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Title of doctoral dissertation (in Polish): Całki dla czterech skorelowanych elektronów w układach atomowych występujące w metodzie Hylleraasa z jednym nieparzystym czynnikiem korelacyjnym

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DESCRIPTION OF DOCTORAL DISSERTATION

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Keywords of doctoral dissertation in Polish: całki jawnie skorelowane, methoda Hylleraasa, funkcje jawnie skorelowane, układy czteroelektronowe

Keywords of doctoral dissertation in English: explicitly correlated integrals, Hylleraas method, explicitly correlated functions, four-electron systems

Summary of doctoral dissertation in Polish: Przedmiotem niniejszej rozprawy jest opracowanie i implementacja metody analitycznego obliczania całek elektronowych funckji jawnie skorelowanych, pojawiających się w obliczeniach dla układów atomowych. Występują one w szczególności w metodzie Hylleraasa z jednym nieparzystym czynnikiem korelacyjnym. W toku pracy zostały opracowane nowe metody teoretyczne, które pozwoliły na uzyskanie wszystkich rozpatrywanych całek w postaci wyrażeń analitycznych zawierających funkcje elementarne oraz dilogarytmy. Dla części całek wzory te nie były nigdy wcześniej publikowane. Poprawność wyprowadzonych wzorów została sprawdzona poprzez porównanie postaci oraz wartości wybranych całek z danymi dostępnymi w liteaturze. Zgodność pomiędzy wartościami otrzymanymi przy pomocy wyrażeniami, a wartościami litraturowymi 40 cyfr znaczących. Uzyskanie tych całek w takiej postaci stanowi ważny krok na drodze do zastosowania metody Hylleraasa w dokładnych obliczeniach układów atomowych i molekularnych mających więcej, niż kilka elektronów.

Summary of doctoral dissertation in English: The subject of this thesis is the development and implementation of a method for the analytical calculation of the electronic integrals of the explicitly correlated functions of the atomic systems, particularly in the Hylleraas method with one odd correlation factor. In the course of the work, new theoretical methods were developed to obtain all considered the integrals as the closed-form analytic expression

with elementary functions and dilogarithms. For some of the integrals, the analytic formulas had never been published before. The correctness of the derived formulae was checked by comparing the form of the expressions and values of the selected integrals with the data available in the literature. The agreement between the values obtained using the derived expressions and the data from previous studies is to 40 significant digits. The derivation of these integrals in this form represents an important step towards the applications of the Hylleraas method in the accurate calculations of atomic and molecular systems with more than a few electrons.

Podziękowania

Chciałbym złożyć serdeczne podziękowania za poświęcony czas, przekazaną wiedzę oraz wsparcie moim promotorom prof Józefowi E. Sienkiewiczowi oraz dr inż Patrykowi Jasikowi.

Podziękowania za pomoc naukową, bez której ukończenie niniejszej rozprawy nie byłoby możliwe składam prof. Krzysztofowi Pachuckiemu.

Dziękuję również rodzinie i bliskim, w szczególności Tacie, Babci Weronice, oraz Oli, za nieustające wsparcie.

Pracę dedykuję pamięci Mamy.

Tymon

Contents

Chapter 1

Introduction

1.1 Thesis statement

In this thesis we show that all integrals called four-electron singly-linked Hylleraas of form

$$\iiiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi}\exp(-w_1r_1-w_2r_2-w_3r_3-w_4r_4)r_1^{n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{12}^{a}r_{13}^{b}r_{14}^{c}r_{23}^{d}r_{24}^{e}r_{34}^{f}, \quad (1.1)$$

with $\{w_1, w_2, w_3, w_4\} \in \mathbb{R}^+ \wedge -1 \leq \{a, b, c, d, e, f, n_1, n_2, n_3, n_4\} \in \mathbb{Z}$ with *at most* three odd parameters among $\{a, b, c, d, e, f\}$ can be obtained as the closed-form analytic expressions involving dilogarithms and elementary functions.

1.2 Motivation

1.2.1 Accurate calculations of the atomic systems

Recent advances in laser spectroscopy have made it possible to the determination of atomic energy levels with accuracies routinely in the range of 0.01–0.0001 cm^{-1} across the periodic table [1]. Meanwhile current theoretical methods, with the exception of the few lightest atomic systems up to five or six electrons, typically do not yield results more accurate than 1 cm^{-1} [2]. Therefore, new theoretical developments in highly accurate methods are essential for the computational prediction of spectra and properties of the atomic systems with more than a few electrons, in order to support and efficiently guide experimental investigations. The most accurate solutions of the Schrodinger equation for atomic and small molecular systems are usually obtained using the variational method based on the quantum mechanical variational principle as it provides both the upper bound on the true energy eigenvalue and reliable methods to improve the energy and estimate the convergence (and consequently accuracy) of the calculations [3]. The method can be summarised as the minimisation of the following functional

$$\varepsilon\left[\Psi(\alpha)\right] = \frac{\langle\Psi(\alpha)|\,\hat{H}\,|\Psi(\alpha)\rangle}{\langle\Psi(\alpha)|\Psi(\alpha)\rangle}, \quad (1.2)$$

where $\varepsilon\left[\Psi(\alpha)\right] \geq E_0$ estimates of the lowest eigenvalue of the Hamiltonian $\hat{H}$ and approaches the exact ground state energy (E_0) of the system described by the Hamiltonian from above as the trial function $\Psi(\alpha)$ approaches the eigenfunction Ψ_0 of the ground state by varying the parameter (or set of parameters) α. Traditionally, the trial function takes the form of a linear combination $\Psi = \sum_i c_i \psi(\alpha)$, which leads to the formulation of the problem in terms of a generalized eigenvalue problem, resulting in method that is commonly called the Ritz method [4]. The Ritz method also allows to easily find also the approximate energies of the excited states as the subsequent larger eigenvalues of the eigenproblem. In order to use the variational method, a suitable set of basis functions $\Psi(\alpha)$ must be chosen. The choice of basis functions is necessarily a compromise between the several factors such as the properties of the trial function must fulfill, the required asymptotic behaviour of the wave function (that variational function converges to), the difficulty and computational cost of obtaining matrix elements, the complexity of the mathematical expressions involved, the availability of existing optimised sets of basis functions and codes to use them, and their suitability for efficient variational optimisation.

The most important and widely used class of basis functions used in variational calculations are linear combinations of the products of the orbital functions [5]. Such functions consist of (usually antisymmetrized) products of one-electron functions [6] of the form

$$\varphi(\mathbf{r}) = R_l(r) Y_l^m(\theta, \phi), \tag{1.3}$$

where r, θ, ϕ are spherical coordinates, $R_l(r)$ is the radial function (that can take various forms) and $Y_l^m(\theta, \phi)$ is the angular function, specifically the spherical harmonic, while $l = 0, 1, 2, 3, ..., m = -l, -l+1, ..., l+1, l$ is the angular momentum and its projection on the z axis. Such a formulation, especially when orbitals are chosen to be orthonormal, allows for extremely efficient evaluation of the matrix elements as well as the formulation of self-consistent field methods, which can be followed by the inclusion of the extensions to this method that describe electron correlation. While it is possible to use various types of orbital functions, including the numerical orbitals on the grid [7, 8], there are two most commonly used functional forms of the orbitals. For the Slater [9] orbitals, the radial function is

$$R_l(r) = N(l, a) r^l \exp(-ar), \tag{1.4}$$

where $N(l, a)$ is normalization factor. In turn, for the Gaussian [10] orbitals radial functions are

$$R_l(r) = M(l, a) r^l \exp(-ar^2) \tag{1.5}$$

where $M(l, a)$ is the normalisation factor this time. While the Slater orbitals are more physically motivated and were discovered 20 years earlier, the Gaussian orbitals that are the most universal and widely used in quantum physics and chemistry nowadays due to extremely efficient algorithms for calculating matrix elements, especially for molecular systems [11]. However, they suffer from the two drawbacks. The first is that since they have a quadratic dependence of the nucleus-electron distance r in the exponent, they decay too quickly for the large values of r (which is immediately obvious when Gaussian orbital is compared against the analytic solution for the hydrogen atom). Secondly, the exact many-electron function that the variational method converges to has to have few known analytical properties at the coalescence of the particles. These conditions are so called Kato cusp conditions after their discoverer [12] and have the form

$$\lim_{r_{ij} \to 0} \left(\frac{\partial \psi (r_{ij})}{\partial r_{ij}} \right)_{av} = \mu_{ij} Q_i Q_j \psi (r_{ij} = 0), \tag{1.6}$$

where av denotes the averaging over the sphere, Q_i, Q_j are the charges of the particles and μ_{ij} is their reduced mass. The Kato cusp condition describes the behaviour of the exact wave function at the coalescence of two particles and additional conditions are known for three particles [13]. The Gaussian orbitals do not fulfil these conditions for neither electron-nucleus nor for electron-electron coalescence. In turn, Slater-type orbitals fulfil the nucleus-electron coalescence condition, but not for electron-electron condition. As a matter of fact all orbital functions fail to fulfil this condition. Nevertheless, while they do converge to the true energy limit in the limit of the infinite number of basis functions this insufficiency results in the slow convergence of methods based on the orbital expansions with respect to the maximum angular momentum l_{max} included in the basis. While the theoretical analysis suggests that the convergence of the orbital functions is proportional to l_{max}^{-4} [14], convergence proportional to l_{max}^{-3} arises from the practical computations [15, 16]. This poses a significant problem when high accuracy of the variational energy or when the accurate wave function is required. The schematic illustration of this problem is presented on the Fig 1. This behaviour, while explained theoretically in greater detail later by Bartlett [17] (and independently by Fock [13]) was first discovered via numerical experiments by Hylleraas [18]. While calculating ionisation energy of the helium atom, he noticed the slow convergence of the variational method using orbital functions. He later, discovered that the

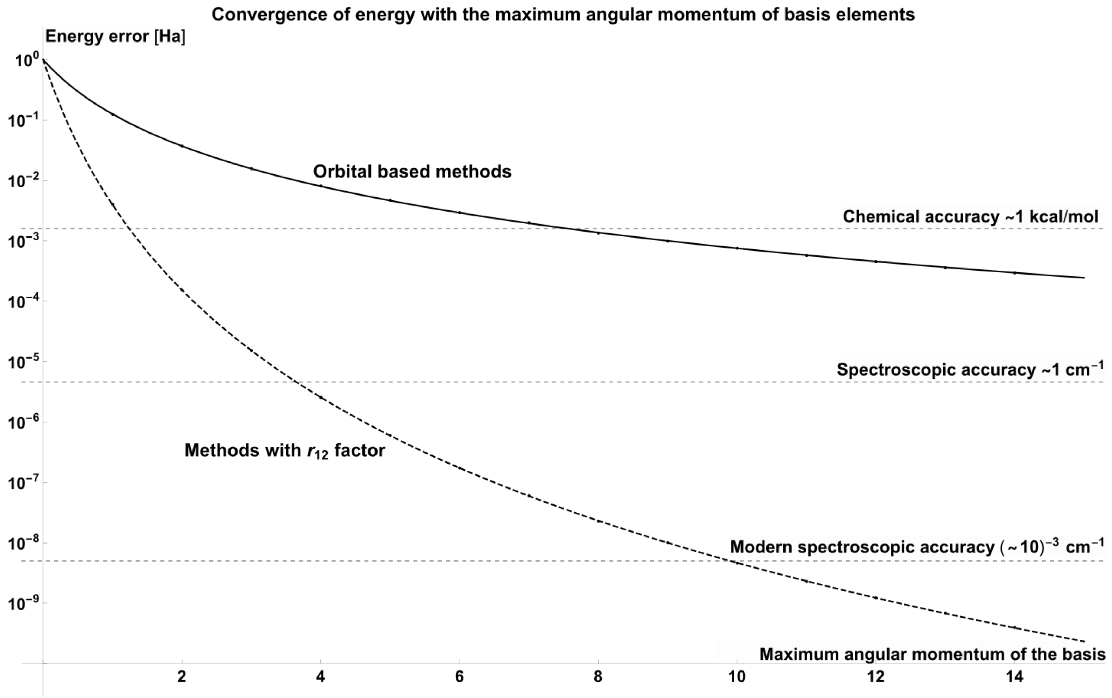

Figure 1.1: Schematic representation of the convergence of energy with maximum angular momentum for orbital and explicitly correlated functions. For the explicitly correlated function l_{max}^{-8} convergence is assumed following the analysis of Kutzelnigg [14], while for orbitals l_{max}^{-3} is assumed because it is the most widely used formula for extrapolation to the complete basis [15,16].

convergence could be significantly improved if the distance between the electrons was introduced into the variational wave function [19]. This improvement allowed to find complete agreement (within 0.01 eV) with the most accurate spectroscopic measurements at the time and quickly opened up a research avenue that led to the accurate calculation of the hydrogen molecule by James and Coolidge [20] and continues to this day, among the others, in the present thesis. Although the idea of introducing interelectronic distances into the trial function was presented earlier by Slater [21] based on a theoretical analysis of the behaviour of the wave function near the Coulomb singularities, he didn't pursue a precise numerical calculation of the ionisation energy of helium. The methods with interelectronic distances explicitly included into the wave functions are named correlated methods [22]. While they have been traditionally used only in highly accurate calculations of few-electron systems [23], recent progress in development of R12/F12 methods [24] has allowed explicitly correlated methods to be applied to large and complex molecular systems [25]. The success of the R12/F12 methods in large systems hasn't fully materialised in the calculations of the atomic [26] and diatomic systems [27] with the intermediate sizes beyond a few electrons, where the large-scale orbital-based calculations still rival the accuracy of the R12/F12 methods [28, 29]. In turn, in the classical, high-accuracy explicitly correlated methods calculations of system with few electrons the two most widely used approaches are [22] the Hylleraas method and its variants and explicitly correlated Gaussian functions. Calculations using these types of functions are currently computationally tractable in systems with no more than six electrons. In my opinion, this means that there is a gap between the extermely accurate methods available for up to six electrons and general methods that are applicable to heavier atoms and large molecular systems. In order to analyse what are the limitations of the many-electron extensions of the existing high-accuracy explicitly correlated variational methods that have been applied beyond the two-electron systems let us consider these methods.

1.2.2 Most accurate explicitly correlated methods

First, we start with the explicitly correlated Gaussian (ECG) functions, as introduced by Boys [30] and Singer [31], which have been extensively described in the recent review [32]. Their general many electron form of a single linear combination of the ECG function is

$$\prod_{1=i<j}^{n} \exp(-a_i r_{ij}^2) \exp(-b r_i^2), \tag{1.7}$$

where n is the number of electrons, the indices numbering the electrons are i, j, while r_i is the distance from the nucleus to the ith electron, the $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the ith and jth electron and $\{a, b\} \in \mathbb{R}^+$ are variational parameters. The main reason for the success of the ECGs is the fact that it is possible to evaluate matrix elements over these functions extremely efficiently using Gaussian Product Theorem, which states that the product of two Gaussian functions centered at $\mathbf{A}$ and $\mathbf{B}$ can be expressed as [10]

$$\exp(-a r_A^2) \exp(-b r_B^2) = \exp(-s r_C^2) \exp(\frac{-ab(\mathbf{AB})^2}{s}), \tag{1.8}$$

where $s = a + b$, $\mathbf{AB} = \mathbf{A} - \mathbf{B}$ and $\mathbf{C} = (a\mathbf{A} + b\mathbf{B})\, s^{-1}$ is the new centre to which the the Gaussian is shifted. Repeated application of this relation and its generalisation allows to calculate all integrals over ECGs analytically. Since the evaluation of the ECG integrals does not pose large difficulty the problem with extension to larger number of electrons must lie elsewhere. There are two significant problems with extending function of type (1.7) to many electrons. The first is that since the function of electrons needs to be antisymmetric this function needs to be antisymmetrized generating $n!$ terms, since all interelectronic distances are present in the function. Secondly, per each linear combination given by equation (1.7) there is a set of $n(n+1)/2$ nonlinear variational parameters. Consequently, the number of nonlinear parameters to optimise for each term in the linear combination of the trial function grows quickly with the number of electrons leading to difficult many-variable optimisation problem. The solution to this problem is possible via restriction of function (1.7) to only single $\exp(-a_i r_{ij}^2)$ leading to functions called Gaussian Type Geminals [33] (GTG). This approach has been studied and applied in the computations involving larger systems, such as neon atom [34] and water molecule [35] in the past, but the accuracy and efficiency of GTG methods were surpassed by the newer R12/F12 methods [24]. Nevertheless, versatility of the ECG functions have been widely used in calculations of few-electron systems and are nowadays essential in obtaining highest-possible accuracy in systems few particles where for atomic systems with more than three electrons they dominate both in terms of accuracy and performance [32]. Furthermore, ECGs have been used to perturbatively calculate the relativistic and QED corrections, include nonadiabatic effects in few-electron atomic and molecular systems, and have recently been employed to solve the Dirac-Coulomb equation, including the no-pair Breit interaction [36]. If not for the factorial scaling with the number of the electrons and steeply growing number of nonlinear parameters in the ECG functions, they would be excellent candidates for highly-accurate method for the systems with more than few electrons. Unfortunately do not see how these two difficulties can be surmounted.

Next, we note that there exists a class of explicitly correlated exponential (ECE) functions (sometimes called explicitly correlated Slater functions) that are analogous to ECG with the functional form of the single term in linear combination that is

$$\prod_{1=i<j}^{n} \exp(-a_i r_{ij}) \exp(-b r_i) \tag{1.9}$$

with symbols having the same meaning as in the definition of ECG functions (equation (1.7)). For two-electron systems such functions are sometimes named Slater type geminals. While these functions have supreme variational convergence properties, the product theorem that would be similarly useful for their evaluation as the one for ECG (given in eq. (1.8)) is not known. Therefore, the integrals with this functions are complicated to evaluate beyond two electrons and such functions are widely used only in the two-electron systems [37–43]. While the analytic formulas for three-electron integrals do exist [44, 45] (and was extended to include complex variational parameters [46]), and we briefly discuss them in section 2.3.1 of this thesis, their evaluation is very involved and it is difficult to control the numerical accuracy and consequently ECE are scarcely utilised in the three-particle atomic systems, with only one study of the three-electron lithium atom [47] that we are aware of. The advantage of ECEs is that the recoil corrections and higher-order QED effects can be efficiently calculated in this basis [48], but so far the calculation of such corrections to the energy levels have realised only in the helium-like systems.

Finally, we turn to the Hylleraas-type functions. The single term of the linear combination in the Hylleraas wave function has the following form for many-electron atoms

$$\prod_{1=i<j}^{n} \exp(-w_i r_i) r_i^{n_i} r_{ij}^{m_{ij}}, \tag{1.10}$$

where, again, n is a number of electrons, i, j are the electron indices, r_i and r_{ij} are nucleus-electron and electron-electron distances, this time raised to the powers $-1 \leq \{n_i, m_{ij}\}$ respectively and $w_i \in \mathbb{R}^+$ are variational parameters. As this function fulfills both Kato cusp conditions and has correct decay for large r_i it is an excellent candidate for basis function and it indeed exhibits exponential convergence to the true energy of the system. Since this form of the function includes all possible distances between the electrons, the calculation of the matrix elements required by the variational method involves integration over coordinates of all electrons. Such integrals cannot be factored to lower dimensional integrals as in the case of the orbitals and the relation similar to the Gaussian Product Theorem is not known for the Hylleraas integrals. Therefore, the integrals quickly become extremely formidable with the increasing number of electrons. As a matter of fact, reliable integration methods for fully correlated Hylleraas function exists only for up to three electrons (the details of the integration methods avaiable for Hylleraas functions are discussed in the next section and in Chapter 2). Beyond that number of electrons, the simplifications of this function are necessary. Hylleraas functions were extensively used in highly-accurate calculations for two- [49–51] and three-electron systems [47, 52] and remains the most accurate method of calculation for the latter. We also note, that Hylleraas basis was successfully used to calculate relativistic [53], QED and recoil corrections [54, 55].

Such simplifications can be preformed by limiting the number of the interelectronic distances in the Hylleraas functions. The limitation may be restricted only to odd powers of r_{ij}, since the even powers can be decomposed into the functions of nucleus-electron distances via the relation $r_{ij}^2 = r_i^2 + r_j^2 - 2r_i r_j \cos(\theta_{ij})$ and $\cos(\theta_{ij})$ may be further transformed, for example using the formula for the cosine of the difference of two angles. Therefore, if function (1.10) is restricted to the single odd power of r_{ij} is called singly-linked Hylleraas function. Analogously, if there are two odd factor of inter-electronic distances such function is called doubly-linked function. Consequently n-tuple linked functions could be constructed up to reconstruction of the original Hylleraas function. After plugging singly-linked Hylleraas function into the expression for the variational energy functional (1.2) it is immediately clear that the integrals of the singly-linked Hylleraas functions involve up to three odd r_{ij}'s, since the first one is from the bra, the second one from the ket and the third one is in Coulomb operator of the Hamiltonian. Therefore, we will restrict our focus to the singly-linked Hylleraas method as it appears to be a reasonable compromise between the properties fulfilled by the trial function and difficulty of integration. The results from the Hylleraas methods are mostly limited to two- [49, 50] and three-electron atomic systems [56–58] with only several studies on the four-electron systems in the singly- [59–61] and doubly-linked [62, 63] Hylleraas basis. While the latter studies did not yield results with leading accuracy it is worth noting, that very small basis sets were used. This indicates, that the bottleneck lied in the evaluation of the matrix elements (since otherwise size of the eigenproblem is the bottleneck of the calculations) and therefore computation of the integrals of the singly- and doubly-linked Hylleraas functions. This observation is an important motivation for the work undertaken in this thesis.

