

# Analytical two-center integrals over Slater geminal functions

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We present analytical formulas for the calculation of the two-center two-electron integrals in the basis of Slater geminals and products of Slater orbitals. Our derivation starts with establishing an inhomogeneous fourth-order ordinary differential equation that is obeyed by the master integral, the simplest integral with inverse powers of all interparticle distances. To solve this equation it was necessary to introduce a new family of special functions which are defined through their series expansions around regular singular points of the differential equation. To increase the power of the interparticle distances under the sign of the integral we developed a family of open-ended recursion relations. A handful of special cases of the integrals is also analyzed with some remarks on simplifications that occur. Additionally, we present some numerical examples of the master integral that validate the correctness and usefulness of the key equations derived in this paper. In particular, we compare our results with the calculations based on the series expansion of the  $\exp(-\gamma r_{12})$  term.

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## I. INTRODUCTION

It has been a well-known fact since the landmark paper of Kato [1] that the exact eigenfunction  $\Psi$  of the Schrödinger Hamiltonian must satisfy certain conditions at the coalescence points of the particles. These are the so-called *cusplike conditions*, expressed mathematically as

$$\lim_{r_{ij} \rightarrow 0} \left( \frac{\partial \Psi}{\partial r_{ij}} \right)_{av} = \mu_{ij} q_i q_j \Psi(r_{ij} = 0), \quad (1)$$

where  $q_i$  are the charges of the particles,  $\mu_{ij}$  is the reduced mass of the particles  $i$  and  $j$ , and the subscript *av* denotes the spherical average over an infinitesimal sphere around  $r_{ij} = 0$ . The above constraint must be satisfied for every single pair of particles in the system. While the nuclear cusp condition is naturally satisfied by the one-electron basis constructed from the Slater orbitals, the electronic cusp condition appears to be a far more difficult problem. Hill [2] analyzed a simple example of a two-electron one-center system with the basis set taken as the partial wave expansion:

$$\Psi(\vec{r}_1, \vec{r}_2) = \sum_{lm}^L Y_{lm}(\theta_1, \varphi_1) Y_{l,-m}(\theta_2, \varphi_2) \times \sum_{nn'}^N f_{nlm}(r_1) f_{n'lm}(r_2), \quad (2)$$

where  $Y_{lm}$  are spherical harmonics,  $(\theta_i, \varphi_i)$ ,  $i = 1, 2$ , are the spherical angles of the vector  $\vec{r}_i$ , and  $f_n$  are some radial factors. He found that the error of the energy decays as  $\sim (L+1)^{-3}$ , so a rather slow convergence is obtained. This saddening corollary can be attributed to the fact that the partial wave expansion has severe difficulties in fulfilling the electronic cusp condition. Much faster convergence can be expected when the basis set is extended to include the  $r_{12}$  factor explicitly. The latter finding is a theoretical underpinning for a vast family of the so-called *explicitly correlated* methods.

Explicitly correlated calculations in quantum mechanics have a long history. The first calculations of this type were performed on the  $1^1S$  state of the helium atom by Hylleraas in his classical 1929 paper [3]. The Hylleraas ansatz for the wave function of He ground state was

$$\Psi_N = e^{-\zeta s} \sum_k^N c_k s^{l_k} t^{2m_k} u^{n_k}, \quad (3)$$

where  $s = r_1 + r_2$ ,  $t = r_1 - r_2$ ,  $u = r_{12}$ , and  $r_i$  are the coordinates of electrons. Using a six-term wave function of the above form with one nonlinear parameter Hylleraas obtained a result with three correct significant digits in the ionization energy of helium [3]. The length of this expansion can be increased and it is a relatively easy task to obtain a nanohartree accuracy. Many authors tried to extend the form of the Hylleraas ansatz. For instance, Kinoshita [4,5] suggested to include negative powers of  $s$  and  $u$ , and Schwartz [6–8] included half-integer powers of the latter quantities. Several researchers [9,10] included logarithmic terms, for example,  $\log(s)$ , in order to satisfy the three-particle coalescence condition of both the electrons and the nucleus. Further extension can be done by considering a so-called “double-basis set” [11–13] in which each combination of powers of  $r_1$ ,  $r_2$ , and  $r_{12}$  is included twice, but with different exponential scale factors and no logarithmic terms. Probably the most well-known calculations in this basis set are those of Drake *et al.* [14], where about 20-significant-digit accuracy on the energy was reached. This idea can further be extended to the “triple basis set” and so forth. Important from the point of view of the present paper is the work of Korobov [15], who obtained a 25-significant-digit accuracy by using Slater-type geminals; that is, the wave function expanded as a linear combination of the functions:

$$\phi_k = e^{-\alpha_k r_1 - \beta_k r_2 - \gamma_k r_{12}}, \quad (4)$$

where  $\alpha_k$ ,  $\beta_k$ , and  $\gamma_k$  are complex parameters which were generated quasirandomly. Recently, Nakashima and Nakatsuji used a method called iterative complement interaction (ICI), described in Ref. [16], and obtained a 40-significant-digit accuracy, which is the highest available until now. At the end

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of this short survey over the helium atom we must admit that the exponentially correlated Gaussian (ECG) functions were also used with success (see Ref. [17]). Of course, all of the methodologies mentioned above can equally well be applied to the excited states and properties [18,19] of the He atom and its isoelectronic series such as  $\text{H}^-$  or  $\text{Li}^+$ . These systems were also subjects of intensive studies in the past [20–23].

The first explicitly correlated calculations on a molecular system, the hydrogen molecule, were carried out in 1933 by James and Coolidge [24] with a basis set, named after them (JC), of the form

$$\xi_1^k \eta_1^l \xi_2^m \eta_2^n r_{12}^\mu e^{-\alpha\xi_1 - \beta\xi_2}, \quad (5)$$

where  $\xi_i$  and  $\eta_i$  are elliptical coordinates. With the advent of computers Kołos and Roothaan used this basis set to obtain a microhartree accuracy in the energy calculations [25,26]. Later on, Kołos and Wolniewicz extended the form of the above basis set to include the Heitler-London function, thereby making it possible to describe the dissociation of the molecule properly [27]. It gave rise to so-called Kołos-Wolniewicz (KW) basis set. The approaches described above were subsequently extended to the excited states of  $\text{H}_2$  (cf. Refs. [28–30]). During the past decades several authors reported calculations in the JC [31–33] or KW [34–38] basis sets with an increasing accuracy. Among other approaches ICI calculations presented by Nakatsuji *et al.* [39] are worth noticing. It is rather astonishing that in the field of  $\text{H}_2$  ECG calculations were proven to be very successful and even competitive with the approaches based on Slater functions [40–43]. Recently, Pachucki, in his *tour de force* paper, derived analytical equations for the integrals over the JC basis set [44]. This made it possible to perform calculations on  $\text{H}_2$  with at least 15-digit accuracy [45]. Let us end this paragraph by remarking that the two-electron analogs of  $\text{H}_2$ ,  $\text{HeH}^+$  [46–50] and  $\text{He}_2^{2+}$  [51–53], were also studied in the literature.

The lithium atom and three-electron ions are probably the last example of when a Hylleraas-type basis set could still successfully be applied. It was possible because analytical equations for the resulting integrals [54–56] and useful recursion relations [57,58] between them are all known. This allowed very accurate calculations, among which those of King [59], Yan *et al.* [22,60], and Puchalski and Pachucki [61] should be mentioned. The results of Hylleraas-CI and ECG calculations for the lithium atom are also available [20]. The accuracy of the calculations for the lithium atom cannot compete with that for helium. Nevertheless, the reported energy values still agree excellently with the best available experimental data [61]. The applicability of the explicitly correlated calculations with the Hylleraas-like ansatz is narrowed dramatically when passing to many-center and/or many-electron systems. Since the Hylleraas-CI and ECG are the only methods that can be used in practice for systems such as the beryllium atom [62–64], the accuracy deteriorates significantly. A similar situation holds for other few-body systems,  $\text{H}_3^+$  [49,65,66],  $\text{H}_3$  [67,68],  $\text{He}_2$  [69], and  $\text{LiH}$  [70].

For many-electron systems explicitly correlated variational calculations are not feasible at present. This is due to the high complexity in the space and permutational symmetry of the wave function. However, basis functions including the explicit dependence on the interelectronic distance  $r_{12}$  can

be introduced into the many-body theory of many-electron systems. Indeed, it was realized as early as 1966 by Byron and Joachain [71,72] and later by Pan and King [73,74], Jeziorski, Szalewicz, and collaborators [75–80], and Adamowicz and Sadlej [81–83] that the pair functions appearing in the energy expressions of the many-body perturbation theory (MBPT), also known as the Møller-Plesset perturbation theory, can be expanded in terms of explicitly correlated functions, provided that the strong orthogonality condition is satisfied. Since the strong orthogonality condition is difficult to meet, Szalewicz *et al.* [77–80] suggested to weaken it without losing the mathematical correctness of the theory. These early explicitly correlated MBPT approaches employed the Hylleraas basis in the case of calculations of Byron and Joachain [71,72] on the beryllium atom and explicitly correlated Gaussian functions in case of the calculations on the Be, LiH, Ne, and  $\text{H}_2\text{O}$  systems [84–87]. In the early 1980s explicitly correlated Gaussian geminals were used with success by Jeziorski and Szalewicz in the coupled cluster (CC) calculations [80]. One important drawback of the approach summarized above is that the perturbation theory and CC calculations involving explicitly correlated basis functions require calculations of three- (and in some cases four-) electron integrals. This makes this kind of calculation prohibitively expensive and limited to small systems. A breakthrough in this respect was suggested by Klopper and Kutzelnigg [88–90] for the MBPT calculations and by Noga and collaborators [91,92] for the CC calculations. These authors suggested to include only terms linear in the interelectronic distance  $r_{12}$  and use an approximate resolution of identity to approximate many-electron integrals with the two-electron integrals. In this way the problem of calculating many-electron integrals was eliminated, although only in an approximate way. Still, this approach was shown to be very successful in many spectroscopic and chemical applications. See, for instance, Ref. [93] for a review. Finally, the most recent advance in this field are the so-called explicitly correlated CC-F12 methods [94–99], in which the interelectronic distance,  $r_{12}$ , is explicitly introduced into the pair functions through the exponential correlation factor  $\exp(-\gamma r_{12})$ . The F12 methods have recently been implemented in an efficient manner [100–102] and shown to accelerate the convergence towards the basis-set limit for a number of properties [103–105]. Unfortunately, the F12 method fails to reproduce accurate interaction potentials of diatomic molecules [106,107], although it was shown to work well in the  $\text{Li} + \text{LiH}$  case [108].

In this paper we introduce a basis set for accurate calculations on diatomic molecules, the basis of Slater geminals. This basis can be used both in the variational calculations and in the many-body MBPT/CC theories. The Slater geminal basis has several advantages over the explicitly correlated basis sets used in molecular calculations thus far. Among others, it satisfies both the electron-nuclei and electron-electron cusp conditions. Similarly to atoms, the exponential correlation factor is expected to improve the convergence of the short-range correlations, while the Slater-type one-electron part will greatly reduce the size of the expansion, thus leading to results much more accurate than possible at present. This is especially important for the new emerging field at the border of chemistry and physics, ultracold molecules. See

the 2012 special issue of Chemical Reviews, in particular papers by Quemener and Julienne [109], Weidemüller and collaborators [110], and by Koch and Shapiro [111]. To better appreciate the importance of high-quality basis sets for molecular calculations on diatomic molecules, let us just quote calculations on the  $\text{Sr}_2$  molecule [112,113], which are currently used in the interpretation of the experimental data for the determination of the time variation of the electron-to-proton mass ratio [114,115]. Another very appealing application of the Slater geminals for diatomic molecules are the calculations of the relativistic effects. Indeed, when the relativistic corrections are calculated in the framework of the perturbation method and with the Breit-Pauli Hamiltonian it is necessary to calculate integrals with the  $1/r_{12}^2$  factor. Analytical calculation of such integrals in the two-center case was impossible until now. It was necessary to use the infinite expansion in the Gegenbauer polynomials, according to the scheme advocated by Wolniewicz [36]. Using our analytical equations for the integrals over the Slater geminal basis, all the necessary relativistic integrals involving the  $1/r_{12}^2$  factor are obtained by a simple one-dimensional numerical integration. A similar scheme was recently successfully applied to calculation of the relativistic corrections for the lithium atom [61].

The paper is organized as follows. In Sec. II we define the master integral,  $f(r)$ , which will serve as a generating integral for the calculations of all the integrals from the family (7) and derive a differential equation satisfied by  $f(r)$ . In Sec. III we show how to solve the homogeneous differential equation, thereby involving a new family of special functions. In Sec. IV we derive solutions of the inhomogeneous differential equation so that an analytical expression for the master integral becomes known explicitly. In Sec. V we establish a family of recursion relations that allow calculations of the integrals with arbitrary powers of all electron-nuclear distances. A similar procedure is adopted in Sec. VI to let arbitrarily grow the power of  $r_{12}$  in the integrals. In Sec. VII we consider a handful of special cases of the integrals that cannot be calculated with the results of the previous sections. In these special cases, an analytical equation for the master integral is found in terms of well-known special functions. In Sec. VIII we present some numerical examples of the master integral that validate the correctness and usefulness of the analytical equations derived in this paper. In particular, we compare our results with the calculations based on the series expansion of the  $\exp(-\gamma r_{12})$  term in the master integral. Finally, in Sec. IX we conclude our paper.

In the paper we rely heavily on the known special functions to simplify the derivation and the final formulas. Our convention for all special functions appearing below is the same as in Ref. [116]. We also use the Meijer  $G$  function, which is defined according to Ref. [117].

## II. THE MASTER INTEGRAL

In this paper, we consider analytical calculation of the two-electron integrals in the basis of Slater geminals and Slater functions for a diatomic molecule. The latter basis set has the general form

$$\phi(\vec{r}_1, \vec{r}_2) = r_{1A}^i r_{1B}^j r_{2A}^k r_{2B}^l r_{12}^n \times e^{-u_3 r_{1A} - u_2 r_{1B} - w_2 r_{2A} - w_3 r_{2B} - w_1 r_{12}}, \quad (6)$$

so it gives rise to a class of two-electron two-center integrals,

$$f_n(i, j, k, l; u_2, u_3, w_2, w_3, w_1) = \int d^3 r_1 \int d^3 r_2 r_{1A}^i r_{1B}^j r_{2A}^k r_{2B}^l r_{12}^n \times e^{-u_3 r_{1A} - u_2 r_{1B} - w_2 r_{2A} - w_3 r_{2B} - w_1 r_{12}}, \quad (7)$$

where we adopted the following notation:  $\vec{r}_i$ ,  $i = 1, 2$ , denotes the coordinates of the electrons and  $\vec{r}_K$ ,  $K = A, B$ , denotes the coordinates of the nuclei. Consequently,  $r_{iK} = |\vec{r}_i - \vec{r}_K|$  and  $r_{12} = |\vec{r}_1 - \vec{r}_2|$  denote the electron-nucleus and interelectronic distances, respectively. The above notation is used throughout the paper.

It is noteworthy that the requirements  $u_2 > 0$ ,  $u_3 > 0$ ,  $w_2 > 0$ ,  $w_3 > 0$ , and  $w_1 > 0$  are sufficient, but much too strong to make the functions (6) square integrable. These requirements can be significantly weakened by demanding only  $u_2 + u_3 + w_1 > 0$  and  $w_2 + w_3 + w_1 > 0$ . Therefore, some of the nonlinear parameters can be negative without violation of the square-integrability principle. This result is reminiscent of the three-body Hylleraas integrals, which is discussed later.

If the basis set is chosen in terms of spherical harmonics multiplied by the radial factor and the exponential correlation factor, then using simple manipulations based on the ordinary trigonometric relations, one can express the resulting integrals in terms of combinations of the integrals from the family (7).

When performing calculations for a two-electron and diatomic system described by the Schrödinger Hamiltonian in the basis set defined by Eq. (6), all the matrix elements of the operators are readily expressed through the integrals (7) except for the kinetic energy operator. To express the latter quantities through the combinations of the integrals from the family (7), a somewhat long derivation is required. So as not to disturb the consistency of the paper, this derivation is reported in Appendix A. As a result, the matrix elements of the Schrödinger Hamiltonian and all the integrals appearing in the nonrelativistic molecular physics on the basis of (6) are expressed fully analytically.

### A. Definition and the momentum space representation

The master integral is defined as the simplest two-electron integral with inverse powers of all electron-nuclear and interelectronic distances, namely,

$$f(r) = \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-u_3 r_{1A}}}{r_{1A}} \frac{e^{-u_2 r_{1B}}}{r_{1B}} \frac{e^{-w_2 r_{2A}}}{r_{2A}} \frac{e^{-w_3 r_{2B}}}{r_{2B}} \frac{e^{-w_1 r_{12}}}{r_{12}} r, \quad (8)$$

where the notation for all appearing quantities is the same as in Eq. (6) and  $r = r_{AB}$  is the internuclear distance. The reason for the choice of the multiplicative constant  $\frac{r}{(4\pi)^2}$  and the particular notation for the nonlinear parameters is clear from the further derivation. Once this integral is known analytically, all integrals  $f_n$  of Eq. (7) can be obtained by multiple differentiations of Eq. (8) over the nonlinear parameters  $u_2$ ,  $u_3$ ,  $w_2$ ,  $w_3$ , and  $w_1$ .

Our first task is to derive an analytical equation for the above integral. We perform a Laplace transform of the master integral with respect to  $r$  and therefore define another integral

$g(u_1)$ :

$$g(u_1) = \int_0^\infty dr f(r) e^{-u_1 r} = \int \frac{d^3 r}{4\pi} \frac{f(r)}{r^2} e^{-u_1 r}. \quad (9)$$

This equality allows us to calculate  $f(r)$  from the inverse Laplace transform formula: integral

$$f(r) = \frac{1}{2\pi i} \int_{-i\infty+\epsilon}^{i\infty+\epsilon} du_1 g(u_1) e^{u_1 r}. \quad (10)$$

The explicit form of the integral  $g(u_1)$  can conveniently be written, after the simple interchange of variables  $\vec{\rho}_1 = \vec{r}_{12}$ ,  $\vec{\rho}_2 = \vec{r}_{2A}$ ,  $\vec{\rho}_3 = \vec{r}_{2B}$ , as

$$g(u_1) = \int \frac{d^3 \rho_1}{4\pi} \int \frac{d^3 \rho_2}{4\pi} \int \frac{d^3 \rho_3}{4\pi} \frac{e^{-u_3 \rho_{12}} e^{-u_2 \rho_{31}}}{\rho_{12} \rho_{31}} \times \frac{e^{-w_2 \rho_2} e^{-w_3 \rho_3} e^{-w_1 \rho_1} e^{-u_1 \rho_{23}}}{\rho_2 \rho_3 \rho_1 \rho_{23}}, \quad (11)$$

with  $\rho_{12} = |\vec{\rho}_1 - \vec{\rho}_2|$  and analogous formulas for  $\rho_{13}$  and  $\rho_{23}$ . The above representation is familiar as it is the generating integral from the theory of three-electron one-center integrals [54,55]. Let us recall the momentum space representation of  $g(u_1)$ :

$$g(u_1) = G(1,1,1,1,1,1), \quad (12)$$

where

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

### B. Differential equation in the momentum space

In this section we establish a differential equation for  $G(1,1,1,1,1,1)$ . Let us first denote the integrand in Eq. (13) by  $\tilde{G}$  with an analogous notation for its parameters:

$$\tilde{G}(m_1, m_2, m_3, m_4, m_5, m_6) = \frac{1}{(k_1^2 + u_1^2)^{m_1}} \frac{1}{(k_2^2 + u_2^2)^{m_2}} \frac{1}{(k_3^2 + u_3^2)^{m_3}} \times \frac{1}{(k_{32}^2 + w_1^2)^{m_4}} \frac{1}{(k_{13}^2 + w_2^2)^{m_5}} \frac{1}{(k_{21}^2 + w_3^2)^{m_6}}. \quad (14)$$

Our derivation is based on the so-called *integration by parts identities* [118,119] and the fact that due to Green's theorem the following family of integrals vanish:

$$0 = I_{ij} = \frac{1}{8\pi^6} \int d^3 k_1 \int d^3 k_2 \int d^3 k_3 \vec{\nabla}_j \cdot [\vec{k}_i \tilde{G}(1,1,1,1,1,1)], \quad (15)$$

where the  $i$  and  $j$  indices can independently take values 1, 2, and 3. The above identity provides nine equations that relate the values of  $G$  with different arguments. These equations can be divided into three sets, the first set being  $I_{13}, I_{23}, I_{33}$  and the

two others obtained by a permutation of the second index. It can be proven that to derive the desired differential equation only one of these sets has to be considered and the results from the others are identical. Therefore, we consider the trio  $I_{13}, I_{23}, I_{33}$ , but this choice is arbitrary. To give an example, we show the derivation for  $I_{13}$ . It follows from the definition that

$$\begin{aligned} \vec{\nabla}_3 \cdot [\vec{k}_1 \tilde{G}(1,1,1,1,1,1)] &= -2\vec{k}_1 \cdot \vec{k}_3 \tilde{G}(1,1,2,1,1,1) \\ &\quad - 2\vec{k}_1 \cdot \vec{k}_{32} \tilde{G}(1,1,1,2,1,1) \\ &\quad + 2\vec{k}_1 \cdot \vec{k}_{13} \tilde{G}(1,1,1,1,2,1). \end{aligned} \quad (16)$$

The scalar (dot) products of several  $\vec{k}$  vectors appearing in the above equation are expanded using the relation  $\vec{k}_i \cdot \vec{k}_j = -\frac{1}{2}[\vec{k}_{ij}^2 - \vec{k}_i^2 - \vec{k}_j^2]$  and similarly for other possible combinations. This makes it possible to rewrite the right-hand side of Eq. (16) as

$$\begin{aligned} &[\vec{k}_{13}^2 - \vec{k}_1^2 - \vec{k}_3^2] \tilde{G}(1,1,2,1,1,1) \\ &+ [\vec{k}_{13}^2 - \vec{k}_{12}^2 - \vec{k}_3^2 + \vec{k}_1^2] \tilde{G}(1,1,1,2,1,1) \\ &+ [\vec{k}_{13}^2 - \vec{k}_3^2 - \vec{k}_1^2] \tilde{G}(1,1,1,1,2,1). \end{aligned} \quad (17)$$

The next step is to make all the coefficients multiplying the different  $\tilde{G}$  functions independent of the  $\vec{k}$  vectors. The latter are absorbed into  $\tilde{G}$  in the following way:

$$\vec{k}_1^2 \tilde{G}(1,1,2,1,1,1) = \tilde{G}(0,1,2,1,1,1) - u_1^2 \tilde{G}(1,1,2,1,1,1). \quad (18)$$

After necessary simplifications the expression for  $I_{13}$  becomes

$$\begin{aligned} I_{13} &= (u_3^2 + u_1^2 - w_2^2) G(1,1,2,1,1,1) \\ &\quad + (w_3^2 + u_3^2 - u_2^2 - w_2^2) G(1,1,1,2,1,1) \\ &\quad + (u_3^2 - u_1^2 - w_2^2) G(1,1,1,1,2,1) + G(1,1,2,1,0,1) \\ &\quad - G(0,1,2,1,1,1) + G(1,1,1,2,0,1) - G(1,1,1,2,1,0) \\ &\quad - G(1,1,0,2,1,1) + G(1,0,1,2,1,1) - G(1,1,0,1,2,1) \\ &\quad + G(0,1,1,1,2,1). \end{aligned} \quad (19)$$

In a very similar way the expressions for  $I_{23}$  and  $I_{33}$  can be derived. The final equations are

$$\begin{aligned} I_{23} &= (u_2^2 + u_3^2 - w_1^2) G(1,1,2,1,1,1) \\ &\quad + (w_3^2 + u_3^2 - u_1^2 - w_1^2) G(1,1,1,1,2,1) \\ &\quad + (u_3^2 - w_1^2 - u_2^2) G(1,1,1,2,1,1) + G(1,0,1,2,1,1) \\ &\quad - G(1,1,0,1,2,1) + G(0,1,1,1,2,1) - G(1,0,2,1,1,0) \\ &\quad - G(1,1,0,2,1,1) + G(1,1,2,0,1,1) - G(1,1,1,1,2,0) \\ &\quad + G(1,1,1,0,2,1), \end{aligned} \quad (20)$$

$$\begin{aligned} I_{33} &= 2u_3^2 G(1,1,2,1,1,1) + (w_2^2 - u_1^2 + u_3^2) G(1,1,1,1,2,1) \\ &\quad + (u_3^2 + w_1^2 - u_2^2) G(1,1,1,2,1,1) + G(1,0,1,2,1,1) \\ &\quad - G(1,1,1,1,1,1) + G(0,1,1,1,2,1) \\ &\quad - G(1,1,0,1,2,1) - G(1,1,0,2,1,1). \end{aligned} \quad (21)$$

By an inspection of these three equations we note that all the  $G$  integrals fall into three classes. The first class consists of integrals with one of the parameters  $m_1, \dots, m_6$  equal to zero.

It is easy to verify by a direct calculation that these integrals belong to the class of the well-known Hylleraas-type helium (three-body) integrals,

$$\Gamma(n_1, n_2, n_3; \alpha, \beta, \gamma) = \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} r_1^{n_1-1} r_2^{n_2-1} r_{12}^{n_3-1} \times e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}, \quad (22)$$

and analytical equations for these integrals are all known since they can be obtained from the generating integral,

$$\Gamma(0, 0, 0; \alpha, \beta, \gamma) = \frac{1}{(\alpha + \beta)(\alpha + \gamma)(\beta + \gamma)}, \quad (23)$$

by a proper differentiation or integration with respect to the nonlinear parameters  $\alpha, \beta, \gamma$ . Recursion relations that enable generation of  $\Gamma$  with arbitrary values of  $n_1, n_2, n_3$  were presented a long time ago by Kołos and co-workers [120]. An analytical expression to generate the integral  $\Gamma(0, 0, 0)$  was derived earlier [121].

The second class of integrals consists of  $G(1, 1, 2, 1, 1, 1)$ ,  $G(1, 1, 1, 2, 1, 1)$ , and  $G(1, 1, 1, 1, 2, 1)$ , and the third class is the

master integral  $G(1, 1, 1, 1, 1, 1)$ . Therefore, we solve the set of three equations (19)–(21) with respect to one of the integrals from the second class. Let us choose  $G(1, 1, 1, 2, 1, 1)$ . The result is

$$\frac{1}{2} \frac{\partial \sigma}{\partial w_1} G(1, 1, 1, 1, 1, 1) - 2w_1 \sigma G(1, 1, 1, 2, 1, 1) + P(w_1, u_1; w_2, u_2; w_3, u_3) = 0, \quad (24)$$

where  $\sigma$  is a polynomial in all nonlinear parameters:

$$\begin{aligned} \sigma = & u_1^2 w_1^2 (u_1^2 - u_2^2 - u_3^2 + w_1^2 - w_2^2 - w_3^2) \\ & + u_2^2 w_2^2 (-u_1^2 + u_2^2 - u_3^2 - w_1^2 + w_2^2 - w_3^2) \\ & + u_3^2 w_3^2 (-u_1^2 - u_2^2 + u_3^2 - w_1^2 - w_2^2 + w_3^2) \\ & + u_1^2 u_2^2 w_3^2 + u_1^2 u_3^2 w_2^2 + u_2^2 u_3^2 w_1^2 + w_1^2 w_2^2 w_3^2. \end{aligned} \quad (25)$$

The function  $P(w_1, u_1; w_2, u_2; w_3, u_3)$  is a combination of integrals from the first class with coefficients being some polynomials in the nonlinear parameters. Its derivation is long and does not present any advance over already published formulas [44, 122], so we list here only the final equation:

$$\begin{aligned} P(w_1, u_1; w_2, u_2; w_3, u_3) = & -u_1 w_1 [(u_1 + w_2)^2 - u_3^2] \Gamma(0, 0, -1; u_1 + w_2, u_3, u_2 + w_1) \\ & - u_1 w_1 [(u_1 + u_3)^2 - w_2^2] \Gamma(0, 0, -1; u_1 + u_3, w_2, w_1 + w_3) \\ & + [u_1^2 w_1^2 + u_2^2 w_2^2 - u_3^2 w_3^2 + w_1 w_2 (u_1^2 + u_2^2 - w_3^2)] \Gamma(0, 0, -1; w_1 + w_2, w_3, u_1 + u_2) \\ & + [u_1^2 w_1^2 - u_2^2 w_2^2 + u_3^2 w_3^2 + w_1 w_3 (u_1^2 + u_3^2 - w_2^2)] \Gamma(0, 0, -1; w_1 + w_3, w_2, u_1 + u_3) \\ & - [u_2 (u_2 + w_1) (u_1^2 + u_3^2 - w_2^2) - u_3^2 (u_1^2 + u_2^2 - w_3^2)] \Gamma(0, 0, -1; u_2 + w_1, u_3, u_1 + w_2) \\ & - [u_3 (u_3 + w_1) (u_1^2 + u_2^2 - w_3^2) - u_2^2 (u_1^2 + u_3^2 - w_2^2)] \Gamma(0, 0, -1; u_3 + w_1, u_2, u_1 + w_3) \\ & + w_1 [w_2 (u_1^2 - u_2^2 + w_3^2) + w_3 (u_1^2 + w_2^2 - u_3^2)] \Gamma(0, 0, -1; w_2 + w_3, w_1, u_2 + u_3) \\ & + w_1 [u_2 (u_1^2 - w_2^2 + u_3^2) + u_3 (u_1^2 + u_2^2 - w_3^2)] \Gamma(0, 0, -1; u_2 + u_3, w_1, w_2 + w_3), \end{aligned} \quad (26)$$

where

$$\Gamma(0, 0, -1; \alpha, \beta, \gamma) = \frac{\ln\left(\frac{\gamma + \alpha}{\gamma + \beta}\right)}{(\alpha - \beta)(\alpha + \beta)}. \quad (27)$$

The above identity can be checked with (e.g., Ref. [123]). Finally, after observing that the identity

$$G(1, 1, 1, 2, 1, 1) = -\frac{1}{2w_1} \frac{\partial g}{\partial w_1} \quad (28)$$

holds, one arrives at the form of the differential equation obeyed by  $g$  in the momentum space:

$$\sigma \frac{\partial g}{\partial w_1} + \frac{1}{2} \frac{\partial \sigma}{\partial w_1} g(u_1) + P(w_1, u_1; w_2, u_2; w_3, u_3) = 0. \quad (29)$$

By exchanging the indices at the  $\vec{k}$  vectors in the definition of  $G(1, 1, 1, 1, 1, 1)$  one can obtain analogous differential equations with respect to the other variables. In particular,

in the derivation the following one will be required:

$$\sigma \frac{\partial g}{\partial u_1} + \frac{1}{2} \frac{\partial \sigma}{\partial u_1} g(u_1) + P(u_1, w_1; u_3, w_3; w_2, u_2) = 0. \quad (30)$$

The latter two equations were recently presented by Pachucki [44]. The solution of Eq. (30) was given by Fromm and Hill [54] and subsequently simplified considerably by Harris [56]. Unfortunately, the explicit form of  $g$  in terms of well-known special functions is too complicated to perform the inverse Laplace transform directly and obtain the two-center integrals as in Eq. (10). Therefore, the differential equation approach seems to be the only way to derive analytical equations for the integrals family (7).

### C. Differential equation in the position space

At this point we depart from the previous works. To obtain a differential equation for the master integral  $f(r)$  we have to perform the inverse Laplace transform of Eq. (30). Pachucki [44] performed such an inversion in the case of  $w_1 = 0$ , so any connection with the geminal basis was lost. Our case

requires a generalization to an arbitrary physically acceptable but nonzero value of  $w_1$ . Let us first rewrite the polynomial  $\sigma$  in the following (convenient) way:

$$\sigma = w_1^2 u_1^4 + \Omega_1 u_1^2 + \Omega_2, \tag{31}$$

$$\begin{aligned} \Omega_1 = & -u_2^2 w_1^2 - u_2^2 w_2^2 + u_2^2 w_3^2 - u_3^2 w_1^2 + u_3^2 w_2^2 \\ & - u_3^2 w_3^2 + w_1^4 - w_1^2 w_2^2 - w_1^2 w_3^2, \end{aligned} \tag{32}$$

$$\begin{aligned} \Omega_2 = & u_2^4 w_2^2 + u_2^2 u_3^2 w_1^2 - u_2^2 u_3^2 w_2^2 - u_2^2 u_3^2 w_3^2 \\ & - u_2^2 w_1^2 w_2^2 + u_2^2 w_2^4 - u_2^2 w_2^2 w_3^2 + u_3^4 w_3^2 \\ & - u_3^2 w_1^2 w_3^2 - u_3^2 w_2^2 w_3^2 + u_3^2 w_3^4 + w_1^2 w_2^2 w_3^2, \end{aligned} \tag{33}$$

so that

$$\frac{\partial \sigma}{\partial u_1} = 4w_1^2 u_1^3 + 2\Omega_1 u_1. \tag{34}$$

By inserting the above identities into Eq. (30) and collecting terms multiplying  $g(u_1)$  and  $\frac{\partial g}{\partial u_1}$  we get

$$\begin{aligned} (w_1^2 u_1^4 + \Omega_1 u_1^2 + \Omega_2) \frac{\partial g}{\partial u_1} + (2w_1^2 u_1^3 + \Omega_1 u_1) g(u_1) \\ + P(u_1, w_1; u_3, w_3; w_2, u_2) = 0. \end{aligned} \tag{35}$$

The inverse Laplace transform of this equation leads to

$$\begin{aligned} w_1^2 r f^{(4)}(r) + 2w_1^2 f^{(3)}(r) + \Omega_1 r f''(r) \\ + \Omega_1 f'(r) + \Omega_2 r f(r) = U(r; w_1, u_2, u_3, w_2, w_3), \end{aligned} \tag{36}$$

where

$$\begin{aligned} U(r; w_1, u_2, u_3, w_2, w_3) \\ = \frac{1}{2\pi i} \int_{-i\infty+\epsilon}^{i\infty+\epsilon} du_1 P(u_1, w_1; u_3, w_3; w_2, u_2) e^{u_1 r}. \end{aligned} \tag{37}$$

The explicit form of  $U(r)$  is obtained by using several Laplace transform identities and reads

$$U(r) = \sum_{i=1}^4 c_i U_i(r) + \sum_{i=5}^8 U_i(r), \tag{38}$$

with

$$c_1 = \frac{1}{2} [w_2 (u_2^2 - u_3^2 - w_1^2) + u_3 (w_2^2 - w_3^2 + w_1^2)], \tag{39}$$

$$c_2 = \frac{1}{2} [w_3 (u_2^2 - u_3^2 + w_1^2) + u_2 (w_2^2 - w_3^2 - w_1^2)], \tag{40}$$

$$c_3 = \frac{1}{2} [w_2 (u_2^2 - u_3^2 - w_1^2) - u_3 (w_2^2 - w_3^2 + w_1^2)], \tag{41}$$

$$c_4 = \frac{1}{2} [u_2 (w_2^2 - w_3^2 - w_1^2) - w_3 (u_2^2 - u_3^2 + w_1^2)], \tag{42}$$

and

$$U_1(r) = e^{r(u_3-w_2)} \text{Ei}[-r(w_1+u_2+u_3)] - e^{r(w_2-u_3)} \text{Ei}[-r(w_1+w_2+w_3)], \tag{43}$$

$$U_2(r) = e^{r(w_3-u_2)} \text{Ei}[-r(w_1+w_2+w_3)] - e^{r(u_2-w_3)} \text{Ei}[-r(w_1+u_2+u_3)], \tag{44}$$

$$\begin{aligned} U_3(r) = & e^{-r(u_3+w_2)} \{ \text{Ei}[-r(w_1+u_2-u_3)] - \text{Ei}[-r(u_2-u_3-w_2+w_3)] \\ & + \text{Ei}[-r(w_1-w_2+w_3)] \} - e^{r(u_3+w_2)} \text{Ei}[-r(u_2+u_3+w_2+w_3)] \\ & + e^{-r(u_3+w_2)} \ln \left| \frac{(w_1+w_2+w_3)(u_2+u_3+w_1)(u_2-u_3-w_2+w_3)}{(w_1-w_2+w_3)(w_1+u_2-u_3)(u_2+u_3+w_2+w_3)} \right|, \end{aligned} \tag{45}$$

$$\begin{aligned} U_4(r) = & e^{-r(u_2+w_3)} \{ \text{Ei}[-r(w_1+u_3-u_2)] - \text{Ei}[-r(u_3-u_2-w_3+w_2)] \\ & + \text{Ei}[-r(w_1-w_3+w_2)] \} - e^{r(u_2+w_3)} \text{Ei}[-r(u_2+u_3+w_2+w_3)] \\ & + e^{-r(u_2+w_3)} \ln \left| \frac{(w_1+w_2+w_3)(u_2+u_3+w_1)(u_2-u_3-w_2+w_3)}{(w_1-w_2+w_3)(w_1+u_2-u_3)(u_2+u_3+w_2+w_3)} \right|, \end{aligned} \tag{46}$$

$$\begin{aligned} U_5(r) = & -\frac{w_1}{r} e^{-r(u_2+w_3)} \left( \frac{1}{r} + u_2 + w_3 \right) + \frac{w_1}{r} e^{-r(u_3+w_1+w_3)} \left( \frac{1}{r} + u_3 + w_1 + w_3 \right) \\ & - e^{-r(u_2+w_3)} w_1 [\gamma (u_2 + w_3) \delta(r) + (1 - \gamma) \delta'(r)] + w_1^2 e^{-r(u_3+w_1+w_3)} \left[ \frac{1}{r} + \gamma \delta(r) \right] \\ & + e^{-r(u_3+w_1+w_3)} [\gamma (u_3 + w_3 + w_1) \delta(r) + (1 - \gamma) \delta'(r)], \end{aligned} \tag{47}$$

$$\begin{aligned} U_6(r) = & -\frac{w_1}{r} e^{-r(u_3+w_2)} \left( \frac{1}{r} + u_3 + w_2 \right) + \frac{w_1}{r} e^{-r(u_2+w_1+w_2)} \left( \frac{1}{r} + u_2 + w_1 + w_2 \right) \\ & - e^{-r(u_3+w_2)} w_1 [\gamma (u_3 + w_2) \delta(r) + (1 - \gamma) \delta'(r)] + w_1^2 e^{-r(u_2+w_1+w_2)} \left[ \frac{1}{r} + \gamma \delta(r) \right] \\ & + e^{-r(u_2+w_1+w_2)} [\gamma (u_2 + w_2 + w_1) \delta(r) + (1 - \gamma) \delta'(r)], \end{aligned} \tag{48}$$

$$U_7(r) = w_1^2 \delta(r) \ln(w_1 + w_2 + w_3), \quad U_8(r) = w_1^2 \delta(r) \ln(w_1 + u_2 + u_3). \tag{49}$$

The results presented above require some comments. First of all, let us establish the connection with the Pachucki differential equation, the zero limit in  $w_1$  of Eq. (36). By setting  $w_1 = 0$  and observing that

$$p^2 = -\frac{\Omega_2}{\Omega_1} \Big|_{w_1=0}, \quad F(r) = -\frac{U(r; 0, u_2, u_3, w_2, w_3)}{\Omega_1}, \quad (50)$$

one arrives at

$$r f''(r) + f'(r) - p^2 r f(r) + F(r) = 0, \quad (51)$$

which exactly coincides with the result given by Pachucki [44] for the case of orbital basis. Second, at the end of this section we would like to mention that in the further derivation we will make use of two other functions which are obtained as the inverse Laplace transforms of  $P$ , namely,

$$\begin{aligned} W(r; w_1, u_2, u_3, w_2, w_3) \\ = \frac{1}{2\pi i} \int_{-i\infty+\epsilon}^{i\infty+\epsilon} du_1 P(w_1, u_1; w_2, u_2; w_3, u_3) e^{u_1 r}, \end{aligned} \quad (52)$$

$$\begin{aligned} V(r; w_1, u_2, u_3, w_2, w_3) \\ = \frac{1}{2\pi i} \int_{-i\infty+\epsilon}^{i\infty+\epsilon} du_1 P(w_3, u_3; w_2, u_2; w_1, u_1) e^{u_1 r}. \end{aligned} \quad (53)$$

Since explicit formulas for these functions have not been presented in the literature thus far, we list them in Appendix B.

### III. SOLUTION OF THE HOMOGENEOUS DIFFERENTIAL EQUATION

First, we solve the homogeneous version of the geminal differential equation:

$$\begin{aligned} w_1^2 r f_H^{(4)}(r) + 2w_1^2 f_H^{(3)}(r) + \Omega_1 r f_H''(r) + \Omega_1 f_H'(r) \\ + \Omega_2 r f_H(r) = 0, \end{aligned} \quad (54)$$

where the subscript  $H$  was added to designate the solution of the homogeneous equation. The above equation is a homogeneous linear ordinary differential equation (ODE) with nonconstant coefficients. We found it very difficult, if not impossible, to express the solution in terms of well-known special or analytical functions. Any manipulations performed with Eq. (54) were proven fruitless in bringing this equation into a characteristic form, thus enabling an analytical solution. It was also impossible to find the solution by using a symbolic mathematical package such as MATHEMATICA [124].

It is interesting from the mathematical point of view that Eq. (54) can be brought to the form

$$w_1^2 \frac{d^2}{dr^2} \left( r \frac{df_H}{dr} \right) + \Omega_1 \frac{d}{dr} \left( r \frac{df_H}{dr} \right) = -r \Omega_2 f_H(r), \quad (55)$$

so that it can be considered as a generalization of the Sturm-Liouville (S-L) equation to the fourth-order ODE with the weight (or density) function equal to  $r$  and eigenvalue  $-\Omega_2$ .

Because of all the above, we decided to define a family of special functions which, by definition, form the general solution of the differential equation (25). We find its form by using the generalized version of the Fröbenius method (see, e.g., Ref. [125]). Precisely, we find a solution in terms of the series expansion around two singular points, zero and infinity.

Our first ansatz is an ordinary regular expansion around  $r = 0$ :

$$f_H(r) = \sum_{k=0}^{\infty} a_k r^k. \quad (56)$$

We insert this ansatz into Eq. (54), collect terms multiplying the same power of  $r$ , and make them zero to make the differential equation satisfied for all values of  $r$ . This establishes the recurrence relation that connects the values of  $a_k$  with different  $k$ . The final result reads

$$\begin{aligned} w_1^2(k+1)(k+2)^2(k+3)a_{k+3} + \Omega_1(k+1)^2 a_{k+1} \\ + \Omega_2 a_{k-1} = 0 \quad \text{for } k \geq 1, \end{aligned} \quad (57)$$

and the indicial equation is

$$12w_1^2 a_3 + \Omega_1 a_1 = 0. \quad (58)$$

Equations (57) and (58) need to be simultaneously satisfied. However, there is a freedom in the choice of three initial parameters  $a_0$ ,  $a_1$ , and  $a_2$ . Therefore, we specify three new special functions  $L_i(r)$ ,  $i = 1, 2, 3$ , using their expansions around  $r = 0$  given by Eq. (56) and the recurrence relation (57). The choice of the three initial parameters is conventional and we put

$$\begin{aligned} L_1(r) \quad \text{with } a_0 = 1, a_1 = 0, a_2 = 0, \\ L_2(r) \quad \text{with } a_0 = 0, a_1 = 1, a_2 = 0, \\ L_3(r) \quad \text{with } a_0 = 0, a_1 = 0, a_2 = 1. \end{aligned} \quad (59)$$

This convention is used throughout the paper. Let us justify the choice of the formulas (59). One may argue that choice  $a_0 = 1$  in  $L_1$  is very special but by putting  $a_0 = C \neq 1$ , we obtain a function which is just  $L_1$  multiplied by  $C$ . The choice of a multiplicative constant is immaterial in our context and, consequently, so is the choice of  $C$ . The same is true for the values of  $a_1$  and  $a_2$  in  $L_2$  and  $L_3$ , respectively. Similarly, by defining a function with  $a_0 = 1, a_1 = 1$ , for example, we obtain a linear combination of  $L_1$  and  $L_2$ . Because of these properties, we find the convention (59) justified.

It is clear that the three functions obtained in the previous paragraph are not sufficient to give the general solution of the homogeneous geminal differential equation. Our second trial for the expansion around  $r = 0$  is somewhat less obvious:

$$f_H(r) = L_i(r) \ln(r) + \sum_{k=0}^{\infty} b_k r^k, \quad (60)$$

where the coefficients  $b_k$  are to be determined by inserting the expression (60) into the homogeneous differential equation and collecting terms multiplying  $r^k$  and  $r^k \ln(r)$ . This results in the recurrence relation:

$$2\Omega_1 a_1 + 28w_1^2 a_3 + \Omega_1 b_1 + 12w_1^2 b_3 = 0, \quad (61)$$

$$\begin{aligned} 2k\Omega_1 a_k + 2(k+1)(2k^2 + 4k + 1)w_1^2 a_{k+2} + \Omega_2 b_{k-2} \\ + k^2 \Omega_1 b_k + w_1^2 k(k+1)^2(k+2)b_{k+2} = 0. \end{aligned} \quad (62)$$

Additionally, as soon as  $w_1 \neq 0$  the above ansatz requires  $a_0 = 0$ ,  $a_1 = 1$ ,  $a_2 = 0$ . As before, we have three parameters which can be chosen freely,  $b_0$ ,  $b_1$ , and  $b_2$ . Since we seek for only one function, let us put  $b_0 = 0$ ,  $b_1 = 1$ ,  $b_2 = 0$ , which

leads to

$$L_4(r) = L_2(r)\ln(r) + \sum_{k=1}^{\infty} b_k r^k. \quad (63)$$

One can show that any function constructed with a different choice of  $b_0, b_1$ , and  $b_2$  can be expressed as a linear combination of  $L_1(r), L_2(r), L_3(r), L_4(r)$ . This formally completes the solution of the homogeneous differential equation (36).

The expansions around  $r = 0$  presented above are convergent for all finite values of  $r$  since the coefficients multiplying the powers of  $r$  decay faster than any polynomial when  $k \rightarrow \infty$ . However, the rate of convergence of these series can be expected to be poor for large values of  $r$  and therefore prohibit an accurate calculation in this regime. As a result, it might be beneficial to obtain their asymptotic expansion, which will be valid and rapidly convergent for large values of  $r$ . The latter expansion can be constructed from the ansatz

$$f_H(r) = e^{tr} \sum_{k=0}^{\infty} a_k r^{-k-\rho}, \quad (64)$$

where  $a_k, t$  and  $\rho$  are coefficients to be determined. By inserting this trial function into the differential equation and grouping coefficients multiplying the same powers of  $1/r$  one obtains indicial equations specifying  $\rho$  and  $t$ ,

$$w_1^2 t^4 + \Omega_1 t^2 + \Omega_2 = 0, \quad (65)$$

$$\rho = \frac{1}{2}, \quad (66)$$

and the recursion relation for  $a_k$  with the value of  $\rho$  already fixed at  $1/2$ ,

$$\frac{1}{4}\Omega_1 a_0 + \frac{3}{2}t^2 w_1^2 a_0 - 2\Omega_1 t a_1 - 4t^3 w_1^2 a_1 = 0, \quad (67)$$

$$-3t w_1^2 a_0 + \frac{9}{4}\Omega_1 a_1 + \frac{27}{2}t^2 w_1^2 a_1 - 4\Omega_1 t a_2 - 8t^3 w_1^2 a_2 = 0, \quad (68)$$

and for  $k > 2$ ,

$$\begin{aligned} 0 = & \frac{1}{16} w_1^2 a_k (2k+3)^2 (2k+1)(2k+5) \\ & - t w_1^2 a_{k+1} (k+2)(2k+3)(2k+5) \\ & + \frac{1}{4} (2k+5)^2 a_{k+2} (\Omega_1 + 6t^2 w_1^2) \\ & - 2(k+3) a_{k+3} (\Omega_1 t + 2t^3 w_1^2). \end{aligned} \quad (69)$$

Equation (65) has four solutions  $t_i, i = 1, \dots, 4$ , which correspond to four functions determining the general solution of the homogeneous differential equation. We see that it is dependent on the sign of  $t_i$  whether convergent or divergent expansion is obtained. The final result can be written as

$$f_H(r) = \frac{e^{tr}}{\sqrt{r}} \sum_{k=0}^{\infty} \frac{a_k}{r^k}, \quad (70)$$

where  $a_0$  can freely be chosen.

It is interesting to establish a connection between the new special functions  $L_i$  and the modified Bessel functions of the first,  $I_0(r)$ , and the second,  $K_0(r)$ , kind. By setting  $w_1 = 0$

Eqs. (57) and (58) become

$$\Omega_1(k+1)^2 a_{k+1} + \Omega_2 a_{k-1} = 0, \quad a_1 = 0, \quad (71)$$

so that the recursion can be solved explicitly to give

$$a_{2k} = \frac{-\frac{\Omega_2}{\Omega_1} \Big|_{w_1=0}^k}{2^{2k} k!^2} = \frac{p^{2k}}{2^{2k} k!^2}, \quad a_{2k-1} = 0, \quad (72)$$

and the series can be brought into the closed form,

$$\sum_{k=0}^{\infty} \frac{p^{2k} r^{2k}}{2^{2k} k!^2} = I_0(pr), \quad (73)$$

coinciding with the Bessel function of the first kind. Similarly, by setting  $w_1 = 0$  in Eqs. (61) and (62) one finds a linear combination of  $I_0(pr)$  and  $K_0(pr)$  to be the  $w_1 = 0$  limit of  $L_4(r)$ . One could force the exact relationship

$$\lim_{w_1 \rightarrow 0} L_4(r) = K_0(pr) \quad (74)$$

by a proper choice of the initial parameters. Our choice was made for the sake of simplicity as indicated before. Similar result is found with the asymptotic expansions of  $L_i(r)$ . Whenever  $w_1 = 0$ , Eq. (65) has two solutions,

$$t_{\pm} = \pm \sqrt{-\frac{\Omega_2}{\Omega_1}} = \pm p, \quad (75)$$

so that Eq. (70) becomes the asymptotic expansion of  $I_0$  (with  $t = p$ ) or  $K_0$  (with  $t = -p$ ).

We believe that because of the interesting properties of the  $L_i(r)$  functions and their strong connection with the Bessel functions they can be understood as a generalization to the fourth-order differential equation. Therefore, we give them the name *hyper-Bessel functions*. In analogy,  $L_1, L_2, L_3$  functions are hyper-Bessel functions of the first kind and  $L_4$  is the hyper-Bessel function of the second kind.

#### IV. SOLUTION OF THE INHOMOGENEOUS DIFFERENTIAL EQUATION

The next step in our derivation is to use the properties of the functions introduced in Sec. III to obtain solution of the inhomogeneous differential equation (36). In this work we decided to use the method based on the Wronskian determinants. Starting with the general solution of the homogeneous equation:

$$f_H(r) = c_1 L_1(r) + c_2 L_2(r) + c_3 L_3(r) + c_4 L_4(r), \quad (76)$$

we make coefficients  $c_i$  explicit functions of  $r, y_i(r)$ , and require the combination

$$\begin{aligned} f(r) = & y_1(r)L_1(r) + y_2(r)L_2(r) \\ & + y_3(r)L_3(r) + y_4(r)L_4(r), \end{aligned} \quad (77)$$

to satisfy the inhomogeneous geminal equation (36). Differentiation of the above equation leads to

$$\begin{aligned} f'(r) = & [y_1(r)L_1'(r) + y_2(r)L_2'(r) \\ & + y_3(r)L_3'(r) + y_4(r)L_4'(r)] \\ & + [y_1'(r)L_1(r) + y_2'(r)L_2(r) \\ & + y_3'(r)L_3(r) + y_4'(r)L_4(r)]. \end{aligned} \quad (78)$$



The requirement that the second expression vanishes identically for all  $r$ ,

$$0 \equiv y_1'(r)L_1(r) + y_2'(r)L_2(r) + y_3'(r)L_3(r) + y_4'(r)L_4(r), \quad (79)$$

enables us bring the first derivative into the form

$$f'(r) = y_1(r)L_1'(r) + y_2(r)L_2'(r) + y_3(r)L_3'(r) + y_4(r)L_4'(r). \quad (80)$$

Similarly, higher-order derivatives are found to be

$$f''(r) = y_1(r)L_1''(r) + y_2(r)L_2''(r) + y_3(r)L_3''(r) + y_4(r)L_4''(r), \quad (81)$$

$$f^{(3)}(r) = y_1(r)L_1^{(3)}(r) + y_2(r)L_2^{(3)}(r) + y_3(r)L_3^{(3)}(r) + y_4(r)L_4^{(3)}(r), \quad (82)$$

$$f^{(4)}(r) = [y_1(r)L_1^{(4)}(r) + y_2(r)L_2^{(4)}(r) + y_3(r)L_3^{(4)}(r) + y_4(r)L_4^{(4)}(r)] + [y_1'(r)L_1^{(3)}(r) + y_2'(r)L_2^{(3)}(r) + y_3'(r)L_3^{(3)}(r) + y_4'(r)L_4^{(3)}(r)], \quad (83)$$

where additional constraints on  $y_i(r)$  were imposed

$$y_1'(r)L_1'(r) + y_2'(r)L_2'(r) + y_3'(r)L_3'(r) + y_4'(r)L_4'(r) \equiv 0, \quad (84)$$

$$y_1'(r)L_1''(r) + y_2'(r)L_2''(r) + y_3'(r)L_3''(r) + y_4'(r)L_4''(r) \equiv 0. \quad (85)$$

