d^2}{d\,r^2} + \sigma_2 \frac{d}{d\,r}\,r\,\frac{d}{d\,r} + \sigma_0\,r\right] f(r) = F(r), \tag{5}$$

where

$$\begin{aligned} \sigma_0 &= w_1^2\,(u + w - x - y)\,(u - w + x - y)\,(u - w - x + y)\,(u + w + x + y) \\ &\quad + 16\,(w\,x - u\,y)\,(u\,x - w\,y)\,(u\,w - x\,y) \\ &= \sigma_{00} + w_1^2\,\sigma_{02}\,, \\ \sigma_2 &= w_1^4 - 2\,w_1^2\,(u^2 + w^2 + x^2 + y^2) + 16\,u\,w\,x\,y \\ &= \sigma_{20} + w_1^2\,\sigma_{22} + w_1^4\,, \\ \sigma_4 &= w_1^2\,, \end{aligned} \tag{6}$$

with the inhomogeneous term given by

$$
\begin{aligned}
F(r) \;=\; & w_1 \left(\frac{1}{r^2} + \frac{2\,w_1 + u + w + x - y}{r} \right) e^{-r\,(u+w+w_1+x-y)} \\
& + w_1 \left(\frac{1}{r^2} + \frac{2\,w_1 + u + w - x + y}{r} \right) e^{-r\,(u+w+w_1-x+y)} \\
& - w_1 \left(\frac{1}{r^2} + \frac{u + w - x - y}{r} \right) e^{-r\,(u+w-x-y)} \\
& - w_1 \left(\frac{1}{r^2} + \frac{u + w + x + y}{r} \right) e^{-r\,(u+w+x+y)} \\
& + \left[\frac{w_1^2}{2}\,(u - w + x - y) + 2\,u\,w\,(y - x) + 2\,x\,y\,(w - u) \right] F_1 \\
& + \left[\frac{w_1^2}{2}\,(u - w - x + y) + 2\,u\,w\,(x - y) + 2\,x\,y\,(w - u) \right] F_2 \\
& + \left[\frac{w_1^2}{2}\,(u + w + x + y) + 2\,u\,w\,(x + y) + 2\,x\,y\,(u + w) \right] F_3 \\
& + \left[\frac{w_1^2}{2}\,(u + w - x - y) - 2\,u\,w\,(x + y) + 2\,x\,y\,(u + w) \right] F_4 \,, \qquad (7)
\end{aligned}
$$

where

$$
\begin{aligned}
F_1 \;=\; & \mathrm{Ei}[-r\,(w_1 + 2\,u)]\,\exp[r\,(u - w + x - y)] - \mathrm{Ei}[-r\,(w_1 + 2\,w)]\,\exp[-r\,(u - w + x - y)] \,, \\
F_2 \;=\; & \mathrm{Ei}[-r\,(w_1 + 2\,u)]\,\exp[r\,(u - w - x + y)] - \mathrm{Ei}[-r\,(w_1 + 2\,w)]\,\exp[-r\,(u - w - x + y)] \,, \\
F_3 \;=\; & \mathrm{Ei}[-2\,r\,(u + w)]\,\exp[r\,(u + w + x + y)] + \Big\{ \mathrm{Ei}[2\,r\,(x + y)] - \mathrm{Ei}[-r\,(w_1 - 2\,x)] \\
& - \mathrm{Ei}[-r\,(w_1 - 2\,y)] - \ln\left[\frac{(w_1 + 2\,u)\,(w_1 + 2\,w)\,(x + y)}{(u + w)\,(w_1 - 2\,x)\,(w_1 - 2\,y)} \right] \Big\}\,\exp[-r\,(u + w + x + y)] \,, \\
F_4 \;=\; & \mathrm{Ei}[-2\,r\,(u + w)]\,\exp[r\,(u + w - x - y)] + \Big\{ \mathrm{Ei}[-2\,r\,(x + y)] - \mathrm{Ei}[-r\,(w_1 + 2\,x)] \\
& - \mathrm{Ei}[-r\,(w_1 + 2\,y)] - \ln\left[\frac{(w_1 + 2\,u)\,(w_1 + 2\,w)\,(x + y)}{(u + w)\,(w_1 + 2\,x)\,(w_1 + 2\,y)} \right] \Big\}\,\exp[-r\,(u + w - x - y)] \,,
\end{aligned}
\qquad (8)
$$

and Ei is the exponential integral function. The function $f(r)$ is the solution of this differential equation, which vanishes at the small r and has a Taylor expansion in w_1.

From the differential equation (5) and similar differential equations for derivatives of f over nonlinear parameters, one can obtain recurrence relations in n_i for the integrals $f(r, n_0, n_1, n_2, n_3, n_4)$ [22, 23]. These recurrences however, have various spurious singularities which make their practical use very cumbersome. For these reason in our former calculations

we have generated explicit expression for derivatives of the master integral for three special cases. The James-Coolidge (JC) basis, where $x = y = 0$ [25]; the generalized Heitler-London basis, where $x = w, y = -u$ [25]; and the HeH^+ basis, where $x = w, y = u$ [26], and in all these cases $w_1 = 0$ is assumed. The results obtained for the ground electronic states of H_2 and HeH^+ were accurate to $10^{-12} - 10^{-15}$ au. These special cases do not work well for excited states in the intermediate region of r, where the general basis with arbitrary nonlinear parameters is needed. In a more recent work [27], we have developed a computational method for exponentially correlated basis functions, namely that with $w_1 \neq 0$. This basis is very flexible and can be used for the calculations of relativistic and QED effects. However, the high computational cost and spurious singularities make this basis rather difficult in application.