It is worth pointing out that there exists another method of simplifying Hylleraas function. It was independently proposed by Sims and Hagstrom [64] under the name of Hylleraas-Configuration Interaction (Hy-CI) and by Woźnicki [65] who named method Superposition of Correlated Configurations (SSC). In this method the wave function takes general form of a CI expansion

$$\Psi = \sum_k C_k \Phi_k \tag{1.11}$$

with

$$\Phi_k = \hat{\mathcal{A}}\hat{O}(L_z)\left[\chi_k r_{ij}^{v_k} \prod_{m=1}^{N} \varphi_{k_m}\right], \tag{1.12}$$

where the power v_k of interelectronic distance is equal to either 0 or 1, $\hat{\mathcal{A}}$ is the antisymmetrizing operator, $\hat{O}(L_z)$ is the angular momentum projector operator and χ_k is an appropriate linearly independent spin function and φ_{k_m} are the one-electron orbitals or linear combinations of them. The orbitals can in principle be either Slater or Gaussian type orbitals and while the original development used the Slater functions, variants with Gaussian orbitals were also developed. This method is in essence very similar to the singly-linked Hylleraas method. The similarity becomes clear if one uses Legendre polynomial expansion to expand the terms $\cos(\theta_{ij})$ in the even powers of $r_{ij}^2 = r_i^2 + r_j^2 - 2r_i r_j \cos(\theta_{ij})$ resulting in products of spherical harmonics which may be summed using addition theorem. Analogously to the Hylleraas methods it is possible to define doubly-linked Hylleraas-CI methods and higher-linked analogues. Similarly to singly-linked Hylleraas method the resulting integrals have at most three inter-electronic distances. The resulting integrals are however quite different in for these methods, since in the case of Hy-CI/SSC methods the presence of the spherical harmonics requires careful angular integration and leads to natural partition of the integration procedure to the angular and radial integration. Extensive descriptions of the methods to evaluate Hylleraas-CI integrals with Slater orbitals were given by Sims [66–68], Belen-Ruiz [69–72] and Harris [73–75].

The possibility of extension of the Hylleraas-CI/SSC method to systems with more than four electrons is clear after the inspection of the function as it comes down to having more terms in the product in equation (1.12) and was realised by Clary and Handy for neon atom. Furthermore, many-electron Hylleraas-CI wave function can be immediately partitioned to four-electron part and the remaining one-electron functions. This allows for straightforward integration by factoring and evaluating the integral over the correlated and the orbital part separately. In order to illustrate the procedure let us perform it for the single six-electron integral of the Hylleraas-CI function with the correlation factor of form $r_{12}r_{23}r_{24}^{-1}$. The integration proceeds as follows

$$\begin{aligned}
&\int \mathrm{d}^3\mathbf{r}_1\,\mathrm{d}^3\mathbf{r}_2\,\mathrm{d}^3\mathbf{r}_3\,\mathrm{d}^3\mathbf{r}_4\,\mathrm{d}^3\mathbf{r}_5\,\mathrm{d}^3\mathbf{r}_6\frac{r_{12}r_{23}}{r_{24}}\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)\varphi(\mathbf{r}_3)\varphi(\mathbf{r}_4)\varphi(\mathbf{r}_5)\varphi(\mathbf{r}_6)\\
&=\int \mathrm{d}^3\mathbf{r}_1\,\mathrm{d}^3\mathbf{r}_2\,\mathrm{d}^3\mathbf{r}_3\,\mathrm{d}^3\mathbf{r}_4\frac{r_{12}r_{23}}{r_{24}}\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)\varphi(\mathbf{r}_3)\varphi(\mathbf{r}_4)\int \mathrm{d}^3\mathbf{r}_5\varphi(\mathbf{r}_5)\int \mathrm{d}^3\mathbf{r}_6\varphi(\mathbf{r}_6).
\end{aligned}\tag{1.13}$$

Therefore, after all possible integrals with three r_{ij}'s are solved, the integration of many-electron problem does not pose further difficulty in Hy-CI/SSC method (at least for the moderate numbers of electrons).

A lot of research on the Hy-CI/SSC methods was done by several groups resulting in many accurate results for two- [51, 76, 77] three- [78–82] and four-electron [83–87] atomic systems. While the calculations of the energy of the five-electron boron atom using Hy-CI/SSC method were made [88], obtained results had significantly lower accuracy than those obtained with ECGs at the time [89]. The 1976 study of Clary and Handy [90] reports application of the Hy-CI method for system as large as neon atom. Although the accuracy of calculations was severely hindered by computational power available at the time, the feat of using explicitly correlated function (without the approximations used in R12/F12 methods) for system with ten electron remains unparalleled until this day. The Hylleraas-CI was the first [91] and the most extensively used explicitly correlated method employed to solve Dirac-Colomb equation [92–95] (and until very recently [36] the only one). A detailed, recent review of the Hylleraas-CI/SSC method is available [96]. It is also worth mentioning that Exponentially-correlated Hylleraas-CI method, which adds exponential (Slater) correlation factor into the Hylleraas-CI function, is being recently developed, but so far the applications are limited to two-electron systems [97–99]. The largest drawback of the Hylleraas-CI method appears to be that, to the best of our knowledge, QED and recoil corrections were never calculated using this method, while the relativistic corrections were obtained only for the helium atom in by directly solving the Dirac-Coulomb equation.

1.2.3 Singly-linked Hylleraas method beyond four electrons

The extendability of the singly-linked Hylleraas function to many electrons while maintaining the simple integrals is not so clear at first. Since many r_{ij}'s with even powers may be present under the integral it cannot be immediately factored to integral products as is the case for Hylleraas-CI/SSC function. However, one may immediately notice, that decomposition of the even powers of r_{ij}'s that do not share both of the indices with the interelectronic distances with the odd powers leads to the linear combinations of products of four-electron singly-linked integrals and one-electron integrals. Let us illustrate this with an example integral, similar to the one shown for the Hy-CI function, and for simplicity we take five electrons and only single square power of inter-electronic distances that does not share both indices, namely r_{25}. The integral is as follows

$$\int \mathrm{d}^3\mathbf{r}_1\,\mathrm{d}^3\mathbf{r}_2\,\mathrm{d}^3\mathbf{r}_3\,\mathrm{d}^3\mathbf{r}_4\,\mathrm{d}^3\mathbf{r}_5\frac{r_{12}r_{23}}{r_{24}}r_{13}^2r_{14}^2r_{34}^2r_{25}^2\varphi(r_1)\varphi(r_2)\varphi(r_3)\varphi(r_4)\varphi(r_5)\tag{1.14}$$

may be rearranged to the following form

$$\begin{aligned}
&\int \mathrm{d}^3\mathbf{r}_1\,\mathrm{d}^3\mathbf{r}_2\,\mathrm{d}^3\mathbf{r}_3\,\mathrm{d}^3\mathbf{r}_4\,\mathrm{d}^3\mathbf{r}_5 \frac{r_{12}r_{23}}{r_{24}} r_{13}^2 r_{14}^2 r_{34}^2 (r_2^2 + r_5^2 - 2\mathbf{r}_2\cdot\mathbf{r}_5)\\
&= \int \mathrm{d}^3\mathbf{r}_1\,\mathrm{d}^3\mathbf{r}_2\,\mathrm{d}^3\mathbf{r}_3\,\mathrm{d}^3\mathbf{r}_4 \frac{r_{12}r_{23}}{r_{24}} r_{13}^2 r_{14}^2 r_{34}^2 r_2^2 \varphi(r_1)\varphi(r_2)\varphi(r_3)\varphi(r_4) \int \mathrm{d}^3\mathbf{r}_5 \varphi(r_5)\\
&+ \int \mathrm{d}^3\mathbf{r}_1\,\mathrm{d}^3\mathbf{r}_2\,\mathrm{d}^3\mathbf{r}_3\,\mathrm{d}^3\mathbf{r}_4 \frac{r_{12}r_{23}}{r_{24}} r_{13}^2 r_{14}^2 r_{34}^2 \varphi(r_1)\varphi(r_2)\varphi(r_3)\varphi(r_4) \int \mathrm{d}^3\mathbf{r}_5 r_5^2 \varphi(r_5)\\
&- 2\int \mathrm{d}^3\mathbf{r}_1\,\mathrm{d}^3\mathbf{r}_2\,\mathrm{d}^3\mathbf{r}_3\,\mathrm{d}^3\mathbf{r}_4\,\mathrm{d}^3\mathbf{r}_5 \frac{r_{12}r_{23}}{r_{24}} r_{13}^2 r_{14}^2 r_{34}^2 \varphi(r_1)\varphi(r_2)\varphi(r_3)\varphi(r_4)\varphi(r_5)\mathbf{r}_2\cdot\mathbf{r}_5
\end{aligned} \tag{1.15}$$

by simply using the law of cosines $r_{ij}^2 = r_i^2 + r_j^2 - 2r_ir_j\cos\theta_{12}$ and the fact that in the Euclidean space dot product may be written as $r_ir_j\cos(\theta_{ij}) = \mathbf{r}_i \cdot \mathbf{r}_j$, multiplying the terms and factoring the integral. While the uncoupling may seem unsuccessful because of the last integral with the scalar product is not separated. However, let us point out that

$$\begin{aligned}
&\int \mathrm{d}^3\mathbf{r}_1\,\mathrm{d}^3\mathbf{r}_2\,\mathrm{d}^3\mathbf{r}_3\,\mathrm{d}^3\mathbf{r}_4\,\mathrm{d}^3\mathbf{r}_5 \frac{r_{12}r_{23}}{r_{24}} r_{13}^2 r_{14}^2 r_{34}^2 \varphi(r_1)\varphi(r_2)\varphi(r_3)\varphi(r_4)\varphi(r_5)\mathbf{r}_2\cdot\mathbf{r}_5\\
&= \int \mathrm{d}^3\mathbf{r}_1\,\mathrm{d}^3\mathbf{r}_2\,\mathrm{d}^3\mathbf{r}_3\,\mathrm{d}^3\mathbf{r}_4 \frac{r_{12}r_{23}}{r_{24}} r_{13}^2 r_{14}^2 r_{34}^2 \varphi(r_1)\varphi(r_2)\varphi(r_3)\varphi(r_4) \int \mathrm{d}^3\mathbf{r}_5 \varphi(r_5)\mathbf{r}_2\cdot\mathbf{r}_5 = 0
\end{aligned} \tag{1.16}$$

since (the rearrangement of the order of integration in the line above is to emphasise which electron needs to be integrated over fist; in this case – the one that does not share an index with any r_{ij} raised to the odd power)

$$\begin{aligned}
&\int \mathrm{d}^3\mathbf{r}_5 \varphi(r_5)\mathbf{r}_2\cdot\mathbf{r}_5 = \int \mathrm{d}^3\mathbf{r}_5 \varphi(r_5) r_2 r_5 \cos(\theta_{25})\\
&= r_2 \int_0^\infty \mathrm{d}r r_5^3 \varphi(r_5)\Big(\cos(\theta_2)\int_0^\pi \mathrm{d}\theta_5 \sin(\theta_5)\cos(\theta_5)\int_0^{2\pi}\mathrm{d}\phi_5\\
&+ \sin(\theta_2)\cos(\phi_2)\int_0^\pi \mathrm{d}\theta_5 \sin(\theta_5)^2 \int_0^{2\pi}\mathrm{d}\phi_5 \cos(\phi_5)\\
&+ \sin(\theta_2)\sin(\phi_2)\int_0^\pi \mathrm{d}\theta_5 \sin(\theta_5)^2 \int_0^{2\pi}\mathrm{d}\phi_5 \sin(\phi_5)\Big) = 0,
\end{aligned} \tag{1.17}$$

where we us formula for the cosine between the two vectors in the spherical coordinates $\cos(\theta_{25}) = \sin(\theta_2)\sin(\theta_5)\cos(\phi_2 - \phi_5) + \cos(\theta_2)\cos(\theta_5)$ and the formula for the difference of the cosine, $\cos(\phi_2 - \phi_5) = \sin(\phi_2)\sin(\phi_5) + \cos(\phi_2)\cos(\phi_5)$. The first integral in (1.17) vanishes after the integration over θ_5 and the integral over ϕ_5 is zero for the two remaining terms of the sum. Therefore, we have shown that the integral (1.14) has been decomposed into the linear combination of the product of the four-electron singly-linked Hylleraas integral and products of the one electron functions. Of course, the angular integration would be more involved with more r_{ij} terms to the even powers present under the integral, but since the functions $\varphi(r_i)$ are spherically symmetric, such scalar products can always be expanded and the angular integration of the scalar products can always be performed in the coordinates of the electrons that are not present in the r_{ij}'s with the odd powers. We believe that this opens up a way to extend the singly-linked Hylleraas methods to systems with more than four electrons, if the efficient methods of evaluating four-electron singly-linked Hylleraas integrals can be found. Therefore we pursue development of such integration method.

1.2.4 Summary of the motivation

To sum up, we pursue analytic evaluation of the singly-linked four-electron integrals for two main reasons. Firstly, we believe that current methods for evaluation of these integrals are lacking, which results in unrealised potential of the singly-linked Hylleraas method in the calculations of the four-electron atomic systems. Secondly, we believe that singly-linked Hylleraas method offers a promising avenue to develop an accurate computational method that will be applicable to light atomic systems with more than few electrons. However, in order to test that claims, efficient method to obtain matrix elements with four electrons must exist first. In addition to that scientific curiosity and formidable challenge of analytic evaluation of explicitly correlated integrals also motivated us to pursue topic presented in this thesis. Therefore, we proceed to evaluation of singly-linked four-electron integrals.

1.3 Existing research on the evaluation of the Hylleraas integrals

1.3.1 Methods for evaluation of the integrals of the Hylleraas-type functions

In general, the methods of evaluation of electronic integrals with the explicitly-correlated functions can be divided to several types – direct numerical integration, expansions into sums, direct analytic evaluation that leads to closed-form formulas. All of these methods of evaluation face the following challenges. First, the correlated functions of many electrons are usually high-dimensional (compared to traditional three- or six-dimensional integration of one- and two-electron functions), with non-trivial spatial dependence in both angular and radial dimensions. The standard techniques such as separation to radial and angular integration are much more difficult to apply in case of the explicitly correlated functions. Furthermore, the integrals involved in the evaluation of the matrix elements for the variational methods include (integrable) Culombic singularities – expressions like $1/r_i, 1/r_{ij}$ – that make the convergence of numerical integration around the singular points slow, unless some method (usually involving some form of regularization) is applied to alleviate this issue. Finally, the problem of evaluating integrals with several-electronic distances is made more difficult by the requirement of having many correct digits, since the values of evaluated integrals are used in eigenproblems to find accurate energies and properties of the considered atomic systems. When high-accuracy energies are required, use of extended-precision arithmetic (such as quadruple precision) is often necessary and evaluated values of the integrals should be accurate up to this precision. Although the methods of integration of explicitly correlated Hylleraas functions have been developed for nearly hundred years (starting from the seminal work of Hylleraas [19]) so far only two- and three-electron integrals have been solved in satisfactory manner.

The first, most obvious class of methods that deals with integration of correlated functions is the one that involves direct numerical evaluation of the integrals by quadratures. Despite the amazing progress in available computation power in recent decades, available computational facilities are still insufficient for direct attack on the problem like numerical integration of the high-dimensional function on the grid with sufficient accuracy and speed for accurate atomic calculations. This mostly stems from the curse of dimensionality – in order to evaluate N-dimensional integral, the number of grid points scales as h^N, where h is the number of grid points in one dimension. Although various schemes that adapt numerical integration methods to the multi-dimensional problems are available, the purely numerical integration methods remain largely unsuccessful for systems beyond two-electrons. Such approach was pursued in work of Guevara, Harris and Turbiner [100] where they have used numerical integration to pursue exponentially correlated functions for lithium atom. Since they used simple, few-parameter “ultra-compact” trial functions that yield reasonable overall accuracy instead of large basis expansion to get maximum accuracy their function was limited to only six terms. This basis resulted in three correct digits of energy, which wile impressive for such short function, is absolutely insufficient for accurate calculations of the atomic and small molecular systems. Even though the clever use of the coordinate transformation has allowed them to reduce the numerical integration to six dimensions and using state-of-the-art parallelized numerical integration algorithms, the authors concluded, that "Because of the complicated profiles of the integrands, the numerical calculations are very difficult and if not done with great care can lead to a serious loss of accuracy. By comparing numerical and analytical evaluations of some of the simpler matrix elements, it was verified that the numerical methods were reliable at least to six significant digits.". We believe that this excellent study shows what kind of challenge the explicitly correlated functions pose to multi-dimensional numerical integration. Therefore, it is of no surprise that we are not aware of any methods that use numerical quadratures to evaluate four-electron singly-linked Hylleraas integrals. We note, that while direct numerical integration of the multi-dimensional functions appears to be hopeless task, the use of one- and two- dimensional numerical integration is widespread in explicitly correlated methods. When the many-dimensional integrals can be analytically transformed to the one- [101] or two-dimensional [102] integrals. In such case, the use of numerical integration, particularly when adapted quadratures are available [103], can be extremely beneficial both in terms of numerical accuracy and computational cost [104] and even allow for the evaluation of some expressions for which other integration methods are unknown [105].

The second, most classical group of methods to calculate explicitly correlated integrals involve expansions into the (sometimes infinite) but convergent sums. An excellent review of this approach (along with some others) was given by King [106] and therefore we will describe only the silent details and developments that happened after this review was published. The most widely used expansion is the well-known (and used across all areas of physics) Laplace expansion

$$\frac{1}{r_{ij}} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l\left(\cos\theta_{ij}\right), \tag{1.18}$$

where $r_< = \min\left\{r_i, r_j\right\}$ and $r_> = \max\left\{r_i, r_j\right\}$. Its most widely used generalisation is the Sack expansion [107]

$$r_{ij}^l = \sum_{l_1=0}^{\infty} R_{ll_1}\left(r_i, r_j\right) P_{l_1}\left(\cos\theta_{ij}\right), \tag{1.19}$$

where $R_{ll_1}\left(r_1, r_2\right)$ is a Sack radial function, but for example expansion for the linear r_{ij} term [108] appeared only four years after the seminal works of Hylleraas. These kinds of expansions allow to decouple the angular and radial integration via expressing r_{ij}^n as series. Angular integration is typically performed using expansion of Legendre polynomials and standard techniques for coupling of the spherical harmonics. In turn, radial integrals are typically expressed in terms of sums of auxiliary integrals that are integrals over the radial coordinates. While for the two-electron integrals these series are finite, the situation is more complicated in case of the three-electron Hylleraas integrals. The most daunting situation happens, when all three r_{ij} terms are raised to the odd powers. In this case, the resulting series are convergent but infinite. While this has limited the accuracy of the computations using Hylleraas functions for a long time, since the trial functions were constructed in a way to avoid this difficulty [109–111]. This difficulties were later surmounted using convergence acceleration techniques [112,113] and asymptotic expansion method [114] and have allowed for extremely accurate calculations. The extension of these techniques to four-electron Hylleraas integrals have resulted in only a partial success. While a lot has been written on the four-electron integrals occurring in the Hylleraas-CI method [66–75](which are in principle a subset of Hylleraas integrals), the general four electrons have resulted in moderate amount of attention [115–121]. We note, that some preliminary work was done for selected limited of five-electron Hylleraas integrals [122,123]

The third class of methods to evaluate Hylleraas integrals involve direct analytic evaluation in order to obtain closed-form analytic expressions. The techniques involve wide spectrum methods for analytic integration of the multi-dimensional integrals such as Fourier transforms, transformations of the coordinates, integration using the residue theorem among the other methods of mathematical physics. Since we extensively rely on this type approach through this thesis, we describe it for the Hylleraas integrals in the next chapter. We go into the great detail starting from simple one-electron integrals and finishing at the four-electron singly-linked Hylleraas integrals. Another technique worth mentioning here is the one introduced by Pachucki, Puchalski and Remiddi [124]. It originates form the techniques used for evaluation of Feynman integrals and allows to generate a scheme of multi-dimensional recurrence relations to calculate Hylleraas integrals, starting from a set of the master integrals. While we use this technique to obtain the analytic expressions in the present thesis and describe it in the next chapter, we would like to point out, that the master integrals can be evaluated numerically and the recurrence relations can be applied to calculate all the remaining integrals in a purely numerical manner.

1.3.2 Analytic evaluation of four-electron singly-linked Hylleraas integrals

Now, we focus on the existing results concerning directly the topic of our thesis – the analytic evaluation of the four-electron singly-linked Hylleraas integrals. Not a lot of work was done using this approach. Padhy [125] has used Fourier representation of the four-electron exponential integrals to obtain closed-form analytic formulas for the four singly-linked Hylleraas integrals, that in our notation (see eq. (1.1)) have the following values of the parameters: $\{n_1, n_2, n_3, n_4\} = -1$ in all integrals and $\{a = 1, b = 1, c = -1\}$, $\{a = 1, d = -1, f = 1\}$, $\{a = 1, d = 1, f = -1\}$ and $\{a = 1, b = -1, f = 1\}$ with the remaining parameters not included in braces are equal to zero. King has published two papers concerned with the analytic evaluation of some singly-linked Hylleraas integrals [121,126]. In the first paper, the classical approach based on the Sack expansion was used to obtain analytic expressions for four-electron integrals with up to four odd powers of r_{ij}, but with the limitation some of the powers of $\{r_1, r_2, r_3, r_4\}$ are equal to zero when there are four odd powers of r_{ij}'s. In the second paper, King has generalized his approach to explicitly correlated exponential functions and gave results slightly more general than those of Padhy. For us, the most interesting are limiting cases where exponential factors are taken to zero which correspond to Hylleraas-type functions. We note, that while King had evaluated Hylleraas integral with $(r_1 r_2 r_{12} r_{13} r_{23} r_{24})^{-1}$ in [121] neither of the works considers integrals with odd $r_{12} r_{23} r_{13}$ and simultaneously at least one even r_{14}, r_{24}, r_{34}.

Chapter 2

Methods

2.1 Introduction

In this chapter we describe a method we developed to obtain closed-form analytic formulas[1] for one center singly-linked Hylleraas integrals. While methods allowing to calculate some of the singly-linked Hylleraas integrals exist in the literature, we are not aware of any method that allows to efficiently obtain all such integrals as closed-form analytic expressions.

The presentation of the developed method is as follows. First, we introduce one- two- and three-electron Hylleraas integrals necessary to bootstrap four-electron calculations as well as describe methods we use to obtain them in closed form. After that, we proceed to discuss the four-electron integrals in general. Next, we discuss newly developed recurrence relations for four-electron Hylleraas integrals. Then, we proceed to discuss our developed methods to obtain singly-linked Hylleraas integrals as closed-form analytic formulas. The Figure 2.1 serves as general guide for the method. Each of the blocks corresponds to the section that describes a part of the calculations. Finally, we show how to obtain all the remaining singly-linked Hylleraas integrals via permutations, using symmetry of the four-electron integrals.

2.1.1 Notation and minor remarks

In our thesis we use notation that is a compromise between the standard notation used in literature and in general in the field of calculation of the electronic integrals, readability, compactness and elegance. We use Roman letters from the start of the alphabet (a, b, c, d, e, f) to denote the powers of the distances between the pairs of electrons sorted by increasing indices, namely $r_{12}, r_{13}, r_{14}, r_{23}, r_{24}, r_{34}$. Powers of distances of electrons r_1, r_2, r_3, r_4 from the origin of the coordinate system are denoted as n_1, n_2, n_3, n_4. The w_1, w_2, w_3, w_4 are positive real variational parameters. We also often use shorthand notation r_i, r_{ij} and w_i with implicit $i, j = 1, 2, 3, 4$ in case of four-electron integrals and $i, j = 1, 2, 3$ in case of the three-electron ones. By $\mathrm{d}^3\mathbf{r}_i$ we

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[1] Here, by closed-form analytic formulas we understand mathematical expressions that may involve special functions, but contain no infinite sums, products or continued fractions, limits, and derivatives or integrals to be performed numerically. This makes such expressions readily available for efficient evaluation with arbitrary precision.

indicate integration over all spatial coordinates of the ith electron over the whole space (from $-\infty$ to $+\infty$ in Cartesian coordinates).

We divide all integrals by factor $(4\pi)^n$, where n is the number of electrons that are integrated over their whole respective spaces. Since the functions we consider do not directly contain spherical harmonics (though they are indirectly "present" in Hylleraas-type functions via the even powers of r_{ij})[2], the integration over angular coordinates of each electron results in 4π. This cancels with the $(4\pi)^n$ factor by which we divide all the integrals.

2.2 One and two electron integrals

2.2.1 One-electron integrals with exponential functions

One-electron integrals are the most elementary integrals in atomic calculations. Closed-form formulas are straightforward to obtain for atomic systems, since the spherical symmetry allows for the separation of the radial and angular integration. The general formula for the exponential one-electron integrals is

$$I_1(i;\alpha) = \int \frac{\mathrm{d}^3\mathbf{r}}{4\pi}\exp(-\alpha r)r^i = \int\limits_0^\infty \mathrm{d}r\exp(-\alpha r)r^{i+2} = \frac{(i+2)!}{\alpha^{i+3}}, \tag{2.1}$$

with the parameters limited to $\alpha > 0$ and $i \geq -2$. The extension of these parameters beyond this range is possible (and necessary, for example, in the case where effective QED operators are calculated), but is beyond the scope of this thesis.

2.2.2 Two-electron integrals of Hylleraas and exponential-type functions

The case of two-electron integrals is slightly more complicated, but easily manageable using some handy methods for evaluation of spherically-symmetric double volume integrals. This makes the two-electron systems a benchmark test for development of the electronic structure methods that are candidates for few-, as well as many-electron atomic systems.

Integrals of the two-electron functions of the Hylleraas type have the following form

$$I_2(l,m,n;\alpha,\beta) = \iint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\exp(-\alpha r_1 - \beta r_2)r_1^l r_2^m r_{12}^n \tag{2.2}$$

where $\alpha, \beta > 0$ and $l, m, n \geq -1$. We will proceed with their evaluation by considering integrals of more general form and evaluate integrals of type (2.2) as their special case.

The more general as well as symmetric integrals are the two-electron exponential integrals. They have the following form

$$\Gamma(l,m,n;\alpha,\beta,\gamma) = \iint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\exp(-\alpha r_1 - \beta r_2 - \gamma r_{12})r_1^{l-1} r_2^{m-1} r_{12}^{n-1}, \tag{2.3}$$

---

[2] The expression for the square of the distance between the pair of electrons $r_{ij}^2 = r_i^2 + r_j^2 - 2r_i r_j \cos(\theta_{ij})$ can be directly related to spherical harmonics using expansion of $\cos(\theta_{ij})$ into Legendre polynomials and Spherical Harmonics Addition Theorem.

with $\alpha, \beta, \gamma > 0$ and $l, m, n \geq 0$. These integrals have a very symmetric form and an advantageous property, that the integrals with increased powers of r_1, r_2, r_{12} can obtained from one integral (so-called master integral) via the differentiation over the parameters α, β, γ

$$\Gamma(l, m, n; \alpha, \beta, \gamma) = \left(-\frac{\partial}{\partial\alpha}\right)^l \left(-\frac{\partial}{\partial\beta}\right)^m \left(-\frac{\partial}{\partial\gamma}\right)^n \Gamma(0, 0, 0; \alpha, \beta, \gamma). \tag{2.4}$$

Method of calculation of closed-form expressions for the two-electron integrals

The remaining task is to calculate $\Gamma(0, 0, 0; \alpha, \beta, \gamma)$ and now we proceed with that evaluation. This integral can be calculated in rather straightforward way using clever change of coordinates [127–129]. The coordinates are obtained by starting from spherical system of coordinates and expressing double volume element in terms of r_1, r_2, r_{12} and angles. The $\mathrm{d}^3\mathbf{r}_2$ is transformed using the fact, that coordinate system of vector $\mathbf{r}_2$ can be rotated, so that the polar axis of vector $\mathbf{r}_2$ is colinear with the vector $\mathbf{r}_1$, and the triangle is formed from the sides r_1, r_2, r_{12}, such that polar angle of $\mathbf{r}_2$ coincides with angle between r_1 and r_2 (denoted as θ_{12}) and azimuthal angle of $\mathbf{r}_2$ corresponds to rotation over the polar axis of $\mathbf{r}_1$ (denoted as χ). After this rotation the volume element of $\mathbf{r}_2$ becomes $\mathrm{d}^3\mathbf{r}_2 = r_2^2\,\mathrm{d}r_2 \sin(\theta_{12})\,\mathrm{d}\theta_{12}\,\mathrm{d}\chi$. Next, we use the law of cosines

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2\cos(\theta_{12}) \tag{2.5}$$

by applying the total derivative to both sides of the equation (with r_1, r_2 fixed)

$$2r_{12}\,\mathrm{d}r_{12} = 2r_1r_2\sin(\theta_{12})\,\mathrm{d}\theta_{12} \tag{2.6}$$

we obtain

$$\sin(\theta_{12})\,\mathrm{d}\theta_{12} = \frac{r_{12}}{r_1r_2}. \tag{2.7}$$

The upper and lower integration limits become $\sqrt{r_1^2 + r_2^2} = r_1 + r_2$ and $\sqrt{r_1^2 - r_2^2} = |r_1 - r_2|$ respectively (since $r_1 \wedge r_2 \geq 0 \Rightarrow \max r_{12} = r_1 + r_2$ and $\min r_{12} = |r_1 - r_2|$) leading to

$$\begin{aligned}\Gamma(0,0,0;\alpha,\beta,\gamma) = \frac{1}{2}\Bigg(&\int_0^\infty \mathrm{d}r_1 \exp(-\alpha r_1) \int_{r_1}^\infty \mathrm{d}r_2 \exp(-\beta r_2) \int_{r_2-r_1}^{r_1+r_2} \mathrm{d}r_{12} \exp(-\gamma r_{12}) \\ &+ \int_0^\infty \mathrm{d}r_2 \exp(-\beta r_2) \int_{r_2}^\infty \mathrm{d}r_1 \exp(-\alpha r_1) \int_{r_1-r_2}^{r_1+r_2} \mathrm{d}r_{12} \exp(-\gamma r_{12})\Bigg)\end{aligned} \tag{2.8}$$

(2.8)

that can be straightforwardly evaluated yielding

$$\Gamma(0, 0, 0; \alpha, \beta, \gamma) = \frac{1}{(\alpha + \beta)(\alpha + \gamma)(\beta + \gamma)}. \tag{2.9}$$

Formulas for the remaining integrals with $\{l, m, n\} > 0$ are obtained by applying formula (2.4).

The only remaining type of the two-electron integral (that is needed to calculate the three-electron integrals we are interested in) is when one of the parameters $\{l, m, n\}$ is equal to -1. These are so-called extended integrals and they are used as boundary terms in evaluation of three-electron integrals. The master integral for extended integrals $\Gamma(-1,0,0;\alpha,\beta,\gamma)$ can be obtained by following the same procedure as in equation (2.8) (with r_1^{-1} under the integral), or by noticing that it can be obtained using direct integration of the equation (2.9) to yield

$$\begin{aligned}\Gamma(-1,0,0;\alpha,\beta,\gamma) &= \int_\alpha^\infty \mathrm{d}\alpha \Gamma(0,0,0;\alpha,\beta,\gamma) \\ &= \int_\alpha^\infty \mathrm{d}\alpha \frac{1}{(\alpha+\beta)(\alpha+\gamma)(\beta+\gamma)} = \frac{\ln\left(\frac{\alpha+\beta}{\alpha+\gamma}\right)}{\beta^2-\gamma^2}.\end{aligned} \tag{2.10}$$

Remaining types of the extended integrals can be obtained by differentiation (similarly to equation (2.4)) and from the symmetry via the permutations of the parameters. These integrals complete the set of formulas of the two-electron integrals that are required to analytically evaluate three- (and consequently four-) electron integrals of Hylleraas type.

2.3 Three-electron integrals

The problem of the correlated three-electron integrals is an order of magnitude more complicated than for integrals involving two electrons. With the addition of a third electron the integrals over their all coordinates are, in general nine-dimensional (3 dimensions per electron) integrals of general form

$$\iiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi} f(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3). \tag{2.11}$$

Consequently, if one wishes to construct a spherically-symmetric function with interelectronic coordinates, there are six distances between the particles – three from nucleus to electron and three between the electrons:

$$f(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = f(r_1,r_2,r_3,r_{12},r_{13},r_{23}). \tag{2.12}$$

These two facts severely complicate three-electron integrals compared against two-electron ones. However, large progress has been made in the evaluation of these integrals, and for the case of Hylleraas-type functions this problem is essentially solved for integrals required in non-relativistic [124], relativistic [130] and lowest-order QED calculations [131].

2.3.1 Fromm-Hill integral

Surprisingly, the first major breakthrough in analytic evaluation of three-electron integrals of Hylleraas type came in 1987 *tour de force* paper authored by Fromm and Hill [44] where even more general integral, namely of exponential type, was directly evaluated analytically by using Fourier integral representation of $r^{-1}\exp(-\alpha r)$ and ingenious application of contour integration. The Fromm-Hill integral has the following form

$$I(w_1,w_2,w_3,u_{12},u_{13},u_{23}) = \iiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\exp(-w_1r_1-w_2r_2-w_3r_3-u_{12}r_{12}-u_{13}r_{13}-u_{23}r_{23})}{r_1r_2r_3r_{12}r_{13}r_{23}}, \tag{2.13}$$

with $\{w_1, w_2, w_3, u_{12}, u_{13}, u_{23}\} \in \mathbb{R}^+$. We will not present its analytic form after integration, as it is rather unwieldy. It involves combinations of dilogarithms with complex arguments that involve the square root of a homogeneous sixth-degree polynomial in parameters w_i, u_{ij} and requires careful branch tracking for numerical evaluation.

Analytic evaluation of the Fromm-Hill integral has allowed to obtain expressions for even more general function, that has arbitrary powers of r_i and r_{ij}

$$\begin{aligned} J(n_1, n_2, n_3, n_{12}, n_{13}, n_{23}; w_1, w_2, w_3, u_{12}, u_{13}, u_{23}) = \iiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_2}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_3}{4\pi} r_1^{n_1-1} r_2^{n_2-1} r_3^{n_3-1} \\ \times r_{12}^{n_{12}-1} r_{13}^{n_{13}-1} r_{23}^{n_{23}-1} \exp(-w_1 r_1 - w_2 r_2 - w_3 r_3 - u_{12} r_{12} - u_{13} r_{13} - u_{23} r_{23}) \end{aligned} \tag{2.14}$$

available via differentiation similarly to the two-electron case

$$\begin{aligned} J(n_1, n_2, n_3, n_{12}, n_{13}, n_{23}; w_1, w_2, w_3, u_{12}, u_{13}, u_{23}) = \left(-\frac{\partial}{\partial w_1}\right)^{n_1} \left(-\frac{\partial}{\partial w_2}\right)^{n_2} \left(-\frac{\partial}{\partial w_3}\right)^{n_3} \\ \times \left(-\frac{\partial}{\partial u_{12}}\right)^{n_{12}} \left(-\frac{\partial}{\partial u_{13}}\right)^{n_{13}} \left(-\frac{\partial}{\partial u_{23}}\right)^{n_{23}} I(w_1, w_2, w_3, u_{12}, u_{13}, u_{23}). \end{aligned} \tag{2.15}$$

The result was difficult in practical realisation via the computer program that could be used in large-scale calculations of atomic systems. Next, there appeared a new result by Remiddi [132] in 1991 where he independently gave analytic formulas for simpler case of $I(w_1, w_2, w_3, 0, 0, 0)$, namely the most fundamental three-electron integral of Hylleraas type (along with several other integrals). Significant simplification of Fromm-Hill formulas was given in 1997 by Harris [45]. He managed to turn integral $I(w_1, w_2, w_3, u_{12}, u_{13}, u_{23})$ to a form involving Clausen function, that does not require branch tracking. He also reconciled results of Fromm-Hill and Remiddi and has shown that it is possible to obtain Remiddi's result as a special case of Fromm-Hill integral (with $u_{ij} = 0$.

2.3.2 Three-electron integrals of Hylleraas-type functions

If we use Hylleraas-type functions to represent wavefunction for three-electron atomic system, the integrals have the following form

$$f(a, b, c, n_1, n_2, n_3; w_1, w_2, w_3) = \iiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_2}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_3}{4\pi} \exp(-w_1 r_1 - w_2 r_2 - w_3 r_3) r_{12}^{a} r_{13}^{b} r_{23}^{c} r_1^{n_1} r_2^{n_2} r_3^{n_3}, \tag{2.16}$$

where $-1 \leq \{a, b, c, n_1, n_2, n_3\} \in \mathbb{Z}$ are powers of distances electron-electron distances and the nucleus-electron distances and $\{w_1, w_2, w_3\} \in \mathbb{R}^+$ are nonlinear parameters. These integrals have the following symmetry

$$\begin{aligned} f(a, b, c, n_1, n_2, n_3; w_1, w_2, w_3) &= f(b, a, c, n_2, n_1, n_3, w_2, w_1, w_3) \\ &= f(c, b, a, n_3, n_1; w_3, w_2, w_1) = f(a, c, b, n_1, n_3, n_2; w_1, w_3, w_2). \end{aligned} \tag{2.17}$$

2.3.3 Three-electron Hylleraas-type master integral

The most fundamental integral is the one with all powers equal to -1 (it also corresponds to special case of the Fromm-Hill integral with all $u_{ij} = 0$)

$$\begin{aligned} &f(-1,-1,-1,-1,-1,-1; w_1, w_2, w_3) = I(w_1, w_2, w_3, 0, 0, 0) = \\ &\iiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\exp(-w_1 r_1 - w_2 r_2 - w_3 r_3)}{r_{12} r_{13} r_{23} r_1 r_2 r_3}. \end{aligned} \tag{2.18}$$

The derivation of the resulting expression by Remiddi also involves Fourier representation of $r^{-1}\exp(-\alpha r)$ but uses sophisticated choice of variable transformations, quadratic forms, derivatives, asymptotic expansions and factor cancellations that yield the final result

$$\begin{aligned} &f(-1,-1,-1,-1,-1,-1; w_1, w_2, w_3) \\ &= \frac{-1}{2\,w_1\,w_2\,w_3}\biggl\{\ln\left(\frac{w_3}{w_1+w_2}\right)\,\ln\left(1+\frac{w_3}{w_1+w_2}\right) + \mathrm{Li}_2\left(-\frac{w_3}{w_1+w_2}\right) + \mathrm{Li}_2\left(1-\frac{w_3}{w_1+w_2}\right) \\ &+ \ln\left(\frac{w_2}{w_3+w_1}\right)\,\ln\left(1+\frac{w_2}{w_1+w_3}\right) + \mathrm{Li}_2\left(-\frac{w_2}{w_1+w_3}\right) + \mathrm{Li}_2\left(1-\frac{w_2}{w_1+w_3}\right) \\ &+ \ln\left(\frac{w_1}{w_2+w_3}\right)\,\ln\left(1+\frac{w_1}{w_1+w_2}\right) + \mathrm{Li}_2\left(-\frac{w_1}{w_2+w_3}\right) + \mathrm{Li}_2\left(1-\frac{w_1}{w_2+w_3}\right)\biggr\}, \end{aligned} \tag{2.19}$$

where Li_2 is the dilogarithm function defined as

$$\mathrm{Li}_2(\mathrm{z}) = -\int_0^{\mathrm{z}} \mathrm{du}\frac{\ln(1-\mathrm{u})}{\mathrm{u}}. \tag{2.20}$$

Increased powers of r_i's can again be straightforwardly obtained via differentiation over respective parameters

$$\begin{aligned} &f(-1,-1,-1,n_1,n_2,n_3; w_1, w_2, w_3) \\ &= \left(-\frac{\partial}{\partial w_1}\right)^{n_1}\left(-\frac{\partial}{\partial w_2}\right)^{n_2}\left(-\frac{\partial}{\partial w_3}\right)^{n_3} f(-1,-1,-1,-1,-1,-1; w_1, w_2, w_3). \end{aligned} \tag{2.21}$$

However, increased powers of r_{ij}'s are not available this way for Hylleraas-type functions. Although they can be (and have been) obtained via application of the same techniques Remiddi used for the direct evaluation of the integral $f(-1,-1,-1,-1,-1,-1; w_1, w_2, w_3)$ the procedure is rather cumbersome and unpractical especially for the higher powers of r_{ij}s, since both the resulting and the intermediate expression lengths increases significantly.

2.3.4 Recurrence relations for three-electron Hylleraas-type integrals

Resolution of this difficulty was found by Pachucki, Puchalski and Remiddi [124] (PPR) in 2004. They have managed to derive closed-form recurrence relations, that allow to express three-electron Hylleraas-type integrals with increased powers of r_{ij} via the integrals with lower powers and some two-electron integrals. This powerful technique paved a way for analytic (and consequently numerical) evaluation of integrals of the Hylleraas-type functions with arbitrary powers of r_{ij}'s. The recurrence relations were obtained by applying the technique of integration by part identities [133, 134] commonly used in analytical calculations of Feynman diagrams. Since the full derivation of these identities is rather lengthy and the details were given in [124] we give only the most salient details of the derivation. First, the following nine identities in the momentum representation are given

$$\begin{aligned} 0 \equiv \mathrm{id}_3(i,j) = \iiint d^3\mathbf{k}_1 d^3\mathbf{k}_2 d^3\mathbf{k}_3 \frac{\partial}{\partial \mathbf{k}_i}\Big(&\mathbf{k}_j (k_1^2+u_1^2)^{-m_1}(k_2^2+u_2^2)^{-m_2} \\ \times (k_3^2+u_3^2)^{-m_3}(k_{32}^2+w_1^2)^{-m_4}&(k_{13}^2+w_2^2)^{-m_5}(k_{21}^2+w_3^2)^{-m_6}\Big), \end{aligned} \tag{2.22}$$

where $i, j \in 1, 2, 3$. Expanding the r.h.s of all the identities in equation (2.22) results in nine equations involving the functions of the following form

$$\begin{aligned} &G(m_1, m_2, m_3, m_4, m_5, m_6) \\ &= \iiint \frac{d^3\mathbf{k}_1 d^3\mathbf{k}_2 d^3\mathbf{k}_3}{8\pi^6} (k_1^2+u_1^2)^{-m_1}(k_2^2+u_2^2)^{-m_2}(k_3^2+u_3^2)^{-m_3} \\ &\times (k_{32}^2+w_1^2)^{-m_4}(k_{13}^2+w_2^2)^{-m_5}(k_{21}^2+w_3^2)^{-m_6}. \end{aligned} \tag{2.23}$$

Next, since we are interested in relations of the integrals of the Hylleraas-type functions, we set $m_1 = m_2 = m_3 = 1$ and differentiate over u_1, u_2, u_3 at $u_1 = u_2 = u_3 = 0$. We introduce functions h_3 defined as

$$\begin{aligned} &h_3(n_1, n_2, n_3, m_4, m_5, m_6) \\ &= (-1)^{n_1} \frac{\partial^{n_1}}{\partial u_1^{n_1}}\bigg|_{u_1=0} (-1)^{n_2} \frac{\partial^{n_2}}{\partial u_2^{n_2}}\bigg|_{u_2=0} (-1)^{n_3} \frac{\partial^{n_3}}{\partial u_3^{n_3}}\bigg|_{u_3=0} G(1, 1, 1, m_4, m_5, m_6), \end{aligned} \tag{2.24}$$

which are in turn connected to the three-electron Hylleraas-type integrals via the relation

$$\begin{aligned} &f(a, b, c, n_1, n_2, n_3; w_1, w_2, w_3) \\ &= \left(-\frac{\partial}{\partial w_1}\right)^{n_1} \left(-\frac{\partial}{\partial w_2}\right)^{n_2} \left(-\frac{\partial}{\partial w_3}\right)^{n_3} h_3(n_1, n_2, n_3, 1, 1, 1) \end{aligned} \tag{2.25}$$

and the following Fourier representation

$$\frac{\exp(-wr)}{r} = \frac{1}{(2\pi)^3} \int \mathrm{d}^3\mathbf{k} \frac{4\pi \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}}{k^2+w^2}, \tag{2.26}$$

and (in distributional sense)

$$\delta^3(\mathbf{r}) = \frac{1}{(2\pi)^3} \int \mathrm{d}^3\mathbf{k} 4\pi \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}. \tag{2.27}$$

The recursion relations are obtained by solving the nine identities from relations (2.22) in a way that yields expressions that allow to increase powers a, b, c and n_1, n_2, n_3. Such expressions correspond to $h_3(n_1+2, n_2, n_3, m_4, m_5, m_6)$, $h_3(n_1, n_2, n_3, m_4+1, m_5, m_6)$ and respective formulas for increased n_2, n_3 and m_5, m_6. Since there are nine equations for six unknowns there is some freedom in exact form of the solutions. PPR chose solution in a way that decouples recursions to the ones that increase powers of r_{ij}'s and separate set for increasing r_i's leading to expressions for $f(a+2, b, c, -1, -1, -1)$, $f(a, b+2, c, -1, -1, -1)$, $f(a, b, c+2, -1, -1, -1)$ as well as $f(a, b, c, n_1+, n_2, n_3)$, $f(a, b, c, n_1, n_2+1, n_3)$, and $f(a, b, c, n_1, n_2, n_3+1)$ respectively (with dependence of f on w_1, w_2, w_3 was omitted). For more details of the derivation we refer the reader to original source and proceed to applications of the results obtained by PPR.

Since powers of r_i's can be increased via the differentiation over w_i's we use only recursions that increase powers or r_{ij}. Therefore, as we are interested in analytic evaluation of the three-electron integrals we present only the recursion that increases powers of r_{ij}

$$\begin{aligned}
&f(a, b, c+2, -1, -1, -1) \\
&= \frac{1+c}{2}\left\{\frac{1}{w_1^2}\left[\frac{b(b-1)}{c+1} f(a, b-2, c+2, -1, -1, -1)\right.\right. \\
&+ (a+2b+c+2) f(a, b, c, -1, -1, -1) + \frac{1}{c+1} f(a, b, c+2, \star, -1, -1) \\
&+ \frac{b(b-1)}{a+1} f(a+2, b-2, c, -1, -1, -1) + \frac{1}{a+1} f(a+2, b, c, -1, -1, \star) \\
&\left. - \frac{\delta_b}{c+1} f(a, \star, c+2, -1, -1, -1) - \frac{\delta_b}{a+1} f(a+2, \star, c, -1, -1, -1)\right] \\
&+ \frac{1}{w_2^2}\left[\frac{a(a-1)}{c+1} f(a-2, b, c+2, -1, -1, -1)\right. \\
&+ (2a+b+c+2) f(a, b, c, -1, -1, -1) + \frac{1}{c+1} f(a, b, c+2, -1, \star, -1) \\
&+ \frac{a(a-1)}{b+1} f(a-2, b+2, c, -1, -1, -1) + \frac{1}{b+1} f(a, b+2, c, -1, -1, \star) \\
&\left. - \frac{\delta_a}{c+1} f(\star, b, c+2, -1, -1, -1) - \frac{\delta_a}{b+1} f(\star, b+2, c, -1, -1, -1)\right] \\
&- \frac{w_3^2}{w_1^2 w_2^2}\left[\frac{c(c-1)}{b+1} f(a, b+2, c-2, -1, -1, -1)\right. \\
&+ (a+b+2c+2) f(a, b, c, -1, -1, -1) + \frac{1}{b+1} f(a, 2+b, c, \star, -1, -1) \\
&+ \frac{c(c-1)}{a+1} f(a+2, b, c-2, -1, -1, -1) + \frac{1}{a+1} f(a+2, b, c, -1, \star, -1) \\
&\left.\left. - \frac{\delta_c}{b+1} f(a, b+2, \star, -1, -1, -1) - \frac{\delta_c}{a+1} f(a+2, b, \star, -1, -1, -1)\right]\right\},
\end{aligned} \tag{2.28}$$

where the symbol δ_n denotes the Kronecker delta $\delta_{n,0}$ and the $\star$ in the argument denotes the integral f with respective r_{ij} or r_i replaced with Dirac delta multiplied by 4π

$$\begin{aligned}
&f(\star, b, c, n_1, n_2, n_3) \\
&= \iiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\exp(-w_1 r_1 - w_2 r_2 - w_3 r_3) 4\pi\delta^3(r_{23}) r_{31}^b r_{12}^c r_1^{n_1} r_2^{n_2} r_3^{n_3}
\end{aligned} \tag{2.29}$$

and

$$\begin{aligned}
&f(a, b, c, \star, n_2, n_3) \\
&= \iiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\exp(-w_1 r_1 - w_2 r_2 - w_3 r_3) r_{23}^a r_{31}^b r_{12}^c 4\pi\delta^3(r_1) r_2^{n_2} r_3^{n_3}.
\end{aligned} \tag{2.30}$$

The above integrals with Dirac delta result in two-electron integrals that belong to classes discussed in the section about two-electron integrals. Respective recursions that increase b and c are straightforwardly found by applying symmetry relations given in equation (2.17). Since larger n_1, n_2, n_3 can be found via differentiations over w_1, w_2, w_3 the only remaining task is to find the three-electron integrals necessary to use the recursion for increasing a, b, c. The formula for the first integral $f(-1,-1,-1,-1,-1,-1; w_1, w_2, w_3)$ was given in equation (2.19). Since recursion given in equation (2.28) changes the powers of r_{ij} by two, the remaining necessary three-electron integrals to use it are $f(0,0,0,-1,-1,-1; w_1, w_2, w_3)$, $f(0,0,-1,-1,-1,-1; w_1, w_2, w_3)$, and $f(0,-1,-1,-1,-1,-1; w_1, w_2, w_3)$. All of the remaining necessary integrals are straightforward to obtain by using symmetry of the three-electron Hylleraas-type integrals as given in equation (2.17).

2.3.5 Remaining three-electron Hylleraas-type master integrals

The remaining master integrals for the recursions for the three-electron integrals can be directly calculated by using the same technique as in the equation (**??**) by transforming the coordinates of $\mathbf{r}_2$ to r_{23} (alternatively $\mathbf{r}_1$ could be changed instead)

$$\begin{aligned}
f(0,-1,-1,-1,-1,-1; w_1, w_2, w_3) &= \iiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\exp(-w_1r_1-w_2r_2-w_3r_3)}{r_{13}r_{23}r_1r_2r_3} \\
&= \frac{1}{2}\iint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\exp(-w_1r_1-w_3r_3)}{r_{13}r_1r_3}\int_0^\infty \mathrm{d}r_2\exp(-w_2r_2)r_2\int_{|r_3-r_2|}^{r_1+r_3}\mathrm{d}r_{23}\frac{1}{r_2r_3} \\
&= \frac{1}{2w_2^2}\iint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\exp(-w_1r_1-w_3r_3)}{r_{13}r_1r_3}\left(\frac{2}{r_3}-\frac{2\exp(-r_3w_2)}{r_3}\right) \\
&= \frac{1}{w_2^2}\iint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\left(\frac{\exp(-w_1r_1-w_3r_3)}{r_1r_3^2r_{13}}-\frac{\exp(-w_1r_1-(w_2+w_3)r_3)}{r_1r_3^2r_{13}}\right)
\end{aligned} \tag{2.31}$$

leading to a combination of the two-electron integrals that can be evaluated via the equation (2.10) to yield

$$\begin{aligned}
f(0,-1,-1,-1,-1,-1; w_1, w_2, w_3) =& \frac{1}{w_2^2}\Big(\Gamma(0,-1,0; w_1, w_3, 0) - \Gamma(0,-1,0; w_1, w_2+w_3, 0)\Big) \\
&= \frac{1}{w_2^2}\left(\frac{\ln(\frac{w_1+w_3}{w_3})}{w_1^2}-\frac{\ln(\frac{w_1+w_2+w_3}{w_2+w_3})}{w_1^2}\right) \\
&= -\frac{1}{w_1^2w_2^2}\ln(\frac{w_3(w_1+w_2+w_3)}{(w_1+w_3)(w_2+w_3)}.
\end{aligned} \tag{2.32}$$

The two remaining basic integrals are straightforwardly evaluated as either products of one- and two-electron (equations (2.1) and (2.9) respectively)

$$\begin{aligned}
f(0,0,-1,-1,-1,-1; w_1, w_2, w_3) &= \iiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\exp(-w_1r_1-w_2r_2-w_3r_3)}{r_{23}r_1r_2r_3} \\
&= \iint \frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\exp(-w_2r_2-w_3r_3)}{r_{23}r_2r_3}\int \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\exp(-w_1)}{r_1} \\
&= \Gamma(0,0,0; w_2, w_3, 0)I_1(-1; w_1) = \frac{1}{w_2w_3(w_2+w_3)w_1^2}
\end{aligned} \tag{2.33}$$

or only one-electron

$$\begin{aligned}f(0,0,-1,-1,-1,-1;w_1,w_2,w_3) &= \iiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\exp(-w_1r_1-w_2r_2-w_3r_3)}{r_1r_2r_3}\\ &= \int \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\exp(-w_1)}{r_1}\int \frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\exp(-w_2)}{r_2}\int \frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\exp(-w_3)}{r_3}\\ &= I_1(-1;w_1)I_1(-1;w_2)I_1(-1;w_3) = \frac{1}{w_1^2w_2^2w_3^2}\end{aligned} \tag{2.34}$$

integrals. Together with symmetry relations given in equation (2.17) this completes the full set of formulas necessary to calculate all considered three-electron integrals of Hylleraas-type using recurrence relations given in eq (2.28) and differentiation over w_i.

2.3.6 Extended three-electron Hylleraas-type integrals

The typical range of parameters for three-electron Hylleraas-type integral, as given in equation (2.16) is restricted to integers $\{a,b,c,n_1,n_2,n_3\} \geq -1$. However, when one wants to consider relativistic corrections, using for example, expectation values for Breit-Pauli Hamiltonian [135] it is necessary with parameters beyond the standard range of parameters. In such extended integrals one of the parameters takes the value of -2 leading to the integrals with either r_{ij}^{-2} (if it is one of the parameters a,b,c) or r_i^{-2} (in case of n_1,n_2,n_3). While in this thesis we solve the four-electron Hylleraas-type integrals that occur in the non-relativistic calculations, some of the extended three-electron integrals are required in order to calculate the four-electron ones in our method.

The extended three-electron Hylleraas-type integrals that we require in our calculations are the ones with $n_1 = -2$ (and their permutations), leading to integral of interest of form

$$f(a,b,c,-2,n_2,n_3;w_1,w_2,w_3) = \iiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\exp(-w_1r_1-w_2r_2-w_3r_3)r_{12}^ar_{13}^br_{23}^cr_1^{-2}r_2^{n_2}r_3^{n_3} \tag{2.35}$$

with regular bounds of parameters. Calculation of such integrals is more involved than the regular Hylleraas-type integrals and although it was solved in [130], the technique developed there uses numerical integration and therefore is adapted for numerical calculations. Since we need analytic formulas we will solve the integral (2.35) analytically.

The simplest way to obtain analytic formulas for the extended integral given in equation (2.35) is to simply integrate it over the parameter, using the fact, that since the differentiation over the parameters w_i works also for integrals with r_1^{-2} we have

$$\left(-\frac{\partial}{\partial w_1}\right) f(a,b,c,-2,n_2,n_3;w_1,w_2,w_3) = -f(a,b,c,-1,n_2,n_3;w_1,w_2,w_3). \tag{2.36}$$

Therefore[3]

$$f(a,b,c,-2,n_2,n_3;w_1,w_2,w_3) = \int_{w_1}^{\infty} \mathrm{d}w_1 f(a,b,c,-1,n_2,n_3;w_1,w_2,w_3). \tag{2.37}$$

---

[3] Since for $n \in \mathbb{N}^+ \wedge w \in \mathbb{R}^+$ we have $\left(-\frac{\partial}{\partial w}\right)\exp(-wr)r^n = \exp(-wr)r^{n+1}$ and $\lim\limits_{w\to\infty}\exp(-wr)\,r^{n+1} \to 0$.

Although the direct analytic integration using formula (2.37) would be troublesome (but possible) in the case of the three odd parameters a, b and c, such situation never occurs in the four-electron Hylleraas-type integrals of our interest. Therefore, the integration can be performed analytically resulting in formulas with elementary functions only.

2.4 Four-electron integrals

Extension of the three-electron exponentially-correlated integrals to four electrons has the following form

$$\begin{aligned}
&K(a,b,c,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4,u_{12},u_{13},u_{14},u_{23},u_{24},u_{34}) = \\
&\iiiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi}\frac{\exp(-w_1r_1-w_2r_2-w_3r_3-w_4r_4)}{r_1^{-n_1}r_2^{-n_2}r_3^{-n_3}r_4^{-n_4}r_{12}^{-a}r_{13}^{-b}r_{14}^{-c}r_{23}^{-d}r_{24}^{-e}r_{34}^{-f}} \\
&\times \exp(-u_{12}r_{12}-u_{13}r_{13}-u_{14}r_{14}-u_{23}r_{23}-u_{24}r_{24}-u_{34}r_{34}),
\end{aligned} \tag{2.38}$$

while the four-electron Hylleraas-type integrals are

$$\begin{aligned}
&g(a,b,c,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4) \\
&= \iiiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi}\frac{\exp(-w_1r_1-w_2r_2-w_3r_3-w_4r_4)}{r_1^{-n_1}r_2^{-n_2}r_3^{-n_3}r_4^{-n_4}r_{12}^{-a}r_{13}^{-b}r_{14}^{-c}r_{23}^{-d}r_{24}^{-e}r_{34}^{-f}}
\end{aligned} \tag{2.39}$$

with (similarly to the three-electron case) $\{w_1, w_2, w_3, w_4\} \in \mathbb{R}^+$ being the nonlinear parameters and $-1 \leq \{a, b, c, d, e, f, n_1, n_2, n_3, n_4\} \in \mathbb{Z}$ are powers of the electron-electron distances and the nucleus-electron distances.

These integrals are symmetric with respect to the exchange of the indices of electrons. There are $4! = 24$ such permutations. Furthermore, similarly to the two- and three-electron Hylleraas functions it is possible to differentiate over the parameters w_1, w_2, w_3, w_4 in order to increase powers of r_1, r_2, r_3, r_4 getting

$$\begin{aligned}
&g(a,b,c,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4) \\
&= \left(-\frac{\partial}{\partial w_1}\right)^{n_1}\left(-\frac{\partial}{\partial w_2}\right)^{n_2}\left(-\frac{\partial}{\partial w_3}\right)^{n_3}\left(-\frac{\partial}{\partial w_4}\right)^{n_4} g(a,b,c,d,e,f,-1,-1,-1,-1;w_1,w_2,w_3,w_4)
\end{aligned} \tag{2.40}$$

The analytic formulas for the master integrals (with all powers or r_i and r_{ij} equal to -1) are not known, neither for the exponentially-correlated, nor for the Hylleraas-type functions. Therefore, at the present moment it is not possible to directly generalise approach used for three-electron integrals. As a result it is necessary to restrict the parameters in order to obtain a set of integrals that are possible to solve analytically.

2.4.1 Recurrence relations for four-electron Hylleraas integrals

In order to calculate singly-linked Hylleraas-type integrals we use the technique inspired by PPR approach to develop a set of the recurrence relations that will allow to obtain analytic formulas for the singly-linked Hylleraas integrals. We develop and use integration-by-parts identities, but in the space (instead of momentum) representation. We emphasise, that the recurrence relations presented here apply for general four-electron Hylleraas integrals and are not limited to singly-linked type only.

Integration by parts identities

We use the sixteen following identities[4]

$$0 = id(i,j) = \iiiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi}\nabla_i \cdot \mathbf{r}_j \frac{\exp(-w_1 r_1 - w_2 r_2 - w_3 r_3 - w_4 r_4)}{r_1^{-n_1} r_2^{-n_2} r_3^{-n_3} r_4^{-n_4} r_{12}^{-a} r_{13}^{-b} r_{14}^{-c} r_{23}^{-d} r_{24}^{-e} r_{34}^{-f}}, \tag{2.41}$$

with $\{i,j\} \in \{1,2,3,4\}$ to obtain the recurrence relations for Hylleraas-type integrals g. The detailed derivation of the recurrence relations are presented in Appendix A in section A.1.2. Here, we present only the final results that are directly applied in calculations. Out of the sixteen recurrences we use the three that increase indices $a,\ b,\ c$. This is possible, because we take the integrals given in equation (2.47) as the starting point and develop the strategy to obtain non-zero indices $a,\ b,\ c$ for a given set of $\{d, e, f, n_1, n_2, n_3, n_4\}$.

Formulas for recurrence relations

The three recurrences developed to obtain analytic formulas for the singly-linked Hylleraas integrals are[5]

$$\begin{aligned}
&g(a+2,b,c,d,e,f,-1,-1,-1,-1) = g(a,b,c,d,e,f,-1,1,-1,-1)\\
&+\frac{1}{2w_1}\Big[(3a+b+c+6)g(a,b,c,d,e,f,0,-1,-1,-1)\\
&+a\big(g(a-2,b,c,d,e,f,0,1,-1,-1) - g(a-2,b,c,d,e,f,2,-1,-1,-1)\big)\\
&+b\big(g(a,b-2,c,d,e,f,0,-1,1,-1) - g(a,b-2,c,d,e,f,2,-1,-1,-1)\\
&-2g(a,b-2,c,d+2,e,f,0,-1,-1,-1) + 2g(a+2,b-2,c,d,e,f,0,-1,-1,-1)\big)\\
&+c\big(g(a,b,c-2,d,e,f,0,-1,-1,1) - g(a,b,c-2,d,e,f,2,-1,-1,-1)\\
&-2g(a,b,c-2,d,e+2,f,0,-1,-1,-1) + 2g(a+2,b,c-2,d,e,f,0,-1,-1,-1)\big)\Big],
\end{aligned} \tag{2.42a}$$

$$\begin{aligned}
&g(a,b+2,c,d,e,f,-1,-1,-1,-1) = g(a,b,c,d,e,f,-1,-1,1,-1)\\
&+\frac{1}{2w_1}\Big[(a+3b+c+6)g(a,b,c,d,e,f,0,-1,-1,-1)\\
&+a\big(g(a-2,b,c,d,e,f,0,1,-1,-1) - g(a-2,b,c,d,e,f,2,-1,-1,-1)\\
&-2g(a-2,b,c,d+2,e,f,0,-1,-1,-1) + 2g(a-2,b+2,c,d,e,f,0,-1,-1,-1)\big)\\
&+b\big(g(a,b-2,c,d,e,f,0,-1,1,-1) - g(a,b-2,c,d,e,f,2,-1,-1,-1)\big)\\
&+c\big(g(a,b,c-2,d,e,f,0,-1,-1,1) - g(a,b,c-2,d,e,f,2,-1,-1,-1)\\
&-2g(a,b,c-2,d,e,f+2,0,-1,-1,-1) + 2g(a,b+2,c-2,d,e,f,0,-1,-1,-1)\big)\Big],
\end{aligned} \tag{2.42b}$$

---

[4] The identities are proven in section A.1.1 of Appendix A.

[5] The recurrence relations are derived in section A.1.2 of Appendix A.

$$
\begin{aligned}
&g(a,b,c+2,d,e,f,-1,-1,-1,-1) = g(a,b,c,d,e,f,-1,-1,-1,1)\\
&+\frac{1}{2w_1}\Big[(a+b+3c+6)g(a,b,c,d,e,f,0,-1,-1,-1)\\
&+a\big(g(a-2,b,c,d,e,f,0,1,-1,-1)-g(a-2,b,c,d,e,f,2,-1,-1,-1)\\
&-2g(a-2,b,c,d,e+2,f,0,-1,-1,-1)+2g(a-2,b,c+2,d,e,f,0,-1,-1,-1)\big)\\
&+b\big(g(a,b-2,c,d,e,f,0,-1,1,-1)-g(a,b-2,c,d,e,f,2,-1,-1,-1)\\
&-2g(a,b-2,c,d,e,f+2,0,-1,-1,-1)+2g(a,b-2,c+2,d,e,f,0,-1,-1,-1)\big)\\
&+c\big(g(a,b,c-2,d,e,f,0,-1,-1,1)-g(a,b,c-2,d,e,f,2,-1,-1,-1)\big)\Big].
\end{aligned}
\tag{2.42c}
$$

These three equations allow to increase the indices a, b and c by two, similarly as the recurrences for the three-electron integrals. However, there are significant differences between the three electron recurrence given in equation (2.28) and the derived four-electron recurrences given in equations (2.42a), (2.42b) and (2.42c).

Comparison with three-electron recurrences

Firstly, contrarily to the three electron case, in the four-electron case we didn't manage to separate indices corresponding to powers of distances between the two electrons from powers corresponding to distances between the electrons and nucleus. Therefore, the recurrences for four-electron integrals cannot be separated to the two set of recursions yielding a method that increases powers of r_{ij} for arbitrary powers of r_i. The second important difference between the three- and four-electron recurrences is that the four-electron recurrences do not terminate for powers below -1. In the three-electron case the integrals with powers lowered by two are multiplied by factor that equals to zero, for example the term:

$$
b=0 \lor b=1 \Rightarrow \frac{b(b-1)}{c+1} f(a,b-2,c+2,-1,-1,-1)=0 \tag{2.43}
$$

in equation (2.28) guarantees that the recursions terminate for both odd and even powers of b (and similarly for a and c).

Derived four-electron recurrences terminate only for $\{a,b,c\}=0$. This is immediately obvious, since equations (2.42) contain terms only such as

$$
\begin{aligned}
&b=0 \Rightarrow\\
&b\Big[g(a,b-2,c,d,e,f,0,-1,1,-1)-g(a,b-2,c,d,e,f,2,-1,-1,-1)-\\
&2g(a,b-2,c,d+2,e,f,0,-1,-1,-1)+2g(a+2,b-2,c,d,e,f,0,-1,-1,-1)\Big]=0,
\end{aligned}
\tag{2.44}
$$

and these terms are not multiplied by $b-1$ which would guarantee that the recurrences terminate for odd powers of b (again, the same argument is valid for a and c). This prompts the development of the alternative technique to calculate the odd powers.

2.4.2 Four-electron singly-linked Hylleraas integrals

Because of the lack of both the master integrals as well as the sufficiently general recurrences for general four-electron Hylleraas integrals, we restrict our interest to the so-called integrals over the four-electron singly-linked Hylleraas functions. These functions have the form

$$\begin{aligned} &h(a,b,c,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4) \\ &= \exp(-w_1 r_1 - w_2 r_2 - w_3 r_3 - w_4 r_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{12}^{a} r_{13}^{b} r_{14}^{c} r_{23}^{d} r_{24}^{e} r_{34}^{f}, \end{aligned} \tag{2.45}$$

with $\{w_1,w_2,w_3,w_4\} \in \mathbb{R}^+ \wedge 1 \leq \{a,b,c,d,e,f,n_1,n_2,n_3,n_4\} \in \mathbb{Z}$ and $\{a,b,c,d,e,f\}$ further restricted to have only one odd parameter (with the rest of them being even). In turn, when such function is taken as the basis function in variational calculations of non-relativistic Schrodinger equation it results in matrix elements that have the form of the integrals of the following type

$$\begin{aligned} &g(a,b,c,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4) \\ &= \iiiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi} h(a,b,c,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4) \\ &= \iiiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi} \exp(-w_1 r_1 - w_2 r_2 - w_3 r_3 - w_4 r_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{12}^{a} r_{13}^{b} r_{14}^{c} r_{23}^{d} r_{24}^{e} r_{34}^{f}, \end{aligned} \tag{2.46}$$

with $\{w_1,w_2,w_3,w_4\} \in \mathbb{R}^+ \wedge -1 \leq \{a,b,c,d,e,f,n_1,n_2,n_3,n_4\} \in \mathbb{Z}$ and $\{a,b,c,d,e,f\}$ restricted to at most three odd and consequently at least three even values. From now we will call these integrals the singly-linked Hylleraas type integrals. The name comes from the fact, that only such integrals arise as matrix elements of the non-relativistic Hamiltonian of atomic system when at most single odd power of r_{ij} factor is allowed in each basis function[6].

The only difference between the singly-linked Hylleraas integrals (2.46) and the general Hylleraas integral (2.39) is in the restriction of the parameter space to at most three odd parameters. Therefore singly-linked Hylleraas functions and integrals are subset of the generic Hylleraas functions and integrals. We emphasise, that consequently all of the relations and methods we derived are generic and apply to generic four-electron Hylleraas-type integrals. So far, we have found our developed methods to suffice in obtaining analytic formulas only for the subset restricted to the singly-linked Hylleraas integrals.

Because of the symmetry properties of the four-electron Hylleraas integrals from now we consider singly-linked Hylleraas-type integrals that have at most one odd factor in the first three indices (a,b,c) and only the index a can be odd. Consequently, for the considered class of integrals, if a is odd there are at most two odd number among indices fourth to six (d,e,f), and three if a is even. This can be done without any loss of generality, since all the remaining singly-linked Hylleraas integrals can be obtained from such integrals via symmetry operations as explained in section 2.4.8. Therefore, in this thesis we develop efficient method to obtain analytic formulas (involving dilogarithmic functions, since they are already present in three-electron subsets of four-electron integrals) for all singly-linked Hylleraas integrals. The general scheme of the method is presented in figure 2.1.

---

[6] There at most three odd factors in the resulting integral, since one comes from the bra of the matrix element, second from the ket and the third one from the Coulomb operator which has form r_{ij}^{-1}.

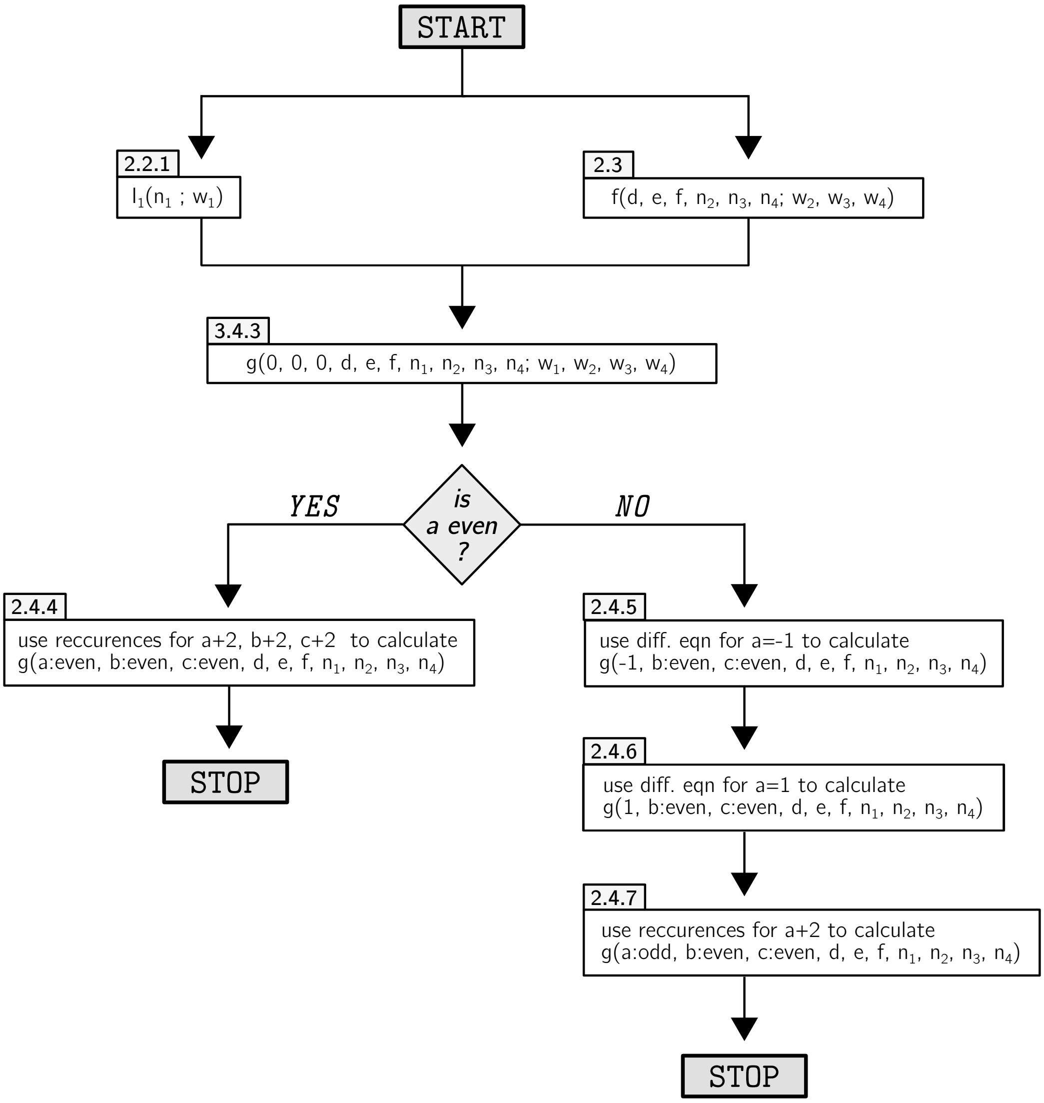


Figure 2.1: Flowchart of the method developed to analytically calculate singly-linked Hylleraas integrals. Number at the top left corner of each block corresponds to the section of this chapter, which describes the given part of the procedure.

2.4.3 Four-electron integrals reducible to simpler integrals

There exists simplest class of singly-linked Hylleraas integrals, that can be expressed either as the three-electron integrals multiplied by integration over the fourth electron or as the products of two-electron integrals (there are also integrals that factor further, to the one-electron integrals). These two types of such integrals are for example

$$
\begin{aligned}
&g(0,0,0,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4)\\
&=\int \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\exp(-w_1r_1)r_1^{n_1}\iiint \frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi}\exp(-w_2r_2-w_3r_3-w_4r_4)r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{23}^{d}r_{24}^{e}r_{34}^{f}=\\
&I_1(n_1;w_1)f(d,e,f,n_2,n_3,n_4;w_2,w_3,w_4)
\end{aligned}
\tag{2.47}
$$

and

$$
\begin{aligned}
&g(a,0,0,0,0,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4)\\
&=\iint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\exp(-w_1r_1-w_2r_2)r_1^{n_1}r_2^{n_2}r_{12}^{a}\iint \frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi}\exp(-w_3r_3-w_4r_4)r_3^{n_3}r_4^{n_4}r_{34}^{f}=\\
&\Gamma(n_1+1,n_2+1,a+1;w_1,w_2,0)\Gamma(n_3+1,n_4+1,f+1;w_3,w_4,0).
\end{aligned}
\tag{2.48}
$$

The first equation (2.47) is used as a starting point to calculate more complicated four-electron integrals. The integrals with two non-overlapping indices r_{ij} are separable into the products of two-electron integrals (such as the one given in equation (2.48) and its permutations with respect to electron indices). Since our method of calculation of the singly-linked Hylleraas integral general and allows to independently calculate such integrals, we use formula (2.48) and other integrals of this kind to validate the correctness developed method.

2.4.4 Application of recurrence relations for even a, b, c

In the case of even a, b, c, application of the four-electron recurrence relations is rather straightforward as all the necessary master integrals are the three-electron integrals multiplied by one-electron integral. As an example we will show how to use recurrences to obtain formulas allowing to calculate first few integrals. First, we use equation (2.42a) to start from $g(0,0,0,d,e,f,-1,-1,-1,-1)$ in order to get

$$
\begin{aligned}
&g(2,0,0,d,e,f,-1,-1,-1,-1)=g(0,0,0,d,e,f,-1,1,-1,-1)\\
&+\frac{6}{2w_1}g(0,0,0,d,e,f,0,-1,-1,-1),
\end{aligned}
\tag{2.49}
$$

where $g(0,0,0,d,e,f,-1,1,-1,-1)$ and $g(0,0,0,d,e,f,0,-1,-1,-1)$ are straightforwardly obtained via the differentiation of $g(0,0,0,d,e,f,-1,-1,-1,-1)$ over the respective parameters w_i as per equation (2.40). Integrals $g(0,2,0,d,e,f,-1,-1,-1,-1)$ and $g(0,0,2,d,e,f,-1,-1,-1,-1)$ are obtained in the same way as equation (2.49) using equations (2.42b) and (2.42c) respectively.

Next, we proceed to use equation (2.42b) with $a = 2, b = 0, c = 0$ which yields

$$\begin{aligned}
&g(2, 2, 0, d, e, f, -1, -1, -1, -1) = g(2, 0, 0, d, e, f, -1, -1, 1, -1) \\
&+ \frac{1}{2w_1}\Big[8g(2, 0, 0, d, e, f, 0, -1, -1, -1) \\
&+ 2\big(g(0, 0, 0, d, e, f, 0, 1, -1, -1) - g(0, 0, 0, d, e, f, 2, -1, -1, -1) \\
&- 2g(0, 0, 0, d + 2, e, f, 0, -1, -1, -1) + 2g(0, 0 + 2, 0, d, e, f, 0, -1, -1, -1)\big)\Big].
\end{aligned} \tag{2.50}$$

All necessary integrals on the right-hand side of the equation above are either already calculated or straightforwardly computed via the differentiation over w_i. Equation (2.42c) with $a = 2$ can be used in the same way to get $g(2, 0, 2, d, e, f, -1, -1, -1, -1)$, while equation (2.42c) with $b = 2$ can be used to get $g(0, 2, 2, d, e, f, -1, -1, -1, -1)$.

Then, we can calculate integral $g(2, 2, 2, d, e, f, -1, -1, -1, -1)$ by, for example[7], applying formula (2.42c) with $a = 2, b = 2, c = 0$ getting

$$\begin{aligned}
&g(2, 2, 2, d, e, f, -1, -1, -1, -1) = g(2, 2, 0, d, e, f, -1, -1, -1, 1) \\
&+ \frac{1}{2w_1}\Big[10g(2, 2, 0, d, e, f, 0, -1, -1, -1) \\
&+ 2\big(g(0, 2, 0, d, e, f, 0, 1, -1, -1) - g(0, 2, 0, d, e, f, 2, -1, -1, -1) \\
&- 2g(0, 2, 0, d, e + 2, f, 0, -1, -1, -1) + 2g(0, 2, 2, d, e, f, 0, -1, -1, -1)\big) \\
&+ 2\big(g(2, 0, 0, d, e, f, 0, -1, 1, -1) - g(2, 0, 0, d, e, f, 2, -1, -1, -1) \\
&- 2g(2, 0, 0, d, e, f + 2, 0, -1, -1, -1) + 2g(2, 0, 2, d, e, f, 0, -1, -1, -1)\big)\Big].
\end{aligned} \tag{2.51}$$

Again, all required integrals on the right-hand side of equation (2.51) are readily computed.

The procedure of applying equations (2.42a), (2.42b) and (2.42c) to increase a, b and c by 2 can be continued to arbitrarily large even values. The only requirement is that all possible combinations of even a, b and c are calculated before the sum $a + b + c$ is increased by two. This ensures that all expressions on the right-hand side of the recurrences given in (2.42) are available or can be computed via the differentiation over the parameters w_i.

2.4.5 Differential equation for $a = -1$ and even b, c

Since the nature of the obtained four-electron recurrences (given in equations (2.42)) requires integrals with indices a, b and c lowered by 2 and 4, to calculate any odd power a of r_{12} we need to calculate two specific cases $a = -1$ and $a = 1$ to start the recurrences for the given set of $\{d, e, f\}$. In order to do so, we developed a technique based on the integration of Poisson equation with the specifically chosen class of functions. It is used to obtain identities that allow us to find the two aforementioned specific cases of four-electron Hylleraas integrals. We call these identities Laplacian identities as they are result of applying Laplacian on the particular Hylleraas-type functions. Since the full derivation of these identities is rather involved, here

---

[7] Alternatively, it can be obtained by applying equation (2.42b) with $a = 2, b = 0, c = 2$ or equation (2.42a) with $a = 0, b = 2, c = 2$.

we present only the final result, while the full derivation is available in the section A.2 of the Appendix A.

The first Laplacian identity (involving $a = -1$) for four-electron Hylleraas integrals is

$$\begin{aligned} &{w_1}^2 g(-1, b, c, d, e, f, 0, -1, -1, -1) - w_1(2 + b + c) g(-1, b, c, d, e, f, -1, -1, -1, -1) \\ &\quad = -r_{-1}(-1, b, c, d, e, f, -1, -1, -1, -1) \end{aligned} \tag{2.52}$$

where the four-electron Hylleraas integral $g(...)$ is defined as in equation (2.39) while

$$\begin{aligned} &r_{-1}(-1, b, c, d, e, f, -1, -1, -1, -1; w_1, w_2, w_3, w_4) \\ &\quad = (b + c + 1)(bg(-1, b - 2, c, d, e, f, 0, -1, -1, -1) + cg(-1, b, c - 2, d, e, f, 0, -1, -1, -1)) \\ &\quad - bcg(-1, b - 2, c - 2, d, e, f + 2, 0, -1, -1, -1) \\ &\quad + w_1 \big(bg(-1, b - 2, c, d, e, f, -1, -1, 1, -1) - bg(-1, b - 2, c, d, e, f, 1, -1, -1, -1) \\ &\quad + cg(-1, b, c - 2, d, e, f, -1, -1, -1, 1) - cg(-1, b, c - 2, d, e, f, 1, -1, -1, -1)\big) \\ &\quad + f(b + d, c + e, f, -2, -1, -1; w_1 + w_2, w_3, w_4) \end{aligned} \tag{2.53}$$

denotes the the inhomogeneous term that is assumed to be composed of the known functions of w_1, w_2, w_3, w_4 and its exact form depends on the values of the parameters b, c, d, e, f. Using the fact (coming from the presence of $e^{-w_1 r_1}$ term in the integral g), that

$$\frac{\partial}{\partial w_1} g(a, b, c, d, e, f, -1, -1, -1, -1) = -g(a, b, c, d, e, f, 0, -1, -1, -1), \tag{2.54}$$

and introducing more compact notation where $g(a, ...) = g(a, b, c, d, e, f, -1, -1, -1, -1)$, we arrive at the differential equation

$$-w_1^2 \frac{\partial}{\partial w_1} g(-1, ...) - w_1(2 + b + c) g(-1, ...) = -r_{-1}(-1, ...). \tag{2.55}$$

This equation has to be solved for $g(-1, ...)$. The solution of the equation (2.55) is

$$g(-1, ...) = \frac{1}{w_1^{2+b+c}} \int w_1^{b+c} \, r_{-1}(-1, ...) \, \mathrm{d}w_1, \tag{2.56}$$

and the constant of integration is fixed in such a way, that there are no terms of order w_1^{-2-b-c} in $g(-1, ...)$. The detailed discussion of a method to obtain this solution and the boundary conditions is given in section A.3 of the Appendix A.

Iterative procedure of finding r_{-1} to find $g(-1, ...)$

Although at first it may seem, that getting the solution of integral $g(-1, ...)$ using presented method is impossible, because of presence of the $g(-1, ...)$ integrals in the inhomogeneous term $r_{-1}(-1, ...)$ (as defined in equation (2.53)), it can be obtained using the iterative procedure with right order of calculation of the integrals. By doing this in a way, that ensures the inhomogeneous term always consists of already integrated terms, it simply becomes a known function of w_1 and the equation can be straightforwardly solved. The procedure is relatively simple as it only requires, that the integrals are calculated starting from lowest possible values of the parameters $b = 0$ and $c = 0$. Then, these values are increased by two (with the condition that both b and c are increased independently). Cases such as $b = 2, c = 4$ can be straightforwardly obtained from $b = 4, c = 2$ by permuting the indices 2 and 3 of the electrons, but we prefer to calculate both of these cases independently. Next, we illustrate this procedure for first few values of b and c.

First, we start with simplest case, namely when both $b = 0$ and $c = 0$ (for a given set of $\{d, e, f\}$). It leads to very simple expression

$$r_{-1}(-1, 0, 0, d, e, f, -1, -1, -1, -1) = -f(d, e, f, -2, -1, -1; w_1 + w_2, w_3, w_4) \tag{2.57}$$

as we just set $b = c = 0$ in equation (2.53). The $f(b + d, c + e, f, -2, -1, -1; w_1 + w_2, w_3, w_4)$ is an extended three-electron integral and its evaluation was discussed in section 2.3.6. Thus, after the integration of this three-electron integral over $\mathrm{d}^3\mathbf{r}_2, \mathrm{d}^3\mathbf{r}_3, \mathrm{d}^3\mathbf{r}_4$, the inhomogeneous term becomes an explicit function of w_1. Next, by plugging this explicit function into the formula (2.56) (and ensuring that boundary conditions as given in section A.3.2 in the Appendix A are fulfilled) we finally obtain the value of integral $g(-1, 0, 0, d, e, f, -1, -1, -1, -1)$.

Next, we proceed to set $b = 2, c = 0$ and, again, use equation (2.53) to get

$$\begin{aligned}
&r_{-1}(-1, 2, 0, d, e, f, -1, -1, -1, -1)\\
&= -6g(-1, 0, 0, d, e, f, 0, -1, -1, -1) + 2w_1 g(-1, 0, 0, d, e, f, -1, -1, 1, -1)\\
&- 2g(-1, 0, 0, d, e, f, 1, -1, -1, -1) + f(2 + d, e, f, -2, -1, -1; w_1 + w_2, w_3, w_4).
\end{aligned} \tag{2.58}$$

The $f(2 + d, e, f, -2, -1, -1; w_1 + w_2, w_3, w_4)$ is, again, an extended three-electron integral, and the integral $g(-1, 0, 0, d, e, f, -1, -1, -1, -1)$ is redily obtained by plugging the term obtained from the eq. (2.57) to the solution of the equation (2.55) given by the formula (2.56). There are two more terms with increased powers n_i that remain to be found. They are straightforwardly obtained from the term $g(-1, 0, 0, d, e, f, -1, -1, -1, -1)$ via differentiation over w_i parameters as given in the equation (2.40). This way we get $g(-1, 2, 0, d, e, f, -1, -1, -1, -1)$ and consequently $g(-1, 2, 0, d, e, f, n_1, n_2, n_3, n_4)$ (with arbitrary values of n_1, n_2, n_3, n_4), since it can be immediately obtained via differentiation over the respective parameters w_1, w_2, w_3, w_4. Integrals $g(-1, 0, 2, d, e, f, n_1, n_2, n_3, n_4)$ are obtained in the similar way.

For $b = 2, c = 2$ case, the expression (2.53) becomes

$$\begin{aligned}
&r_{-1}(-1, 2, 2, d, e, f, -1, -1, -1, -1)\\
&= 5(2g(-1, 0, 2, d, e, f, 0, -1, -1, -1) + 2g(-1, 2, 0, d, e, f, 0, -1, -1, -1))\\
&- 4g(-1, 0, 0, d, e, f + 2, 0, -1, -1, -1)\\
&+ w_1\big(2g(-1, 0, 2, d, e, f, -1, -1, 1, -1) - 2g(-1, 0, 2, d, e, f, 1, -1, -1, -1)\\
&+ 2g(-1, 2, 0, d, e, f, -1, -1, -1, 1) - 2g(-1, 2, 0, d, e, f, 1, -1, -1, -1)\big)\\
&+ f(2 + d, 2 + e, f, -2, -1, -1; w_1 + w_2, w_3, w_4).
\end{aligned} \tag{2.59}$$

As previously all terms on the right-hand side of the equation (2.59) are already evaluated previously using equations (2.57), (2.58), and differentiation over parameters (as per equation (2.40)) to increase n_i and solved via the formula (2.56).

From this point the procedure follows analogously for $r_{-1}(-1,4,2,d,e,f,-1,-1,-1,-1)$ and $g(-1,4,2,d,e,f,-1,-1,-1,-1)$, $r_{-1}(-1,2,4,d,e,f,-1,-1,-1,-1)$ in order to calculate $g(-1,2,4,d,e,f,-1,-1,-1,-1)$, followed by using $r_{-1}(-1,4,4,d,e,f,-1,-1,-1,-1)$ to obtain $g(-1,4,4,d,e,f,-1,-1,-1,-1)$ et cetera. Consequently, repeated application of this procedure yields formula for any[8] integral of type $g(-1,b,c,d,e,f,-1,-1,-1,-1)$ with even b and c.

2.4.6 Differential equation for $a = 1$ and even b, c

Similarly to the case of $a = -1$ we use method of applying Laplacian (described in detail in section A.2 of Appendix A) to obtain the second Laplacian expression

$$\begin{aligned}&{w_1}^2 g(1,b,c,d,e,f,0,-1,-1,-1) - w_1(2+b+c)g(1,b,c,d,e,f,-1,-1,-1,-1)\\&= -r_1(1,b,c,d,e,f,-1,-1,-1,-1)\end{aligned} \tag{2.60}$$

that leads to the identical form of the differential equation as with with $a = -1$ (see eq. (2.55)) namely

$$-{w_1}^2 \frac{\partial}{\partial w_1} g(1,...) - w_1(2+b+c)g(1,...) = -r(1,...). \tag{2.61}$$

with only the (slight) difference in the inhomogeneous term

$$\begin{aligned}&r_1(1,b,c,d,e,f,-1,-1,-1,-1;w_1,w_2,w_3,w_4)\\&= (b+c+1)(bg(1,b-2,c,d,e,f,0,-1,-1,-1) + cg(1,b,c-2,d,e,f,0,-1,-1,-1))\\&- bcg(1,b-2,c-2,d,e,f+2,0,-1,-1,-1)\\&+ w_1\big(bg(1,b-2,c,d,e,f,-1,-1,1,-1) - bg(1,b-2,c,d,e,f,1,-1,-1,-1)\\&+ cg(1,b,c-2,d,e,f,-1,-1,-1,1) - cg(1,b,c-2,d,e,f,1,-1,-1,-1)\big)\\&- 2g(-1,b,c,d,e,f,-1,-1,-1,-1).\end{aligned} \tag{2.62}$$

This differential equation is, again, solved (as described in section A.3 of Appendix A) to yield

$$g(1,...) = \frac{1}{w_1^{2+b+c}} \int w_1^{b+c} r_1(1,...)\, \mathrm{d}w_1. \tag{2.63}$$

The main difference with the integrals with $a = -1$ is that $g(-1,...)$ is a part of the inhomogeneous term $r_1(1,...)$ (in place of the extended three-electron integral present for the former case). Thus, it must be solved first, in order to solve for $g(1,...)$. The last term in the right-hand side of the equation (2.62) requires the integral $g(-1,b,c,d,e,f,-1,-1,-1,-1)$ to be already calculated. Therefore, in order to calculate the integral with $a = 1$ for each set of values of $\{b,c,d,e,f\}$ the integral with $a = -1$ must be solved first.

---

[8] In the case of the singly-linked Hylleraas integrals we are interested in, there would be at most only two odd values among the parameters $\{d,e,f\}$. This makes the integration given in the equation (2.63) simple, as it is over only elementary functions. In the case of the three odd parameters the integration becomes significantly more difficult, since the integrand consists of non-elementary dilogarithmic functions (defined in equation (2.20)) which are more difficult to integrate.

The rest of the iterative procedure is identical with the one described in the previous section 2.4.5. Application of this procedure allows us to find any[9] integral with $a = 1$, even $b \geq 0$ and even $c \geq 0$, and (in principle) arbitrary $\{d, e, f\} \geq -1$.

2.4.7 Application of recurrence relation for odd $a > 1$ and even b, c

When the four-electron Hylleraas-type integrals with $a = -1$ as well as $a = 1$ are solved for a given set of values of $\{b, c, d, e, f, -1, -1, -1, -1\}$ it is finally possible to use recurrence relation to increase a by two to obtain closed-form formulas for the integrals with arbitrary odd values of $a > 1$, even b, c and any values of $\{d, e, f\}$.

The procedure is rather straightforward since it only requires repeated application of recurrence relation (2.42a) and differentiation over parameters w_i while all necessary integrals are already obtained using methods described in the previous sections.

In order to illustrate what are required integrals and how they can be calculated using presented methods here we present application of the recurrence relation to obtain $a = 3$ for non negative even b, c and arbitrary $\{d, e, f\} \geq -1$.

The equation (2.42a) with $a = 1$ takes form

$$\begin{aligned}
&g(3, b, c, d, e, f, -1, -1, -1, -1) = g(1, b, c, d, e, f, -1, 1, -1, -1)\\
&+ \frac{1}{2w_1}\Big[(3 + b + c + 6)g(1, b, c, d, e, f, 0, -1, -1, -1)\\
&+ 1\big(g(-1, b, c, d, e, f, 0, 1, -1, -1) - g(-1, b, c, d, e, f, 2, -1, -1, -1)\big)\\
&+ b\big(g(1, b - 2, c, d, e, f, 0, -1, 1, -1) - g(1, b - 2, c, d, e, f, 2, -1, -1, -1)\\
&- 2g(1, b - 2, c, d + 2, e, f, 0, -1, -1, -1) + 2g(1, b - 2, c, d, e, f, 0, -1, -1, -1)\big)\\
&+ c\big(g(1, b, c - 2, d, e, f, 0, -1, -1, 1) - g(1, b, c - 2, d, e, f, 2, -1, -1, -1)\\
&- 2g(1, b, c - 2, d, e + 2, f, 0, -1, -1, -1) + 2g(1, b, c - 2, d, e, f, 0, -1, -1, -1)\big)\Big].
\end{aligned} \tag{2.64}$$

It is immediately evident that all integrals appearing on the right-hand side of the equation (2.64) can be calculated using methods from sections 2.4.5 and 2.4.6 and using the differentiation over parameters w_i to increase n_i (as given in the equation (2.40)). The differentiation can also be used to increase last four indices of $g(3, b, c, d, e, f, -1, -1, -1, -1)$, so more general integrals of form $g(3, b, c, d, e, f, n_1, n_2, n_3, n_4)$ are straightforwardly obtained.

From this point, the repeated application of (2.42a) can be used to increase a further, up to the arbitrarily high odd values. This way, we complete the method of obtaining closed-form analytic formulas for singly-linked Hylleraas integrals with odd $a \geq -1$, even non negative b, c and arbitrary $d, e, f \geq -1$. The final remaining task is to show how to get remaining integrals, such as the ones with odd b, even a, c and arbitrary d, e, f.

---

[9] Again, with the disclaimer that the integrand with three odd parameters d, e, f makes integration (2.63) significantly more difficult than the case of one or two odd parameters.

2.4.8 Remaining singly-linked Hylleraas integrals obtained via symmetry

Although in principle the same methods that were presented in previous sections, namely using recurrence relations or Laplacian identities followed by solution of differential equations and applying recurrences, could be used to obtain the remaining integrals, there exists a much simpler way to do so. The task of obtaining the remaining integrals, namely the ones where either b is odd and a, c are even or c is odd and a, b are even is straightforward if we use symmetry properties of four-electron Hylleraas integrals. For example we can permute electrons 2 and 3 which results in the permutation of electron indices $\{1 \to 1, 2 \to 3, 3 \to 2, 4 \to 4\}$ directly to the definition of the Hylleraas integral eq. (2.39) to obtain

$$\begin{aligned}
&g(a,b,c,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4)\\
&= \iiiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi}\frac{\exp(-w_1r_1-w_2r_2-w_3r_3-w_4r_4)}{r_1^{-n_1}r_2^{-n_2}r_3^{-n_3}r_4^{-n_4}r_{12}^{-a}r_{13}^{-b}r_{14}^{-c}r_{23}^{-d}r_{24}^{-e}r_{34}^{-f}}\\
&= \iiiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi}\frac{\exp(-w_1r_1-w_3r_3-w_2r_2-w_4r_4)}{r_1^{-n_1}r_3^{-n_2}r_2^{-n_3}r_4^{-n_4}r_{13}^{-a}r_{12}^{-b}r_{14}^{-c}r_{32}^{-d}r_{34}^{-e}r_{24}^{-f}}\\
&= g(b,a,c,d,f,e,n_1,n_3,n_2,n_4;w_1,w_2,w_3,w_4).
\end{aligned} \tag{2.65}$$

Similarly, electrons 3 and 4 can be changed, resulting in the following permutation of the electron indices $\{1 \to 1, 4 \to 2, 3 \to 3, 2 \to 4\}$ to yield

$$g(a,b,c,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4) = g(c,b,a,f,e,d,n_1,n_4,n_3,n_2;w_1,w_2,w_3,w_4). \tag{2.66}$$

This way, the integrals with odd b or c can be calculated using formulas for integrals with odd a. For example, using formula (2.65) we can easily get

$$g(2,1,4,1,0,-1,1,2,3,4;w_1,w_2,w_3,w_4) = g(1,2,4,1,-1,0,1,3,2,4;w_1,w_2,w_3,w_4). \tag{2.67}$$

Finally, we note that in the numerical evaluation of four-electron singly-linked Hylleraas integrals it is far more efficient to permute values of the nonlinear parameters w_1, w_2, w_3, w_4 in such a way, that formulas with odd a and even b, c are used for numerical evaluation, rather than to explicitly implement formulas for cases with odd b and c. This significantly reduces the number of equations that has to be implemented in the code. Furthermore, additional reduction of the number of the formulas for the integrals is possible for even a, b, c via the assumption that $a \geq b \geq c$ and subsequent use of suitable permutations for the remaining cases.

Chapter 3

Results

3.1 Simplification of the analytic formulas

While method developed in the previous chapter allows us to obtain all closed-form analytic formulas for the singly-linked Hylleraas integrals, direct application of the method results in quick growth of the expression size. Naive application of the recurrences leads to sizable formulas after only few iterations. Such long formulas are unfavourable in the numerical implementations. In order to circumvent expression growth we have developed strategy to simplify and shorten the expressions using mathematical transformations. The expression growth starts already with the three-electron Hylleraas integrals, which serve as input for the four-electron integrals, so first we show how to put them in the maximally compact form. Next, we progress to the singly-linked four-electron Hylleraas integrals.

In order to keep the expressions for integrals within the reasonable length, we introduce the following function

$$
\begin{aligned}
&l(w_1, w_2, w_3) = \\
&= -\frac{1}{2}\Bigg\{\ln\left(\frac{w_3}{w_1 + w_2}\right) \ln\left(1 + \frac{w_3}{w_1 + w_2}\right) + \mathrm{Li}_2\left(-\frac{w_3}{w_1 + w_2}\right) + \mathrm{Li}_2\left(1 - \frac{w_3}{w_1 + w_2}\right) \\
&+ \ln\left(\frac{w_2}{w_3 + w_1}\right) \ln\left(1 + \frac{w_2}{w_1 + w_3}\right) + \mathrm{Li}_2\left(-\frac{w_2}{w_1 + w_3}\right) + \mathrm{Li}_2\left(1 - \frac{w_2}{w_1 + w_3}\right) \\
&+ \ln\left(\frac{w_1}{w_2 + w_3}\right) \ln\left(1 + \frac{w_1}{w_1 + w_2}\right) + \mathrm{Li}_2\left(-\frac{w_1}{w_2 + w_3}\right) + \mathrm{Li}_2\left(1 - \frac{w_1}{w_2 + w_3}\right)\Bigg\}.
\end{aligned}
\tag{3.1}
$$

It contains the dilogarithmic functions along with some logarithm expressions. Using it allows us to compactly express, for example, the three-electron integral defined in equation (2.19) as

$$
f(-1, -1, -1, -1, -1, -1; w_1, w_2, w_3) = \frac{l(w_1, w_2, w_3)}{w_1 w_2 w_3}. \tag{3.2}
$$

Using $l(w_1, w_2, w_3)$ to write the formulas for the integrals has three advantages. It separates out the part of the expression that has the special function, it allows to separate out and compactly write the derivatives of $l(w_1, w_2, w_3)$, and it permits computation of $l(w_1, w_2, w_3)$ and its derivatives as a separate procedure in the numerical implementation.

3.1.1 Illustration of the expression growth

In order to show the problem of expression growth we will start with the simple example.

Simple application of the three-electron recurrence relation as given in the equation (2.28), modified using the symmetry of the three-electron Hylleraas integrals to increase the first index by two

$$
\begin{aligned}
&f(-1,-1,1,-1,-1,-1;w_1,w_2,w_3)\\
&=\frac{l\left(w_1,w_2,w_3\right)}{w_1w_2^3w_3}+\frac{l\left(w_1,w_2,w_3\right)}{w_1w_2w_3^3}-\frac{w_1l\left(w_1,w_2,w_3\right)}{w_2^3w_3^3}-\frac{1}{w_2^2w_3^2\left(w_1+w_3\right)}\\
&-\frac{1}{w_2^2\left(w_1+w_2\right)w_3^2}+\frac{\log\left(w_2\right)}{w_1w_2^2w_3^2}-\frac{\log\left(w_1+w_2\right)}{w_1w_2^2w_3^2}+\frac{\log\left(w_3\right)}{w_1w_2^2w_3^2}-\frac{\log\left(w_1+w_3\right)}{w_1w_2^2w_3^2}\\
&-\frac{\log\left(w_1\right)}{w_2^3w_3^2}+\frac{\log\left(w_1+w_2\right)}{w_2^3w_3^2}-\frac{\log\left(w_3\right)}{w_2^3w_3^2}+\frac{\log\left(w_2+w_3\right)}{w_2^3w_3^2}-\frac{\log\left(w_1\right)}{w_2^2w_3^3}\\
&-\frac{\log\left(w_2\right)}{w_2^2w_3^3}+\frac{\log\left(w_1+w_3\right)}{w_2^2w_3^3}+\frac{\log\left(w_2+w_3\right)}{w_2^2w_3^3}.
\end{aligned}
\tag{3.3}
$$

The only simplification for this case involves collecting terms with function l and logarithms resulting in slightly more compact expression

$$
\begin{aligned}
&f(-1,-1,1,-1,-1,-1;w_1,w_2,w_3)\\
&=\left(-\frac{w_1}{w_2^3w_3^3}+\frac{1}{w_2^3w_3w_1}+\frac{1}{w_2w_3^3w_1}\right)l(w_1,w_2,w_3)\\
&-\frac{1}{w_2^2w_3^2\left(w_1+w_3\right)}-\frac{1}{w_2^2\left(w_1+w_2\right)w_3^2}+\left(\frac{1}{w_3^3w_2^2}+\frac{1}{w_3^2w_2^3}\right)\log\left(\frac{w_2+w_3}{w_1}\right)+\\
&\left(\frac{1}{w_2^2w_3^3}-\frac{1}{w_1w_2^2w_3^2}\right)\log\left(\frac{w_1+w_3}{w_2}\right)+\left(\frac{1}{w_2^3w_3^2}-\frac{1}{w_1w_2^2w_3^2}\right)\log\left(\frac{w_1+w_2}{w_3}\right).
\end{aligned}
\tag{3.4}
$$

The difference becomes much more pronounced for simply calculated

$$
\begin{aligned}
&f(-1,0,1,-1,-1,-1;w_1,w_2,w_3)\\
&=-\frac{1}{2w_2^2w_3^3\left(w_2+w_3\right)}+\frac{3}{2w_1w_2^2\left(w_1+w_2\right)w_3^2}+\frac{1}{2w_1w_2\left(w_1+w_2\right)^2w_3^2}\\
&-\frac{1}{2w_2^2\left(w_1+w_2\right)^2w_3^2}+\frac{1}{2w_2^2w_3^2\left(w_2+w_3\right)^2}+\frac{1}{2w_2w_3^3\left(w_2+w_3\right)^2}\\
&+\frac{3\log\left(w_2\right)}{2w_1^2w_2^2w_3^2}-\frac{3\log\left(w_2\right)}{2w_2^2w_3^4}-\frac{3\log\left(w_1+w_2\right)}{2w_1^2w_2^2w_3^2}-\frac{3\log\left(w_2+w_3\right)}{2w_1^2w_2^2w_3^2}\\
&+\frac{3\log\left(w_1+w_2+w_3\right)}{2w_1^2w_2^2w_3^2}-\frac{3\log\left(\frac{w_2(w_1+w_2+w_3)}{(w_1+w_2)(w_2+w_3)}\right)}{2w_1^2w_2^2w_3^2}\\
&-\frac{2\log\left(\frac{w_2(w_1+w_2+w_3)}{(w_1+w_2)(w_2+w_3)}\right)}{w_1^2w_3^4}+\frac{3\log\left(w_1+w_2\right)}{2w_2^2w_3^4}+\frac{3\log\left(w_2+w_3\right)}{2w_2^2w_3^4}\\
&-\frac{3\log\left(w_1+w_2+w_3\right)}{2w_2^2w_3^4}+\frac{3\log\left(\frac{w_2(w_1+w_2+w_3)}{(w_1+w_2)(w_2+w_3)}\right)}{2w_2^2w_3^4},
\end{aligned}
\tag{3.5}
$$

which after performing partial fraction decomposition with respect to w_1, collecting the logarithms and using their properties results in very compact expression

$$
\begin{aligned}
&f(-1,0,1,-1,-1,-1;w_1,w_2,w_3)\\
&=\frac{1}{w_1^2w_2^2w_3^2}-\frac{1}{w_1^2\left(w_1+w_2\right)^2w_3^2}-\frac{2\log\left(\frac{w_2(w_1+w_2+w_3)}{(w_1+w_2)(w_2+w_3)}\right)}{w_1^2w_3^4}.
\end{aligned}
\tag{3.6}
$$

Therefore, we have developed a systematic way to simplify integral expressions. The simplification is performed for each integral and the optimised expression is used as an input in the recurrences and Laplacian expressions.

3.1.2 Three-electron Hylleraas integrals simplification

The resulting formulas for the three-electron Hylleraas integrals can be grouped into the four main categories. This separation depends on the number of odd and even parameters among the a, b, c in the integral $f(a,b,c,-1,-1,-1;w_1,w_2,w_3)$. This follows from the fact, that different kind of master integral corresponds to each of this situation. The most complicated one occurs when there are three odd parameters, simpler one with the two and one odd parameter, and the simplest one is the case of three even parameters.

In general there are three kinds of expressions to simplify: the ones with the function $l(w_1,w_2,w_3)$, the logarithms and the rational functions of w_1,w_2,w_3. In order to simplify the rational functions, we first perform partial fraction decomposition three times one after another. Once over w_1, then w_2 and finally w_3. Next, we perform partial fraction decomposition over each of them once again and choose expression with the shortest length. We have found this procedure to efficiently reduce the length of the rational expressions. In case of the expressions with the function $l(w_1,w_2,w_3)$ the only operation we perform is to collect together the factors that multiply the function l and its derivatives. In case of the logarithms we try to collect as many factors w_i (where $i=1,2,3$) under the single logarithm and collect all factors multiplying these collected logarithms. We have found that this procedure allows for significant cancellations among these factors.

Application of these aforementioned techniques is applied depending on what number of powers of r_{ij} are odd. In case of the three odd powers, all techniques are applied, in case of two odd powers the techniques for reducing logarithms and partial fraction decomposition. Finally when there is only one or there are none even powers we use only partial fractions decomposition. In case of the derivatives applied simplification techniques are practically identical to the case of $f(a,b,c,-1,-1,-1;w_1,w_2,w_3)$ with the only difference lying in the fact that with three odd powers of r_{ij} there are extra terms coming from the derivatives of the function l.

In order to illustrate efficiency of these simplification techniques, below we attach Table 3.1 that presents the expression length, counted as the number of the terms in the sum, of the several three-electron Hylleraas integrals. For example, the length of the formula (3.3) is 17, while for its simplified counterpart given in the equation (3.4) it is 11. For equations (3.5) and (3.6) it is 17 and 3 respectively.

Table 3.1: The length of the expressions for the selected three-electron Hylleraas integrals before and after the reduction of the expression length. Columns Integral, Naive, Simplified, and Ratio contain the type of the integral, the number of the terms in the naive application of the recurrence formulas and differentiation, the number of the terms after the simplification and ratio of the non-simplified to the simplified expression.

Integral	Naive	Simplified	Ratio
$f(1,1,-1,-1,-1,-1)$	59	33	1.8
$f(1,1,1,-1,-1,-1)$	124	54	2.3
$f(2,-1,-1,-1,-1,-1)$	18	8	2.2
$f(2,0,-1,-1,-1,-1)$	19	4	4.8
$f(2,2,-1,-1,-1,-1)$	65	11	5.9
$f(3,1,-1,-1,-1,-1)$	147	69	2.1
$f(2,2,2,-1,-1,-1)$	205	7	29.3
$f(4,2,0,-1,-1,-1)$	202	6	33.7
$f(3,3,3,-1,-1,-1)$	832	239	3.5
$f(4,4,4,-1,-1,-1)$	989	19	52.1
$f(1,-1,-1,0,-1,-1)$	37	13	2.8
$f(1,1,-1,0,-1,-1)$	95	36	2.6
$f(1,1,1,0,-1,-1)$	197	60	3.3
$f(1,-1,-1,1,-1,-1)$	69	20	3.5
$f(1,1,-1,1,-1,-1)$	171	55	3.1
$f(1,1,1,1,-1,-1)$	378	94	4.0
$f(1,-1,-1,2,-1,-1)$	159	25	6.4
$f(1,1,-1,2,-1,-1)$	314	66	4.8
$f(1,1,1,2,-1,-1)$	696	112	6.2
$f(1,-1,-1,0,0,-1)$	28	20	1.4
$f(1,1,-1,0,0,-1)$	88	50	1.8
$f(1,1,1,0,0,-1)$	180	89	2.0
$f(1,-1,-1,0,1,-1)$	35	27	1.3
$f(1,1,-1,0,1,-1)$	110	66	1.7
$f(1,1,1,0,1,-1)$	214	113	1.9
$f(1,-1,-1,1,0,-1)$	35	29	1.2
$f(1,1,-1,1,0,-1)$	109	64	1.7
$f(1,1,1,1,0,-1)$	222	113	2.0
$f(1,-1,-1,1,1,-1)$	47	38	1.2
$f(1,1,-1,1,1,-1)$	137	88	1.6
$f(1,1,1,1,1,-1)$	265	155	1.7
$f(1,-1,-1,2,0,-1)$	42	36	1.2
$f(1,1,-1,2,0,-1)$	130	80	1.6
$f(1,1,1,2,0,-1)$	264	143	1.8
$f(1,-1,-1,2,1,-1)$	57	47	1.2
$f(1,1,-1,2,1,-1)$	164	103	1.6
$f(1,1,1,2,1,-1)$	316	183	1.7

3.1.3 Four-electron Hylleraas integrals simplification

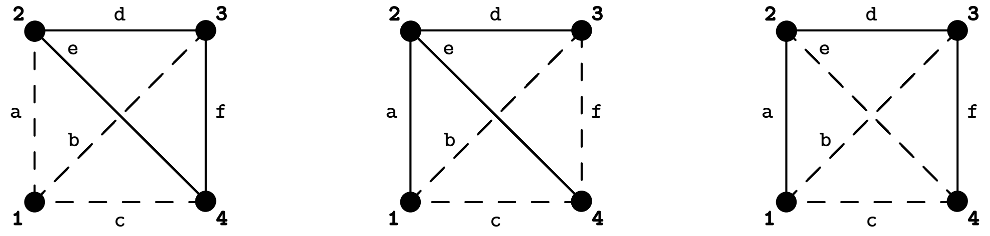
For the four-electron Hylleraas the situation with expression length is similar to the three-electron integrals. First, all input three-electron integrals are taken simplified. Then, we perform partial fraction decomposition and collect logarithms, function l and its derivatives. The procedure, especially partial fraction decomposition can be quite time consuming, but since the resulting expressions are shorter it makes the calculation of the higher powers of r_{ij} significantly faster and results in more compact final expression.

Table 3.2: The length of the expressions for the selected four-electron Hylleraas integrals before and after the reduction of the expression length. Columns Integral, Naive, Simplified, and Ratio contain the type of the integral, the number of the terms in the naive application of the recurrence formulas and differentiation, the number of the terms after the simplification and ratio of the non-simplified to the simplified expression.

Integral	Naive	Simplified	Ratio
g(-1, 0, 0, 0, 1, 1, -1, -1, -1, -1)	30	17	2.2
g(-1, 0, 0, 0, 3, -1, -1, -1, -1, -1)	36	20	1.7
g(-1, 2, 0, 0, 0, 0, -1, -1, -1, -1)	8	4	0.0
g(-1, 4, 0, 0, 0, 0, -1, -1, -1, -1)	18	6	0.0
g(-1, 2, 2, 0, 0, 0, -1, -1, -1, -1)	35	14	0.0
g(-1, 2, 0, -1, 0, -1, -1, -1, -1, -1)	247	20	0.0
g(-1, 2, 0, -1, -1, 0, -1, -1, -1, -1)	491	51	0.0

3.2 Explicit formulas for the first few four-electron Hylleraas integrals

In general there are three main types of singly-linked Hylleraas integrals. The first type, we will call "triangle" integral involves three linked odd powers of r_{ij}. This means that two indices of the three electron are present in each r_{ij} with odd power. The example of this type of the integrals we will present are integrals with odd r_{23}, r_{24} and r_{34} and consequently even r_{12}, r_{13}, r_{14}. The second distinct type of the singly-linked Hylleraas integrals involves a single electron index that is repeated in all odd powers of distances between the electrons. An example of such integrals would be integral with odd powers r_{12}, r_{23}, r_{24} and even remaining powers. This type of integral is called "star" integral, since there is single electron (electron 2 in the given example) that "connects" to the rest of the electron with the odd powers of r_{ij}. The last, third type is a singly-linked Hylleraas integral called "chain" integral. It consists of expressions where each electron index is repeated at most twice. Example of such integral would be the one with odd r_{12}, r_{23} and r_{24}. The name comes from the fact that each electron is sequentially "chained" to the next one via odd power of r_{ij}. These are possible types of singly-linked Hylleraas integrals with three odd powers of interelectronic distances. Integrals with less that three odd powers are easily represented as products of three-, two- and one-electron integrals and are much simpler so they do not have separate names. Finally it is worth emphasizing, that for singly-linked Hylleraas integrals there exist only these three classes of integrals for any number of electrons. This is a consequence of the simple simple geometric fact, that the aforementioned types are the only possible connected line segments independently on how many edges are present.



(A) (B) (C)

Figure 3.1: Classification of the four-electron singly-linked Hylleraas integrals. Dots with the electrons schematically represented by dots with numbers, dashed lines representing the even and solid lines odd powers of the distances between the electrons with small letters (a-e) corresponding to parameters in the definition of singly-lined. Each of the three cases of triangle (A), star (B), and chain (C) integral corresponds to a different integral topology and cannot be obtained by permuting different cases.

Since as mentioned in section 2.4.8 it is possible to obtain remaining singly-linked Hylleraas integrals via permutations here we only present the analytic formulas for some example integrals of the types mentioned in the previous paragraph. Furthermore, we restrict ourselves to lowest powers of r_{ij} as the expressions become increasingly long with for larger powers.

3.2.1 Triangle integrals

In order to keep the expression for triangle integrals within reasonable length, we introduce the following compact notation for the derivatives of the function l

$$\left(\frac{\partial}{\partial w_2}\right)^i \left(\frac{\partial}{\partial w_3}\right)^j \left(\frac{\partial}{\partial w_4}\right)^k l(w_2, w_3, w_4) = l^{(i,j,k)}\left(w_2, w_3, w_4\right). \tag{3.7}$$

The simplest triangle integral with even powers of the remaining r_{ij}'s is

$$\begin{aligned} & g(2,0,0,-1,-1,-1,-1,-1,-1,-1) \\ & = \left(\frac{3}{w_1^4 w_2 w_3 w_4} + \frac{2}{w_1^2 w_2^3 w_3 w_4}\right) l\left(w_2, w_3, w_4\right) \\ & - \frac{2 l^{(1,0,0)}\left(w_2, w_3, w_4\right)}{w_1^2 w_2^2 w_3 w_4} + \frac{l^{(2,0,0)}\left(w_2, w_3, w_4\right)}{w_1^2 w_2 w_3 w_4} \end{aligned} \tag{3.8}$$

with the next two being

$$
\begin{aligned}
&g(4,0,0,-1,-1,-1,-1,-1,-1,-1)\\
&=\left(\frac{71}{w_1^6 w_2 w_3 w_4}+\frac{32}{w_1^4 w_2^3 w_3 w_4}+\frac{24}{w_1^2 w_2^5 w_3 w_4}\right) l\left(w_2,w_3,w_4\right)\\
&+\left(-\frac{32}{w_1^4 w_2^2 w_3 w_4}-\frac{24}{w_1^2 w_2^4 w_3 w_4}\right) l^{(1,0,0)}\left(w_2,w_3,w_4\right)\\
&+\left(\frac{16}{w_1^4 w_2 w_3 w_4}+\frac{12}{w_1^2 w_2^3 w_3 w_4}\right) l^{(2,0,0)}\left(w_2,w_3,w_4\right)\\
&-\frac{4 l^{(3,0,0)}\left(w_2,w_3,w_4\right)}{w_1^2 w_2^2 w_3 w_4}+\frac{l^{(4,0,0)}\left(w_2,w_3,w_4\right)}{w_1^2 w_2 w_3 w_4}
\end{aligned}
\tag{3.9}
$$

and

$$
\begin{aligned}
&g(2,2,0,-1,-1,-1,-1,-1,-1,-1)\\
&=\frac{2}{w_1^4 w_3^2\left(w_2+w_3\right) w_4^2}+\frac{2}{w_1^4 w_3^2 w_4^2\left(w_2+w_4\right)}+\left(\frac{2 w_2}{w_1^4 w_3^3 w_4^3}+\frac{71}{w_1^6 w_3 w_4 w_2}\right.\\
&\left.+\frac{16}{w_1^4 w_3^3 w_4 w_2}-\frac{2}{w_1^4 w_3 w_4^3 w_2}+\frac{14}{w_1^4 w_3 w_4 w_2^3}+\frac{4}{w_1^2 w_3^3 w_4 w_2^3}\right) l\left(w_2,w_3,w_4\right)\\
&+\left(\frac{2}{w_1^4 w_2 w_3^2 w_4^2}-\frac{2}{w_1^4 w_3^3 w_4^2}\right)\log\left(\frac{w_2+w_3}{w_4}\right)+\left(\frac{2}{w_1^4 w_2 w_3^2 w_4^2}\right)\\
&-\left(\frac{2}{w_1^4 w_3^2 w_4^3}\right)\log\left(\frac{w_2+w_4}{w_3}\right)+\left(-\frac{2}{w_1^4 w_4^3 w_3^2}-\frac{2}{w_1^4 w_4^2 w_3^3}\right)\log\left(\frac{w_3+w_4}{w_2}\right)\\
&+\left(-\frac{18}{w_1^4 w_2 w_3^2 w_4}-\frac{4}{w_1^2 w_2^3 w_3^2 w_4}\right) l^{(0,1,0)}\left(w_2,w_3,w_4\right)+\left(\frac{9}{w_1^4 w_2 w_3 w_4}\right.\\
&\left.+\frac{2}{w_1^2 w_2^3 w_3 w_4}\right) l^{(0,2,0)}\left(w_2,w_3,w_4\right)+\left(-\frac{14}{w_1^4 w_2^2 w_3 w_4}-\frac{4}{w_1^2 w_2^2 w_3^3 w_4}\right) l^{(1,0,0)}\left(w_2,w_3,w_4\right)\\
&+\frac{4 l^{(1,1,0)}\left(w_2,w_3,w_4\right)}{w_1^2 w_2^2 w_3^2 w_4}-\frac{2 l^{(1,2,0)}\left(w_2,w_3,w_4\right)}{w_1^2 w_2^2 w_3 w_4}+\left(\frac{7}{w_1^4 w_2 w_3 w_4}\right.\\
&\left.+\frac{2}{w_1^2 w_2 w_3^3 w_4}\right) l^{(2,0,0)}\left(w_2,w_3,w_4\right)-\frac{2 l^{(2,1,0)}\left(w_2,w_3,w_4\right)}{w_1^2 w_2 w_3^2 w_4}+\frac{l^{(2,2,0)}\left(w_2,w_3,w_4\right)}{w_1^2 w_2 w_3 w_4}.
\end{aligned}
\tag{3.10}
$$

3.2.2 Star integrals

The first, most fundamental integral of star type is given by

$$\begin{aligned}
&g\left(-1,0,0,-1,-1,0,-1,-1,-1,-1\right)\\
&=\left(\frac{w_2}{w_1^2w_3^2w_4^2}+\frac{1}{w_1^2w_3w_4^2}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3\right)}{\left(w_1+w_2\right)\left(w_2+w_3\right)}\right)\\
&+\left(\frac{w_2}{w_1^2w_3^2w_4^2}+\frac{1}{w_1^2w_3^2w_4}\right)\log\left(\frac{w_2\left(w_1+w_2+w_4\right)}{\left(w_1+w_2\right)\left(w_2+w_4\right)}\right)\\
&+-\frac{\log\left(\frac{(w_1+w_2)(w_1+w_2+w_3+w_4)}{(w_1+w_2+w_3)(w_1+w_2+w_4)}\right)}{w_1w_3^2w_4^2}\\
&+\left(-\frac{w_2}{w_1^2w_3^2w_4^2}-\frac{1}{w_1^2w_3^2w_4}-\frac{1}{w_1^2w_3w_4^2}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3+w_4\right)}{\left(w_1+w_2\right)\left(w_2+w_3+w_4\right)}\right)
\end{aligned}\tag{3.11}$$

while the next one is

$$\begin{aligned}
&g\left(1,0,0,-1,-1,0,-1,-1,-1,-1\right)\\
&=\frac{3}{w_1^2w_2w_3^2w_4^2}-\frac{1}{w_1^2w_3^2\left(w_2+w_3\right)w_4^2}-\frac{1}{w_1^2w_3^2w_4^2\left(w_2+w_4\right)}-\frac{1}{w_1^2w_3^2w_4^2\left(w_2+w_3+w_4\right)}\\
&+\left(\frac{2w_2}{w_1^4w_3^2w_4^2}+\frac{2}{w_1^4w_3w_4^2}+\frac{2}{w_1^3w_3^2w_4^2}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3\right)}{\left(w_1+w_2\right)\left(w_2+w_3\right)}\right)\\
&+\left(\frac{2w_2}{w_1^4w_3^2w_4^2}+\frac{2}{w_1^4w_3^2w_4}+\frac{2}{w_1^3w_3^2w_4^2}\right)\log\left(\frac{w_2\left(w_1+w_2+w_4\right)}{\left(w_1+w_2\right)\left(w_2+w_4\right)}\right)\\
&+\left(\frac{2}{w_1^2w_3^2w_4^2\left(w_2+w_3+w_4\right)}-\frac{2}{w_1^2w_2w_3^2w_4^2}\right)\log\left(\frac{w_1+w_2+w_3+w_4}{\left(w_2+w_3\right)\left(w_2+w_4\right)}\right)\\
&+\left(-\frac{2w_2}{w_1^4w_3^2w_4^2}-\frac{2}{w_1^4w_3^2w_4}+\frac{2}{w_1^2w_3^2w_4^2\left(w_2+w_3+w_4\right)}-\frac{2}{w_1^4w_3w_4^2}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3+w_4\right)}{\left(w_1+w_2\right)\left(w_2+w_3+w_4\right)}\right).
\end{aligned}\tag{3.12}$$

Integral with increased e is

$$\begin{aligned}
&g(-1,0,0,-1,1,0,-1,-1,-1,-1)\\
&=\frac{1}{w_1^2w_2w_3^2w_4^2}-\frac{1}{w_1^2\left(w_1+w_2\right)w_3^2w_4^2}-\frac{1}{w_1^2w_3^2\left(w_2+w_3\right)w_4^2}+\frac{1}{w_1^2w_3^2\left(w_1+w_2+w_3\right)w_4^2}\\
&+\left(\frac{2w_2}{w_1^2w_3^2w_4^4}+\frac{2}{w_1^2w_3w_4^4}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3\right)}{\left(w_1+w_2\right)\left(w_2+w_3\right)}\right)\\
&+\left(\frac{2w_2}{w_1^2w_3^2w_4^4}+\frac{2}{w_1^2w_3^2w_4^3}\right)\log\left(\frac{w_2\left(w_1+w_2+w_4\right)}{\left(w_1+w_2\right)\left(w_2+w_4\right)}\right)\\
&-\frac{2\log\left(\frac{(w_1+w_2)(w_1+w_2+w_3+w_4)}{(w_1+w_2+w_3)(w_1+w_2+w_4)}\right)}{w_1w_3^2w_4^4}\\
&+\left(-\frac{2w_2}{w_1^2w_3^2w_4^4}-\frac{2}{w_1^2w_3^2w_4^3}-\frac{2}{w_1^2w_3w_4^4}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3+w_4\right)}{\left(w_1+w_2\right)\left(w_2+w_3+w_4\right)}\right)
\end{aligned}\tag{3.13}$$

while the increased d results in

$$\begin{aligned}
&g(-1,0,0,1,-1,0,-1,-1,-1,-1)\\
&=\frac{1}{w_1^2w_2w_3^2w_4\left(w_2+w_4\right)}-\frac{1}{w_1^2\left(w_1+w_2\right)w_3^2w_4\left(w_1+w_2+w_4\right)}\\
&+\left(\frac{2w_2}{w_1^2w_3^4w_4^2}+\frac{2}{w_1^2w_3^3w_4^2}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3\right)}{\left(w_1+w_2\right)\left(w_2+w_3\right)}\right)\\
&+\left(\frac{2w_2}{w_1^2w_3^4w_4^2}+\frac{2}{w_1^2w_3^4w_4}\right)\log\left(\frac{w_2\left(w_1+w_2+w_4\right)}{\left(w_1+w_2\right)\left(w_2+w_4\right)}\right)\\
&-\frac{2\log\left(\frac{(w_1+w_2)(w_1+w_2+w_3+w_4)}{(w_1+w_2+w_3)(w_1+w_2+w_4)}\right)}{w_1w_3^4w_4^2}\\
&+\left(-\frac{2w_2}{w_1^2w_3^4w_4^2}-\frac{2}{w_1^2w_3^4w_4}-\frac{2}{w_1^2w_3^3w_4^2}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3+w_4\right)}{\left(w_1+w_2\right)\left(w_2+w_3+w_4\right)}\right).
\end{aligned}\tag{3.14}$$

To show the star integral with the increased b we present

$$\begin{aligned}
&g(-1,2,0,-1,-1,0,-1,-1,-1,-1)\\
&=-\frac{4}{w_1^3w_3^4}+\frac{2}{w_1^2w_3^3w_4^2}-\frac{8w_2}{w_1^3w_3^3w_4^2}-\frac{4}{w_1^3w_3^2w_4^2}-\frac{1}{w_1^2\left(w_1+w_2\right)w_3^2w_4^2}\\
&-\frac{1}{w_1^2w_3^2\left(w_2+w_3\right)w_4^2}+\frac{2}{w_1^2w_3^4w_4}-\frac{8w_2}{w_1^3w_3^4w_4}-\frac{20}{3w_1^3w_3^3w_4}\\
&+\frac{1}{w_1^2w_3^2w_4^2\left(w_1+w_2+w_4\right)}+\frac{1}{w_1^2w_3^2w_4^2\left(w_2+w_3+w_4\right)}\\
&+\left(-\frac{4w_2^3}{3w_1^4w_3^4w_4^2}+\frac{6w_2}{w_1^4w_3^2w_4^2}+\frac{6w_2}{w_1^2w_3^4w_4^2}+\frac{14}{3w_1^4w_3w_4^2}+\right.\\
&\left.\frac{2}{w_1^3w_3^2w_4^2}+\frac{2}{w_1^2w_3^3w_4^2}+\frac{4}{w_1w_3^4w_4^2}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3\right)}{\left(w_1+w_2\right)\left(w_2+w_3\right)}\right)\\
&\left(-\frac{4w_2^3}{3w_1^4w_3^4w_4^2}-\frac{4w_2^2}{w_1^4w_3^4w_4}+\frac{6w_2}{w_1^4w_3^2w_4^2}+\frac{6w_2}{w_1^2w_3^4w_4^2}-\frac{4w_2}{w_1^4w_3^4}-\frac{4w_4}{3w_1^4w_3^4}+\right.\\
&\left.\frac{6}{w_1^4w_3^2w_4}+\frac{6}{w_1^2w_3^4w_4}+\frac{2}{w_1^3w_3^2w_4^2}+\frac{4}{w_1w_3^4w_4^2}\right)\log\left(\frac{w_2\left(w_1+w_2+w_4\right)}{\left(w_1+w_2\right)\left(w_2+w_4\right)}\right)\\
&\left(\frac{12w_2^2}{w_1^4w_3^4w_4}+\frac{12w_2^2}{w_1^4w_3^3w_4^2}+\frac{24w_2}{w_1^4w_3^3w_4}+\frac{12w_2}{w_1^4w_3^2w_4^2}+\frac{12w_2}{w_1^4w_3^4}\right.\\
&\left.+\frac{4w_4}{w_1^4w_3^4}+\frac{14}{w_1^4w_3^2w_4}+\frac{6}{w_1^4w_3w_4^2}+\frac{12}{w_1^4w_3^3}\right)\log\left(\frac{w_1+w_2+w_3+w_4}{\left(w_2+w_3\right)\left(w_2+w_4\right)}\right)\\
&-\frac{2\log\left(\frac{(w_1+w_2)(w_1+w_2+w_3+w_4)}{(w_1+w_2+w_3)(w_1+w_2+w_4)}\right)}{3w_1w_3^4w_4^2}+\left(\frac{16w_2^3}{3w_1^4w_3^4w_4^2}+\frac{16w_2^2}{w_1^4w_3^4w_4}+\frac{12w_2^2}{w_1^4w_3^3w_4^2}\right.\\
&+\frac{24w_2}{w_1^4w_3^3w_4}+\frac{8w_2}{w_1^4w_3^2w_4^2}-\frac{6w_2}{w_1^2w_3^4w_4^2}+\frac{16w_2}{w_1^4w_3^4}+\frac{16w_4}{3w_1^4w_3^4}+\frac{8}{w_1^4w_3^2w_4}\\
&\left.-\frac{6}{w_1^2w_3^4w_4}+\frac{4}{3w_1^4w_3w_4^2}-\frac{2}{w_1^2w_3^3w_4^2}+\frac{12}{w_1^4w_3^3}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3+w_4\right)}{\left(w_1+w_2\right)\left(w_2+w_3+w_4\right)}\right).
\end{aligned}\tag{3.15}$$

3.2.3 Chain integrals

The most fundamental chain integral is

$$\begin{aligned}
&g\left(-1,0,0,-1,0,-1,-1,-1,-1,-1\right)\\
&=-\frac{\log\left(\frac{w_2(w_1+w_2+w_3)}{(w_1+w_2)(w_2+w_3)}\right)}{w_1^2w_3w_4^2}+\frac{\log\left(\frac{w_2(w_1+w_2+w_3+w_4)}{(w_1+w_2)(w_2+w_3+w_4)}\right)}{w_1^2w_4^2\left(w_3+w_4\right)}\\
&-\frac{\log\left(\frac{w_3(w_2+w_3+w_4)}{(w_2+w_3)(w_3+w_4)}\right)}{w_1^2w_2w_4^2}+\frac{\log\left(\frac{w_3(w_1+w_2+w_3+w_4)}{(w_1+w_2+w_3)(w_3+w_4)}\right)}{w_1^2\left(w_1+w_2\right)w_4^2}.
\end{aligned}\tag{3.16}$$

The index increase leads to

$$\begin{aligned}
&g\left(1,0,0,-1,0,-1,-1,-1,-1,-1\right)\\
&=-\frac{1}{w_1^2w_2^2\left(w_2+w_3\right)w_4^2}+\frac{1}{w_1^2w_2^2w_4^2\left(w_2+w_3+w_4\right)}+\left(-\frac{2}{w_1^4w_3w_4^2}\right.\\
&\left.-\frac{2}{w_1^4w_4^2w_2}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3\right)}{\left(w_1+w_2\right)\left(w_2+w_3\right)}\right)-\frac{2\log\left(\frac{w_3(w_2+w_3+w_4)}{(w_2+w_3)(w_3+w_4)}\right)}{w_1^2w_2^3w_4^2}\\
&-\frac{2\log\left(\frac{w_3(w_1+w_2+w_3+w_4)}{(w_1+w_2+w_3)(w_3+w_4)}\right)}{w_1^3w_2\left(w_1+w_2\right)w_4^2}+\left(\frac{2}{w_1^4w_4^2\left(w_3+w_4\right)}+\frac{2}{w_1^3w_2w_4^2\left(w_1+w_2\right)}\right.\\
&\left.+\frac{2}{w_1^4w_4^2\left(w_1+w_2\right)}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3+w_4\right)}{\left(w_1+w_2\right)\left(w_2+w_3+w_4\right)}\right)
\end{aligned}\tag{3.17}$$

and

$$\begin{aligned}
&g\left(-1,0,0,1,0,-1,-1,-1,-1,-1\right)\\
&=\frac{1}{3w_1^2w_2w_3^2w_4^2}-\frac{1}{3w_1^2\left(w_1+w_2\right)w_3^2w_4^2}+\frac{1}{3w_1^2w_2^2w_3w_4^2}-\frac{1}{3w_1^2\left(w_1+w_2\right)^2w_3w_4^2}\\
&-\frac{1}{3w_1^2w_2w_4^2\left(w_3+w_4\right)^2}+\frac{1}{3w_1^2\left(w_1+w_2\right)w_4^2\left(w_3+w_4\right)^2}-\frac{1}{3w_1^2w_2^2w_4^2\left(w_3+w_4\right)}\\
&+\frac{1}{3w_1^2\left(w_1+w_2\right)^2w_4^2\left(w_3+w_4\right)}-\frac{2\log\left(\frac{w_2(w_1+w_2+w_3)}{(w_1+w_2)(w_2+w_3)}\right)}{3w_1^2w_3^3w_4^2}-\frac{2\log\left(\frac{w_3(w_2+w_3+w_4)}{(w_2+w_3)(w_3+w_4)}\right)}{3w_1^2w_2^3w_4^2}\\
&+\frac{2\log\left(\frac{w_3(w_1+w_2+w_3+w_4)}{(w_1+w_2+w_3)(w_3+w_4)}\right)}{3w_1^2\left(w_1+w_2\right)^3w_4^2}+\frac{2\log\left(\frac{w_2(w_1+w_2+w_3+w_4)}{(w_1+w_2)(w_2+w_3+w_4)}\right)}{3w_1^2w_4^2\left(w_3+w_4\right)^3}
\end{aligned}\tag{3.18}$$

as well as

$$\begin{aligned}
&g\left(-1,0,0,-1,0,1,-1,-1,-1,-1\right)\\
&=-\frac{1}{w_1^2w_3^2\left(w_2+w_3\right)w_4^2}+\frac{1}{w_1^2w_3^2\left(w_1+w_2+w_3\right)w_4^2}\\
&+\left(-\frac{2}{w_1^2w_4^4w_3}-\frac{2}{w_1^2w_4^2w_3^3}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3\right)}{\left(w_1+w_2\right)\left(w_2+w_3\right)}\right)\\
&-\frac{2\log\left(\frac{w_3(w_2+w_3+w_4)}{(w_2+w_3)(w_3+w_4)}\right)}{w_1^2w_2w_4^4}+\frac{2\log\left(\frac{w_3(w_1+w_2+w_3+w_4)}{(w_1+w_2+w_3)(w_3+w_4)}\right)}{w_1^2\left(w_1+w_2\right)w_4^4}+\frac{2\log\left(\frac{w_2(w_1+w_2+w_3+w_4)}{(w_1+w_2)(w_2+w_3+w_4)}\right)}{w_1^2w_4^4\left(w_3+w_4\right)}.
\end{aligned}\tag{3.19}$$

With $b = 2$ the chain integral has form

$$\begin{aligned}
&g\left(-1,2,0,-1,0,-1,-1,-1,-1,-1\right)\\
&= \frac{4}{3w_1^3w_3^2w_4^2} - \frac{1}{3w_1^2\left(w_1+w_2\right)w_3^2w_4^2} - \frac{1}{3w_1^2\left(w_1+w_2\right)^2w_3w_4^2} - \frac{4}{3w_1^3\left(w_1+w_2\right)w_3w_4^2}\\
&- \frac{1}{w_1^2w_3^2\left(w_2+w_3\right)w_4^2} - \frac{4}{3w_1^3w_4^2\left(w_3+w_4\right)^2} + \frac{1}{3w_1^2\left(w_1+w_2\right)w_4^2\left(w_3+w_4\right)^2}\\
&+ \frac{1}{3w_1^2\left(w_1+w_2\right)^2w_4^2\left(w_3+w_4\right)} + \frac{4}{3w_1^3\left(w_1+w_2\right)w_4^2\left(w_3+w_4\right)}\\
&+ \frac{1}{w_1^2w_4^2\left(w_3+w_4\right)^2\left(w_2+w_3+w_4\right)} + \left(\frac{4w_2^2}{3w_1^4w_3^3w_4^2} - \frac{6}{w_1^4w_3w_4^2}\right.\\
&\left.- \frac{2}{w_1^2w_3^3w_4^2}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3\right)}{\left(w_1+w_2\right)\left(w_2+w_3\right)}\right) + \left(\frac{14}{3w_1^4w_4^2\left(w_1+w_2\right)}\right.\\
&\left.+ \frac{8}{3w_1^3w_4^2\left(w_1+w_2\right)^2} + \frac{2}{3w_1^2w_4^2\left(w_1+w_2\right)^3}\log\left(\frac{w_3\left(w_1+w_2+w_3+w_4\right)}{\left(w_1+w_2+w_3\right)\left(w_3+w_4\right)}\right)\right.\\
&+ \left(-\frac{4w_2^2}{3w_1^4w_4^2\left(w_3+w_4\right)^3} + \frac{6}{w_1^4w_4^2\left(w_3+w_4\right)}\right.\\
&\left.+ \frac{2}{w_1^2w_4^2\left(w_3+w_4\right)^3}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3+w_4\right)}{\left(w_1+w_2\right)\left(w_2+w_3+w_4\right)}\right)
\end{aligned} \tag{3.20}$$

while for $e = 2$ we get

$$\begin{aligned}
&g\left(-1,0,0,-1,2,-1,-1,-1,-1,-1\right)\\
&= \frac{8}{3w_1\left(w_1+w_2\right)^3w_4^3} + \frac{4w_1}{3w_2^2\left(w_1+w_2\right)^3w_4^3} + \frac{4}{w_2\left(w_1+w_2\right)^3w_4^3} - \frac{1}{w_1^2w_2^2\left(w_2+w_3\right)w_4^2}\\
&+ \frac{1}{w_1^2\left(w_1+w_2\right)^2\left(w_1+w_2+w_3\right)w_4^2} - \frac{1}{3w_1w_2\left(w_1+w_2\right)w_4^2\left(w_3+w_4\right)^2}\\
&- \frac{4}{3w_1\left(w_1+w_2\right)^2w_4^3\left(w_3+w_4\right)} - \frac{4}{3w_2\left(w_1+w_2\right)^2w_4^3\left(w_3+w_4\right)}\\
&- \frac{1}{3w_2^2\left(w_1+w_2\right)^2w_4^2\left(w_3+w_4\right)}, - \frac{2}{3w_1w_2\left(w_1+w_2\right)^2w_4^2\left(w_3+w_4\right)}\\
&- \frac{14\log\left(\frac{w_2\left(w_1+w_2+w_3\right)}{\left(w_1+w_2\right)\left(w_2+w_3\right)}\right)}{3w_1^2w_3w_4^4} + \left(\frac{4w_3^2}{3w_1^2w_2^3w_4^4} - \frac{2}{w_1^2w_2^3w_4^2} - \frac{6}{w_1^2w_2w_4^4}\right)\log\left(\frac{w_3\left(w_2+w_3+w_4\right)}{\left(w_2+w_3\right)\left(w_3+w_4\right)}\right)\\
&+ \left(-\frac{4w_3^2}{3w_1^2\left(w_1+w_2\right)^3w_4^4} + \frac{2}{w_1^2\left(w_1+w_2\right)^3w_4^2} + \frac{6}{w_1^2\left(w_1+w_2\right)w_4^4}\right)\log\left(\frac{w_3\left(w_1+w_2+w_3+w_4\right)}{\left(w_1+w_2+w_3\right)\left(w_3+w_4\right)}\right)\\
&+ \left(\frac{14w_3^2}{3w_1^2w_4^4\left(w_3+w_4\right)^3} + \frac{12w_3}{w_1^2w_4^3\left(w_3+w_4\right)^3} + \frac{8}{w_1^2w_4^2\left(w_3+w_4\right)^3}\right)\log\left(\frac{w_2\left(w_1+w_2+w_3+w_4\right)}{\left(w_1+w_2\right)\left(w_2+w_3+w_4\right)}\right).
\end{aligned} \tag{3.21}$$

3.3 Comparison with the existing results

3.3.1 Comparison of analytical formulas

First, we compare our formulas against those most recently derived by King [126]. We report that our formulas agree (after rescaling by $(4\pi)^4$) with formulas (24), (30), (42), (54) of King. However, despite the agreement between (42) of King and our equation (3.16) we did not manage to reproduce the value in equation (43). We suppose that there is some kind of mistake in this value. Next, we look at the earlier work of King [121], where we confirm agreement of our results with his formulas (37), (40) (which is equal to (42) form [126] and our equation (3.16)). Interestingly we confirm (41) from [121] which is in disagreement with his latter value of (43) form [126].

3.3.2 Numerical values of integrals

Next, we compare our values with the ones available from King [126]. First, we note that there is a misprint in King's Table 1 where the value of p should be equal to -1, not 1. When taking this (and rescaling of our integrals by $(4\pi)^4$) into account, our results agree with King's values for all 41 digits given in Table 1 and Table 2 of [126]. As an example, we show in Table 3.3 our results of the integral $g(1,0,0,1,0,-1,n_1,n_2,0,0;w_1,w_2,w_3,w_4)$.

Table 3.3: Present numerical values for selected values of the singly-linked Hylleraas integral g with $a=1, b=0, c=0, d=1, e=0, f=-1, n_3=0, n_4=0$.

n_1	n_2	w_1	w_2	w_3	w_4	Value of integral g(1, 0, 0, 1, 0, -1, $n_1, n_2, 0, 0; w_1, w_2, w_3, w_4$)
-1	-1	1.0	1.0	1.0	1.0	3.4553924355488356174760578385009478547888 $\times 10^5$
-1	-1	1.1	1.1	1.1	1.1	1.2110939689740175952300900736535233573747 $\times 10^5$
-1	-1	1.10	1.85	2.37	2.91	2.2399251764521981887632798244478194342854 $\times 10^2$
0	0	1.0	1.0	1.0	1.0	2.4131839593234774164104657085980726616233 $\times 10^6$
0	0	1.1	1.1	1.1	1.1	6.9901343476796004567999755497809669560957 $\times 10^5$
0	0	1.10	1.85	2.37	2.91	8.0393101779695602061205053725304366496571 $\times 10^2$

Next, we have checked the values from earlier work of King [121], where we have 40 digit agreement between values from table Table 1 and Table 2 therein and using our formulas.

Chapter 4

Conclusions

4.1 Summary

We have been able to successfully derive general method to obtain all singly-linked Hylleraas integrals in terms of closed-form analytic formulas. In order to develop the method of their calculation new theoretical tools have been developed: recurrences for the four-electron Hylleraas functions, Laplacian identities that have allowed us to obtain integrals necessary to start the derived recurrences, and the method that has allowed to solve the Laplacian identities using the three-electron Hylleraas integrals. A program to compute closed-form analytical expressions for both the three- and the four-electron integrals has been developed. Since the expression length becomes significant, procedures to simplify and keep the formulas as compact as possible have been developed. Excellent agreement, reaching forty significant digits, was obtained with the existing results for the four-electron Hylleraas in was confirmed, including both the numerical and analytical verification.

We believe, that this contribution is a first step towards the construction of the accurate method for evaluating of the properties and energy levels of the light atomic systems beyond a few electrons. We plan to apply obtained results in order to develop an efficient method for numerical evaluation of the analytic formulas. While existing formulas provide accurate benchmark for other implementations, the practical numerical program must inevitably deal with finite-precision arithmetics. Therefore, it remains to be seen whether the method we have developed will be widely adopted in the calculations of atomic systems.

In summary, we claim, that we have fulfilled the thesis statement presented at the beginning of this thesis and developed a method to obtain closed-form analytic expressions for all singly-linked Hylleraas integrals. While the lengthy expressions for higher powers of the distances between the electrons in the integrals cause the method to slow down, it in principle works for arbitrary values of these powers. Furthermore, since the calculation of the derivatives is a relatively simple procedure, a mixed symbolic-numerical approach can be adopted for this case.

4.2 Possible extensions of the present work

4.2.1 Large scale calculations of the energy levels of the four-electron systems

The first and most natural extension of the present work is of course the preparation of a program to evaluate matrix elements in singly-linked Hylleraas basis that utilises the developed formulas. While care must be taken in order to avoid loss of numerical accuracy, the analytical expressions allow for extensive tests and manipulations in order to transform them into a more robust method. The highly accurate calculation in a large basis would be the ultimate tests of the strength and correctness of the obtained results. While the properties of the four-electron atoms are calculated quite extensively, methods that yield highly-accurate wave functions allow to improve the accuracy of second-order properties that strongly depend on the quality of the wave function.

4.2.2 Doubly-and fully-linked Hylleraas method for four electron systems

Another worthwhile direction of extending the present work would be to try to generalise the method to the Hylleraas integrals with functions involving more than the odd powers of distances between the electron. On the other hand, the present accuracy of the explicitly correlated Gaussians seem to be sufficient in four-electron systems appear to be sufficient for any practical purposes. Therefore such pursuit would have mostly purely intellectual value, since the perspectives to extend the doubly-linked method beyond the systems with more than four electrons seem limited.

4.2.3 Extensions of the developed integration techniques towards more electrons

While the method to deal with singly-linked Hylleraas functions with more electrons has been sketched in section 1.2.3 of the appendix, the practical implementation of a such method has many challenges. Efficient algorithm that scales well with the number of the electrons in the system must be developed if the method is extended beyond the few electrons. Furthermore, the antisymmetrization of a wave function becomes a formidable challenge when explicitly correlated functions are used. Promising direction to deal with this problem has been shown by Nakashima [136].

4.2.4 Beyond non-relativistic energy

Yet another line of work is to extend the current method of integral evaluation to include integrals that is necessary in calculations beyond solving the non-relativistic Schrodinger equation. Such calculations include computations of the relativistic and QED effects, recoil corrections, dipole and quadrupole moments, upper bound to energy and many others. For these types of calculations additional matrix elements must be calculated, some of which are not expressed as integrals considered in this thesis. For the inclusion of the relativistic effects it seems, that the approach taken with the Hylleraas functions in lithium [130] should be possible to apply to the singly-linked Hylleraas four-electron integrals.

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Appendix A

Mathematical details and derivations

A.1 Derivation of the recurrence relations

A.1.1 Integration by parts identities in coordinate space representation

Integration by parts (IBP) identities is a technique, developed for computing Feynman integrals in quantum field theory [133, 134], that allows to derive useful relations between certain kinds of multi-dimensional integrals, and subsequently form a differential equation satisfied by master integrals. In our work, we use IBPs to derive the recurrence relations for the increasing powers of r_{ij} in many-electron integrals with the Hylleraas-type functions. The coordinate space IBP relations derived here can be generalised to the Hylleraas type integrals with arbitrary number of electrons.

Vanishing integral of the divergence of electron's position vector with Hylleraas-type spherically-symmetric two-electron function

We show below, that for $-1 \leq \{l, n, m\} \in \mathbb{Z} \wedge \{\alpha, \beta\} \in \mathbb{R}^+$ the following integral is equal to zero

$$\iint \mathrm{d}^3\mathbf{r}_1\, \mathrm{d}^3\mathbf{r}_2 \nabla_1 \cdot \mathbf{r}_2 \exp(-\alpha r_1 - \beta r_2) r_1^l r_2^m r_{12}^n = 0. \tag{A.1}$$

Using the divergence theorem we transform the triple integral over $\mathrm{d}^3\mathbf{r}_1$ to the surface integral over the boundary of the infinite sphere (with $\hat{\mathbf{r}}_1$ as the outward pointing unit vector on the spherical surface)

$$\begin{aligned}&\iint \mathrm{d}^3\mathbf{r}_1\, \mathrm{d}^3\mathbf{r}_2 \nabla_1 \cdot \mathbf{r}_2 \exp(-\alpha r_1 - \beta r_2) r_1^l r_2^m r_{12}^n \\ &= \int \mathrm{d}^3\mathbf{r}_2 \exp(-\beta r_2) r_2^m \mathbf{r}_2 \cdot \lim_{r_1 \to \infty} \oiint \mathrm{d}^2\hat{\mathbf{r}}_1 \exp(-\alpha r_1) r_1^l r_{12}^n\end{aligned} \tag{A.2}$$

expanding r_{12}^n using cosine law and factoring r_1 outside the square root we get

$$\int \mathrm{d}^3\mathbf{r}_2 \exp(-\beta r_2) r_2^m \mathbf{r}_2 \cdot \lim_{r_1 \to \infty} \oiint \mathrm{d}^2\hat{\mathbf{r}}_1 \exp(-\alpha r_1) r_1^{l+n} \left(1 + \frac{r_2^2}{r_1^2} + 2\frac{r_2}{r_1}\cos(\theta_{12})\right)^{n/2}. \tag{A.3}$$

In the surface integral, we integrate only over the angles, so the limit can be taken under the surface integral which results in

$$\oiint \mathrm{d}^2\hat{\mathbf{r}}_1 \lim_{r_1\to\infty} \exp(-\alpha r_1) r_1^{l+n} \left(1+\frac{r_2^2}{r_1^2}+2\frac{r_2}{r_1}\cos(\theta_{12})\right)^{n/2} = 0, \tag{A.4}$$

as the limit under the integral goes to 0 (since $\cos(\theta_{12})$ is in range $[-1, 1]$ and at the infinity exponential function vanishes faster than any polynomial of r_1). Therefore the relation (A.1) is proven.

General result for bound many-electron functions

The analogous result holds for a larger number of electrons and other combinations of the indices of ∇_i and $\mathbf{r}_j$, including $i = j$ (which can be shown in the similar way as above). The only difference in the case of more electrons is in the additional powers of r_j coming from more r_{jk} factors, which does not change the final result.

Therefore, the general result which can be written in the following way

$$\int\!\cdots\!\int \mathrm{d}^3\mathbf{r}_i\, \mathrm{d}^3\mathbf{r}_j\, \mathrm{d}^3\mathbf{r}_k \ldots \nabla_i \cdot \mathbf{r}_j g(r_i, r_j, r_k, r_{ij}, r_{ik}, r_{jk}, \ldots) = 0, \tag{A.5}$$

which holds for any scalar, many-electron, square-integrable function g that is sufficiently smooth (specifically Lipschitz continuous[1]) and vanishes at the infinity. Commonly used atomic Slater- and Gaussian-type functions, whether they include (sufficiently well-behaved) explicit correlation factors or not, fulfill these conditions. Furthermore, this relation can be rather straightforwardly extended to two- and many-centre problems after slight modification. Additionally, it's possible to find more analogous relations by finding second Green's identity analogue to the equation (A.5).

A.1.2 Derivation of the four-electron recurrence relations

We now proceed to derive the recurrence relations for the case of our interest, namely the four-electron Hylleraas-type integrals. We write equation (A.5) with four-electron Hylleraas-type functions. This leads to set of sixteen identities that have the following form

$$\begin{aligned} 0 = id(i,j) = \iiiint \mathrm{d}^3\mathbf{r}_1\, \mathrm{d}^3\mathbf{r}_2\, \mathrm{d}^3\mathbf{r}_3\mathbf{r}_2\, \mathrm{d}^3\mathbf{r}_4 \nabla_i \cdot \mathbf{r}_j \exp(-r_1 w_1 - r_2 w_2 - r_3 w_3 - r_4 w_4) \\ \times\, r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f} \end{aligned} \tag{A.6}$$

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[1] