# Integrals for relativistic nonadiabatic energies of $H_2$ in an exponential basis

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Accurate predictions for hydrogen molecular levels require the treatment of electrons and nuclei on equal footing. While nonrelativistic theory has been effectively formulated this way, calculation of relativistic and quantum electrodynamic effects using an exponential basis with explicit correlations that ensure well-controlled numerical precision is much more challenging. In this work, we derive a complete set of integrals for the relativistic correction and demonstrate their application to several of the lowest rovibrational levels. Together with similar advancements for quantum electrodynamic corrections, this will improve the accuracy beyond $10^{-9}$ and hopefully explain discrepancies with recent experimental values.

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## I. INTRODUCTION

Molecular hydrogen is the most abundant molecule in the universe [1]. It is also the dominant component of the atmosphere of giant planets in the solar system [2]. Hence, it draws the attention of astronomers and laboratory physicists [3–6]. In particular, laboratory spectroscopy provides indispensable data for, e.g., constructing astronomical models and databases [7–10], determining physical constants [11,12], and searching for new physics beyond the standard model [13–15]. In recent years, precision spectroscopy of molecular hydrogen has reached an accuracy that enables testing the QED theory at an accuracy level of several parts per billion [16–21].

In several recent studies, a systematic discrepancy on the level of 1.5–2.0 MHz ($\sim$5–7 $\times 10^{-5}\,\mathrm{cm}^{-1}$) between theoretical and experimental vibrational transition energies of $H_2$, HD, and $D_2$ was reported [19–22]. This inconsistency corresponds to $1\sigma-3\sigma$ of theoretical uncertainty. As an illustration, we can quote the currently most accurate experimental energy for the $S_2(0)$ rovibrational transition in $H_2$: 252 016 361.164(8)MHz [20]. The corresponding theoretical prediction is 252 016 358.6(16)MHz [23] and differs from the measured value by 2.6 MHz, i.e., 1.6$\sigma$. Given that the theoretical nonrelativistic energy is known with kilohertz ($\sim 10^{-7}\,\mathrm{cm}^{-1}$) accuracy, incomplete accounting for nuclear motion in relativistic and/or QED components of the total energy is most likely the source of these discrepancies.

In this study, we tackle relativistic correction by treating electrons and nuclei on equal footing. We introduce a computational method that achieves an accuracy of a few kilohertz, similar to that for nonrelativistic energies. We employ the nonadiabatic James-Coolidge (naJC) basis function, which was previously used to solve the four-body Schrödinger equation [24], yielding the nonrelativistic energy of rovibrational levels with a relative accuracy of $10^{-13}-10^{-14}$ [25–28]. This approach retains its accuracy for rotationally and vibrationally excited states. Additionally, this accuracy surpasses the uncertainty arising from the imprecise nuclear masses. The naJC wave function fully accounts simultaneously for both the electron correlation and the movement of the nuclei. This means that there is no need to separate the electronic and nuclear degrees of freedom or introduce common approximations such as the one-electron and Born-Oppenheimer approximations. Evaluation of matrix elements with the nonrelativistic Hamiltonian necessitated finding a new class of integrals, which was the main difficulty in constructing the naJC-based method.

Applying the naJC wave function to relativistic and QED corrections is even more involved. Matrix elements of the relativistic Breit-Pauli Hamiltonian in the basis of naJC functions require the evaluation of unknown classes of integrals. Determination of these integrals is the *sine qua non* of developing this approach and of achieving the accuracy needed for testing QED. This paper presents methods and techniques employed in the evaluation of three new classes of such relativistic integrals and presents a proof of concept for the lowest rovibrational levels of $H_2$.

### A. Wave function

The nonadiabatic James-Coolidge basis function is a special case of a general four-particle exponential function of the

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form

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_A, \vec{r}_B; \{w_j, u_j, n_i\}) = e^{-w_1 r_{12} - w_2 r_{2A} - w_3 r_{2B} - u_1 r_{AB} - u_2 r_{1B} - u_3 r_{1A}} \times r_{AB}^{n_0} r_{12}^{n_1} (r_{1A} - r_{1B})^{n_2} (r_{2A} - r_{2B})^{n_3} (r_{1A} + r_{1B})^{n_4} (r_{2A} + r_{2B})^{n_5}. \quad (1)$$

This function contains all interparticle distances $r_{ij} = |\vec{r}_i - \vec{r}_j|$, with $\vec{r}_1$ and $\vec{r}_2$ pointing at electrons and $\vec{r}_A$ and $\vec{r}_B$ pointing at nuclei. The nonlinear parameters $w_j$ and $u_j$ are assumed to be positive real numbers, and the exponents $n_i$ are non-negative integers. Matrix elements of the nonrelativistic Hamiltonian evaluated with these general exponential functions lead to integrals of the form

$$g(w_1, w_2, w_3, u_1, u_2, u_3, \{n_i\}) = \int \frac{d^3 r_{12}}{4\pi} \int \frac{d^3 r_{2A}}{4\pi} \int \frac{d^3 r_{2B}}{4\pi} \frac{e^{-w_1 r_{12}}}{r_{12}} \frac{e^{-w_2 r_{2A}}}{r_{2A}} \frac{e^{-w_3 r_{2B}}}{r_{2B}} \frac{e^{-u_1 r_{AB}}}{r_{AB}} \frac{e^{-u_2 r_{1B}}}{r_{1B}} \frac{e^{-u_3 r_{1A}}}{r_{1A}} \times r_{AB}^{n_0} r_{12}^{n_1} (r_{1A} - r_{1B})^{n_2} (r_{2A} - r_{2B})^{n_3} (r_{1A} + r_{1B})^{n_4} (r_{2A} + r_{2B})^{n_5}. \quad (2)$$

The sequence of integer exponents $n_0, n_1, n_2, n_3, n_4, n_5$ is denoted as $\{n_i\}$. When this symbol is omitted, it means $\{0\} \equiv 0, 0, 0, 0, 0, 0$, and the corresponding integral is called the master integral. It is convenient to express the function (1) in ellipticlike variables:

$$\zeta_1 = r_{1A} + r_{1B}, \quad \eta_1 = r_{1A} - r_{1B}, \quad \zeta_2 = r_{2A} + r_{2B}, \quad \eta_2 = r_{2A} - r_{2B}, \quad R = r_{AB}, \quad (3)$$

which entails introducing new symbols for linear combinations of parameters

$$w_2 = w + x, \qquad w_3 = w - x, \qquad u_2 = u - y, \qquad u_3 = u + y, \qquad u_1 = t. \quad (4)$$

In this notation

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_A, \vec{r}_B; t, w_1, y, x, u, w, \{n_i\}) = e^{-t R - w_1 r_{12} - y \eta_1 - x \eta_2 - u \zeta_1 - w \zeta_2} R^{n_0} r_{12}^{n_1} \eta_1^{n_2} \eta_2^{n_3} \zeta_1^{n_4} \zeta_2^{n_5}, \quad (5)$$

and corresponding integrals assume the following form:

$$g(t, w_1, y, x, u, w, \{n_i\}) = \int dV \frac{e^{-t R} e^{-w_1 r_{12}} e^{-y \eta_1} e^{-x \eta_2} e^{-u \zeta_1} e^{-w \zeta_2}}{R\, r_{12}\, r_{1A}\, r_{1B}\, r_{2A}\, r_{2B}} \times R^{n_0} r_{12}^{n_1} \eta_1^{n_2} \eta_2^{n_3} \zeta_1^{n_4} \zeta_2^{n_5}, \quad (6)$$

where we introduced the shorthand notation $\int dV \equiv \int \frac{d^3 r_{12}}{4\pi} \int \frac{d^3 r_{2A}}{4\pi} \int \frac{d^3 r_{2B}}{4\pi}$. Unfortunately, such integrals are difficult to handle [29,30], which prompts a slight simplification of the general function (1). This simplification is achieved by setting

$$w_1 = 0, \qquad y = 0, \qquad x = 0, \qquad w = u. \quad (7)$$

The corresponding function

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_A, \vec{r}_B; t, u, \{n_i\}) = e^{-t R - u(\zeta_1 + \zeta_2)} R^{n_0} r_{12}^{n_1} \eta_1^{n_2} \eta_2^{n_3} \zeta_1^{n_4} \zeta_2^{n_5} \quad (8)$$

was named the nonadiabatic James-Coolidge function because of its resemblance to the two-electron James-Coolidge function used in clamped nuclei calculations with $H_2$ [31].