III. TAYLOR EXPANSION APPROACH

Here we overcame the above problems, and were able to present an efficient way to calculate two-centre two-electron integrals with Kołos-Wolniewicz functions (1) by using the Taylor expansion in r. This Taylor expansion has already been proposed in Ref. [23], and here we prove that it works in practice by the calculation of Born-Oppenheimer energies for excited states of H_2. First of all, this expansion is absolutely convergent for an arbitrary r [19]. In the typical situation near the equilibrium distance $r = 1.4$ au one needs about 60 terms to obtain the integral with quadruple precision. For larger distances ($r \sim 12$ au) the number of terms grows to about 200. Coefficients of the expansion are obtained using arbitrary precision arithmetic [20]. The evaluation time of all integrals on a single Intel Xenon core for the largest basis of 3003 functions, using 64 digits arithmetic, was about 30 minuts, in comparison to about 60 minutes of quadruple precision linear algebra (DSPGVX, LAPACK routine [21]). In fact the main issue in these calculations is not the evaluation time of integrals, but the numerical instabilities in decomposition of the overlap matrix.

The complete set of recursions for the Taylor expansion of $f(r)$ and its derivatives with respect to parameters can be obtained from the above differential equation. It is, however, more convenient to use the following formulas for derivatives which were obtained in Ref.

[27]

$$
\begin{aligned}
(w_1^2 - 4\,w^2)\,\frac{\partial f'(r)}{\partial w} &= -\frac{r\,f(r)}{2}\,\frac{\partial \sigma_{02}}{\partial w} - 2\,r\,w\,f''(r) + \frac{-F_1 - F_2 + F_3 + F_4}{2}\,,\\
(w_1^2 - 4\,u^2)\,\frac{\partial f'(r)}{\partial u} &= -\frac{r\,f(r)}{2}\,\frac{\partial \sigma_{02}}{\partial u} - 2\,r\,u\,f''(r) + \frac{F_1 + F_2 + F_3 + F_4}{2}\,,\\
(w_1^2 - 4\,x^2)\,\frac{\partial f'(r)}{\partial x} &= -\frac{r\,f(r)}{2}\,\frac{\partial \sigma_{02}}{\partial x} - 2\,r\,x\,f''(r) + \frac{F_1 - F_2 + F_3 - F_4}{2}\,,\\
(w_1^2 - 4\,y^2)\,\frac{\partial f'(r)}{\partial y} &= -\frac{r\,f(r)}{2}\,\frac{\partial \sigma_{02}}{\partial y} - 2\,r\,y\,f''(r) + \frac{-F_1 + F_2 + F_3 - F_4}{2}\,,
\end{aligned}
\tag{9}
$$

where σ_{02} is defined in Eq. (6), the inhomogeneous F_i terms are given by Eq. (8) and $f'(r)$ means derivative with respect to r. The derivative with respect to w_1 can be easily obtained from the fact that function $r^{-2}\,f(r)$ is dimensionless, which entails that

$$
w_1\,\frac{\partial f(r)}{\partial w_1} = -w\,\frac{\partial f(r)}{\partial w} - u\,\frac{\partial f(r)}{\partial u} - x\,\frac{\partial f(r)}{\partial x} - y\,\frac{\partial f(r)}{\partial y} + r\,f'(r) - 2\,f(r)\,. \tag{10}
$$

The recurrence relations for the Taylor expansion of $f(r, n_0, n_1, n_2, n_3, n_4)$ are obtained as follows. The master integral $f(r)$ has the following expansion in r:

$$
f(r) = \sum_{n=1}^{\infty} \left[f_n^{(1)}\,(\ln(r) + \gamma_{\rm E}) + f_n^{(2)}\right] r^n\,, \tag{11}
$$

(where $\gamma_{\rm E}$ is the Euler constant), and so have all its derivatives $f(r, n_0, n_1, n_2, n_3, n_4)$. To get recursions in n_0 we divide each equation in (9) by the corresponding parameter, sum up and use Eq. (10). The resulting equation expanded in r is

$$
\begin{aligned}
f_n^{(1)}(n_0,0,0,0,0) &= \frac{1}{4\,n\,(n+n_0)}\left(F_{n-1}^{(1)}(n_0) - 4\,\frac{\sigma_{00}}{\sigma_{20}}\,f_{n-2}^{(1)}(n_0,0,0,0,0)\right.\\
&\quad + \frac{n}{u}\,f_n^{(1)}(n_0-2,0,0,1,0) + \frac{n}{w}\,f_n^{(1)}(n_0-2,0,0,0,1)\\
&\quad \left. + \frac{n}{x}\,f_n^{(1)}(n_0-2,0,1,0,0) + \frac{n}{y}\,f_n^{(1)}(n_0-2,1,0,0,0)\right)\,,
\end{aligned}
\tag{12}
$$

$$
\begin{aligned}
f_n^{(2)}(n_0,0,0,0,0) &= \frac{1}{4\,n\,(n+n_0)}\left(F_{n-1}^{(2)}(n_0) - \frac{4\,\sigma_{00}}{\sigma_{20}}\,f_{n-2}^{(2)}(n_0,0,0,0,0)\right.\\
&\quad - 4\,(2\,n+n_0)\,f_n^{(1)}(n_0,0,0,0,0)\\
&\quad + \frac{1}{u}\big(f_n^{(1)}(n_0-2,0,0,1,0) + n\,f_n^{(2)}(n_0-2,0,0,1,0)\big)\\
&\quad + \frac{1}{w}\big(f_n^{(1)}(n_0-2,0,0,0,1) + n\,f_n^{(2)}(n_0-2,0,0,0,1)\big)\\
&\quad + \frac{1}{x}\big(f_n^{(1)}(n_0-2,0,1,0,0) + n\,f_n^{(2)}(n_0-2,0,1,0,0)\big)\\
&\quad \left. + \frac{1}{y}\big(f_n^{(1)}(n_0-2,1,0,0,0) + n\,f_n^{(2)}(n_0-2,1,0,0,0)\big)\right)\,,
\end{aligned}
\tag{13}
$$