By inserting Eqs. (81), (82), and (83) into the differential equation and noting that the functions  $L_i(r)$  satisfy the homogeneous differential equation, one arrives at

$$U(r) = w_1^2 r [y_1'(r)L_1^{(3)}(r) + y_2'(r)L_2^{(3)}(r) + y_3'(r)L_3^{(3)}(r) + y_4'(r)L_4^{(3)}(r)]. \quad (86)$$

$$+ y_3'(r)L_3^{(3)}(r) + y_4'(r)L_4^{(3)}(r)]. \quad (87)$$

The above equation together with Eqs. (79), (84), and (85) specify the four-dimensional system of linear equations

$$\begin{bmatrix} L_1^{(3)}(r) & L_2^{(3)}(r) & L_3^{(3)}(r) & L_4^{(3)}(r) \\ L_1''(r) & L_2''(r) & L_3''(r) & L_4''(r) \\ L_1'(r) & L_2'(r) & L_3'(r) & L_4'(r) \\ L_1(r) & L_2(r) & L_3(r) & L_4(r) \end{bmatrix} \begin{bmatrix} y_1'(r) \\ y_2'(r) \\ y_3'(r) \\ y_4'(r) \end{bmatrix} = \begin{bmatrix} \frac{U(r)}{w_1^2 r} \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad (88)$$

which can easily be solved symbolically for  $y_i'(r)$  by using the Cramer's rule. The result reads

$$y_1'(r) = \frac{U(r) W_1(r)}{w_1^2 r W(r)}, \quad (89)$$

where  $W(r)$  is the Wronskian determinant of the functions  $L_1(r), L_2(r), L_3(r), L_4(r)$ ,

$$W(r) = \begin{vmatrix} L_1^{(3)}(r) & L_2^{(3)}(r) & L_3^{(3)}(r) & L_4^{(3)}(r) \\ L_1''(r) & L_2''(r) & L_3''(r) & L_4''(r) \\ L_1'(r) & L_2'(r) & L_3'(r) & L_4'(r) \\ L_1(r) & L_2(r) & L_3(r) & L_4(r) \end{vmatrix}, \quad (90)$$

and  $W_k(r)$  are the same as  $W(r)$  apart from the fact that the  $k$ th column was replaced by the unit vector  $[1, 0, 0, 0]$ , for example:

$$W_1(r) = \begin{vmatrix} 1 & L_2^{(3)}(r) & L_3^{(3)}(r) & L_4^{(3)}(r) \\ 0 & L_2''(r) & L_3''(r) & L_4''(r) \\ 0 & L_2'(r) & L_3'(r) & L_4'(r) \\ 0 & L_2(r) & L_3(r) & L_4(r) \end{vmatrix} = \begin{vmatrix} L_2''(r) & L_3''(r) & L_4''(r) \\ L_2'(r) & L_3'(r) & L_4'(r) \\ L_2(r) & L_3(r) & L_4(r) \end{vmatrix}. \quad (91)$$

Some degree of suspicion may be connected with the fact that the Wronskian appears in the denominator. However, since the functions  $L_1(r), L_2(r), L_3(r)$ , and  $L_4(r)$  span the space of solutions of the homogeneous differential equation they cannot be linearly dependent and thus  $W(r)$  cannot vanish identically. Equation (89) can now formally be integrated,

$$y_1(r) = \int dr \frac{U(r) W_1(r)}{w_1^2 r W(r)}, \quad (92)$$

so that the solution of the inhomogeneous differential equation is

$$f(r) = \sum_{i=1}^4 L_i(r) \int dr \frac{U(r) W_i(r)}{w_1^2 r W(r)}, \quad (93)$$

where the initial conditions have not been imposed yet. At this point we observe that the solution is rather complicated because of the presence of five determinants, including the Wronskian itself, which is the most cumbersome in the calculations. Therefore, it will be advantageous to introduce some simplifications in the above formula. It turns out that the appearance of the Wronskian can be eliminated altogether by using the so-called Abel's identity, which states that for any  $n$ th-order homogeneous differential equation of the form

$$y^{(n)}(x) + p_{n-1}(x)y^{(n-1)}(x) + \dots + p_0(x)y(x) = 0, \quad (94)$$

the Wronskian constructed from  $n$  linearly independent solutions can be expressed as

$$W(x) = W(x_0) \exp\left(-\int_{x_0}^x dx' p_{n-1}(x')\right), \quad (95)$$

provided that  $p_{n-1}(x)$  is continuous on the interval  $[x_0, x]$ . In the case of the geminal differential equation  $p_{n-1}(r) = \frac{2}{r}$  (continuous on  $0 < r \leq \infty$ ), so that integration can easily be carried out and the Abel's identity is

$$W(r) = W(r_0) \left(\frac{r_0}{r}\right)^2. \quad (96)$$

We need to specify the point  $r_0$ . Our choice  $r_0 = 1$  is motivated by the fact that the above equation takes a very simple form and that  $r_0 = 1$  is sufficiently close to  $r = 0$  at which series expansions of  $L_i(r)$  are provided. It allows a robust calculation of  $W(1)$  for any values of the nonlinear parameters. By inserting the identity

$$W(r) = W(1) \frac{1}{r^2}, \quad (97)$$

into the solution (93) considerable simplifications occur:

$$f(r) = \sum_{i=1}^4 \frac{L_i(r)}{w_1^2 W(1)} \int dr r U(r) W_i(r). \quad (98)$$

Despite considerable effort we did not manage to simplify this equation further, at least in the general case. Such a simplification will occur for a special case considered in the next subsection.

Finally, we have to impose four initial conditions on the above solution to make it consistent with the definition of the master integral. The first three initial conditions are natural:

$$f(0) = 0, \quad \lim_{r \rightarrow \infty} f(r) = 0, \quad \lim_{r \rightarrow \infty} f'(r) = 0. \quad (99)$$

The fourth initial condition is somehow more complicated, but we see that whenever  $r \rightarrow 0$  then  $r_{1B} \rightarrow r_{1A} = r_1$ , etc., so that in the  $r = 0$  limit the derivative of the master integral becomes the well-known integral:

$$f'(0) = \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-(u_3+u_2)r_1}}{r_1^2} \frac{e^{-(w_2+w_3)r_2}}{r_2^2} \frac{e^{-w_1 r_{12}}}{r_{12}}. \quad (100)$$

Analytical formula for this integral is well known (cf. Eq. (34) of Ref. [123]). After the four initial conditions are imposed the master integral becomes

$$\begin{aligned} f(r) = & \frac{L_1(r)}{w_1^2 W(1)} \int_0^r dr' r' U(r') W_1(r') \\ & - \frac{L_2(r)}{w_1^2 W(1)} \int_r^\infty dr' r' U(r') W_2(r') \\ & - \frac{L_3(r)}{w_1^2 W(1)} \int_r^\infty dr' r' U(r') W_3(r') \\ & + \frac{L_4(r)}{w_1^2 W(1)} \int_0^r dr' r' U(r') W_4(r'). \end{aligned} \quad (101)$$

One can check that the above formula satisfies the initial conditions (99) and (100) and therefore is the solution of the inhomogeneous differential geminal equation. In the further derivation we also need the values of  $f'(r)$ ,  $f''(r)$ , and  $f^{(3)}(r)$ . Higher-order derivatives can be obtained recursively by differentiation of Eq. (36):

$$\begin{aligned} f^{(n+4)}(r) = & \frac{U^{(n)}(r)}{r w_1^2} - \frac{n+2}{r} f^{(n+3)}(r) - \frac{\Omega_1}{w_1^2} f^{(n+2)}(r) \\ & - \frac{\Omega_1(n+1)}{r w_1^2} f^{(n+1)}(r) - \frac{\Omega_2}{w_1^2} f^{(n)}(r) - \frac{\Omega_2 n}{r w_1^2} f^{(n-1)}(r). \end{aligned} \quad (102)$$

The first derivative of the master integral with respect to  $r$  is obtained directly from the representation (101):

$$\begin{aligned} f'(r) = & \frac{L_1'(r)}{w_1^2 W(1)} \int_0^r dr' r' U(r') W_1(r') \\ & - \frac{L_2'(r)}{w_1^2 W(1)} \int_r^\infty dr' r' U(r') W_2(r') \\ & - \frac{L_3'(r)}{w_1^2 W(1)} \int_r^\infty dr' r' U(r') W_3(r') \end{aligned}$$

$$\begin{aligned} & + \frac{L_4'(r)}{w_1^2 W(1)} \int_0^r dr' r' U(r') W_4(r') \\ & + \sum_{i=1}^4 \frac{L_i(r)}{w_1^2 W(1)} r U(r) W_i(r). \end{aligned} \quad (103)$$

The nonintegral term is equal to

$$\sum_{i=1}^4 \frac{L_i(r)}{w_1^2 W(1)} r U(r) W_i(r) = \sum_{i=1}^4 L_i(r) y_i'(r), \quad (104)$$

so it vanishes identically on the basis of the initial assumption (79). The first derivative of  $f(r)$  becomes

$$\begin{aligned} f'(r) = & \frac{L_1'(r)}{w_1^2 W(1)} \int_0^r dr' r' U(r') W_1(r') \\ & - \frac{L_2'(r)}{w_1^2 W(1)} \int_r^\infty dr' r' U(r') W_2(r') \\ & - \frac{L_3'(r)}{w_1^2 W(1)} \int_r^\infty dr' r' U(r') W_3(r') \\ & + \frac{L_4'(r)}{w_1^2 W(1)} \int_0^r dr' r' U(r') W_4(r'). \end{aligned} \quad (105)$$

Similarly, using the conditions (84) and (85), explicit formulas for  $f''(r)$  and  $f^{(3)}(r)$  are obtained:

$$\begin{aligned} f''(r) = & \frac{L_1''(r)}{w_1^2 W(1)} \int_0^r dr' r' U(r') W_1(r') \\ & - \frac{L_2''(r)}{w_1^2 W(1)} \int_r^\infty dr' r' U(r') W_2(r') \\ & - \frac{L_3''(r)}{w_1^2 W(1)} \int_r^\infty dr' r' U(r') W_3(r') \\ & + \frac{L_4''(r)}{w_1^2 W(1)} \int_0^r dr' r' U(r') W_4(r'), \end{aligned} \quad (106)$$

$$\begin{aligned} f^{(3)}(r) = & \frac{L_1^{(3)}(r)}{w_1^2 W(1)} \int_0^r dr' r' U(r') W_1(r') \\ & - \frac{L_2^{(3)}(r)}{w_1^2 W(1)} \int_r^\infty dr' r' U(r') W_2(r') \\ & - \frac{L_3^{(3)}(r)}{w_1^2 W(1)} \int_r^\infty dr' r' U(r') W_3(r') \\ & + \frac{L_4^{(3)}(r)}{w_1^2 W(1)} \int_0^r dr' r' U(r') W_4(r'), \end{aligned} \quad (107)$$

so that values of the latter three quantities can be calculated with an insignificant additional cost once the numerical integration of the integrals appearing in  $f(r)$  is done.

## V. RECURSION RELATIONS FOR THE POWERS OF $r_{1A}, r_{1B}, r_{2A}, r_{2B}$

With the analytical expression for the master integral at hand, we turn to the calculation of the integrals with arbitrary powers of  $r_{1A}, r_{1B}, r_{2A}, r_{2B}$ . They are obtained by differentiation of the master integral with respect to the nonlinear parameters. Explicit differentiation of Eq. (55) is cumbersome and connected with painful and expensive numerical integrations. Therefore, to start the recursion relations,

we must establish an equation that connects the value of the derivative of the master integral with respect to, say,  $w_3$ , to the master integral and optionally its derivatives with respect to  $r$ . The latter quantities can be computed by using the theory presented in the previous section.

The desired recursion relation can be derived from two differential equations in the momentum space. The first was already derived in the Sec. II B,

$$\sigma \frac{\partial g}{\partial u_1} + \frac{1}{2} \frac{\partial \sigma}{\partial u_1} g(u_1) + P(u_1, w_1; u_3, w_3; w_2, u_2) = 0, \quad (108)$$

and the second is obtained by the proper exchange of the nonlinear parameters, making use of the fact that both  $g$  and  $\sigma$  are invariant under the latter operations:

$$\sigma \frac{\partial g}{\partial w_3} + \frac{1}{2} \frac{\partial \sigma}{\partial w_3} g(u_1) + P(w_3, u_3; w_2, u_2; w_1, u_1) = 0. \quad (109)$$

By taking the inverse Laplace transform of both equations one obtains

$$-w_1^2 r f^{(4)}(r) - 2w_1^2 f^{(3)}(r) - \Omega_1 r f''(r) - \Omega_1 f'(r) - \Omega_2 r f(r) + U(r; w_1, u_2, u_3, w_2, w_3) = 0, \quad (110)$$

$$w_1^2 \frac{\partial f^{(4)}}{\partial w_3} + \Omega_1 \frac{\partial f''}{\partial w_3} + \Omega_2 \frac{\partial f}{\partial w_3} + \frac{1}{2} \frac{\partial \Omega_1}{\partial w_3} f''(r) + \frac{1}{2} \frac{\partial \Omega_2}{\partial w_3} f(r) + V(r; w_1, u_2, u_3, w_2, w_3) = 0, \quad (111)$$

and by differentiation of the first equation with respect to  $w_3$  one obtains a pair,

$$\begin{aligned} E_1 &\equiv -w_1^2 r \frac{\partial f^{(4)}}{\partial w_3} - 2w_1^2 \frac{\partial f^{(3)}}{\partial w_3}(r) \\ &\quad - \frac{\partial \Omega_1}{\partial w_3} r f''(r) - \Omega_1 r \frac{\partial f''}{\partial w_3} - \frac{\partial \Omega_1}{\partial w_3} f'(r) - \Omega_1 \frac{\partial f'}{\partial w_3} \\ &\quad - \frac{\partial \Omega_2}{\partial w_3} r f(r) - \Omega_2 r \frac{\partial f}{\partial w_3} + \frac{\partial U(r)}{\partial w_3} = 0, \\ E_2 &\equiv w_1^2 \frac{\partial f^{(4)}}{\partial w_3} + \Omega_1 \frac{\partial f''}{\partial w_3} + \Omega_2 \frac{\partial f}{\partial w_3} + \frac{1}{2} \frac{\partial \Omega_1}{\partial w_3} f''(r) \\ &\quad + \frac{1}{2} \frac{\partial \Omega_2}{\partial w_3} f(r) + V(r) = 0, \end{aligned} \quad (112)$$

where the notation for the nonlinear parameters in  $U$  and  $V$  was suppressed for brevity. These two equations provide a starting point to establish an explicit recursion relation. However, its derivation is still a nontrivial task since  $E_1, E_2$ , apart from the desired term  $\frac{\partial f}{\partial w_3}$ , consist of the derivatives of the latter with respect to  $r$  up to the fourth order. Our approach was based on the following three additional identities that are defined as

$$E_3 = \frac{\partial}{\partial r} (E_1 + r E_2), \quad (113)$$

$$E_4 = \frac{\partial}{\partial r} (r E_3 - 2 E_1), \quad (114)$$

$$E_5 = \frac{\partial}{\partial r} (E_4 - 4 E_2). \quad (115)$$

The reason for making the combinations above is as follows. At each step we cancel out the fourth-order derivative of  $\frac{\partial f}{\partial w_3}$  with respect to  $r$  and then create it back by doing a differentiation

with respect to  $r$ . By repeating this procedure three times we figure out that the Eq. (113) is a set of equations with five unknown quantities,

$$\frac{\partial f}{\partial w_3}, \frac{\partial f'}{\partial w_3}, \frac{\partial f''}{\partial w_3}, \frac{\partial f^{(3)}}{\partial w_3}, \frac{\partial f^{(4)}}{\partial w_3},$$

so it can be solved analytically. The differentiation performed at each step guarantees that  $E_i, i = 1, 5$ , are linearly independent as long as none of the coefficients multiplying the unknown quantities in the initial equations for  $E_1$  and  $E_2$  vanishes. Higher-order derivatives of  $\frac{\partial f}{\partial w_3}$  over  $r$  do not appear. The final result is

$$\begin{aligned} \frac{\partial f}{\partial w_3} &= 2w_1^2 \frac{\Omega_2}{D_0} \left\{ 6V(r) + 2rV'(r) + 2 \frac{\partial U'(r)}{\partial w_3} \right. \\ &\quad \left. + \frac{\partial \Omega_2}{\partial w_3} [f(r) + r f'(r)] \right. \\ &\quad \left. - \frac{\partial \Omega_1}{\partial w_3} [f''(r) + r f^{(3)}(r)] \right\} + \frac{\Omega_1^2}{D_0} \left\{ -4V(r) - 2rV'(r) \right. \\ &\quad \left. - 2 \frac{\partial U'(r)}{\partial w_3} + \frac{\partial \Omega_2}{\partial w_3} r f'(r) + \frac{\partial \Omega_1}{\partial w_3} [2f''(r) + r f^{(3)}(r)] \right\} \\ &\quad + w_1^2 \frac{\Omega_1}{D_0} \left\{ -10V''(r) - 2rV^{(3)}(r) - 2 \frac{\partial U^{(3)}(r)}{\partial w_3} \right. \\ &\quad \left. + \frac{\partial \Omega_2}{\partial w_3} [f''(r) + r f^{(3)}(r)] + \frac{\partial \Omega_1}{\partial w_3} [3f^{(4)}(r) + r f^{(5)}(r)] \right\}, \end{aligned} \quad (116)$$

where  $D_0$  is the common denominator:

$$D_0 = 2\Omega_2 (\Omega_1^2 - 4w_1^2 \Omega_2). \quad (117)$$

It is noteworthy that the procedure in which the required set  $E_i, i = 1, 5$ , was obtained is somehow ambiguous. Only the first step of this procedure, formation of  $E_3$ , is unique since there is only one correct method to obtain a useful equation by canceling out the fourth-order derivative of  $\frac{\partial f}{\partial w_3}$ . In the further steps such an elimination can be performed using different equations which were obtained previously and the number of possibilities grows with the number of steps taken. We cannot prove that the particular choice of equations for  $E_i, i = 1, 5$ , which we used here is “the best.” However, in our procedure we tried to minimize the order of the derivatives of functions  $U(r)$  and  $V(r)$  that appeared in the final result. It leads to Eq. (116), which turns out to be regular.