### B. Integrals in the James-Coolidge basis

The whole class of integrals appearing in the matrix elements of the nonrelativistic Hamiltonian in the naJC basis (8) was implemented [24]. Arbitrary $\{n_i\}$ integrals can be formally defined as multiple derivatives with respect to nonlinear parameters present in the general master integral $g(t, w_1, y, x, u, w)$ of Eq. (6),

$$G(t, u; \{n_i\}) = \left(-\frac{\partial}{\partial t}\right)^{n_0} \left(-\frac{\partial}{\partial w_1}\right)^{n_1}_{w_1=0} \left(-\frac{\partial}{\partial y}\right)^{n_2}_{y=0} \left(-\frac{\partial}{\partial x}\right)^{n_3}_{x=0} \left(-\frac{\partial}{\partial u}\right)^{n_4}_{u=w} \left(-\frac{\partial}{\partial w}\right)^{n_5} g(t, w_1, y, x, u, w). \quad (9)$$

In the above formulas and in what follows, we use the notation in which simplified versions of integrals $g$ will be denoted by a capital $G$ and will appear in two variants, one with $w = u$ and the other one with $w \neq u$:

$$G(t, u; \{n_i\}) \equiv g(w_1 = 0, y = 0, x = 0, w = u), \quad (10)$$

$$G(t, u, w; \{n_i\}) \equiv g(w_1 = 0, y = 0, x = 0). \quad (11)$$

Hence, we write explicitly

$$G(t, u; \{n_i\}) = \int dV \frac{e^{-t R} e^{-u(\zeta_1 + \zeta_2)}}{R\, r_{12}\, r_{1A}\, r_{1B}\, r_{2A}\, r_{2B}} \times R^{n_0} r_{12}^{n_1} \eta_1^{n_2} \eta_2^{n_3} \zeta_1^{n_4} \zeta_2^{n_5}, \quad (12)$$

$$G(t, u) = \int dV \frac{e^{-t R} e^{-u(\zeta_1 + \zeta_2)}}{R\, r_{12}\, r_{1A}\, r_{1B}\, r_{2A}\, r_{2B}}. \quad (13)$$

From now on, we also assume that the condition $t > 2u$ is satisfied, and formulas for $-2u \leqslant t \leqslant 2u$ are obtained by analytic continuation.

Techniques developed by one of the authors to evaluate such integrals were described in Refs. [32,33]. In short, this approach relies on a set of partial differential equations (PDEs) to which the integrals $g$ are solutions. All these PDEs can be written as

$$\sigma\,\frac{\partial g}{\partial\beta}+\frac{1}{2}\,\frac{\partial\sigma}{\partial\beta}\,g+P_\beta=0, \tag{14}$$

where $\beta$ is one of the six parameters $t$, $w_1$, $y$, $x$, $u$, and $w$ and $\sigma$ is the following polynomial in these six parameters:

$$\begin{aligned}\sigma &= w_1^2\,t^4+w_1^2\,(u+w-x-y)(u-w+x-y)\\ &\quad\times(u-w-x+y)(u+w+x+y)\\ &\quad+t^2\big[w_1^4-2\,w_1^2(u^2+w^2+x^2+y^2)+16u\,w\,x\,y\big]\\ &\quad-16(u\,y-w\,x)(u\,x-w\,y)(u\,w-x\,y).\end{aligned} \tag{15}$$

Properly manipulating these equations leads to recurrence relations in all variables, which enables finding arbitrary nonrelativistic integrals of Eq. (12). In particular, the explicit formulas for the master integrals are

$$\begin{aligned}G(t,u,w) &= \frac{1}{4u\,w}\left[\frac{\ln\frac{2u\,w}{(t+u+w)(u+w)}}{t+u+w}-\frac{\ln\frac{2u}{t+u+w}}{t-u+w}\right.\\ &\quad\left.-\frac{\ln\frac{2\,w}{t+u+w}}{t+u-w}+\frac{\ln\frac{2\,(u+w)}{t+u+w}}{t-u-w}\right],\end{aligned} \tag{16}$$

$$G(t,u)=\frac{1}{4u^2}\left[\frac{\ln\frac{u}{t+2u}}{t+2u}-\frac{2\ln\frac{2u}{t+2u}}{t}+\frac{\ln\frac{4u}{t+2u}}{t-2u}\right]. \tag{17}$$

Similarly, we proceed with the relativistic integrals resulting from evaluating matrix elements with the Breit-Pauli Hamiltonian. The new relativistic integrals can be divided into three classes:

$$\begin{aligned}G_{AB}(t,u;\{n_i\}) &= \int dV\,\frac{e^{-t\,R}\,e^{-u\,(\zeta_1+\zeta_2)}}{R^2\,r_{12}\,r_{1A}\,r_{1B}\,r_{2A}\,r_{2B}}\\ &\quad\times R^{n_0}\,r_{12}^{n_1}\,\eta_1^{n_2}\,\eta_2^{n_3}\,\zeta_1^{n_4}\,\zeta_2^{n_5},\end{aligned} \tag{18}$$

$$\begin{aligned}G_{12}(t,u;\{n_i\}) &= \int dV\,\frac{e^{-t\,R}\,e^{-u\,(\zeta_1+\zeta_2)}}{R\,r_{12}^2\,r_{1A}\,r_{1B}\,r_{2A}\,r_{2B}}\\ &\quad\times R^{n_0}\,r_{12}^{n_1}\,\eta_1^{n_2}\,\eta_2^{n_3}\,\zeta_1^{n_4}\,\zeta_2^{n_5},\end{aligned} \tag{19}$$

$$\begin{aligned}G_{1B}(t,u;\{n_i\}) &= \int dV\,\frac{e^{-t\,R}\,e^{-u\,(\zeta_1+\zeta_2)}}{R\,r_{12}\,r_{1A}\,r_{1B}^2\,r_{2A}\,r_{2B}}\\ &\quad\times R^{n_0}\,r_{12}^{n_1}\,\eta_1^{n_2}\,\eta_2^{n_3}\,\zeta_1^{n_4}\,\zeta_2^{n_5}.\end{aligned} \tag{20}$$

The remaining integrals ($G_{1A}$, $G_{2A}$, and $G_{2B}$) can be obtained by a permutation of variables. To find integrals (18)–(20) from their master integrals, we need to established the recurrence relation for all six indices $n_0$, $n_1$, $n_2$, $n_3$, $n_4$, and $n_5$. Each type of these integrals requires a different treatment. Therefore, a separate section will be devoted to each of them. In each section, we will describe the derivation of the pertinent master integral first and then the recursive relations in all variables.

## II. $G_{AB}$ INTEGRALS

Let us first note that

$$G_{AB}(t,u;\{n_i\})=G(t,u;n_0-1,n_1,n_2,n_3,n_4,n_5), \tag{21}$$

so all the integrals with $n_0 \geqslant 1$ are considered to be known. What we need are the remaining $G_{AB}$ integrals with $n_0 = 0$, in particular, the master integral

$$G_{AB}(t,u)=\int dV\,\frac{e^{-t\,R}\,e^{-u\,(\zeta_1+\zeta_2)}}{R^2\,r_{12}\,r_{1A}\,r_{1B}\,r_{2A}\,r_{2B}}. \tag{22}$$

The $G_{AB}(t,u)$ master integral can be found analytically by direct integration of $G(t,u)$ over $t$. For this purpose, we first rearrange Eq. (17),

$$G(t,u)=-\frac{t\ln 2-2u\ln\frac{t+2u}{2u}}{tu(t-2u)\,(t+2u)}. \tag{23}$$

Then, relying on the integral

$$\frac{e^{-t\,R}}{R^2}=\int_t^\infty dt\,\frac{e^{-t\,R}}{R}, \tag{24}$$

we evaluate

$$G_{AB}(t,u)=\int_t^\infty dt\;G(t,u) \tag{25}$$

and express the result in terms of dilogarithms ($\mathrm{Li}_2$), namely,

$$G_{AB}(t,u)=\frac{1}{2u^2}\left[\frac{1}{2}\,\mathrm{Li}_2\!\left(\frac{t-2u}{t+2u}\right)-\mathrm{Li}_2\!\left(\frac{t}{t+2u}\right)+\frac{\pi^2}{12}\right]. \tag{26}$$

The integration in Eq. (25) can also be performed numerically and confronted with the analytic result to verify its accuracy. All other $G_{AB}(t,u;0,n_1,n_2,n_3,n_4,n_5)$ integrals were evaluated by numerical integration with respect to $t$ of corresponding $G(t,u;0,n_1,n_2,n_3,n_4,n_5)$ functions; therefore, no recurrences are needed in this case.

## III. $G_{12}$ INTEGRALS

### A. The $G_{12}(t,u)$ master integral

Let us note that

$$G_{12}(t,u;\{n_i\})=G(t,u;n_0,n_1-1,n_2,n_3,n_4,n_5), \tag{27}$$

which means that all the $G_{12}$ integrals with $n_1 \geqslant 1$ are identical to the corresponding nonrelativistic integrals $G$. Of interest to us are the remaining $G_{12}$ integrals with $n_1 = 0$. We start with the evaluation of the master integral

$$G_{12}(t,u)=\int dV\,\frac{e^{-t\,R}\,e^{-u\,(\zeta_1+\zeta_2)}}{R\,r_{12}^2\,r_{1A}\,r_{1B}\,r_{2A}\,r_{2B}}. \tag{28}$$

Because this integral does not depend explicitly on the $w_1$ parameter (related to the $r_{12}$ variable), the direct integration method applied to $G_{AB}$ functions will not work, and a more sophisticated method, described below, must be applied.

Let $g(-w_1) = g(t, w_1, y, x, u, w)$ [see Eq. (6)], and consider the following Hankel's contour integral (see Eq. (6.1.4) of Ref. [34] and Fig. 1):

$$g_\alpha=\hat{\Omega}(\omega^{-\alpha}\,g(\omega))\equiv\frac{1}{2\,\pi\,i}\int_{-\infty}^{(0^+)}g(\omega)\,\omega^{-\alpha}\,d\omega \tag{29}$$

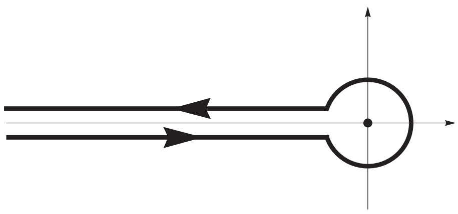

FIG. 1. Integration path for Hankel's integral in Eq. (29).

for an arbitrary real $\alpha$. We show that, subject to $y=0$, $x=0$, and $w=u$,

$$g_0' \equiv \left.\frac{dg_\alpha}{d\alpha}\right|_{\alpha=0} = G_{12}(t,u). \tag{30}$$

If in Eq. (29) we change the order of $dV$ with $d\omega$ integrations, then the $\omega$ integral takes the form

$$\frac{r_{12}^{\alpha-2}}{\Gamma(\alpha)} = \frac{1}{2\pi i}\int_{-\infty}^{(0^+)} \frac{e^{\omega r_{12}}}{r_{12}}\,\omega^{-\alpha}\,d\omega. \tag{31}$$

Because the derivative at $\alpha=0$ on the left side is

$$\left.\frac{d}{d\alpha}\right|_{\alpha=0}\frac{r_{12}^{\alpha-2}}{\Gamma(\alpha)} = \left.\frac{d}{d\alpha}\right|_{\alpha=0}\alpha\, r_{12}^{\alpha-2} = \frac{1}{r_{12}^2}, \tag{32}$$

Eq. (30) is proved.

Consider now two PDEs of Eq. (14), the first with $\beta=w_1$ and the second with $\beta=t$, where $\sigma(y=0,x=0,w=u) = w_1^2\,t^2\,(w_1^2+t^2-4u^2)$ and where $P_{w_1}$ and $P_{u_1}$ are taken from Appendix A. We transform the first equation by substituting $w_1=-\omega$ and multiplying by $t^{-2}\,\omega^{-3-\alpha}$,

$$\omega^{-\alpha-1}(t^2-4u^2+\omega^2)\frac{\partial g(\omega)}{\partial\omega} + \omega^{-\alpha-2}(t^2-4u^2+2\omega^2)g(\omega) - t^{-2}\,\omega^{-\alpha-3}P_{w_1}(\omega) = 0. \tag{33}$$

In the next step, we apply $\hat\Omega$ from Eq. (29) to the above equation and use the relation

$$\hat\Omega\left(\omega^{-\alpha}\frac{\partial g(\omega)}{\partial\omega}\right) = \alpha\,\hat\Omega(\omega^{-\alpha-1}g(\omega)) \tag{34}$$

to obtain

$$(\alpha+2)(t^2-4u^2)\,\hat\Omega(\omega^{-\alpha-2}g(\omega)) + (\alpha+1)\,\hat\Omega(\omega^{-\alpha}g(\omega)) - t^{-2}\,\hat\Omega(\omega^{-\alpha-3}P_{w_1}(\omega)) = 0. \tag{35}$$

Recalling the definition of $g_\alpha$ in Eq. (29), we get

$$(\alpha+2)(t^2-4u^2)g_{\alpha+2} + (\alpha+1)g_\alpha - G_{w_1}(\alpha+3) = 0, \tag{36}$$

where

$$G_\beta(\alpha) = \frac{1}{t^2}\,\hat\Omega(\omega^{-\alpha}P_\beta(\omega)), \tag{37}$$

and hence,

$$g_{\alpha+2} = \frac{-(\alpha+1)g_\alpha + G_{w_1}(\alpha+3)}{(\alpha+2)(t^2-4u^2)}. \tag{38}$$

Now, let us transform the second PDE. Again, we set $w_1 = -\omega$; next, we multiply it by $t^{-1}\,\omega^{-4-\alpha}$ and then apply the $\hat\Omega$ operator to get

$$t\,(t^2-4u^2)\,\frac{\partial g_{\alpha+2}}{\partial t} + t\,\frac{\partial g_\alpha}{\partial t} + 2\,(t^2-2u^2)\,g_{\alpha+2} + g_\alpha = -t\,G_{u_1}(\alpha+4). \tag{39}$$

Now, we insert $g_{\alpha+2}$ from Eq. (38) and multiply the result by $(2+\alpha)(t^2-4u^2)$, obtaining

$$t\,(t^2-4u^2)\frac{\partial g_\alpha}{\partial t} + [t^2\,(2+\alpha)-4u^2]\,g_\alpha = H_\alpha, \tag{40}$$

where

$$H_\alpha = -(2+\alpha)\,t\,(t^2-4u^2)\,G_{u_1}(\alpha+4) - t\,(t^2-4u^2)\frac{\partial G_{w_1}(\alpha+3)}{\partial t} + 4u^2\,G_{w_1}(\alpha+3). \tag{41}$$

Differentiation of Eq. (40) with respect to $\alpha$ at $\alpha=0$, bearing in mind that $g_0=0$, yields the partial differential equation of the form

$$t\,(t^2-4u^2)\frac{\partial g_0'(t)}{\partial t} + \left(2\,t^2-4u^2\right)g_0'(t) = H_0'. \tag{42}$$

The solution to this equation is the master integral $g_0'$ we are looking for. First, however, we must find an explicit formula for $H_0'$. For this purpose, we evaluate

$$\begin{aligned} H_0' &= \left.\frac{\partial H_\alpha}{\partial\alpha}\right|_{\alpha=0} \\ &= -t\,(t^2-4u^2)\,G_{u_1}(4) - 2\,t\,(t^2-4u^2)\,G_{u_1}'(4) \\ &\quad - t\,(t^2-4u^2)\frac{\partial G_{w_1}'(3)}{\partial t} + 4u^2\,G_{w_1}'(3). \end{aligned} \tag{43}$$

Explicit formulas for $G_\beta$ functions can be obtained from the corresponding $P_\beta$ polynomials [see Eq. (37)] and are listed in Appendix B. After insertion of these formulas into Eq. (43), $H_0'$ simplifies greatly to its final form:

$$H_0' = -\frac{\pi^2}{12} + 2\,\mathrm{Li}_2\left(\frac{t}{t+2u}\right). \tag{44}$$

We can now return to Eq. (42) and solve it for $g_0'$:

$$g_0' = G_{12}(t,u) = \frac{1}{t\,\sqrt{t^2-4u^2}}\int_{2u}^{t} dt\,\frac{H_0'}{\sqrt{t^2-4u^2}}. \tag{45}$$

The lower integration limit is $2u$, because $g_0'$ must be finite at every positive $t$, including $t=2u$.