where

$$F_n^{(i)}(n_0) \;=\; \frac{1}{2}\left[\left(\frac{1}{u}-\frac{1}{w}+\frac{1}{x}-\frac{1}{y}\right)F_{1,n}^{(i)}(n_0,0,0,0,0)+\left(\frac{1}{u}-\frac{1}{w}-\frac{1}{x}+\frac{1}{y}\right)F_{2,n}^{(i)}(n_0,0,0,0,0)\right.$$
$$\left.+\left(\frac{1}{u}+\frac{1}{w}+\frac{1}{x}+\frac{1}{y}\right)F_{3,n}^{(i)}(n_0,0,0,0,0)+\left(\frac{1}{u}+\frac{1}{w}-\frac{1}{x}-\frac{1}{y}\right)F_{4,n}^{(i)}(n_0,0,0,0,0)\right]. \tag{14}$$

Recursions in n_1, n_2, n_3 and n_4 are obtained by differentiation of the corresponding equation. For example, in n_4 they are the following

$$f_n^{(1)}(n_0,n_1,n_2,n_3,n_4+1) = -\frac{1}{4\,n\,(n_4+1)\,w^2}\left[\right.$$
$$2\,f_{n-2}^{(1)}(n_0,n_1-2,n_2,n_3,n_4-1) - 2\,w\,f_{n-2}^{(1)}(n_0,n_1-2,n_2,n_3,n_4)$$
$$-4\,f_{n-2}^{(1)}(n_0,n_1-1,n_2-1,n_3-1,n_4) + 4\,u\,f_{n-2}^{(1)}(n_0,n_1-1,n_2-1,n_3,n_4)$$
$$+4\,x\,f_{n-2}^{(1)}(n_0,n_1-1,n_2,n_3-1,n_4) - 4\,y\,f_{n-2}^{(1)}(n_0,n_1-1,n_2,n_3,n_4-1)$$
$$-4\,(u\,x-w\,y)\,f_{n-2}^{(1)}(n_0,n_1-1,n_2,n_3,n_4) + 2\,f_{n-2}^{(1)}(n_0,n_1,n_2-2,n_3,n_4-1)$$
$$-2\,w\,f_{n-2}^{(1)}(n_0,n_1,n_2-2,n_3,n_4) + 4\,y\,f_{n-2}^{(1)}(n_0,n_1,n_2-1,n_3-1,n_4)$$
$$-4\,x\,f_{n-2}^{(1)}(n_0,n_1,n_2-1,n_3,n_4-1) - 4\,(u\,y-x\,w)\,f_{n-2}^{(1)}(n_0,n_1,n_2-1,n_3,n_4)$$
$$+2\,f_{n-2}^{(1)}(n_0,n_1,n_2,n_3-2,n_4-1) - 2\,w\,f_{n-2}^{(1)}(n_0,n_1,n_2,n_3-2,n_4)$$
$$-4\,u\,f_{n-2}^{(1)}(n_0,n_1,n_2,n_3-1,n_4-1) + 4\,(u\,w-x\,y)\,f_{n-2}^{(1)}(n_0,n_1,n_2,n_3-1,n_4)$$
$$-2\,f_{n-2}^{(1)}(n_0,n_1,n_2,n_3,n_4-3) + 6\,w\,f_{n-2}^{(1)}(n_0,n_1,n_2,n_3,n_4-2)$$
$$+2\,(u^2-3\,w^2+x^2+y^2)\,f_{n-2}^{(1)}(n_0,n_1,n_2,n_3,n_4-1)$$
$$+2\,(w^3-u^2\,w-w\,x^2+2\,u\,x\,y-w\,y^2)\,f_{n-2}^{(1)}(n_0,n_1,n_2,n_3,n_4)$$
$$-n\,(n_4+1)\,f_n^{(1)}(n_0-2,n_1,n_2,n_3,n_4+1) - 2\,n\,(n-2\,n_4+1)\,f_n^{(1)}(n_0,n_1,n_2,n_3,n_4-1)$$
$$+2\,n\,(n-4\,n_4-1)\,w\,f_n^{(1)}(n_0,n_1,n_2,n_3,n_4) - \frac{1}{2}\big[-F_{1,n-1}^{(1)}(n_0,n_1,n_2,n_3,n_4)$$
$$\left.-F_{2,n-1}^{(1)}(n_0,n_1,n_2,n_3,n_4)+F_{3,n-1}^{(1)}(n_0,n_1,n_2,n_3,n_4)+F_{4,n-1}^{(1)}(n_0,n_1,n_2,n_3,n_4)\big]\right], \tag{15}$$

$$
\begin{aligned}
f_n^{(2)}(n_0,n_1,n_2,n_3,n_4+1) = &-\frac{1}{4\,n\,(n_4+1)\,w^2}\Bigg[\\
&-(n_4+1)\,f_n^{(1)}(n_0-2,n_1,n_2,n_3,n_4+1) - 2\,(2\,n-2\,n_4+1)\,f_n^{(1)}(n_0,n_1,n_2,n_3,n_4-1) \\
&+2\,(2\,n-4\,n_4-1)\,w\,f_n^{(1)}(n_0,n_1,n_2,n_3,n_4) + 4\,(n_4+1)\,w^2\,f_n^{(1)}(n_0,n_1,n_2,n_3,n_4+1) \\
&+2\,f_{n-2}^{(2)}(n_0,n_1-2,n_2,n_3,n_4-1) - 2\,w\,f_{n-2}^{(2)}(n_0,n_1-2,n_2,n_3,n_4) \\
&-4\,f_{n-2}^{(2)}(n_0,n_1-1,n_2-1,n_3-1,n_4) + 4\,u\,f_{n-2}^{(2)}(n_0,n_1-1,n_2-1,n_3,n_4) \\
&+4\,x\,f_{n-2}^{(2)}(n_0,n_1-1,n_2,n_3-1,n_4) - 4\,y\,f_{n-2}^{(2)}(n_0,n_1-1,n_2,n_3,n_4-1) \\
&-4\,(u\,x-w\,y)\,f_{n-2}^{(2)}(n_0,n_1-1,n_2,n_3,n_4) + 2\,f_{n-2}^{(2)}(n_0,n_1,n_2-2,n_3,n_4-1) \\
&-2\,w\,f_{n-2}^{(2)}(n_0,n_1,n_2-2,n_3,n_4) + 4\,y\,f_{n-2}^{(2)}(n_0,n_1,n_2-1,n_3-1,n_4) \\
&-4\,x\,f_{n-2}^{(2)}(n_0,n_1,n_2-1,n_3,n_4-1) - 4\,(u\,y-x\,w)\,f_{n-2}^{(2)}(n_0,n_1,n_2-1,n_3,n_4) \\
&+2\,f_{n-2}^{(2)}(n_0,n_1,n_2,n_3-2,n_4-1) - 2\,w\,f_{n-2}^{(2)}(n_0,n_1,n_2,n_3-2,n_4) \\
&-4\,u\,f_{n-2}^{(2)}(n_0,n_1,n_2,n_3-1,n_4-1) + 4\,(u\,w-x\,y)\,f_{n-2}^{(2)}(n_0,n_1,n_2,n_3-1,n_4) \\
&-2\,f_{n-2}^{(2)}(n_0,n_1,n_2,n_3,n_4-3) + 6\,w\,f_{n-2}^{(2)}(n_0,n_1,n_2,n_3,n_4-2) \\
&+2\,(u^2-3\,w^2+x^2+y^2)\,f_{n-2}^{(2)}(n_0,n_1,n_2,n_3,n_4-1) \\
&+2\,(w^3-u^2\,w-w\,x^2+2\,u\,x\,y-w\,y^2)\,f_{n-2}^{(2)}(n_0,n_1,n_2,n_3,n_4) \\
&-n\,(n_4+1)\,f_n^{(2)}(n_0-2,n_1,n_2,n_3,n_4+1) - 2\,n\,(n-2\,n_4+1)\,f_n^{(2)}(n_0,n_1,n_2,n_3,n_4-1) \\
&+2\,n\,(n-4\,n_4-1)\,w\,f_n^{(2)}(n_0,n_1,n_2,n_3,n_4) - \frac{1}{2}\big[-F_{1,n-1}^{(2)}(n_0,n_1,n_2,n_3,n_4) \\
&-F_{2,n-1}^{(2)}(n_0,n_1,n_2,n_3,n_4) + F_{3,n-1}^{(2)}(n_0,n_1,n_2,n_3,n_4) + F_{4,n-1}^{(2)}(n_0,n_1,n_2,n_3,n_4)\big]\Bigg]\,, \qquad (16)
\end{aligned}
$$

where the inhomogeneous terms $F_{k,n}^{(i)}(n_0,n_1,n_2,n_3,n_4)$ are constructed in Appendix A. Together with recursion relations in n_1, n_2, and n_3 they allow for the calculation of all integrals with the condition that x and y are not close to 0. In practice we assume that both x and y are greater than 0.01. The case where $x = 0$ or $y = 0$ is considered in the next Section.

IV. SPECIAL CASES

The obtained recursions work in general cases, with some exceptions. When one of the parameters is close to zero, then these recursions become unstable. We have not been able to find recursions which are safe at small x and y and its evaluation is linear in the length of the Taylor series. Instead, one can perform a Taylor expansion in a small parameter,

for example in x. Coefficients can be obtained from the master differential equation (5) by differentiating over w_1 and x at $w_1 = x = 0$. It becomes then an algebraic equation for $f(n_0, 0, n_2, 0, 0)$. For example the result for the master integral is

$$f(r) = \frac{\sinh(r\,y)}{r\,y}\,\frac{1}{4\,u\,w}\left\{-\mathrm{Ei}(-2\,r\,u)\,\exp(r\,(u-w)) - \mathrm{Ei}(-2\,r\,w)\,\exp(r\,(w-u))\right.$$
$$\left.+\mathrm{Ei}(-2\,r\,(u+w))\,\exp(r\,(u+w)) + \left[\ln\left(\frac{2\,r\,u\,w}{u+w}\right) + \gamma_{\mathrm{E}}\right]\,\exp(-r\,(u+w))\right\}. \quad (17)$$

This expression can also be derived from the Neumann expansion of $1/r_{12}$ in spherical oblate coordinates, see also Appendix B, in which the master integral f is presented in terms of the Neumann expansion. In the calculation performed here, we do not derive explicit expressions for integrals with $w_1 = x = 0$, but adopt the numerical recursion for the Taylor series for the case of $x = 0$. This is done by differentiating the third equation in (9) with respect to all parameters at $w_1 = x = 0$. It then becomes an equation for $f_n^{(i)}(n_0, n_1, n_2, n_3, n_4)$, which gives recursions at $x = 0$, namely

$$f_n^{(1)}(n_0, n_1, n_2, n_3, n_4) = \frac{1}{4\,u\,w\,y}\left[-2\,f_n^{(1)}(n_0, n_1-2, n_2-1, n_3, n_4)\right.$$
$$+ 4\,y\,f_n^{(1)}(n_0, n_1-1, n_2-1, n_3, n_4) + 4\,f_n^{(1)}(n_0, n_1-1, n_2, n_3-1, n_4-1)$$
$$- 4\,w\,f_n^{(1)}(n_0, n_1-1, n_2, n_3-1, n_4) - 4\,u\,f_n^{(1)}(n_0, n_1-1, n_2, n_3, n_4-1)$$
$$+ 4\,u\,w\,f_n^{(1)}(n_0, n_1-1, n_2, n_3, n_4) + 2\,f_n^{(1)}(n_0, n_1, n_2-3, n_3, n_4)$$
$$- 2\,f_n^{(1)}(n_0, n_1, n_2-1, n_3-2, n_4) + 4\,u\,f_n^{(1)}(n_0, n_1, n_2-1, n_3-1, n_4)$$
$$- 2\,f_n^{(1)}(n_0, n_1, n_2-1, n_3, n_4-2) + 4\,w\,f_n^{(1)}(n_0, n_1, n_2-1, n_3, n_4-1)$$
$$- 2\,(u^2+w^2+y^2)\,f_n^{(1)}(n_0, n_1, n_2-1, n_3, n_4) - 4\,y\,f_n^{(1)}(n_0, n_1, n_2, n_3-1, n_4-1)$$
$$+ 4\,w\,y\,f_n^{(1)}(n_0, n_1, n_2, n_3-1, n_4) + 4\,u\,y\,f_n^{(1)}(n_0, n_1, n_2, n_3, n_4-1)$$
$$+ (n+2)\,(n_2+1)\,f_{n+2}^{(1)}(n_0-2, n_1, n_2+1, n_3, n_4)$$
$$+ 2\,(n+2)\,(n-2\,n_2+3)\,f_{n+2}^{(1)}(n_0, n_1, n_2-1, n_3, n_4) + \frac{1}{2}\big[F_{1,n+1}^{(1)}(n_0, n_1, n_2, n_3, n_4)$$
$$\left.- F_{2,n+1}^{(1)}(n_0, n_1, n_2, n_3, n_4) + F_{3,n+1}^{(1)}(n_0, n_1, n_2, n_3, n_4) - F_{4,n+1}^{(1)}(n_0, n_1, n_2, n_3, n_4)\big]\right], \quad (18)$$

$$
\begin{aligned}
f_n^{(2)}(n_0,n_1,n_2,n_3,n_4) = \frac{1}{4\,u\,w\,y}\Big[&(n_2+1)\,f_{n+2}^{(1)}(n_0-2,n_1,n_2+1,n_3,n_4)\\
&+2\,(2\,(n+2)-2\,n_2+1)\,f_{n+2}^{(1)}(n_0,n_1,n_2-1,n_3,n_4)-2\,f_n^{(2)}(n_0,n_1-2,n_2-1,n_3,n_4)\\
&+4\,y\,f_n^{(2)}(n_0,n_1-1,n_2-1,n_3,n_4)+4\,f_n^{(2)}(n_0,n_1-1,n_2,n_3-1,n_4-1)\\
&-4\,w\,f_n^{(2)}(n_0,n_1-1,n_2,n_3-1,n_4)-4\,u\,f_n^{(2)}(n_0,n_1-1,n_2,n_3,n_4-1)\\
&+4\,u\,w\,f_n^{(2)}(n_0,n_1-1,n_2,n_3,n_4)+2\,f_n^{(2)}(n_0,n_1,n_2-3,n_3,n_4)\\
&-2\,f_n^{(2)}(n_0,n_1,n_2-1,n_3-2,n_4)+4\,u\,f_n^{(2)}(n_0,n_1,n_2-1,n_3-1,n_4)\\
&-2\,f_n^{(2)}(n_0,n_1,n_2-1,n_3,n_4-2)+4\,w\,f_n^{(2)}(n_0,n_1,n_2-1,n_3,n_4-1)\\
&-2\,(u^2+w^2+y^2)\,f_n^{(2)}(n_0,n_1,n_2-1,n_3,n_4)-4\,y\,f_n^{(2)}(n_0,n_1,n_2,n_3-1,n_4-1)\\
&+4\,w\,y\,f_n^{(2)}(n_0,n_1,n_2,n_3-1,n_4)+4\,u\,y\,f_n^{(2)}(n_0,n_1,n_2,n_3,n_4-1)\\
&+(n+2)\,(n_2+1)\,f_{n+2}^{(2)}(n_0-2,n_1,n_2+1,n_3,n_4)\\
&+2\,(n+2)\,(n-2\,n_2+3)\,f_{n+2}^{(2)}(n_0,n_1,n_2-1,n_3,n_4)+\frac{1}{2}\big[F_{1,n+1}^{(2)}(n_0,n_1,n_2,n_3,n_4)\\
&-F_{2,n+1}^{(2)}(n_0,n_1,n_2,n_3,n_4)+F_{3,n+1}^{(2)}(n_0,n_1,n_2,n_3,n_4)-F_{4,n+1}^{(2)}(n_0,n_1,n_2,n_3,n_4)\big]\Big]\,. \qquad (19)
\end{aligned}
$$

The assumption of a symmetry with respect to $A \leftrightarrow B$ introduces integrals with $x = y = 0$, and these have already been derived using recursion relations obtained in Ref. [25]. Moreover, functions with $x = y = 0$, the so-called JC basis, work very well for short internuclear distances ($r < 6$ a.u.), as is demonstrated in the next Section. They can also be obtained via the Taylor series, but most probably the best way to calculate integrals with small x or y is by the Neumann expansion, which becomes finite at $x = 0$ or $y = 0$.

For very large internuclear distances, x and y are significantly different from 0 and the Taylor expansion requires many terms. We tried to use a generalized Heitler-London basis, where $x = \pm w$ and $y = \pm u$. The analytic expression for this special type of integral was obtained using recursion relations derived in Ref. [22]. The expression for $f(n_0, n_1, n_2, n_3, n_4)$ involves exponential integral function Ei, the exponential and the master integral $f(r)$. In spite of using explicit expressions, this way of calculation is not much more effective than the Taylor series. This is because the analytic expressions are very long for large n_0 and their evaluation requires the higher precision arithmetic. One cannot exclude that there is a clever way to express long polynomials in terms of some known functions, as is the case for odd n_0 [23], but so far we have not been able to do so. In the appendix B we present a compact Neumann representation for the master integral, which can be helpful in developing

an approach without the use of the Taylor expansion.

V. NUMERICAL RESULTS

The wave function of electronic Σ state of the H_2 molecule is expressed in terms of the basis wave functions ϕ_i in Eq. (1) as follows

$$\psi_\Sigma = \sum_i c_i \left(1 \pm P_{AB}\right) \left(1 \pm P_{12}\right) \phi_i \,, \tag{20}$$

where P_{AB} permutes the nuclei A and B, P_{12} interchanges the two electrons, and c_i are linear coefficients, obtained as components of the eigenvector of the Hamiltonian matrix. The powers n_i of electronic distances in ϕ are chosen by the condition

$$\sum_{i=0}^{4} n_i \leq \Omega \,, \tag{21}$$

with the parameter Ω changing from 5 to 10. The largest value $\Omega = 10$ corresponds to the 3003 length of the general basis and to 1910 in the JC basis. The JC basis is more compact, because the symmetry P_{AB} of Σ_g^+ state restricts certain combinations of n_i, which is not the case of the basis with x or $y \neq 0$.

Table I presents numerical results for the nonrelativistic energy of the first 5 excited electronic $^1\Sigma_g^+$ states of the H_2 molecule obtained for $r = 1.5, 3.0$ au with the JC, and for $r = 6, 12$ au with the general basis. The nonlinear parameters have been optimized against the binding energies for $\Omega = 7$. In the case of the JC basis, we used a double basis sets with two independent set of parameters, and $\Omega_2 = \Omega_1 - 2$. Since the minimization leads to $u \approx w$ in the second set, we impose the additional condition for n_i to eliminate linear dependence of the basis for $u = w$. In the calculations involving general basis, we used only one set of parameters.

In spite of the use of a very simple basis with just 4 independent nonlinear parameters, our results are two- or three-orders of magnitude more accurate than the most accurate results obtained so far, namely those in the Kołos-Wolniewicz basis [12, 13] and explicitly correlated Gaussian (ECG) functions [16]. This improved accuracy is especially visible for higher excited states, see Table I.

TABLE I: Nonrelativistic Born-Oppenheimer energy $E(r)$ of excited electronic $^1\Sigma_g^+$ states of the H_2 molecule at four internuclear distances r, in a.u., calculated with $\Omega = 9, 10$. The results are compared with the previous best available data obtained with KW [12, 13] and ECG [16] wave functions.

State	Ω	$E(1.5)$	$E(3.0)$	$E(6.0)$	$E(12.0)$
$EF\,^1\Sigma_g^+$	9	−0.703 000 246 8	−0.690 747 055 9	−0.694 267 016	−0.628 742 038
	10	−0.703 000 247 0	−0.690 747 056 3	−0.694 267 029	−0.628 742 088
	ECG	−0.703 000 229	−0.690 747 014	−0.694 267 005	−0.628 742 051
	KW	−0.702 999 909	−0.690 746 981	−0.694 263 365	−0.628 730 759
$GK\,^1\Sigma_g^+$	9	−0.639 008 658 8	−0.656 985 931	−0.626 147 966	−0.624 745 652
	10	−0.639 008 659 5	−0.656 985 945	−0.626 147 969	−0.624 745 653
	KW	−0.639 007 737	−0.656 983 847	−0.626 147 852	
$H\bar{H}\,^1\Sigma_g^+$	9	−0.636 334 418 0	−0.630 554 122	−0.583 463 524	−0.604 584 075
	10	−0.636 334 418 5	−0.630 554 134	−0.583 463 574	−0.604 584 280
	KW	−0.636 333 766	−0.630 550 821	−0.583 461 341	−0.604 529 322
$P\,^1\Sigma_g^+$	9	−0.614 073 200	−0.623 922 685	−0.564 424 571	−0.555 682 254
	10	−0.614 073 206	−0.623 922 735	−0.564 424 574	−0.555 682 256
	KW	−0.614 049 795	−0.623 917 301	−0.564 423 608	
$O\,^1\Sigma_g^+$	9	−0.612 886 933	−0.607 984 433	−0.553 905 260	−0.555 533 720
	10	−0.612 886 935	−0.607 984 513	−0.553 905 272	−0.555 533 721
	KW	−0.612 885 514	−0.607 841 139	−0.553 862 823	

VI. SUMMARY

In this paper we have developed a numerical procedure for two-centre two-electron integrals with exponential functions. It is based on the Taylor expansion in the internuclear distance, differential equations for derivatives of the master integral with respect to nonlinear parameters (9), and recursion relations. The whole code is very compact but requires a high precision arithmetic, typically 64 digits. This numerical approach has been applied to the calculation of excited $^1\Sigma_g^+$ states of the H_2 molecule. The obtained results, in a relatively

small and simple basis, are more accurate than any best previous results, see Table I.

As well as being simple, this numerical approach can be extended, we think, to integrals with additional inverse powers of electronic distances which are needed for the calculations of relativistic and QED corrections, including the yet unknown $\alpha^4\,\mathrm{Ry}$ contribution which limits the present accuracy of theoretical predictions for H_2.

Appendix A: Taylor expansion of the inhomogeneous terms

The general recursion relations for the Taylor expansion of two-centre two-electron integrals involve inhomogeneous terms. They are split into the logarithmic and nonlogarithmic parts similarly to Eq. (11). The logarithmic part with $\sigma^{(1)} = \delta_{n_0}\,[1-(-1)^n]/(n_1!\,n_2!\,n_3!\,n_4!)$ is

$$F^{(1)}_{1,n}(n_0,n_1,n_2,n_3,n_4) \;=\; \sigma^{(1)}\,(-1)^{n_2+n_3}\,\frac{(u-w+x-y)^{n-n_1-n_2-n_3-n_4}}{(n-n_1-n_2-n_3-n_4)!}\,, \tag{A1}$$

$$F^{(1)}_{2,n}(n_0,n_1,n_2,n_3,n_4) \;=\; \sigma^{(1)}\,(-1)^{n_1+n_3}\,\frac{(u-w-x+y)^{n-n_1-n_2-n_3-n_4}}{(n-n_1-n_2-n_3-n_4)!}\,, \tag{A2}$$

$$F^{(1)}_{3,n}(n_0,n_1,n_2,n_3,n_4) \;=\; \sigma^{(1)}\,(-1)^{n_1+n_2+n_3+n_4}\,\frac{(u+w+x+y)^{n-n_1-n_2-n_3-n_4}}{(n-n_1-n_2-n_3-n_4)!}\,, \tag{A3}$$

$$F^{(1)}_{4,n}(n_0,n_1,n_2,n_3,n_4) \;=\; \sigma^{(1)}\,(-1)^{n_3+n_4}\,\frac{(u+w-x-y)^{n-n_1-n_2-n_3-n_4}}{(n-n_1-n_2-n_3-n_4)!}\,, \tag{A4}$$

and the nonlogarithmic part with $\sigma^{(2)} = 1/(n_0!\,n_1!\,n_2!\,n_3!\,n_4!)$ is

$$\begin{aligned} F^{(2)}_{1,n}(n_0,n_1,n_2,n_3,n_4) \;=\; \sigma^{(2)}\,\big[&(-1)^{n_2}\,F_E(-u,-w+x-y,n_0,n_3,n-n_1-n_2-n_4)\\ &-(-1)^{n_1}\,F_E(-w,-u-x+y,n_0,n_4,n-n_1-n_2-n_3)\\ &+(-1)^{n_2}\,F_L(-u,-w+x-y,n_0,n_3,n-n_1-n_2-n_4)\\ &-(-1)^{n_1}\,F_L(-w,-u-x+y,n_0,n_4,n-n_1-n_2-n_3)\big]\,, \end{aligned} \tag{A5}$$

$$\begin{aligned} F^{(2)}_{2,n}(n_0,n_1,n_2,n_3,n_4) \;=\; \sigma^{(2)}\,\big[&(-1)^{n_1}\,F_E(-u,-w-x+y,n_0,n_3,n-n_1-n_2-n_4)\\ &-(-1)^{n_2}\,F_E(-w,-u+x-y,n_0,n_4,n-n_1-n_2-n_3)\\ &+(-1)^{n_1}\,F_L(-u,-w-x+y,n_0,n_3,n-n_1-n_2-n_4)\\ &-(-1)^{n_2}\,F_L(-w,-u+x-y,n_0,n_4,n-n_1-n_2-n_3)\big]\,, \end{aligned} \tag{A6}$$

$$
\begin{aligned}
F^{(2)}_{3,n}(n_0,n_1,n_2,n_3,n_4) \;=\; & \sigma^{(2)}\,\big[(-1)^{n_1+n_2}\,F_E(-u-w,x+y,0,n_3+n_4,n-n_1-n_2)\,\delta_{n_0} \\
& +(-1)^{n_1+n_2}\,F_E(x+y,-u-w,0,n_1+n_2,n-n_3-n_4)\,\delta_{n_0} \\
& +(-1)^{n_1+n_2}\,[1+(-1)^n]\,F_L(-u-w,x+y,0,n_3+n_4,n-n_1-n_2)\,\delta_{n_0} \\
& -(-1)^{n_2}\,F_E(x,-u-w-y,n_0,n_2,n-n_1-n_3-n_4) \\
& -(-1)^{n_1}\,F_E(y,-u-w-x,n_0,n_1,n-n_2-n_3-n_4) \\
& -(-1)^{n+n_1+n_2+n_4}\,F_L(-u,w+x+y,n_0,n_3,n-n_1-n_2-n_4) \\
& -(-1)^{n+n_1+n_2+n_3}\,F_L(-w,u+x+y,n_0,n_4,n-n_1-n_2-n_3)\big]\,, \qquad \text{(A7)}
\end{aligned}
$$

$$
\begin{aligned}
F^{(2)}_{4,n}(n_0,n_1,n_2,n_3,n_4) \;=\; & \sigma^{(2)}\,\big[F_E(-u-w,-x-y,0,n_3+n_4,n-n_1-n_2)\,\delta_{n_0} \\
& +F_E(-x-y,-u-w,0,n_1+n_2,n-n_3-n_4)\,\delta_{n_0} \\
& +[1+(-1)^n]\,F_L(-u-w,-x-y,0,n_3+n_4,n-n_1-n_2)\,\delta_{n_0} \\
& -(-1)^{n_1}\,F_E(-x,-u-w+y,n_0,n_2,n-n_1-n_3-n_4) \\
& -(-1)^{n_2}\,F_E(-y,-u-w+x,n_0,n_1,n-n_2-n_3-n_4) \\
& -(-1)^{n+n_4}\,F_L(-u,w-x-y,n_0,n_3,n-n_1-n_2-n_4) \\
& -(-1)^{n+n_3}\,F_L(-w,u-x-y,n_0,n_4,n-n_1-n_2-n_3)\big]\,, \qquad \text{(A8)}
\end{aligned}
$$

where

$$
F_L(b,a;k,m,n) \;=\; \left.\frac{\partial^k}{\partial c^k}\right|_{c=0} \frac{\partial^m}{\partial b^m}\,\frac{(a-b)^n}{n!}\,\ln(-2b-c)\,, \qquad \text{(A9)}
$$

$$
F_E(b,a;k,m,n) \;=\; \left.\frac{\partial^k}{\partial c^k}\right|_{c=0} \frac{\partial^m}{\partial b^m}\,\frac{1}{n!}\,\left.\frac{\partial^n}{\partial r^n}\right|_{r=1} e^{r\,(a-b)}\,\Big(\mathrm{Ei}\big[r(2\,b+c)\big]-\ln\big[r\,(-2b-c)\big]-\gamma_{\mathrm{E}}\Big)\,. \qquad \text{(A10)}
$$

Appendix B: Neumann expansion of the master integral

The Neumann expansion of r_{12}^{-1} or $e^{-w_1\,r_{12}}\,r_{12}^{-1}$ in spherical oblate coordinates has been previously used in the calculation of two-centre two-electron integrals, see [18] and references therein. Here we present a compact formula for $f(r)$ at $w_1=0$

$$
f(r) \;=\; \sum_{n=0}^{\infty}\,\frac{(1+2\,n)}{4}\,r^2\,j_n(r\,x)\,j_n(r\,y)\,\Pi_n(r\,u,r\,w)\,, \qquad \text{(B1)}
$$

where j_n, h_n are modified spherical Bessel functions,

$$\begin{aligned} j_n(x) &= x^n \left(\frac{1}{x}\frac{d}{dx}\right)^n \frac{\sinh(x)}{x}, \\ h_n(x) &= x^n \left(\frac{1}{x}\frac{d}{dx}\right)^n \frac{\exp(-x)}{x}\,, \end{aligned} \tag{B2}$$

and where

$$\begin{aligned} \Pi_n(u,w) &= h_n(-u)\,h_n(-w)\,\mathrm{Ei}\big(-2\,(u+w)\big) + h_n(u)\,h_n(w)\left(\ln\Big(\frac{2\,u\,w}{u+w}\Big) + \gamma_{\mathrm{E}}\right) \\ &\quad +(-1)^n\,h_n(-u)\,h_n(w)\,\mathrm{Ei}(-2\,u) + (-1)^n\,h_n(u)\,h_n(-w)\,\mathrm{Ei}(-2\,w) \\ &\quad +\frac{e^{-u-w}}{u\,w}\,W_n\Big(\frac{1}{u},\frac{1}{w}\Big)\,. \end{aligned} \tag{B3}$$

$W_n(\alpha,\beta)$ is a polynomial in α and β, such that it eliminates $1/r$ singularity in Π_n. It can be constructed recursively as follows,

$$W_i(\alpha,\beta) = -\sum_{k=1}^{i} \frac{2}{i-k+1}\,p_{k,i}(\alpha)\,p_{k,i}(\beta)\,, \tag{B4}$$

where $p_{k,i}$ are polynomials, for which the following recursions work

$$\begin{aligned} p_{k,i}(x) &= p^e_{k,i}(x) + p^o_{k,i}(x), \\ p^e_{1,i}(x) &= 1, \\ p^o_{1,i}(x) &= 0, \\ p^e_{k+1,i}(x) &= p^e_{k,i}(x) + \frac{1+(-1)^k}{2}\,x\,(2\,i-2\,k+1)\,p^o_{k,i}(x), \\ p^o_{k+1,i}(x) &= p^o_{k,i}(x) + \frac{1+(-1)^{k+1}}{2}\,x\,(2\,i-2\,k+1)\,p^e_{k,i}(x). \end{aligned} \tag{B5}$$

We have not been able to prove that the above formula for $f(r)$ solves the differential equation (B3), instead we have shown that first terms of the Taylor expansion in x coincides with that obtained from the differential equation, see the text before Eq. (17), and we have checked its correctness numerically. The principal advantage of this Neumann expansion is the fact that differentiation with respect to nonlinear parameters can be as easily performed as derivatives of spherical Bessel functions and of the polynomial W_n, and this differentiation does not lead to any singularities. In addition $\Pi_n(r\,u, r\,w)$ has very simple integral representation. Namely, if we consider $\Pi_n(r\,u, r\,w)$ as an analytic function of r with branch cut for $r<0$, then it can be expressed by the following dispersion relation

$$\Pi_n(r\,u, r\,w) = \int_0^\infty dr'\,\left(\frac{1}{r} - \frac{1}{r+r'}\right)\,4\,j_n(r'\,u)\,j_n(r'\,w)\,\exp\big(-(r+r')\,(u+w)\big)\,. \tag{B6}$$

which might be convenient for the numerical evaluation.

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