By multiplying both sides of the relation (116) by  $D_0$  and by further differentiation one can calculate arbitrary derivative over the nonlinear parameters, thus advancing the powers of  $r_{1A}, r_{1B}, r_{2A}, r_{2B}$  as much as necessary. The recursion relations for the derivatives over  $w_2, u_3$ , and  $u_2$  that cannot directly be calculated from the above formula are obtained with the use of the symmetry of the master integral. Namely, by permuting  $w_2 \leftrightarrow w_3$  and  $u_2 \leftrightarrow u_3$  (exchange of the nuclei  $A \leftrightarrow B$  in the master integral) and noting that the master integral is invariant with respect to this permutation, analogous recursion relation for  $\frac{\partial f}{\partial w_2}$  is obtained. Similarly, the exchange of  $u_2 \leftrightarrow w_3$  and  $u_3 \leftrightarrow w_2$  (change of the electrons' numbering  $1 \leftrightarrow 2$ ) results in the derivative over  $u_2$ . Finally, the use of both of these permutations gives the derivative over  $u_3$ .

We listed only the formula for  $\frac{\partial f}{\partial w_3}$  despite the fact that by solving the set of equations for  $E_i$ ,  $i = 1, 5$ , its derivatives over  $r$  up to the fourth order are obtained as by-products. From the mathematical point of view equivalent formulas can be derived by differentiating Eq. (116) over  $r$ . Although numerical results obtained in this manner are the same, formulas for higher-order derivatives over  $r$  calculated from the solution of Eqs. (113) are much more transparent. In particular, they do not include higher-order derivatives of the functions  $U(r)$  and  $V(r)$  and of the master integral. Therefore, we list all the missing formulas in Appendix C.

## VI. RECURSION RELATIONS FOR THE POWERS OF $r_{12}$

Since the integrals in the Slater geminal basis considered here already include explicit correlation factor, there is little point in growing powers of  $r_{12}$  in the initial basis set. However, such a possibility is open and we elaborate it in this section. In particular, we derive an analytical equation for the overlap integral over Slater geminals which, despite its simplicity at first glance, has not found analytical solution yet. Our approach is similar to the one presented in the previous section. We establish a relation that connects the value of  $\frac{\partial f}{\partial w_1}$  with the master integral and its derivatives over  $r$ . In the derivation we use the following differential equations for  $g$  in the momentum space:

$$\sigma \frac{\partial g}{\partial u_1} + \frac{1}{2} \frac{\partial \sigma}{\partial u_1} g(u_1) + P(u_1, w_1; u_3, w_3; w_2, u_2) = 0, \quad (118)$$

$$\sigma \frac{\partial g}{\partial w_1} + \frac{1}{2} \frac{\partial \sigma}{\partial w_1} g(u_1) + P(w_1, u_1; w_2, u_2; w_3, u_3) = 0. \quad (119)$$

The first of these equations is differentiated with respect to  $w_1$  and then the inverse Laplace transform is performed to give

$$\begin{aligned} \bar{E}_1 = & -rw_1^2 \frac{\partial f^{(4)}}{\partial w_1} - 2w_1^2 \frac{\partial f^{(3)}}{\partial w_1} - \Omega_1 r \frac{\partial f''}{\partial w_1} \\ & - \Omega_1 \frac{\partial f'}{\partial w_1} - \Omega_2 r \frac{\partial f}{\partial w_1} \\ & - 2rw_1 f^{(4)}(r) - 4w_1 f^{(3)}(r) - r \frac{\partial \Omega_1}{\partial w_1} f''(r) \\ & - \frac{\partial \Omega_1}{\partial w_1} f'(r) - r \frac{\partial \Omega_2}{\partial w_1} f(r) + \frac{\partial U(r)}{\partial w_1} = 0, \quad (120) \end{aligned}$$

$$\begin{aligned} \bar{E}_2 = & w_1^2 \frac{\partial f^{(4)}}{\partial w_1} + \Omega_1 \frac{\partial f''}{\partial w_1} + \Omega_2 \frac{\partial f}{\partial w_1} + w_1 f^{(4)}(r) \\ & + \frac{1}{2} \frac{\partial \Omega_1}{\partial w_1} f''(r) + \frac{1}{2} \frac{\partial \Omega_2}{\partial w_1} f(r) + W(r) = 0. \quad (121) \end{aligned}$$

Using a similar procedure as for the derivatives over  $w_3$  we form a set of equations,

$$\bar{E}_3 = \frac{\partial}{\partial r} (\bar{E}_1 + r\bar{E}_2), \quad (122)$$

$$\bar{E}_4 = \frac{\partial}{\partial r} (\bar{E}_3 + 2\bar{E}_2), \quad (123)$$

$$\bar{E}_5 = \frac{\partial \bar{E}_4}{\partial r}, \quad (124)$$

which are then solved for the following quantities:

$$\frac{\partial f}{\partial w_1}, \frac{\partial f'}{\partial w_1}, \frac{\partial f''}{\partial w_1}, \frac{\partial f^{(3)}}{\partial w_1}, \frac{\partial f^{(4)}}{\partial w_1}.$$

The final equation for  $\frac{\partial f}{\partial w_1}$  is given by

$$\begin{aligned} \frac{\partial f}{\partial w_1} = & -2w_1^2 \frac{\Omega_2}{D_0} \left\{ -6W(r) - 2rW'(r) - 2 \frac{\partial U'(r)}{\partial w_1} - \frac{\partial \Omega_2}{\partial w_1} [f(r) - rf'(r)] \right. \\ & \left. + \frac{\partial \Omega_1}{\partial w_1} [f''(r) + rf^{(3)}(r)] + 6w_1 f^{(4)}(r) + 2w_1 f^{(5)}(r) \right\} \\ & + \frac{\Omega_1^2}{D_0} \left\{ -4W(r) - 2rW'(r) - 2 \frac{\partial U'(r)}{\partial w_1} + \frac{\partial \Omega_2}{\partial w_1} rf'(r) + \frac{\partial \Omega_1}{\partial w_1} [2f''(r) + rf^{(3)}(r)] + 8w_1 f^{(4)}(r) + 2rw_1 f^{(5)}(r) \right\} \\ & + w_1^2 \frac{\Omega_1}{D_0} \left\{ -10W''(r) - 2rW^{(3)}(r) - 2 \frac{\partial U^{(3)}(r)}{\partial w_1} + \frac{\partial \Omega_2}{\partial w_3} [f''(r) + rf^{(3)}(r)] \right. \\ & \left. + \frac{\partial \Omega_1}{\partial w_3} [3f^{(4)}(r) + rf^{(5)}(r)] + 10w_1 f^{(6)}(r) + 2w_1 r f^{(7)}(r) \right\}. \quad (125) \end{aligned}$$

Higher powers of  $r_{12}$  are obtained by further differentiation of the above equation. As before, useful formulas resulting from the solution of the set for  $\bar{E}_i$ ,  $i = 1, 5$ , are listed in Appendix C.

## VII. SPECIAL CASES

In this section we consider four special cases of the integrals corresponding to situations when coefficients  $\Omega_1$  and/or  $\Omega_2$

vanish. From the mathematical point of view the recursion relations for the coefficients  $a_k$  and  $b_k$  remain valid since in their recursive evaluation one never divides by  $\Omega_1$  or  $\Omega_2$ . Therefore, the representation of the master integral given by Eq. (100) is still correct. However, for practical reasons it is useful to consider these two special cases in detail since the solution of the homogeneous differential equation can be expressed in terms of well-known special functions. This makes the implementation of the method much simpler.

### A. Vanishing $\Omega_2$ coefficient

Vanishing  $\Omega_2$  coefficient is probably the most important special case since it occurs for a handful of physically important classes of integrals. This includes an exponentially correlated analog of the symmetric James-Coolidge basis set [24] ( $u_2 = u_3 = w_2 = w_3 = x$ ) and symmetric exchange integrals over atomic orbitals ( $u_3 = w_2 = x$ ,  $u_2 = w_3 = y$ ). Singularities also appear whenever

$$w_1^2 = (u_2^2 w_2^2 - u_3^2 w_3^2) \left( \frac{1}{u_2^2 - w_3^2} - \frac{1}{u_3^2 - w_2^2} \right). \quad (126)$$

Moreover, the recursion relations established in the previous sections are not valid in this case since  $\Omega_2$  appears in the denominator in the key formulas.

In this special case the geminal differential equation takes the form

$$w_1^2 r f^{(4)}(r) + 2w_1^2 f^{(3)}(r) + \Omega_1 r f''(r) + \Omega_1 f'(r) = U(r), \quad (127)$$

so that the homogeneous equation is

$$w_1^2 r f_H^{(4)}(r) + 2w_1^2 f_H^{(3)}(r) + \Omega_1 r f_H''(r) + \Omega_1 f_H'(r) = 0. \quad (128)$$

The simplest way to obtain the solution of the latter equation is to use the recursion relations for the coefficients in the series expansions that were derived for the general case [Eqs. (57), (58), (61), and (62)]. By setting  $\Omega_2 = 0$  they become

$$w_1^2 (k+2)^2 (k+3) a_{k+3} + \Omega_1 (k+1) a_{k+1} = 0 \quad \text{for } k \geq 1, \quad (129)$$

$$12w_1^2 a_3 + \Omega_1 a_1 = 0. \quad (130)$$

As before, there are three initial parameters that can freely be chosen,  $a_0, a_1, a_2$ . Let us make the same choice as in Eq. (59):

$$\begin{aligned} \tilde{L}_1(r) & \text{ with } a_0 = 1, a_1 = 0, a_2 = 0, \\ \tilde{L}_2(r) & \text{ with } a_0 = 0, a_1 = 1, a_2 = 0, \\ \tilde{L}_3(r) & \text{ with } a_0 = 0, a_1 = 0, a_2 = 1. \end{aligned} \quad (131)$$

The solutions of Eq. (128) are denoted by tildes to distinguish them from the solutions in the general case. The resulting functions can be expressed in terms of the generalized hypergeometric function ( ${}_pF_q[a_1, \dots, a_p; b_1, \dots, b_q; z]$ ) and some elementary functions:

$$\tilde{L}_1(r) = 1, \quad (132)$$

$$\tilde{L}_2(r) = r {}_1F_2 \left[ \frac{1}{2}; 1, \frac{3}{2}; -\frac{\Omega_1}{w_1^2} r^2 \right], \quad (133)$$

$$\tilde{L}_3(r) = r^2 {}_2F_3 \left[ 1, 1; \frac{3}{2}, \frac{3}{2}, 2; -\frac{\Omega_1}{w_1^2} r^2 \right]. \quad (134)$$

The recursion relation for the coefficients  $b_k$  becomes

$$2\Omega_1 a_1 + 28w_1^2 a_3 + \Omega_1 b_1 + 12w_1^2 b_3 = 0, \quad (135)$$

$$2k\Omega_1 a_k + 2(k+1)(2k^2 + 4k + 1)w_1^2 a_{k+2} + k^2 \Omega_1 b_k + w_1^2 k(k+1)^2 (k+2) b_{k+2} = 0. \quad (136)$$

At this point it is very useful to depart slightly from the previous approach and choose a little less obvious initial conditions for the series  $b_k$ :

$$b_0 = 0, \quad b_1 = \frac{4}{\pi} \left[ \ln \left( \frac{\sqrt{\Omega_1}}{2w_1} \right) + \gamma - 1 \right], \quad b_2 = 0. \quad (137)$$

With this choice the function  $L_4(r)$  takes a very appealing form:

$$\tilde{L}_4(r) = \pi r \left[ Y_0 \left( \frac{\sqrt{\Omega_1}}{w_1} r \right) H_{-1} \left( \frac{\sqrt{\Omega_1}}{w_1} r \right) \right. \quad (138)$$

$$\left. + Y_1 \left( \frac{\sqrt{\Omega_1}}{w_1} r \right) H_0 \left( \frac{\sqrt{\Omega_1}}{w_1} r \right) \right], \quad (139)$$

where  $Y_\alpha$  is the Bessel function of the second kind and  $H_\alpha$  is the Struve function, both of the order  $\alpha$ . This completes the solution of Eq. (128). In this particular case we found a closed expression for  $f_H(r)$  in terms of the known special functions, so that the implementation and numerical realization become significantly simpler. Since the initial conditions for  $f(r)$  in this special case are the same as in the general case, the solution of (127) takes the form

$$\begin{aligned} f(r) = & \frac{\tilde{L}_1(r)}{w_1^2 \tilde{W}(1)} \int_0^r dr' r' U(r') \tilde{W}_1(r') \\ & - \frac{\tilde{L}_2(r)}{w_1^2 \tilde{W}(1)} \int_r^\infty dr' r' U(r') \tilde{W}_2(r') \\ & - \frac{\tilde{L}_3(r)}{w_1^2 \tilde{W}(1)} \int_r^\infty dr' r' U(r') \tilde{W}_3(r') \\ & + \frac{\tilde{L}_4(r)}{w_1^2 \tilde{W}(1)} \int_0^r dr' r' U(r') \tilde{W}_4(r'), \end{aligned} \quad (140)$$

and the formulas for the derivatives are analogous to Eqs. (105)–(107).

Whenever the  $\Omega_2$  coefficient vanishes, the recursion relations established in the previous sections are no longer correct. Equations for  $E_i$ ,  $i = 1, 5$ , become a system of linear equations with a singular coefficients matrix. To give an example of how to circumvent this problem, let us derive an analytical equation for  $\frac{\partial f}{\partial w_3}$ . In this special case  $E_1$  and  $E_2$  are

$$\begin{aligned} E_1 = & -w_1^2 r \frac{\partial f^{(4)}}{\partial w_3} - 2w_1^2 \frac{\partial f^{(3)}}{\partial w_3}(r) - \frac{\partial \Omega_1}{\partial w_3} r f''(r) \\ & - \Omega_1 r \frac{\partial f''}{\partial w_3} - \frac{\partial \Omega_1}{\partial w_3} f'(r) - \Omega_1 \frac{\partial f'}{\partial w_3} - \frac{\partial \Omega_2}{\partial w_3} r f(r) \\ & + \frac{\partial U(r)}{\partial w_3} = 0, \end{aligned} \quad (141)$$

$$\begin{aligned} E_2 = & w_1^2 \frac{\partial f^{(4)}}{\partial w_3} + \Omega_1 \frac{\partial f''}{\partial w_3} + \frac{1}{2} \frac{\partial \Omega_1}{\partial w_3} f''(r) \\ & + \frac{1}{2} \frac{\partial \Omega_2}{\partial w_3} f(r) + V(r) = 0. \end{aligned} \quad (142)$$

We form the combinations

$$E_3 = \frac{\partial}{\partial r} (E_1 + r E_2), \quad (143)$$

$$E_4 = \frac{\partial}{\partial r} (r E_3 - 2 E_1), \quad (144)$$

and solve Eqs. (141)–(144) for  $\frac{\partial f'}{\partial w_3}$  instead of  $\frac{\partial f}{\partial w_3}$ . The result is

$$\begin{aligned} \frac{\partial f'}{\partial w_3} = & -\frac{1}{2\Omega_1} \left\{ -2rV(r) - 2\frac{\partial U(r)}{\partial w_3} + \frac{\partial \Omega_2}{\partial w_3} r f(r) \right. \\ & + \frac{\partial \Omega_1}{\partial w_3} [2f'(r) + r f''(r)] \left. \right\} - \frac{w_1^2}{\Omega_1^2} \left\{ -8V'(r) - 2rV''(r) \right. \\ & \left. - 2\frac{\partial U''(r)}{\partial w_3} + \frac{\partial \Omega_2}{\partial w_3} r f''(r) + \frac{\partial \Omega_1}{\partial w_3} [2f^{(3)}(r) + r f^{(4)}(r)] \right\}. \end{aligned} \quad (145)$$

This result needs now to be formally integrated over  $r$ . The resulting integrals can be expanded as

$$[r f(r)]^{(-1)} = r f^{(-1)}(r) - f^{(-2)}(r), \quad (146)$$

where the superscript  $(-I)$  was introduced to denote the  $I$ -fold integration over  $r$  with the boundary condition  $f^{(-I)}(\infty) = 0$  (the so-called antidifferentiation). The integrals of  $f(r)$  over  $r$  can be obtained by the consecutive integration of Eq. (127):

$$f^{(-1)}(r) = \frac{1}{\Omega_1} [w_1^2 r f''(r) + \Omega_1 r f'(r) - U^{(-2)}(r)]. \quad (147)$$

The result becomes

$$\begin{aligned} \frac{\partial f}{\partial w_3} = & -\frac{1}{2\Omega_1} \left\{ -2rV^{(-1)}(r) + 2V^{(-2)}(r) - 2\frac{\partial U^{(-1)}(r)}{\partial w_3} + \frac{\partial \Omega_2}{\partial w_3} [r f^{(-1)}(r) - f^{(-2)}(r)] + \frac{\partial \Omega_1}{\partial w_3} [f(r) + r f'(r)] \right\} \\ & - \frac{w_1^2}{\Omega_1^2} \left\{ -8V(r) - 2rV'(r) + 2V(r) - 2\frac{\partial U'(r)}{\partial w_3} + \frac{\partial \Omega_2}{\partial w_3} [r f'(r) - f(r)] + \frac{\partial \Omega_1}{\partial w_3} [f''(r) + r f^{(3)}(r)] \right\}. \end{aligned} \quad (148)$$

Antiderivatives of the functions  $U(r)$  and  $V(r)$  can all be obtained in an analytical way. For example, in the special case  $u_2 = u_3 = w_2 = w_3 = x$  mentioned earlier they are

$$\begin{aligned} \frac{\partial U^{(-1)}(r)}{\partial w_3} = & \frac{w_1 e^{-r(w_1+2x)}}{8(w_1+2x)} \{ -4r w_1 e^{r w_1} (w_1+2x) [2\text{Ei}(-r w_1) - e^{4rx} \text{Ei}(-4rx) - \ln(4r)] \\ & + 2\ln(w_1+2x) - 2\ln(w_1) - \ln(x) \} + 4e^{r w_1} [\gamma r w_1 (w_1+2x) - 4x] + 8(w_1+2x), \end{aligned} \quad (149)$$

$$\begin{aligned} V^{(-1)}(r) = & \frac{w_1 e^{-r(2x+w_1)}}{2r^2(2x+w_1)} \left\{ -r^2 w_1 e^{r w_1} [e^{4rx} (2x+w_1) \text{Ei}(-4rx) - 2(2x+w_1) \text{Ei}(-r w_1) + w_1 \ln(4rx) + 2x \ln(rx) + x \ln(16)] \right. \\ & \left. + e^{r w_1} \left[ -\gamma r^2 w_1 (2x+w_1) + 4r^2 w_1 (2x+w_1) \tanh^{-1} \left( \frac{x}{x+w_1} \right) + 4rx + 2 \right] - 2[r(2x+w_1) + 1] \right\}, \end{aligned} \quad (150)$$

$$\begin{aligned} V^{(-2)}(r) = & \frac{w_1 e^{-r(4x+w_1)}}{4rx(2x+w_1)} \left\{ e^{r(2x+w_1)} \left[ -r w_1^2 e^{4rx} \text{Ei}(-4rx) + 2r w_1^2 e^{2rx} \text{Ei}[-r(2x+w_1)] \right. \right. \\ & \left. - 2rx w_1 e^{4rx} \text{Ei}(-4rx) + 4rx w_1 e^{2rx} \text{Ei}[-r(2x+w_1)] + r w_1^2 \ln(4rx) + \gamma r w_1 (2x+w_1) \right] \\ & \left. + e^{r(2x+w_1)} \left[ 2rx w_1 \ln(rx) + rx w_1 \ln(16) - 4r w_1 (2x+w_1) \tanh^{-1} \left( \frac{x}{x+w_1} \right) - 4x \right] \right. \\ & \left. - 2r w_1 (2x+w_1) \text{Ei}(-r w_1) e^{r(2x+w_1)} + 4x e^{2rx} \right\}. \end{aligned} \quad (151)$$

In a similar way higher-order derivatives over the nonlinear parameters can be calculated. One needs to use the expressions for  $E_1$  and  $E_2$  differentiated the desired number of times over  $u_2, u_3, w_2, w_3$  as a starting point and form the same combinations as in the above example.

### B. Vanishing $\Omega_1$ coefficient

Vanishing  $\Omega_1$  is a by far less troublesome special case than the one considered in the previous section. Conditions under which  $\Omega_1$  vanishes are found by recasting it into a particular form,

$$\Omega_1 = w_1^4 - w_1^2(u_2^2 + u_3^2 + w_2^2 + w_3^2) + (u_2^2 - u_3^2)(w_3^2 - w_2^2), \quad (152)$$

so we may solve  $\Omega_1 = 0$  against  $w_1^2$ . The result is trivially found to be  $w_1^2 = \frac{1}{2}(u_2^2 + u_3^2 + w_2^2 + w_3^2 \pm \sqrt{\Delta})$ , with  $\Delta = (u_2^2 + u_3^2 + w_2^2 + w_3^2)^2 - 4(u_2^2 - u_3^2)(w_3^2 - w_2^2)$ , and we see that  $\Omega_1$  vanishes after some coincidental choice of the nonlinear parameters defined by the above equation rather than for some particular class of the integrals. In this special case the homogeneous differential equation takes the form

$$w_1^2 r f_H^{(4)}(r) + 2w_1^2 f_H^{(3)}(r) + \Omega_2 r f_H(r) = 0. \quad (153)$$

This equation can be solved by using the recursion relations for the coefficients in the series expansions derived in the general case, by setting  $\Omega_1 = 0$  and recognizing the resulting series in terms of the well-known special functions. Since we have

already presented a detailed example of such a procedure, here we only list the final equations in a convenient form. The solutions of Eq. (153) are denoted by double-tilde to distinguish them from the previous ones:

$$\tilde{\tilde{L}}_1(r) = {}_0F_3 \left[ \frac{1}{2}, \frac{3}{4}, \frac{3}{4}; -\frac{\Omega_2}{256w_1^2}r^4 \right], \quad (154)$$

$$\tilde{\tilde{L}}_2(r) = r {}_0F_3 \left[ \frac{3}{4}, 1, \frac{5}{4}; -\frac{\Omega_2}{256w_1^2}r^4 \right], \quad (155)$$

$$\tilde{\tilde{L}}_3(r) = r^2 {}_0F_3 \left[ \frac{5}{4}, \frac{5}{4}, \frac{3}{2}; -\frac{\Omega_2}{256w_1^2}r^4 \right], \quad (156)$$

$$\tilde{\tilde{L}}_4(r) = G_{04}^{20} \left( -\frac{\Omega_2}{256w_1^2}r^4 \middle| \frac{0}{\frac{1}{4}, \frac{1}{4}, 0, \frac{1}{2}} \right), \quad (157)$$

where  $G_{pq}^{mn}(z | \begin{smallmatrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{smallmatrix})$  is the Meijer  $G$  function. The solution of the inhomogeneous equation can now formally be written as

$$\begin{aligned} f(r) = & \frac{\tilde{\tilde{L}}_1(r)}{w_1^2 \tilde{\tilde{W}}(1)} \int_0^r dr' r' U(r') \tilde{\tilde{W}}_1(r') \\ & - \frac{\tilde{\tilde{L}}_2(r)}{w_1^2 \tilde{\tilde{W}}(1)} \int_r^\infty dr' r' U(r') \tilde{\tilde{W}}_2(r') \\ & - \frac{\tilde{\tilde{L}}_3(r)}{w_1^2 \tilde{\tilde{W}}(1)} \int_r^\infty dr' r' U(r') \tilde{\tilde{W}}_3(r') \\ & + \frac{\tilde{\tilde{L}}_4(r)}{w_1^2 \tilde{\tilde{W}}(1)} \int_0^r dr' r' U(r') \tilde{\tilde{W}}_4(r'), \quad (158) \end{aligned}$$

with the definitions of  $\tilde{\tilde{W}}(r)$  and  $\tilde{\tilde{W}}_i(r)$  analogous to Eqs. (90) and (91), respectively.

Since the recursion relations derived in the general case remain valid for  $\Omega_1 = 0$  we can rewrite them as they take much simpler form here, for instance,

$$\begin{aligned} \frac{\partial f}{\partial w_3} = & \frac{1}{4\Omega_2} \left\{ 6V(r) + 2rV'(r) + 2\frac{\partial U'(r)}{\partial w_3} \right. \\ & \left. + \frac{\partial \Omega_2}{\partial w_3} [f(r) + rf'(r)] - \frac{\partial \Omega_1}{\partial w_3} [f''(r) + rf^{(3)}(r)] \right\}, \quad (159) \end{aligned}$$

so that higher-order derivatives over the nonlinear parameters are calculated from the recursion relation for the general case by putting  $\Omega_1 = 0$  at the end of each recursive step.

### C. Vanishing $\Omega_1$ and $\Omega_2$ coefficients

The situation where  $\Omega_1 = 0$  and  $\Omega_2 = 0$  is quite rare since the conditions given in the two previous sections that make  $\Omega_1$  and  $\Omega_2$  vanish must mutually be satisfied. This occurs, for example, when  $u_2 = u_3 = w_2 = w_3 = x$  and additionally  $w_1 = 2x$ . The homogeneous differential equation has a disarmingly simple four linearly independent

solutions:

$$\check{L}_1(r) = 1, \quad (160)$$

$$\check{L}_2(r) = r, \quad (161)$$

$$\check{L}_3(r) = r^2, \quad (162)$$

$$\check{L}_4(r) = r \ln(r) - r. \quad (163)$$

The above solutions were denoted by check mark to separate them from the previous ones. The Wronskian  $W(r)$  and the  $W_i(r)$  determinants can be brought into the closed forms

$$\check{W}(r) = -\frac{2}{r^2}, \quad (164)$$

$$\check{W}_1(r) = r, \quad (165)$$

$$\check{W}_2(r) = 2 - 2 \ln(r), \quad (166)$$

$$\check{W}_3(r) = -\frac{1}{r}, \quad (167)$$

$$\check{W}_4(r) = -2, \quad (168)$$

so that the solution of the inhomogeneous differential equation takes the form

$$\begin{aligned} f(r) = & \frac{1}{w_1^2} \left\{ -\frac{1}{2} \int_0^r dr' r'^2 U(r') \right. \\ & + r \int_r^\infty dr' r' U(r') [1 - \ln(r)] - \frac{1}{2} r^2 \int_r^\infty dr' U(r') \\ & \left. + r [\ln(r) - 1] \int_0^r dr' r' U(r') \right\}, \quad (169) \end{aligned}$$

where, for example, in the case  $u_2 = u_3 = w_2 = w_3 = x$ ,  $w_1 = 2x$ :

$$\begin{aligned} U(r) = & \frac{4xe^{-4rx}}{r^2} \{ 2r^2 x^2 e^{2rx} [e^{4rx} \text{Ei}(-4rx) - 2\text{Ei}(-2rx) \\ & + \ln(rx)] + 6rx + e^{2rx} [2rx(\gamma rx - 1) - 1] + 1 \}. \quad (170) \end{aligned}$$

However, even in such a simple case not all of the above integrals can be calculated fully analytically, so we still need to struggle with the numerical integration. A little bit more difficult is the differentiation of the master integral with respect to the nonlinear parameters. For example, the derivative over  $w_3$  is obtained from the special forms of the two identities which were derived in the previous sections:

$$\begin{aligned} \check{E}_1 = & -w_1^2 r \frac{\partial f^{(4)}}{\partial w_3} - 2w_1^2 \frac{\partial f^{(3)}}{\partial w_3}(r) \\ & - \frac{\partial \Omega_1}{\partial w_3} r f''(r) - \frac{\partial \Omega_1}{\partial w_3} f'(r) \\ & - \frac{\partial \Omega_2}{\partial w_3} r f(r) + \frac{\partial U(r)}{\partial w_3} = 0, \quad (171) \end{aligned}$$

$$\begin{aligned} \check{E}_2 = & w_1^2 \frac{\partial f^{(4)}}{\partial w_3} + \frac{1}{2} \frac{\partial \Omega_1}{\partial w_3} f''(r) \\ & + \frac{1}{2} \frac{\partial \Omega_2}{\partial w_3} f(r) + V(r) = 0. \quad (172) \end{aligned}$$

We take the combination  $(\check{E}_1 + r \check{E}_2)$  to cancel out the term  $\frac{\partial f^{(4)}}{\partial w_3}$  and solve the resulting equation against  $\frac{\partial f^{(3)}}{\partial w_3}$ :

$$\frac{\partial f^{(3)}}{\partial w_3} = \frac{1}{2w_1^2} \left[ \frac{\partial U(r)}{\partial w_3} + rV(r) - \frac{\partial \Omega_1}{\partial w_3} f'(r) - \frac{1}{2} \frac{\partial \Omega_1}{\partial w_3} r f''(r) - \frac{1}{2} \frac{\partial \Omega_2}{\partial w_3} r f(r) \right]. \quad (173)$$

This equation needs now to be antidifferentiated three times to give

$$\frac{\partial f}{\partial w_3} = \frac{1}{2w_1^2} \left\{ \frac{\partial U^{(-3)}(r)}{\partial w_3} + rV^{(-3)}(r) - 3V^{(-4)}(r) - \frac{\partial \Omega_1}{\partial w_3} f^{(-2)}(r) - \frac{1}{2} \frac{\partial \Omega_1}{\partial w_3} [r f^{(-1)}(r) - 3f^{(-2)}(r)] - \frac{1}{2} \frac{\partial \Omega_2}{\partial w_3} [r f^{(-3)}(r) - f^{(-4)}(r)] \right\}. \quad (174)$$

The antiderivatives of the master integral are obtained by consecutive antidifferentiation of the expression

$$w_1^2 r f^{(4)}(r) + 2w_1^2 f^{(3)}(r) = U(r),$$

e.g.,  $f^{(-1)}(r) = r f(r) - \frac{U^{(-4)}(r)}{w_1^2}$ . (175)

Higher-order derivatives with respect to the nonlinear parameters are obtained using the same procedure, albeit  $E_1$  and  $E_2$  need to be differentiated an arbitrary number of times with respect to  $u_2, u_3, w_2, w_3$  before putting  $\Omega_1 = 0$  and  $\Omega_2 = 0$ .

**D. Vanishing  $\Omega_1^2 - 4w_1^2\Omega_2$  coefficient**

In the special case  $\Omega_2 = (\frac{\Omega_1}{2w_1})^2$  two pairs of roots of the  $\sigma$  polynomial [Eqs. (25) and (31)], lying on the same side of the complex plane coincide, so that  $\sigma = w_1^2(t^2 + \frac{\Omega_1}{2w_1})^2$ . As a result, the homogeneous differential equation (54) can be brought into the form

$$w_1^2 \hat{A} [r \hat{A} f_H(r)] = 0, \quad (176)$$

where  $\hat{A}$  is a differential operator defined as

$$\hat{A} = \frac{\partial^2}{\partial r^2} - q^2, \quad (177)$$

with  $q^2 = -\frac{\Omega_1}{2w_1}$ . Equation (176) can be solved by decomposing it into a system of two second-order differential equations:

$$w_1^2 \hat{A} [r h(r)] = 0, \quad (178)$$

$$\hat{A} f_H(r) = h(r). \quad (179)$$

The first of these equations has the form  $r h''(r) + 2h'(r) - r q^2 h(r) = 0$ , so that the general solution is

$$h(r) = C_1 \frac{e^{qr}}{r} + C_2 \frac{e^{-qr}}{r}, \quad (180)$$

and Eq. (179) takes the form

$$f_H''(r) - q^2 f_H(r) = C_1 \frac{e^{qr}}{r} + C_2 \frac{e^{-qr}}{r}. \quad (181)$$

The latter equation is solved with elementary methods. Finally we conclude that Eq. (176) has four linearly independent

solutions that can be chosen as

$$e^{-qr}, e^{qr}, e^{-qr} \text{Ei}[2qr] - e^{qr} \ln[2qr],$$

and  $e^{qr} \text{Ei}[-2qr] - e^{-qr} \ln[2qr]$ . (182)

The solution of the inhomogeneous differential equation takes the form analogous to Eq. (101). Similarly, Eqs. (105)–(107) are the derivatives of the master integral with respect to  $r$ .

Since  $D_0 = \Omega_1^2 - 4w_1^2\Omega_2$  appears in the denominator in nearly all recursion relations derived for the general case they become invalid here. However, this problem can be circumvented by using the same trick as in the  $\Omega_2 = 0$  case, namely solving the system of Eqs. (141)–(144) with respect to  $\frac{\partial f'}{\partial w_3}$  and performing consecutive antidifferentiations. Since the derivation is exactly the same as in the Sec. VII A there is little point in repeating it here.

**VIII. NUMERICAL EXAMPLES**

In this section we present results of calculations on the representative set of master integrals with some hand-picked values of the nonlinear parameters. We implemented a general code that is able to calculate the values of the master integral with arbitrarily chosen nonlinear parameters. The code is written in the C programming language and all the calculations were performed in the quadruple arithmetic precision using the GCC Libquadmath library. A handful of the results presented here were additionally checked using an independent program written in MATHEMATICA with the octuple arithmetic precision. Comparison with the results obtained in the extended precision shows that calculations performed in quadruple precision, using 101 points of the Tanh-Sinh quadrature [126,127] for all numerical integrations, gave an accuracy of at least long double precision (around 20 significant digits) and much better on the average.

It is easy to verify that for the calculation of the master integral one can also use a different procedure, based on the series expansion of  $\exp(-w_1 r_{12})$  around  $w_1 = 0$  under the sign of the integral in Eq. (8). Since the latter expansion is uniformly convergent for any positive value of  $w_1$  one can perform term by term integration what leads to the identity

$$f_0(r; w_1) = \sum_{n=0}^{\infty} f_n(r; 0) \frac{(-1)^n w_1^n}{n!}. \quad (183)$$

The above series is convergent for any value of  $w_1$  and gives exactly the same numerical result as Eq. (101). The prescription for how to calculate the integrals with an arbitrary power of  $r_{12}$  but  $w_1 = 0$ ,  $f_n(r; 0)$ , was recently presented by means of the open-ended recursion relation (cf. Eq. (48) of Ref. [44]). Therefore, Eq. (176) is an interesting alternative to the analytical equation derived in the previous section. It is worth considering in detail how fast the above series expansion converges for a given value of  $w_1$  and how many terms are necessary to obtain long double precision which one can easily get by using Eq. (101) throughout. To make such a comparison possible, we implemented the mentioned recursion relation to advance the power of  $r_{12}$  in  $f_n(r; 0)$  as much as necessary in the MATHEMATICA package. However, the first problem encountered was the numerical stability of this recursion. Although the starting values for the recursion were computed in the octuple arithmetic precision, after  $n = 75$  steps only few digits were



TABLE I. Comparison of the values of the master integral with  $u_2 = w_2 = 1$ ,  $u_3 = w_3 = 2$ ,  $w_1 = 1.0$  calculated according to Eqs. (176) and (101). Calculations performed for  $r = 2$ . [k] denotes  $10^k$ .

Expansion length	$f(r)$ value
10	2.385 283 238 131 237 790 81 [−04]
20	2.391 211 576 428 702 083 23 [−04]
30	2.391 211 701 580 610 513 14 [−04]
40	2.391 211 701 582 629 801 40 [−04]
50	2.391 211 701 582 629 832 84 [−04]
60	2.391 211 701 582 629 832 84 [−04]
70	2.391 211 701 582 629 832 84 [−04]
75	2.391 211 701 582 629 832 84 [−04]
Eq. (101)	2.391 211 701 582 629 832 84 [−04]

estimated to be correct. Therefore, it is rather pointless to go beyond this value of  $n$ . On the other hand, further extension of the arithmetic precision which is already two times bigger than for calculations based on Eq. (101) will slow down the code dramatically and make it inferior to the numerical integration approach. In Tables I–V we present a comparison of the values of the master integral obtained according to the Eq. (176) with different expansion lengths and obtained by numerical integration in Eq. (101). We have chosen representative values of the nonlinear parameters ( $u_2 = w_2 = 1$ ,  $u_3 = w_3 = 2$ ) which were kept fixed and we have varied the value of  $w_1$  to examine the behavior of the expansion Eq. (176) with increasing  $w_1$ . We see that for  $w_1 = 1$  series expansion defined by Eq. (176) converges fast and smoothly towards the correct value and only a few tens of terms are necessary to obtain the long double precision result. An even better behavior is met for lower values of  $w_1$ . However, when  $w_1$  increases beyond one the convergence of Eq. (176) deteriorates and even for  $w_1 = 1.5$  as much as 75 terms of the expansion are not enough to obtain a reliable precision of 21 significant digits. For  $w_1 = 2.5$  only three significant digits are recovered after 75 terms and for  $w_1 = 3.0$  the series converges so badly that no useful information about the value of the master integral is obtained after 75 terms. Moreover, the result for  $w_1 = 3.0$  is clearly wrong since by a simple inspection of Eq. (8) we observe that the value of the master integral is always positive.

TABLE II. Comparison of the values of the master integral with  $u_2 = w_2 = 1$ ,  $u_3 = w_3 = 2$ ,  $w_1 = 1.5$  calculated according to Eqs. (160) and (101). Calculations performed for  $r = 2$ . [k] denotes  $10^k$ .

Expansion length	$f(r)$ value
10	1.329 520 816 045 925 011 91 [−04]
20	1.631 282 021 221 431 126 08 [−04]
30	1.631 651 606 696 872 148 17 [−04]
40	1.631 651 950 791 715 159 95 [−04]
50	1.631 651 951 100 638 063 39 [−04]
60	1.631 651 951 100 914 576 99 [−04]
70	1.631 651 951 100 914 825 55 [−04]
75	1.631 651 951 100 914 825 78 [−04]
Eq. (101)	1.631 651 951 100 914 825 97 [−04]

TABLE III. Comparison of the values of the master integral with  $u_2 = w_2 = 1$ ,  $u_3 = w_3 = 2$ ,  $w_1 = 2.0$  calculated according to Eqs. (176) and (101). Calculations performed for  $r = 2$ . [k] denotes  $10^k$ .

Expansion length	$f(r)$ value
10	−3.630 119 046 255 042 455 73 [−04]
20	1.070 421 921 389 016 547 74 [−04]
30	1.173 671 324 160 235 219 71 [−04]
40	1.175 380 214 096 797 535 24 [−04]
50	1.175 407 461 586 619 038 54 [−04]
60	1.175 407 894 643 606 977 59 [−04]
70	1.175 407 901 555 664 109 29 [−04]
75	1.175 407 901 658 970 039 51 [−04]
Eq. (101)	1.175 407 901 668 450 706 30 [−04]

Although a simple comparison provided in the above clearly shows that the numerical integration approach is superior compared to the series expansion method, we must admit that the numerical integration has its own problems. They appear for small values of  $w_1$ , say, lower than 0.2. In this regime, the integrands in Eq. (101) vanish slowly and significant contribution to the value of the master integral comes from the large  $r'$  in integration over the interval  $[r, +\infty]$ . The treatment of such situations requires an efficient matching of the series expansion around 0 with the asymptotic expansions of the functions  $L_i(r)$ . Moreover, for large  $r'$  accurate calculation of  $W_i(r')$  becomes difficult because significant loss of digits occurs due to the subtraction of two near-equal numbers. Therefore, we believe that the most efficient method of calculation of the master integral will be a suitable union of the two algorithms described here. Series expansion is to be used for small  $w_1$ , where it converges fast and only a handful of terms is required to obtain desired accuracy. For larger  $w_1$  numerical integration is superior and is able to provide arbitrary accuracy. In Table VI we additionally listed values of the master integral with some combinations of the nonlinear parameters corresponding to the general case without comparing them to the series expansion method.

Special cases of the master integral were implemented separately, taking advantage of the fact that  $L_i(r)$  functions are expressed in terms of known special functions. All necessary

TABLE IV. Comparison of the values of the master integral with  $u_2 = w_2 = 1$ ,  $u_3 = w_3 = 2$ ,  $w_1 = 2.5$  calculated according to Eqs. (176) and (101). Calculations performed for  $r = 2$ . [k] denotes  $10^k$ .

Expansion length	$f(r)$ value
10	−3.963 824 548 353 598 661 93 [−03]
20	−7.394 533 803 914 365 183 95 [−04]
30	−3.922 534 357 111 556 877 31 [−05]
40	6.940 930 190 407 504 160 82 [−05]
50	8.555 013 409 879 120 834 54 [−05]
60	8.793 765 644 766 649 249 36 [−05]
70	8.829 222 228 539 903 511 31 [−05]
75	8.837 871 552 224 364 384 80 [−05]
Eq. (101)	8.835 455 860 398 344 467 78 [−05]

TABLE V. Comparison of the values of the master integral with  $u_2 = w_2 = 1$ ,  $u_3 = w_3 = 2$ ,  $w_1 = 3.0$  calculated according to Eqs. (176) and (101). Calculations performed for  $r = 2$ . [k] denotes  $10^k$ .

Expansion length	$f(r)$ value
10	-2.285 092 132 216 817 479 00 [-02]
20	-2.902 204 388 154 522 817 70 [-02]
30	-2.770 162 995 062 714 932 55 [-02]
40	-2.546 625 633 397 138 405 90 [-02]
50	-2.333 510 298 021 168 682 89 [-02]
60	-2.147 292 702 104 883 235 95 [-02]
70	-2.198 741 099 645 234 679 27 [-02]
75	-2.192 990 423 157 987 209 06 [-02]
Eq. (101)	3.896 924 382 867 342 390 05 [-06]

special functions were implemented using Chebyshev interpolation method. In Table VII we give examples of the values of the master integral in one important special case corresponding to the exponential version of the symmetric James-Coolidge basis set, namely  $u_2 = u_3 = w_2 = w_3 = x$  with an arbitrary value of  $w_1$  and  $x$  (vanishing  $\Omega_2$  coefficient).

### IX. OUTLINE FOR THE FUTURE

In this paper we introduced an explicitly correlated basis set for state-of-the-art *ab initio* calculations for diatomic molecules and reported analytical formulas ready to apply for all molecular integrals appearing in the nonrelativistic calculations. While a physical application of the theory presented here will be reported soon, we would like to stress that our theoretical results will find several important applications.

First of all, the Slater geminal basis is expected to improve the convergence of molecular calculations on two-electron diatomic molecules by several orders of magnitude. With the advent of new experimental tools that allow measurements of the dissociation energy of  $H_2$  with an astonishing accuracy of  $10^{-4} \text{ cm}^{-1}$  [128] and with the announcements that this level of accuracy will be improved by two orders of magnitude, new molecular calculations will be necessary to reproduce the experimental data. Especially important in this respect will be the calculation of the relativistic integrals in the basis of the Slater geminals. We expect that the accuracy of the relativistic

TABLE VI. Examples of the values of the master integral with  $u_2 = w_2 = x$ ,  $u_3 = w_3 = y$  calculated according to Eq. (101). The symbol [k] denotes the powers of 10,  $10^k$ .

$w_1$	$x$	$y$	$r$	$f(r)$ value
2.0	2.0	3.0	2.0	1.201 629 296 541 321 185 57 [-06]
2.0	2.0	3.0	6.0	1.856 901 834 734 240 180 70 [-15]
3.0	2.0	3.0	4.0	2.546 518 235 628 700 248 18 [-11]
3.0	2.0	3.0	1.0	1.270 207 041 003 930 246 56 [-04]
2.0	2.5	1.5	5.0	5.468 451 264 859 307 911 42 [-11]
2.0	2.5	1.5	10.0	1.230 852 624 131 342 228 73 [-11]
5.0	1.0	3.5	1.0	1.348 628 792 547 450 383 43 [-04]
5.0	1.0	3.5	3.0	1.124 458 143 821 066 488 15 [-08]
8.0	2.0	4.0	1.0	1.120 127 360 296 310 672 77 [-05]
8.0	2.0	4.0	0.5	2.734 827 621 588 948 643 78 [-04]

TABLE VII. Examples of the values of the master integral with  $u_2 = w_2 = u_3 = w_3 = x$ , calculated according to Eq. (140). The symbol [k] denotes the powers of 10,  $10^k$ .

$w_1$	$x$	$r$	$f(r)$ value
1.0	1.0	1.0	1.703 125 280 928 411 227 96 [-02]
1.0	2.0	1.0	1.014 022 114 173 744 267 56 [-03]
1.0	3.0	1.0	8.004 150 114 345 362 264 69 [-05]
3.0	1.0	1.0	5.951 801 370 434 581 206 93 [-03]
3.0	2.0	1.0	4.274 030 135 492 893 397 48 [-04]
3.0	3.0	1.0	3.729 764 549 603 920 888 36 [-05]
1.0	1.0	6.0	7.056 468 173 179 733 644 15 [-07]
1.0	2.0	6.0	1.844 671 299 421 804 291 18 [-12]
1.0	3.0	6.0	6.550 119 462 337 850 009 32 [-18]
3.0	1.0	6.0	1.434 427 682 763 861 672 06 [-07]
3.0	2.0	6.0	4.476 440 831 180 785 306 69 [-13]
3.0	3.0	6.0	1.768 710 162 179 272 839 12 [-18]

corrections reported in Ref. [129], computed in the basis of explicitly correlated Gaussian geminals, can be improved by a few orders of magnitude. Also, the QED effects could be accounted for in a more accurate way to produce not only state-of-the-art estimates of the dissociation energy, but also of the rotational and vibrational spacings [130].

The second important application of the theory presented above is the numerical calculation of the integrals in the basis set of Slater orbitals for diatomic molecules. While the theoretical background was introduced by Pachucki in 2009 [44], his algorithms for certain classes of integrals turned out to be inefficient for practical implementation. Using the geminal recursion relations and putting the exponent in the correlation factor  $w_1$  equal to zero, one obtains much simpler and numerically more convenient recursion relations.

Also worth mentioning are the calculations of the relativistic integrals in the basis set of the Slater orbitals for diatomic molecules. At present, no *ab initio* program for molecular calculations has available all integrals appearing in the Breit-Pauli theory, even in the Gaussian basis set. We plan to apply our theory to the expressions for the most difficult class involving the  $r_{12}^{-2}$  factor and perform actual calculations with just one numerical integration in one dimension. In this way, accurate calculations of the fine and hyperfine structure of diatomics will become possible.

Finally, the basis set of the Slater geminals can be used in the explicitly correlated MBPT/CC theories, thus greatly improving the accuracy of the present approaches based on the Gaussian orbitals and linear or exponential correlation factors.

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### APPENDIX A: MATRIX ELEMENTS OF THE KINETIC ENERGY OPERATOR

Let us consider the two-center two-electron Schödinger Hamiltonian:

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z_A}{r_{1A}} - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{1B}} - \frac{Z_B}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{r}, \quad (\text{A1})$$

where  $Z_K$  denotes the nuclear charge of the nucleus  $K$  and the notation for the other quantities is the same as in Eq. (7). The basis functions are of the form (6). The overlap integrals between these basis functions and the matrix elements of the nuclear attraction and electronic repulsion operators are obviously expressed through the integrals from the family (7) with proper powers of  $r_{iK}$  and  $r_{12}$ . The only difficulty is to express the matrix elements of the kinetic energy operator through the integrals (7). Let us introduce a shorthand notation that will be used throughout this Appendix:

$$\begin{aligned} |ijkln\rangle &= r_{1A}^i r_{1B}^j r_{2A}^k r_{2B}^l r_{12}^n e^{-u_3 r_{1A} - u_2 r_{1B} - w_2 r_{2A} - w_3 r_{2B} - w_1 r_{12}} \\ &= \varphi_{ij}(1) \varphi_{kl}(2) r_{12}^n e^{-w_1 r_{12}}. \end{aligned} \quad (\text{A2})$$

Our derivation was inspired by the procedure given by Kołos *et al.* [25,26]. In fact, their result is the  $w_1 = w'_1 = 0$  limit of our equation. The matrix element is transformed as

$$\begin{aligned} \langle ijkl | -\nabla_1^2 | i'j'k'l'n' \rangle \\ = \int d^3 r_2 \varphi_{kl}(2) \varphi_{k'l'}(2) \int d^3 r_1 \nabla_1 [\varphi_{ij}(1) r_{12}^n e^{-w_1 r_{12}}] \\ \cdot \nabla_1 [\varphi_{i'j'}(1) r_{12}^{n'} e^{-w'_1 r_{12}}], \end{aligned} \quad (\text{A3})$$

where the Green's theorem was used. Let us now consider only the integration over the coordinates of the first electron. For simplicity we consider the case  $n = n' = 0$ . The general form of the matrix element will then be obtained by differentiating  $n$  times with respect to  $w_1$  and  $n'$  times with respect to  $w'_1$  and multiplying by the factor  $(-1)^{n+n'}$ . The latter integral is

rewritten as

$$\begin{aligned} & \int d^3 r_1 \nabla_1 [\varphi_{ij}(1) e^{-w_1 r_{12}}] \cdot \nabla_1 [\varphi_{i'j'}(1) e^{-w'_1 r_{12}}] \\ &= \int d^3 r_1 \left( [\nabla_1 \varphi_{ij}(1)] [\nabla_1 \varphi_{i'j'}(1)] e^{-(w_1+w'_1)r_{12}} \right. \\ & \quad + w_1 w'_1 \varphi_{ij}(1) \varphi_{i'j'}(1) e^{-(w_1+w'_1)r_{12}} \\ & \quad + \frac{1}{w_1 + w'_1} \{ w'_1 [\nabla_1 \varphi_{ij}(1)] \varphi_{i'j'}(1) \\ & \quad \left. + w_1 \varphi_{ij}(1) [\nabla_1 \varphi_{i'j'}(1)] \} [\nabla_1 e^{-(w_1+w'_1)r_{12}}] \right) \\ &= \int d^3 r_1 \left( w_1 w'_1 \varphi_{ij}(1) \varphi_{i'j'}(1) e^{-(w_1+w'_1)r_{12}} \right. \\ & \quad - \frac{1}{w_1 + w'_1} \{ w'_1 [\Delta_1 \varphi_{ij}(1)] \varphi_{i'j'}(1) \\ & \quad \left. + w_1 \varphi_{ij}(1) [\Delta_1 \varphi_{i'j'}(1)] \} e^{-(w_1+w'_1)r_{12}} \right), \end{aligned} \quad (\text{A4})$$

where the Green's theorem was used in the last step to remove the gradient operator working on terms containing the  $r_{12}$  factor. The equation for the Laplacian of the  $\varphi_{ij}(1)$  is rather straightforward to derive and the final result is

$$\begin{aligned} \Delta_1 \varphi_{ij}(1) &= i(i+j+1)\varphi_{i-2,j}(1) + j(i+j+1)\varphi_{i,j-2}(1) \\ & \quad + (u_3^2 + u_2^2)\varphi_{ij}(1) - u_3 \left( i + \frac{j}{2} + 2 \right) \varphi_{i-1,j}(1) \\ & \quad - u_2 \left( j + \frac{i}{2} + 2 \right) \varphi_{i,j-1}(1) - r^2 i j \varphi_{i-2,j-2}(1) \\ & \quad + \frac{1}{2} i u_2 r^2 \varphi_{i-2,j-1}(1) + \frac{1}{2} j u_3 r^2 \varphi_{i-1,j-2}(1) \\ & \quad + u_2 u_3 [\varphi_{i+1,j-1}(1) + \varphi_{i-1,j+1}(1) - r^2 \varphi_{i-1,j-1}(1)] \\ & \quad - \frac{1}{2} i u_2 \varphi_{i-2,j+1}(1) - \frac{1}{2} j u_3 \varphi_{i+1,j-2}(1). \end{aligned} \quad (\text{A5})$$

By inserting the formulas (A4) and (A5) into Eq. (A3) one arrives at

$$\begin{aligned} \langle ijkl | -\nabla_1^2 | i'j'k'l'0 \rangle &= w_1 w'_1 \langle ijkl | i'j'k'l'0 \rangle - \frac{w'_1}{w_1 + w'_1} \left[ i(i+j+1)(i-2, jkl | i'j'k'l'0) \right. \\ & \quad + j(i+j+1)(ij-2, k | i'j'k'l'0) + (u_3^2 + u_2^2) \langle ijkl | i'j'k'l'0 \rangle \\ & \quad - u_3 \left( i + \frac{j}{2} + 2 \right) \langle i-1, jkl | i'j'k'l'0 \rangle - u_2 \left( j + \frac{i}{2} + 2 \right) \langle ij-1, k | i'j'k'l'0 \rangle \\ & \quad - r^2 i j \langle i-2, j-2, k | i'j'k'l'0 \rangle + \frac{1}{2} i u_2 r^2 \langle i-2, j-1, k | i'j'k'l'0 \rangle \\ & \quad + \frac{1}{2} j u_3 r^2 \langle i-1, j-2, k | i'j'k'l'0 \rangle + u_2 u_3 \langle i+1, j-1, k | i'j'k'l'0 \rangle + u_2 u_3 \langle i-1, j+1, k | i'j'k'l'0 \rangle \\ & \quad - r^2 u_2 u_3 \langle i-1, j-1, k | i'j'k'l'0 \rangle - \frac{1}{2} i u_2 \langle i-2, j+1, k | i'j'k'l'0 \rangle - \frac{1}{2} j u_3 \langle i+1, j-2, k | i'j'k'l'0 \rangle \left. \right] \\ & \quad - \frac{w_1}{w_1 + w'_1} \left[ i'(i'+j'+1) \langle ijkl | i'-2, j'k'l'0 \rangle + j'(i'+j'+1) \langle ij, k | i'j'-2, k'l'0 \rangle \right. \\ & \quad + (u_3^2 + u_2^2) \langle ijkl | i'j'k'l'0 \rangle - u'_3 \left( i' + \frac{j'}{2} + 2 \right) \langle ijkl | i'-1, j'k'l'0 \rangle \\ & \quad \left. - u'_2 \left( j' + \frac{i'}{2} + 2 \right) \langle ijkl | i'j'-1, k'l'0 \rangle - r^2 i' j' \langle ijkl | i'-2, j'-2, k'l'0 \rangle \right] \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2} i' u'_2 r^2 \langle ijkl0 | i' - 2, j' - 1, k' l' 0 \rangle + \frac{1}{2} j' u'_3 r^2 \langle ijkl0 | i' - 1, j' - 2, k' l' 0 \rangle \\
& + u'_2 u'_3 \langle ijkl0 | i' + 1, j' - 1, k' l' 0 \rangle + u'_2 u'_3 \langle ijkl0 | i' - 1, j' + 1, k' l' 0 \rangle - r^2 u'_2 u'_3 \langle ijkl0 | i' - 1, j' - 1, k' l' 0 \rangle \\
& - \frac{1}{2} i' u'_2 \langle ijkl0 | i' - 2, j' + 1, k' l' 0 \rangle - \frac{1}{2} j' u'_3 \langle ijkl0 | i' + 1, j' - 2, k' l' 0 \rangle \Big], \tag{A6}
\end{aligned}$$

where the notation  $\langle ijkl0 | i' j' k' l' 0 \rangle$  was used to designate ordinary overlap integrals which belong to the integral family (7). The above equation is already symmetric with respect to the interchange of primed and nonprimed indices. It is noteworthy that the singularity appearing when  $w_1 = w'_1 = 0$  is only apparent. It can easily be removed by taking first the limit  $w'_1 \rightarrow w_1$  and then putting  $w_1 = 0$ . To obtain the most general matrix element of the kinetic energy operator,  $\langle ijkl n | -\nabla_1^2 | i' j' k' l' n' \rangle$ , one needs to differentiate Eq. (A6) with respect to  $w_1$  and  $w'_1$ . This differentiation is easily carried out explicitly with any symbolic mathematical program. The resulting formulas are quite compact and make their direct implementation straightforward. On the other hand, by multiplying both sides of Eq. (A6) by  $w_1 + w'_1$  and performing consecutive differentiation, it is quite easy to derive a recursion relation that connects the values of  $\langle ijkl n | -\nabla_1^2 | i' j' k' l' n' \rangle$  with different  $n$  and  $n'$ . However, this recursion is inherently unstable with the increasing  $n$  and  $n'$ , and can be considered inferior to the approach based on the analytical equations, at least for larger  $n$  and  $n'$ .

## APPENDIX B: ANALYTICAL FORMULAS FOR THE FUNCTIONS $W(r)$ AND $V(r)$

In this Appendix we list explicit analytical formulas for the functions  $W(r; w_1, u_2, u_3, w_2, w_3)$  and  $V(r; w_1, u_2, u_3, w_2, w_3)$ , which are defined as the inverse Laplace transforms in Eqs. (52) and (53), respectively. We would like to stress that in the formulas given below all the terms proportional to the Dirac  $\delta$  distribution or its derivatives were omitted. This can be done because for  $r > 0$  these terms never contribute to the values of the master integral derivatives calculated from the recursion relations presented in the text. However, the missing terms can be recovered by taking the Laplace transform of the listed equations and comparing with the proper analog of Eq. (26). This can easily be done by using any symbolic mathematical package.

The function  $W(r)$  takes the form

$$W(r) = \sum_{i=1}^6 W_i(r), \tag{B1}$$

with

$$W_1(r) = w_1 e^{-r(u_2+w_1+w_2)} \left( \frac{1}{r^2} + \frac{u_2 + w_1 + w_2}{r} \right), \tag{B2}$$

$$W_2(r) = w_1 e^{-r(u_3+w_1+w_3)} \left( \frac{1}{r^2} + \frac{u_3 + w_1 + w_3}{r} \right), \tag{B3}$$

$$\begin{aligned}
W_3(r) = & \frac{w_1 w_2 (u_2^2 - w_3^2) + u_2^2 w_2^2 - u_3^2 w_3^2}{(w_1 + w_2)^2 - w_3^2} \frac{1}{r} [e^{-r(u_2+w_2+w_1)} - e^{-r(u_2+w_3)}] \\
& + \frac{w_1 (w_1 + w_2)}{(w_1 + w_2)^2 - w_3^2} \frac{1}{r^3} \{-e^{-r(u_2+w_3)} [2 + 2r(u_2 + w_3) + r^2(u_2 + w_3)^2] \\
& + e^{-r(u_2+w_2+w_1)} [2 + 2r(u_2 + w_2 + w_1) + r^2(u_2 + w_2 + w_1)^2]\}, \tag{B4}
\end{aligned}$$

$$\begin{aligned}
W_4(r) = & \frac{w_1 w_3 (u_3^2 - w_2^2) + u_3^2 w_3^2 - u_2^2 w_2^2}{(w_1 + w_3)^2 - w_2^2} \frac{1}{r} [e^{-r(u_3+w_3+w_1)} - e^{-r(u_3+w_2)}] \\
& + \frac{w_1 (w_1 + w_3)}{(w_1 + w_3)^2 - w_2^2} \frac{1}{r^3} \{-e^{-r(u_3+w_2)} [2 + 2r(u_3 + w_2) + r^2(u_3 + w_2)^2] \\
& + e^{-r(u_3+w_3+w_1)} [2 + 2r(u_3 + w_3 + w_1) + r^2(u_3 + w_3 + w_1)^2]\}, \tag{B5}
\end{aligned}$$

$$\begin{aligned}
W_5(r) = & \frac{w_1 u_2 (w_2^2 - u_3^2) + u_2^2 w_2^2 - u_3^2 w_3^2}{(u_2 + w_1)^2 - u_3^2} \frac{1}{r} [e^{-r(u_2+w_2+w_1)} - e^{-r(u_3+w_2)}] \\
& + \frac{u_2^2 - u_3^2 + u_2 w_1}{(u_2 + w_1)^2 - u_3^2} \frac{1}{r^3} \{e^{-r(u_3+w_2)} [2 + 2r(u_3 + w_2) + r^2(u_3 + w_2)^2] \\
& - e^{-r(u_2+w_2+w_1)} [2 + 2r(u_2 + w_2 + w_1) + r^2(u_2 + w_2 + w_1)^2]\}, \tag{B6}
\end{aligned}$$

$$\begin{aligned}
W_6(r) = & \frac{w_1 u_3 (u_2^2 - w_3^2) + u_2^2 w_2^2 - u_3^2 w_3^2}{-(u_2 + w_1)^2 + u_2^2} \frac{1}{r} [e^{-r(u_3+w_3+w_1)} - e^{-r(u_2+w_3)}] \\
& + \frac{u_2^2 - u_3^2 - u_3 w_1}{-(u_3 + w_1)^2 + u_2^2} \frac{1}{r^3} \{e^{-r(u_2+w_3)} [2 + 2r(u_2 + w_3) + r^2(u_2 + w_3)^2] \\
& - e^{-r(u_3+w_3+w_1)} [2 + 2r(u_3 + w_3 + w_1) + r^2(u_3 + w_3 + w_1)^2]\}. \tag{B7}
\end{aligned}$$

Let us denote the permutation  $u_2 \leftrightarrow w_3$ ,  $u_3 \leftrightarrow w_2$  by  $P_{12}$  and the permutation  $u_2 \leftrightarrow u_3$ ,  $w_2 \leftrightarrow w_3$  by  $P_{AB}$ . The reason for adopting such a notation becomes clear when one considers the symmetries of the master integral. Calculation of  $W(r)$  is simplified by the relations

$$P_{AB} W_1(r) = W_2(r), \quad P_{AB} W_3(r) = W_4(r), \quad P_{AB} W_5(r) = W_6(r), \tag{B8}$$

so that the programming effort is halved. Further simplifications occur after observing, for instance, that

$$\frac{e^{-r(u_3+w_2)}}{r^3} [2 + 2r(u_3 + w_2) + r^2(u_3 + w_2)^2] = \frac{\partial^2}{\partial r^2} \left[ \frac{e^{-r(u_3+w_2)}}{r} \right] \tag{B9}$$

so that in the implementation one can concentrate on the calculation of the derivatives of the quantities like  $e^{-ar}/r$  since any derivative of  $W(r)$  with respect to the nonlinear parameters and  $r$  is expressed through them.

The explicit form of  $V(r)$  is expressed conveniently as

$$V(r) = V_1(r) + V_2(r) + V_3(r) + \bar{c}_1 V_4(r) + \bar{c}_2 V_5(r), \tag{B10}$$

with

$$\begin{aligned}
V_1(r) = & \frac{e^{-r(u_3+w_2+w_1)}}{r} (w_1^2 - u_3^2 - u_3 w_3) + \frac{e^{-r(u_3+w_2)}}{r} (-w_1^2 + u_3^2 - u_2 w_3) \\
& + u_3 w_3 \frac{e^{-r(u_2+w_2)}}{r} + u_2 w_3 \frac{e^{-r(u_2+w_2+w_1)}}{r}, \tag{B11}
\end{aligned}$$

$$\begin{aligned}
V_2(r) = & \frac{w_1 w_3 (u_3^2 - w_2^2) + u_3^2 w_3^2 - u_2^2 w_2^2}{(w_1 + w_3)^2 - w_2^2} \frac{1}{r} [e^{-r(u_3+w_3+w_1)} - e^{-r(u_3+w_2)}] \\
& + \frac{w_1(w_1 + w_3)}{(w_1 + w_3)^2 - w_2^2} \frac{1}{r^3} \{-e^{-r(u_3+w_2)} [2 + 2r(u_3 + w_2) + r^2(u_3 + w_2)^2] \\
& + e^{-r(u_3+w_3+w_1)} [2 + 2r(u_3 + w_3 + w_1) + r^2(u_3 + w_3 + w_1)^2]\}, \tag{B12}
\end{aligned}$$

$$\begin{aligned}
V_3(r) = & \frac{w_1 w_3 (w_2^2 - u_3^2) + w_2 w_3 (u_3^2 - u_2^2 + w_1^2)}{(w_1 + w_2)^2 - w_3^2} \frac{1}{r} [e^{-r(u_2+w_2+w_1)} - e^{-r(u_2+w_3)}] \\
& - \frac{w_1 w_3}{(w_1 + w_2)^2 - w_3^2} \frac{1}{r^3} \{-e^{-r(u_2+w_3)} [2 + 2r(u_2 + w_3) + r^2(u_2 + w_3)^2] \\
& \times e^{-r(u_2+w_2+w_1)} [2 + 2r(u_2 + w_2 + w_1) + r^2(u_2 + w_2 + w_1)^2]\}, \tag{B13}
\end{aligned}$$

$$\begin{aligned}
V_4(r) = & e^{-r(u_2+w_3)} \{-\text{Ei}[-r(w_1 + u_3 - u_2)] + \text{Ei}[-r(u_3 - u_2 - w_3 + w_2)] \\
& - \text{Ei}[-r(w_1 - w_3 + w_2)]\} - e^{r(u_2+w_3)} \text{Ei}[-r(u_2 + u_3 + w_2 + w_3)] \\
& + e^{-r(u_2+w_3)} \ln \left| \frac{(w_1 + w_2 - w_3)(w_1 - u_2 + u_3)(u_2 + u_3 + w_2 + w_3)}{(w_1 + w_2 + w_3)(u_2 + u_3 + w_1)(u_2 - u_3 - w_2 + w_3)} \right|, \tag{B14}
\end{aligned}$$

$$V_5(r) = e^{r(w_3-u_2)} \text{Ei}[-r(w_1 + w_2 + w_3)] + e^{r(u_2-w_3)} \text{Ei}[-r(w_1 + u_2 + u_3)], \tag{B15}$$

and

$$\bar{c}_1 = \frac{1}{2} [u_2(w_1^2 - w_2^2 + w_3^2) + w_3(u_2^2 - u_3^2 + w_1^2)], \tag{B16}$$

$$\bar{c}_2 = \frac{1}{2} [u_2(w_1^2 - w_2^2 + w_3^2) - w_3(u_2^2 - u_3^2 + w_1^2)]. \tag{B17}$$

We see that the form of  $V_2(r)$  and  $V_3(r)$  is analogous to the  $W_i(r)$ ,  $i = 3, 6$ . Similarly,  $V_4(r)$  and  $V_5(r)$  are expressed

through the same combinations of functions as  $U_3(r)$  and  $U_2(r)$ , respectively. The only difference is that some terms contribute with the sign reversed. Since the form of  $U_1(r)$  is relatively simple and straightforward to implement, arbitrary derivatives of the function  $V(r)$  can be computed by using a proper union of the algorithms for  $U(r)$  and  $W(r)$  functions.

## APPENDIX C: AUXILIARY RECURSION RELATIONS

In this Appendix we list formulas for the derivatives of  $\frac{\partial f}{\partial w_3}$  and  $\frac{\partial f}{\partial w_1}$  over  $r$  up to the third order which result from the

solution of the set of equations for  $E_i$  and  $\bar{E}_i$ ,  $i = 1, 5$ . Higher-order derivatives can be obtained by successive differentiation of the geminal differential equation:

$$\begin{aligned} \frac{\partial f'}{\partial w_3} = & \frac{\Omega_1}{2(4w_1^2\Omega_2 - \Omega_1^2)} \left\{ -2rV(r) - 2\frac{\partial U(r)}{\partial w_3} + \frac{\partial\Omega_2}{\partial w_3}rf(r) + \frac{\partial\Omega_1}{\partial w_3}[2f'(r) + rf''(r)] \right\} \\ & + \frac{w_1^2}{4w_1^2\Omega_2 - \Omega_1^2} \left\{ -8V'(r) - 2rV''(r) - 2\frac{\partial U''(r)}{\partial w_3} + \frac{\partial\Omega_2}{\partial w_3}rf''(r) + \frac{\partial\Omega_1}{\partial w_3}[2f^{(3)}(r) + rf^{(4)}(r)] \right\}, \end{aligned} \quad (C1)$$

$$\begin{aligned} \frac{\partial f''}{\partial w_3} = & \frac{\Omega_1}{2(4w_1^2\Omega_2 - \Omega_1^2)} \left\{ -2V(r) - 2rV'(r) - 2\frac{\partial U'(r)}{\partial w_3} + \frac{\partial\Omega_2}{\partial w_3}[rf'(r) + f(r)] + \frac{\partial\Omega_1}{\partial w_3}[rf^{(3)}(r) + 3f''(r)] \right\} \\ & + \frac{w_1^2}{4w_1^2\Omega_2 - \Omega_1^2} \left\{ -10V''(r) - 2rV^{(3)}(r) - 2\frac{\partial U^{(3)}(r)}{\partial w_3} + \frac{\partial\Omega_2}{\partial w_3}[rf^{(3)}(r) + f''(r)] + \frac{\partial\Omega_1}{\partial w_3}[rf^{(5)}(r) + 3f^{(4)}(r)] \right\}, \end{aligned} \quad (C2)$$

$$\begin{aligned} \frac{\partial f^{(3)}}{\partial w_3} = & -\frac{\Omega_2}{4w_1^2\Omega_2 - \Omega_1^2} \left\{ -2rV(r) - 2\frac{\partial U(r)}{\partial w_3} + \frac{\partial\Omega_2}{\partial w_3}rf(r) + \frac{\partial\Omega_1}{\partial w_3}[rf''(r) + 2f'(r)] \right\} \\ & - \frac{\Omega_1}{2(4w_1^2\Omega_2 - \Omega_1^2)} \left\{ -8V'(r) - 2rV''(r) - 2\frac{\partial U''(r)}{\partial w_3} + \frac{\partial\Omega_2}{\partial w_3}rf''(r) + \frac{\partial\Omega_1}{\partial w_3}[rf^{(4)}(r) + 2f^{(3)}(r)] \right\}, \end{aligned} \quad (C3)$$

$$\begin{aligned} \frac{\partial f'}{\partial w_1} = & \frac{\Omega_1}{2(4w_1^2\Omega_2 - \Omega_1^2)} \left\{ -2rW(r) - 2\frac{\partial U(r)}{\partial w_1} + \frac{\partial\Omega_2}{\partial w_1}rf(r) + \frac{\partial\Omega_1}{\partial w_1}[2f'(r) + rf''(r)] + 2w_1[4f^{(3)}(r) + rf^{(4)}(r)] \right\} \\ & + \frac{w_1^2}{4w_1^2\Omega_2 - \Omega_1^2} \left\{ -8W'(r) - 2rW''(r) - 2\frac{\partial U''(r)}{\partial w_1} + \frac{\partial\Omega_2}{\partial w_1}rf''(r) \right. \\ & \left. + \frac{\partial\Omega_1}{\partial w_1}[2f^{(3)}(r) + rf^{(4)}(r)] + 2w_1[4f^{(5)}(r) + rf^{(6)}(r)] \right\}, \end{aligned} \quad (C4)$$

$$\begin{aligned} \frac{\partial f''}{\partial w_1} = & \frac{\Omega_1}{2(4w_1^2\Omega_2 - \Omega_1^2)} \left\{ -2W(r) - 2rW'(r) - 2\frac{\partial U'(r)}{\partial w_1} + \frac{\partial\Omega_2}{\partial w_1}[rf'(r) + f(r)] \right. \\ & \left. + \frac{\partial\Omega_1}{\partial w_1}[rf^{(3)}(r) + 3f''(r)] + 2w_1[5f^{(4)}(r) + rf^{(5)}(r)] \right\} + \frac{w_1^2}{4w_1^2\Omega_2 - \Omega_1^2} \left\{ -10W''(r) - 2rW^{(3)}(r) - 2\frac{\partial U^{(3)}(r)}{\partial w_1} \right. \\ & \left. + \frac{\partial\Omega_2}{\partial w_1}[rf^{(3)}(r) + f''(r)] + \frac{\partial\Omega_1}{\partial w_3}[rf^{(5)}(r) + 3f^{(4)}(r)] + 2w_1[5f^{(6)}(r) + rf^{(7)}(r)] \right\}, \end{aligned} \quad (C5)$$

$$\begin{aligned} \frac{\partial f^{(3)}}{\partial w_1} = & -\frac{\Omega_2}{4w_1^2\Omega_2 - \Omega_1^2} \left\{ -2rW(r) - 2\frac{\partial U(r)}{\partial w_1} + \frac{\partial\Omega_2}{\partial w_1}rf(r) + \frac{\partial\Omega_1}{\partial w_1}[rf''(r) + 2f'(r)] + 4w_1[2f^{(3)}(r) + rf^{(4)}(r)] \right\} \\ & - \frac{\Omega_1}{2(4w_1^2\Omega_2 - \Omega_1^2)} \left\{ -8W'(r) - 2rW''(r) - 2\frac{\partial U''(r)}{\partial w_1} + \frac{\partial\Omega_2}{\partial w_1}rf''(r) \right. \\ & \left. + \frac{\partial\Omega_1}{\partial w_1}[rf^{(4)}(r) + 2f^{(3)}(r)] + 2w_1[4f^{(5)}(r) + rf^{(6)}(r)] \right\}. \end{aligned} \quad (C6)$$

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