Integration by parts and appropriate variable changes enable the working representation of the above integral, suitable for effective numerical integration to a desired accuracy:

$$G_{12}(t,u) = \frac{1}{t\,\sqrt{t^2-4u^2}}\left\{H_0'(t,u)\,\ln(\tau+\sqrt{\tau^2-1}) - \int_0^{\sqrt{\frac{\tau-1}{\tau+1}}} dy\,\frac{4\,y}{y^2+1}\,\ln\frac{1-y^2}{2}\,\ln\frac{1-y}{1+y}\right\}, \tag{46}$$

where $\tau = t/(2u)$. The numerical integration is performed over a bounded interval with the upper limit $\sqrt{\frac{\tau-1}{\tau+1}} < 1$, and the integrand is a monotonic function of $y$. Therefore, the convergence of a numerical quadrature is fast.

### B. Recurrences

Our next goal is to establish recurrence relations which enable the evaluation of an arbitrary integral $G_{12}(t,u;\{n_i\})$ from integrals with lower values of exponents $n_i$. We proceed like in the derivation of the master integral. The main difference is that we set $y=0$, $x=0$, and $w=u$ only after differentiation with $\hat{D}$ in Eq. (53). We start by employing the PDE (14) with $\beta=w_1$ and $\sigma$ from Eq. (15). For clarity, we write the latter as

$$\sigma = w_1^4 A_{w_1} + w_1^2 B_{w_1} + C_{w_1} \tag{47}$$

and

$$\frac{1}{2}\frac{\partial\sigma}{\partial w_1} = 2\,w_1^3 A_{w_1} + w_1 B_{w_1}, \tag{48}$$

where

$$A_{w_1} = t^2, \tag{49}$$

$$\begin{aligned} B_{w_1} = {} & t^4 - 2t^2(u^2+w^2+x^2+y^2) \\ & + (u+w-x-y)(u-w+x-y) \\ & \times (u-w-x+y)(u+w+x+y), \end{aligned} \tag{50}$$

$$C_{w_1} = 16t^2uwxy - 16(uy-wx)(ux-wy)(uw-xy). \tag{51}$$

Subsequently, we set $w_1=-\omega$, multiply the PDE by $\omega^{-\alpha-3}$, apply the operator $\hat{\Omega}$ defined in Eq. (29), and use Eqs. (34) and (37). As a result, we get

$$\begin{aligned} & (\alpha+1)A_{w_1}\,g_\alpha + (\alpha+2)B_{w_1}g_{\alpha+2} + (\alpha+3)C_{w_1}g_{\alpha+4} \\ & - t^2 G_{w_1}(\alpha+3) = 0. \end{aligned} \tag{52}$$

The obtained equation is differentiated using the following operator:

$$\begin{aligned} \hat{D} \equiv {} & (-1)^{n_2+n_3+n_4+n_5} \\ & \times \left(\frac{\partial}{\partial w}\right)^{n_5}\bigg|_{w=u}\left(\frac{\partial}{\partial u}\right)^{n_4}\left(\frac{\partial}{\partial x}\right)^{n_3}\bigg|_{x=0}\left(\frac{\partial}{\partial y}\right)^{n_2}\bigg|_{y=0}. \end{aligned} \tag{53}$$

The resulting expression is a long combination of multiple derivatives of $g_\alpha$, $g_{\alpha+2}$, and $g_{\alpha+4}$ of the order of at most $n_2+n_3+n_4+n_5$ plus a single $G_{w_1}$ term [see Eq. (37)]. Among them, one $g_\alpha$ function and one $g_{\alpha+2}$ function occur with the highest *shell* of exponents $n_2$, $n_3$, $n_4$, and $n_5$. Let us extract this $g_{\alpha+2}$ function to obtain the relation

$$g_{\alpha+2}(t,u;n_2,n_3,n_4,n_5) = (\cdots)\,g_\alpha(t,u;n_2,n_3,n_4,n_5) + \cdots \tag{54}$$

needed for recursion in the parameter $\alpha$.

Next, we employ another PDE (14) with $\beta=y$. This time,

$$\frac{1}{2}\frac{\partial\sigma}{\partial y} = w_1^2 A_y + B_y, \tag{55}$$

where

$$A_y = -2(t^2y - 2uwx + u^2y + w^2y + x^2y - y^3), \tag{56}$$

$$\begin{aligned} B_y = {} & 8t^2uwx + 8x(-wx+uy)(ux-wy) \\ & + 8w(-wx+uy)(uw-xy) \\ & - 8u(ux-wy)(uw-xy). \end{aligned} \tag{57}$$

We treat this PDE in a way similar to the first one; we set $w_1=-\omega$, multiply it by $\omega^{-\alpha-4}$, and apply the $\hat{\Omega}$ operator, obtaining

$$\begin{aligned} & A_y\,g_{\alpha+2} + B_y\,g_{\alpha+4} + A_{w_1}\frac{\partial g_\alpha}{\partial y} + B_{w_1}\frac{\partial g_{\alpha+2}}{\partial y} \\ & + C_{w_1}\frac{\partial g_{\alpha+4}}{\partial y} + t^2\,G_y\,(\alpha+4) = 0, \end{aligned} \tag{58}$$

which we differentiate using $\hat{D}$. There are two functions with arguments from the maximal shell, $g_\alpha(t,u;n_2+1,n_3,n_4,n_5)$ and $g_{\alpha+2}(t,u;n_2+1,n_3,n_4,n_5)$. We use Eq. (54) to eliminate $g_{\alpha+2}(t,u;n_2+1,n_3,n_4,n_5)$ to get the new relation

$$g_\alpha(t,u;n_2+1,n_3,n_4,n_5) = \cdots, \tag{59}$$

which expresses $g_\alpha$ in terms of the other $g_\alpha$, $g_{\alpha+2}$, and $g_{\alpha+4}$ from lower shells, as well as by functions $G_{w_1}$ and $G_y$ originating from inhomogeneous terms.

Now, we can repeat this procedure for the other pairs of parameters (and pertinent PDEs), $(w_1,x)$, $(w_1,u)$, and $(w_1,w)$, each time obtaining the corresponding recursive relation for

$$g_\alpha(t,u;n_2,n_3+1,n_4,n_5) = \cdots, \tag{60}$$

$$g_\alpha(t,u;n_2,n_3,n_4+1,n_5) = \cdots, \tag{61}$$

$$g_\alpha(t,u;n_2,n_3,n_4,n_5+1) = \cdots. \tag{62}$$

From the obtained set of five $g_\alpha$ relations for arbitrary $\alpha$, we get corresponding relations at $\alpha=0$ and derivatives in $\alpha$ at $\alpha=0$. The final 10 relationships together with the initial $g_0'$ of Eq. (45) form an exhaustive set of recurrences needed to evaluate the function $g_0'$ with arbitrary $n_2$, $n_3$, $n_4$, and $n_5$:

$$g_0'(t,u;n_2,n_3,n_4,n_5) = G_{12}(t,u;0,0,n_2,n_3,n_4,n_5). \tag{63}$$

Other functions $g_0$, $g_2$, $g_4$, $g_2'$, and $g_4'$ appearing within these relationships are just auxiliary and serve only to maintain the complete scheme of recurrences.

The last step is to construct $G_{12}$ integrals for any exponent $n_0$ from the relation

$$\begin{aligned} & G_{12}(t,u;n_0,0,n_2,n_3,n_4,n_5) \\ & = \left(-\frac{\partial}{\partial t}\right)^{n_0} G_{12}(t,u;0,0,n_2,n_3,n_4,n_5). \end{aligned} \tag{64}$$

Inspection of the achieved explicit expressions permits the writing of functions to be differentiated in a general form:

$$\begin{aligned} & G_{12}(t,u;0,0,n_2,n_3,n_4,n_5) \\ & = u^{-(n_2+n_3+n_4+n_5)}\sum_{i=0}^{3} c_i(x)\,f_i, \end{aligned} \tag{65}$$

where $x=2u/t$,

$$\begin{aligned} & f_0 = u^2G_{12}(t,u), && f_1 = \frac{\pi^2}{24} - \mathrm{Li}_2\left(\frac{t}{t+2u}\right), \\ & f_2 = \log\left(\frac{2u}{t+2u}\right), && f_3 = 1 \end{aligned} \tag{66}$$

and where the coefficients $c_i(x)$ are simple rational functions of $x$, for example,

$$G_{12}(t,u;0,0,0,0,1,0)=\frac{1}{u^3}\,\frac{2\,f_0+f_1}{x^2-1}, \tag{67}$$

$$G_{12}(t,u;0,0,1,1,0,0)=-\frac{1}{u^4}\,\frac{2\,f_0\,(x^2-4)-f_1\,(x^2+2)+f_2\,(x-1)(x^2-2)+(x-1)^2}{(x^2-1)^2}, \tag{68}$$

$$G_{12}(t,u;0,0,0,2,0,0)=\frac{x^2}{u^4}\,\frac{f_2\,(x-1)\,x^4-f_1\,(x^2-4)\,x^2+2\,f_0\,\big(x^4-2x^2+4\big)+(x-1)^2}{16\,(x^2-1)^2}. \tag{69}$$

Differentiating such functions does not pose any particular difficulties.

## IV. $G_{1B}$ INTEGRALS

### A. The $G_{1B}(t,u)$ master integral

We are going to derive here an explicit formula for the master integral

$$G_{1B}(t,u)=\int dV\,\frac{e^{-t\,R}\,e^{-u\,(\zeta_1+\zeta_2)}}{R\,r_{12}\,r_{1A}\,r_{1B}^2\,r_{2A}\,r_{2B}}. \tag{70}$$

For this purpose we express this integral in terms of the derivative of the function $g$:

$$G_{1B}(t,u)=\int_{u_2}^{\infty}du_2\,g(t,u_2,u_3,w)\Big|_{u_2=u_3=u} \tag{71}$$

$$=-\int_u^{\infty}du_2\int_t^{\infty}dt\,\frac{\partial g(t,u_2,u,w)}{\partial t} \tag{72}$$

$$=-\int_t^{\infty}dt\int_u^{\infty}du_2\,\frac{\partial g(t,u_2,u,w)}{\partial t}. \tag{73}$$

Because $g$ satisfies the PDE (14) with $\beta=t=u_1$, $\sigma=(u_2-u_3)^2\,(u_2+u_3)^2\,w^2$, and $\frac{\partial\sigma}{\partial t}=0$, its derivative can be found immediately:

$$\frac{\partial g(t,u_2,u_3,w)}{\partial t}=-\frac{P_{u_1}}{\sigma}. \tag{74}$$

Hence, we arrive at

$$G_{1B}(t,u)=-\int_t^{\infty}dt\int_{u_2}^{\infty}du_2\,\Big(-\frac{P_{u_1}}{\sigma}\Big)\Big|_{u_2=u_3=u}. \tag{75}$$

The function $P_\beta$, for arbitrary arguments, is presented in Appendix A. It is a combination of logarithms and simple rational functions; thus, the integral in $u_2$ can readily be performed, and the result for $w=u$ is

$$G_{1B}(t,u)=-\int_t^{\infty}dt\,\frac{1}{4u^2}\left[\frac{g_1(t,u)}{t-2u}-\frac{g_1(t,u)}{t}+\frac{g_2(t,u)}{t}-\frac{g_2(t,u)}{t+2u}\right], \tag{76}$$

where

$$g_1(t,u)=\frac{\pi^2}{12}-\frac{1}{2}\ln^2\left(\frac{2u}{t+2u}\right)-\mathrm{Li}_2\left(\frac{t}{t+2u}\right)+\mathrm{Li}_2\left(\frac{t-2u}{t+2u}\right), \tag{77}$$

$$g_2(t,u)=\frac{\pi^2}{12}+\frac{1}{2}\ln^2\left(\frac{2u}{t+2u}\right)-2\,\mathrm{Li}_2\left(\frac{t}{t+2u}\right)+\mathrm{Li}_2\left(\frac{t-2u}{t+2u}\right). \tag{78}$$

Repeating the above derivation but with $w\neq u$, we obtain

$$G_{1B}(t,u,w)=-\int_t^{\infty}dt\,\frac{\partial G_{1B}(t,u,w)}{\partial t}, \tag{79}$$

$$\frac{\partial G_{1B}(t,u,w)}{\partial t}=\frac{1}{4uw}\left[\frac{g_1(t,u,w)}{t-u-w}-\frac{g_1(t,u,w)}{t+u-w}+\frac{g_2(t,u,w)}{t-u+w}-\frac{g_2(t,u,w)}{t+u+w}\right], \tag{80}$$

where

$$g_1(t,u,w)=\mathrm{Li}_2\left(\frac{t-u-w}{t+u+w}\right)-\mathrm{Li}_2\left(\frac{t+u-w}{t+u+w}\right)-\mathrm{Li}_2\left(-\frac{u}{w}\right)-\frac{1}{2}\ln^2\left(\frac{2w}{t+u+w}\right), \tag{81}$$

$$g_2(t,u,w)=\mathrm{Li}_2\left(\frac{t-u-w}{t+u+w}\right)-2\,\mathrm{Li}_2\left(\frac{t-u+w}{t+u+w}\right)+\mathrm{Li}_2\left(-\frac{u}{w}\right)+\frac{1}{2}\ln^2\left(\frac{2w}{t+u+w}\right)+\frac{\pi^2}{6}. \tag{82}$$

For the recurrence relations discussed in the following section, we will also need derivatives of the master integral with respect to $u$ and $w$:

$$\frac{\partial G_{1B}(t,u,w)}{\partial u}=-\frac{G_{1B}(t,u,w)}{u}-\frac{1}{4uw}\left[\frac{g_1(t,u,w)}{t-u-w}+\frac{g_1(t,u,w)}{t+u-w}+\frac{g_2(t,u,w)}{t-u+w}+\frac{g_2(t,u,w)}{t+u+w}\right], \tag{83}$$

$$\frac{\partial G_{1B}(t,u,w)}{\partial w} = -\frac{G_{1B}(t,u,w)}{w} - \frac{1}{4uw}\left[\frac{g_1(t,u,w)}{t-u-w} - \frac{g_1(t,u,w)}{t+u-w} - \frac{g_2(t,u,w)}{t-u+w} + \frac{g_2(t,u,w)}{t+u+w}\right]. \tag{84}$$

These derivatives can be obtained from Eqs. (79) and (80) as follows:

$$\begin{aligned}\frac{\partial G_{1B}(t,u,w)}{\partial w} &= \frac{\partial}{\partial w}\left(-\int_t^\infty dt\,\frac{\partial G_{1B}(t,u,w)}{\partial t}\right)\\ &= -\int_t^\infty dt\,\frac{\partial}{\partial w}\frac{1}{4uw}\left[\frac{g_1(t,u,w)}{t-u-w} - \frac{g_1(t,u,w)}{t+u-w} + \frac{g_2(t,u,w)}{t-u+w} - \frac{g_2(t,u,w)}{t+u+w}\right]\\ &= -\frac{G_{1B}(t,u,w)}{w} - \frac{1}{4uw}\int_t^\infty dt\,\frac{\partial}{\partial w}\left[\frac{g_1(t,u,w)}{t-u-w} - \frac{g_1(t,u,w)}{t+u-w} + \frac{g_2(t,u,w)}{t-u+w} - \frac{g_2(t,u,w)}{t+u+w}\right]\\ &= -\frac{G_{1B}(t,u,w)}{w} - \frac{1}{4uw}\int_t^\infty dt\left\{\frac{\partial}{\partial t}\left[-\frac{g_1(t,u,w)}{t-u-w} + \frac{g_1(t,u,w)}{t+u-w} + \frac{g_2(t,u,w)}{t-u+w} - \frac{g_2(t,u,w)}{t+u+w}\right] + X\right\},\end{aligned} \tag{85}$$

where

$$X = \left(\frac{1}{t-u-w} - \frac{1}{t+u-w}\right)\left(\frac{\partial}{\partial w} + \frac{\partial}{\partial t}\right)g_1(t,u,w) + \left(\frac{1}{t-u+w} - \frac{1}{t+u+w}\right)\left(\frac{\partial}{\partial w} - \frac{\partial}{\partial t}\right)g_2(t,u,w) \equiv 0. \tag{86}$$

Hence, Eq. (84) is proved.

The direct integral representation of $G_{1B}(t,u,w)$, namely,

$$G_{1B}(t,u,w) = \int_0^\infty dk\, g(t, u+k, u, w), \tag{87}$$

where

$$\begin{aligned}g(t,u_2,u_3,w) = \frac{1}{2\,w(u_2-u_3)(u_2+u_3)}\bigg[&-\mathrm{Li}_2\left(\frac{t-u_3-w}{t+u_2+w}\right) + \mathrm{Li}_2\left(\frac{t-u_3+w}{t+u_2+w}\right) + \mathrm{Li}_2\left(\frac{t+u_2-w}{t+u_2+w}\right)\\ &+ \mathrm{Li}_2\left(\frac{t-u_2-w}{t+u_3+w}\right) - \mathrm{Li}_2\left(\frac{t-u_2+w}{t+u_3+w}\right) - \mathrm{Li}_2\left(\frac{t+u_3-w}{t+u_3+w}\right)\bigg],\end{aligned} \tag{88}$$

will also be needed to derive the recurrences. The latter formula was obtained using

$$g(t,u_2,u_3,w) = -\int_t^\infty dt\,\frac{\partial g}{\partial t}(t,u_2,u_3,w) \tag{89}$$

with the integrand taken from Eq. (74).

### B. Recurrences

In this section we derive formulas for $G_{1B}(t,u;\{n_i\})$ in Eq. (20) for arbitrary $n_i$, and the subsequent steps of this derivation are as follows.

#### 1. Recurrence in $n_3$

In the first step, we obtain formulas for the standard integral $g(t,w_1,x,u_2,u_3,w;n_3)$ at $w_1 = x = 0$. For this purpose, we employ the PDE (14) with $\beta = x$. For $w_1 = 0$, we take

$$\sigma = 16t^2uwxy - 16(-wx+uy)(ux-wy)(uw-xy) \tag{90}$$

and $P_x = P_{w_2} - P_{w_3}$ (see Appendix A). Next, we differentiate this PDE $n_3$ times with respect to $x$, set $x=0$, and extract the highest-order derivative

$$g(n_3) \equiv g(t,w_1,x,u_2,u_3,w;n_3)\big|_{x=0} = (-1)^{n_3}\frac{\partial^{n_3} g}{\partial x^{n_3}}\bigg|_{x=0}. \tag{91}$$

The obtained recursive formula enables the $n_3$th derivative $g(n_3)$ to be evaluated from lower-order derivatives of $g$ and the derivative of the inhomogeneous term $P_x(n_3) \equiv (-1)^{n_3}\frac{\partial^{n_3}P_x}{\partial x^{n_3}}|_{x=0}$,

$$\begin{aligned}g(n_3) = &-\frac{(2n_3-1)(t^2-u^2-w^2-y^2)}{2uwy}g(n_3-1)\\ &-\frac{(n_3-1)^2(u^2w^2+u^2y^2+w^2y^2)}{u^2\,w^2\,y^2}g(n_3-2)\\ &-\frac{(n_3-2)(2n_3-3)(n_3-1)}{2uwy}g(n_3-3)\\ &+\frac{P_x(n_3-1)}{16u^2w^2y^2}.\end{aligned} \tag{92}$$

The $g(n_3)$ obtained from this relation is the starting point for the next recurrence.

#### 2. Recurrence in $n_1$

In the second step, we will obtain formulas for $g(t,w_1,x,u_2,u_3,w;n_1,n_3)$ at $w_1 = x = 0$. In a way similar to that above, we use the PDE (14) with $\beta = w_1$, $\sigma$ from Eq. (15), and $P_{w_1}$ taken from Appendix A. We differentiate this equation $n_1$ times with respect to $w_1$ and set $w_1 = 0$. Then, we differentiate the obtained relationship again $n_3$ times with respect to $x$ and set $x = 0$. These operations yield

$$g(n_1, n_3) \equiv (-1)^{n_1+n_3} \frac{\partial^{n_3}}{\partial x^{n_3}} \frac{\partial^{n_1}}{\partial w_1^{n_1}} g\Big|_{w_1=x=0}, \tag{93}$$

with the following recursion relations:

$$\begin{aligned} g(n_1, n_3) &\\ = \frac{c_1\,(n_1-1)^2\,(n_3-1)\,n_3\,g(n_1-2, n_3-2)}{8u^2w^2y^2} &- \frac{c_2\,(n_1-1)^2\,g(n_1-2, n_3)}{16\,u^2\,w^2\,y^2} - \frac{c_3\,(n_3-1)\,n_3\,g(n_1, n_3-2)}{u^2\,w^2\,y^2}\\ - \frac{c_4\,n_3\,g(n_1, n_3-1)}{u\,w\,y} &- \frac{(n_1-3)\,(n_1-2)^2\,(n_1-1)\,t^2\,g(n_1-4, n_3)}{16\,u^2\,w^2\,y^2} - \frac{(n_3-2)\,(n_3-1)\,n_3\,g(n_1, n_3-3)}{u\,w\,y}\\ - \frac{(n_1-1)^2\,(n_3-3)\,(n_3-2)\,(n_3-1)\,n_3\,g(n_1-2, n_3-4)}{16\,u^2\,w^2\,y^2} &+ \frac{(n_1-1)^2\,n_3\,g(n_1-2, n_3-1)}{2\,u\,w\,y} + \frac{P_{w_1}(n_1-1, n_3)}{16\,u^2\,w^2\,y^2}, \end{aligned} \tag{94}$$

where

$$\begin{aligned} c_1 &= t^2+u^2+w^2+y^2, & c_2 &= t^4-2\,t^2u^2+u^4-2t^2w^2-2u^2\,w^2+w^4-2\,t^2\,y^2-2u^2y^2-2w^2y^2+y^4,\\ c_3 &= u^2w^2+u^2\,y^2+w^2y^2, & c_4 &= -t^2+u^2+w^2+y^2 \end{aligned} \tag{95}$$

and we have defined $g(0, n_3) \equiv g(n_3)$ in Eq. (92) and $P_{w_1}(n_1, n_3) \equiv (-1)^{n_1+n_3} \frac{\partial^{n_3}}{\partial x^{n_3}} \frac{\partial^{n_1}}{\partial w_1^{n_1}} P_{w_1}\Big|_{w_1=x=0}$.

#### 3. Integration with respect to $u_2$

In the third step, we perform analytic integration of $g(t, u_2, u_3, w; n_1, n_3)$ with respect to $u_2$ in order to obtain a function with an additional power of $1/r_{1B}$,

$$\begin{aligned} G_{1B}&(t, u, w; 0, n_1, 0, n_3, 0, 0)\\ &= \int_0^\infty dk\, g(t, u+k, u, w; n_1, n_3)\Big|_{w_1=x=0}. \end{aligned} \tag{96}$$

The integrand combines $\mathrm{Li}_2$, logarithmic, and rational functions of $t$, $u$, $w$, and $k$. The $\mathrm{Li}_2$ functions always appear in the same combination as in Eq. (88); namely, they form $g(t, u+k, u, w)$, and we use this equation to express the integral in terms of $G_{1B}(t, u, w)$ according to Eq. (87). Further on, the integration of logarithmic functions gives dilogarithms $\mathrm{Li}_2$ in such a combination, which can always be expressed in terms of $g_1$ and $g_2$ functions defined in Eqs. (81) and (82). What remains after the integration are the logarithmic and rational functions of $t$, $u$, and $w$.

#### 4. Recurrence in $n_4$ and $n_5$

In the fourth step, we derive $G_{1B}(t, u; 0, n_1, 0, n_3, n_4, n_5)$ by taking derivatives with respect to $u$ and $w$ of $G_{1B}(t, u, w; 0, n_1, 0, n_3, 0, 0)$,

$$\begin{aligned} G_{1B}&(t, u; 0, n_1, 0, n_3, n_4, n_5)\\ &= \left(-\frac{\partial}{\partial w}\right)^{n_5}_{w=u} \left(-\frac{\partial}{\partial u}\right)^{n_4} G_{1B}(t, u, w; 0, n_1, 0, n_3, 0, 0), \end{aligned} \tag{97}$$

and in this operation we make use of Eqs. (83) and (84).

#### 5. Recurrence in $n_2$

Recurrence in the $n_2$ exponent can be found from an algebraic relation between variables,

$$\frac{\eta_1^{n_2}}{r_{1B}} = \eta_1^{n_2-1}\left(\frac{\zeta_1}{r_{1B}} - 2\right), \tag{98}$$

which leads directly to the following formula:

$$\begin{aligned} G_{1B}&(t, u; 0, n_1, n_2, n_3, n_4, n_5)\\ &= G_{1B}(t, u; 0, n_1, n_2-1, n_3, n_4+1, n_5)\\ &\quad - 2\,G(t, u; 0, n_1, n_2-1, n_3, n_4, n_5). \end{aligned} \tag{99}$$

As we can see, apart from $G_{1B}$ integrals of lower order in $n_2$, it also involves standard integrals $G$ from Eq. (12).

#### 6. Recurrence in $n_0$

The last exponent for which we need to find a recurrence is $n_0$, which relates to the internuclear variable $R$ and the nonlinear parameter $t$. Because of the presence of the parameter $t$ in the naJC basis function [Eq. (8)], the $n_0 = 0$ integrals have an explicit dependence on $t$, e.g.,

$$\begin{aligned} G_{1B}&(t, u; 0, 0, 0, 0, 0, 1)\\ &= \frac{1}{2tu}\left[2t\,G_{1B}(t, u) + \frac{g_1(t, u)}{t-2u} - \frac{g_2(t, u)}{t+2u}\right], \end{aligned} \tag{100}$$

$$\begin{aligned} G_{1B}&(t, u; 0, 1, 0, 0, 0, 0)\\ &= \frac{1}{2tu\,(t+2u)} \ln\left(\frac{2u}{t+2u}\right), \end{aligned} \tag{101}$$

$$\begin{aligned} G_{1B}&(t, u; 0, 1, 1, 0, 0, 0)\\ &= \frac{1}{t\,(t+2u)^2}\left[\frac{1}{2\,u} + \frac{1}{t}\ln\left(\frac{2u}{t+2u}\right)\right]. \end{aligned} \tag{102}$$

TABLE I. Numerical values of the master integrals, defined in Eqs. (22), (28), and (70), evaluated for $t = 38.38$ and $u = 1.956$, are shown with a precision of 32 significant digits.

| Master integral | Value |
|---|---|
| $G_{AB}(t,u)$ | 0.007 321 991 591 821 939 899 610 091 538 52 |
| $G_{12}(t,u)$ | 0.002 007 747 417 108 337 201 534 734 124 51 |
| $G_{1B}(t,u)$ | 0.002 832 386 807 422 208 953 576 913 409 21 |

Therefore, it is sufficient to perform a direct differentiation of pertinent $G_{1B}$ integrals with respect to this variable,

$$G_{1B}(t,u;\{n_i\}) = \left(-\frac{\partial}{\partial t}\right)^{n_0} G_{1B}(t,u;0,n_1,n_2,n_3,n_4,n_5), \tag{103}$$

using Eq. (76) to obtain formulas for an arbitrary $n_0$. This concludes the derivation of explicit formulas for an arbitrary $G_{1B}$ integral. A few examples of moderate-size formulas are as follows:

$$\begin{aligned} &G_{1B}(t,u;1,0,0,0,0,1)\\ &= -\frac{t^2-4tu+2u^2}{2t^2u^2\,(t-2u)^2}\,g_1(t,u) - \frac{t^2+4tu+2u^2}{2t^2u^2\,(t+2u)^2}\,g_2(t,u)\\ &\quad + \frac{8u}{t\,(t-2u)^2(t+2u)^2}\,\ln 2\\ &\quad - \frac{t^3-3t^2u-12u^3}{t^2u\,(t-2u)^2(t+2u)^2}\,\ln\frac{2u}{t+2u}, \end{aligned} \tag{104}$$

$$\begin{aligned} &G_{1B}(t,u;1,1,0,0,0,0)\\ &= \frac{1}{2tu\,(t+2u)^2}\left[1+\frac{2(t+u)}{t}\ln\frac{2u}{t+2u}\right], \end{aligned} \tag{105}$$

$$\begin{aligned} &G_{1B}(t,u;1,1,1,0,0,0)\\ &= \frac{1}{t^2\,(t+2u)^3}\left[\frac{3\,t+4u}{2u}+\frac{4(t+u)}{t}\ln\frac{2u}{t+2u}\right]. \end{aligned} \tag{106}$$

## V. NUMERICAL RESULTS

In this section, we present a small selection of numerical results that can be helpful in the reproduction and numerical implementation of the equations derived in previous sections. Among many formulas employed to produce the full set of the relativistic integrals, those for the master integrals seem to be the most important. Because they are the seeds of all recurrences, their numerical values must be known to a sufficiently high precision. Every step of the recurrence in $n_i$ may introduce a small round-off error, which when accumulated would deteriorate the precision of the highest-order terms. Because the target precision imposed on all the integrals is about 64 digits, the master integrals must be evaluated to a significantly higher accuracy. This goal was achieved using MPFR libraries [35] coupled with a MPFUN library [36] and linked to a source code in FORTRAN 95. Numerical values of the master integrals representing three different classes of relativistic integrals are listed in Table I.

The total energy of a rovibrational level of a light molecule described by the vibrational $v$ and rotational $J$ quantum numbers is represented as a series in powers of the fine-structure constant $\alpha$,

$$E^{(v,J)} = \alpha^2 E^{(v,J)}_{\rm nr} + \alpha^4 E^{(v,J)}_{\rm rel} + \alpha^5 E^{(v,J)}_{\rm qed} + \cdots. \tag{107}$$

Our ultimate purpose, for which the integrals described above are indispensable, is an accurate prediction of the relativistic correction $E^{(v,J)}_{\rm rel}$ for rovibrational states of $H_2$ and its isotopologues. This correction is evaluated as an expectation value $\langle\Psi|H_{\rm BP}|\Psi\rangle$ of the mass-dependent Breit-Pauli Hamiltonian (in atomic units, $m = 1$),

$$\begin{aligned} H_{\rm BP} = &-\frac{p_1^4}{8\,m^3} - \frac{p_2^4}{8\,m^3} - \frac{p_A^4}{8\,m_A^3} - \frac{p_B^4}{8\,m_B^3} + \frac{\pi}{m^2}\,\delta^{(3)}(r_{12}) + \frac{\pi}{2}\left(\frac{1}{m^2}+\frac{\delta_{I_A}}{m_A^2}\right)[\delta^{(3)}(r_{1A})+\delta^{(3)}(r_{2A})]\\ &+\frac{\pi}{2}\left(\frac{1}{m^2}+\frac{\delta_{I_B}}{m_B^2}\right)[\delta^{(3)}(r_{1B})+\delta^{(3)}(r_{2B})] - \frac{1}{2\,m^2}\,p_1^i\left(\frac{\delta^{ij}}{r_{12}}+\frac{r_{12}^i\,r_{12}^j}{r_{12}^3}\right)p_2^j - \frac{1}{2\,m_A\,m_B}\,p_A^i\left(\frac{\delta^{ij}}{r_{AB}}+\frac{r_{AB}^i\,r_{AB}^j}{r_{AB}^3}\right)p_B^j\\ &+\frac{1}{2\,m\,m_A}\,p_1^i\left(\frac{\delta^{ij}}{r_{1A}}+\frac{r_{1A}^i\,r_{1A}^j}{r_{1A}^3}\right)p_A^j + \frac{1}{2\,m\,m_B}\,p_1^i\left(\frac{\delta^{ij}}{r_{1B}}+\frac{r_{1B}^i\,r_{1B}^j}{r_{1B}^3}\right)p_B^j\\ &+\frac{1}{2\,m\,m_A}\,p_2^i\left(\frac{\delta^{ij}}{r_{2A}}+\frac{r_{2A}^i\,r_{2A}^j}{r_{2A}^3}\right)p_A^j + \frac{1}{2\,m\,m_B}\,p_2^i\left(\frac{\delta^{ij}}{r_{2B}}+\frac{r_{2B}^i\,r_{2B}^j}{r_{2B}^3}\right)p_B^j, \end{aligned} \tag{108}$$

with the wave function $\Psi$ expanded in the basis of the naJC functions [Eq. (8)]. In the above equation, subscripts $A$ and $B$, accompanying symbols of mass $m$, momentum $p$, and the coordinate $r$, concern nuclei, while 1 and 2 refer to electrons. The nuclear-spin factor $\delta_I$, present in Dirac delta terms, depends on the nucleus's spin $I$: $\delta_I = 1$ for $I = 1/2$ and $\delta_I = 0$ otherwise. All the electron spin-dependent terms are omitted as they vanish for the ground electronic state of $^1\Sigma_g^+$ symmetry, while nuclear-spin-dependent terms are also omitted because we do not consider the fine and hyperfine structures. Due to its negligible magnitude, we have also omitted the nucleus-nucleus Dirac delta term.

Table II contains preliminary numerical results of the relativistic correction obtained for the three lowest rovibrational levels of $H_2$. $E^{(v,J)}_{\rm rel}$ was evaluated with a sequence of wave functions of growing quality, which enables estimation of

TABLE II. Convergence of the relativistic correction $E_{\rm rel}^{(v,J)}$ (in a.u.) calculated using the nonadiabatic James-Coolidge wave function for the $(v, J)$ rovibrational level of $H_2$. $K$ is the size of the nonadiabatic James-Coolidge basis set employed, governed by $\Omega$, the largest shell enabled. Calculations were performed using the nuclear mass $M/m = 1836.152\,673\,43(11)$ [40].

| $\Omega$ | $K$ | $E_{\rm rel}^{(0,0)}$ | $K$ | $E_{\rm rel}^{(0,1)}$ | $K$ | $E_{\rm rel}^{(0,2)}$ |
|---|---|---|---|---|---|---|
| 9 | 28 756 | −0.204 547 752 0 | 49 042 | −0.204 326 998 3 | 49 042 | −0.203 890 204 8 |
| 10 | 42 588 | −0.204 547 538 4 | 73 164 | −0.204 326 718 0 | 73 164 | −0.203 889 953 8 |
| 11 | 61 152 | −0.204 547 467 0 | 105 840 | −0.204 326 616 4 | 105 840 | −0.203 889 881 7 |
| 12 | 85 904 | −0.204 547 434 3 | 149 408 | −0.204 326 587 7 | 149 408 | −0.203 889 846 0 |
| 13 | 117 936 | −0.204 547 423 1 | | | | |
| 14 | 159 120 | −0.204 547 417 6 | | | | |
| | $\infty$ | −0.204 547 412(5) | $\infty$ | −0.204 326 56(3) | $\infty$ | −0.203 889 81(3) |

its numerical accuracy. The size of the wave-function expansions was determined by the shell parameter $\Omega$, limiting from above the sum of the exponents $n_1 + n_2 + n_3 + n_4 + n_5$ of the naJC basis functions (8) included. The extrapolation to the infinite basis size was performed at the level of individual operators present in the Hamiltonian (108). The relativistic integrals were evaluated for integer exponents fulfilling the following conditions: $n_1 + n_2 + n_3 + n_4 + n_5 \leqslant 35$ and $n_0 \leqslant 85$, which enables application of wave functions with a shell $\Omega$ up to 14 for $J = 0$ and up to 12 for $J > 0$.

For the rotationless level ($J = 0$), analogous results are available in the literature. In 2018, Wang and Yan [37] reported $E_{\rm rel}^{(0,0)} = -0.204\,544(5)$ a.u., in agreement with our results, whereas Puchalski *et al.* [38] obtained $E_{\rm rel}^{(0,0)} = -0.204\,547\,56(4)$ a.u., which is off by $4\sigma$ from the new result. Reinvestigating the convergence of the latter correction revealed that the error-bar estimation was too optimistic. Calculations performed by Stanke and Adamowicz [39] in 2013 yielded $E_{\rm rel}^{(0,0)} = -0.201\,3$ a.u. The uncertainty of this number is unknown. Assuming that all the digits quoted are significant, we note a considerable disagreement with all the other values.

In contrast to the nonadiabatic explicitly correlated Gaussian functions [38,39], the naJC wave function exhibits the correct behavior at interparticle distances tending to zero or infinity. This results in fast convergence of the relativistic operators, allowing for a total relativistic correction with an accuracy of $10^{-8}$. This level of accuracy is essential given the present and upcoming measurements.

For the rotationally excited levels there are no analogous data available in the literature. A comparison can be made to the relativistic correction obtained within the adiabatic approximation, e.g., within the nonadiabatic perturbation theory (NAPT) implemented in the publicly available H2SPECTRE program [23,41]. For $J = 1$, NAPT yields $E_{\rm rel}^{(0,1)} = -0.204\,326\,8(2)$ a.u., which agrees to within $1.2\sigma$ with the direct nonadiabatic (DNA) result in Table II. The uncertainty of the NAPT result is due to neglected higher-order finite-nuclear-mass effects; the comparison with the DNA value validates the method of uncertainty estimation. For $J = 2$, NAPT gives $E_{\rm rel}^{(0,2)} = -0.203\,889\,6(2)$ a.u., which is in agreement with the DNA result.

## VI. CONCLUSIONS

The naJC wave function, together with the nuclear-mass-dependent Breit-Pauli Hamiltonian in Eq. (108), fully takes into account nonadiabatic effects (nuclear recoil) in the relativistic correction. However, the expectation values of the operators present in this Hamiltonian evaluated in the naJC basis require access to new, previously unknown classes of integrals. The mathematical techniques reported in this paper enabled the evaluation of such extended integrals, allowing an unprecedented relative accuracy of $3 \times 10^{-8}$ for the relativistic correction of the ground state of $H_2$. Regarding the dissociation energy of a rovibrational level, this corresponds to an absolute accuracy of $6 \times 10^{-8}\,{\rm cm}^{-1}$ (~2kHz). Previous calculations, apart from the rotationless cases mentioned above, were performed in the framework of the adiabatic approximation using the second-order NAPT with the inclusion of the relativistic terms proportional to the electron-to-nucleus mass ratio. The new DNA method, which is 2 orders of magnitude more accurate, removes the uncertainty caused by unknown higher-order terms of the NAPT expansion and allows the error estimation of the NAPT computation to be verified.

One of the essential features opened up by the extended classes of integrals is the possibility of accurately determining the relativistic correction for higher rotational levels. As in the case of the nonrelativistic energy [24–28], the accuracy now achieved allows the error from the relativistic correction to be neglected in the total error budget. From now on, the missing recoil contribution to the QED correction and the unknown higher-order-in-$\alpha$ corrections will be the only factors that determine the overall energy uncertainty.

Apart from the relativistic correction itself, the new classes of integrals will also enable an extension of the field of application of the naJC wave function to the evaluation of the operators present in the QED term of the expansion (107) as well as to various electric and magnetic properties of the hydrogen molecule.

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## APPENDIX A: INHOMOGENEOUS TERMS $P_\beta$

The PDE (14) is satisfied by the general four-body integral of Eq. (2). These equations involve inhomogeneous terms $P_\beta$ with $\beta = u_i, w_i$. All these terms can be expressed by a single general function $P$:

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

The explicit formula for $P$ was obtained in [33] and is repeated here for completeness:

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

In the main text, we often referred to Eq. (14) with $\beta$ being a linear combination of $w_i$ and $u_i$ as in Eq. (4). In such a case, $P_\beta$ can be obtained from one of the following equations:

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

## APPENDIX B: EXPLICIT FORMULAS FOR $G_\beta(\alpha)$ FUNCTIONS AND THEIR DERIVATIVES

The functions $G_\beta(\alpha)$ were defined in Eq. (37). Explicit formulas for these functions and their derivatives with respect $\alpha$, $G'_\beta(\alpha)$, needed for the evaluation of $H'_0$ in Eq. (43), are as follows:

$$G_{u_1}(4) = \frac{-t+u}{tu(t+2u)^2}, \tag{B1}$$

$$\begin{aligned}
G'_{u_1}(4) &= -\frac{1}{8tu^2} + \frac{5}{4u(t+2u)^2} + \frac{1}{8u^2(t+2u)} \\
&\quad + \frac{\ln(2u)}{tu(t+2u)} - \frac{3\ln(t+2u)}{t\,(t+2u)^2},
\end{aligned} \tag{B2}$$

$$\begin{aligned}
G'_{w_1}(3) &= -\frac{1}{2u^2} - \frac{\pi^2}{48u^2} + \frac{2}{u(t+2u)} - \frac{\ln(2u)}{2u^2} \\
&\quad + \frac{2\ln(t+2u)}{u(t+2u)} - \frac{\ln\left(\frac{t+2u}{2u}\right)}{tu} + \frac{\mathrm{Li}_2\left(\frac{t}{t+2u}\right)}{2u^2},
\end{aligned} \tag{B3}$$

$$\begin{aligned}
\frac{\partial G'_{w_1}(3)}{\partial t} &= -\frac{1}{2tu^2} + \frac{1}{2u^2(t+2u)} \frac{2(t+u)\ln\left(\frac{t+2u}{2u}\right)}{t^2u(t+2u)} \\
&\quad - \frac{2\ln(t+2u)}{u(t+2u)^2}.
\end{aligned} \tag{B4}$$


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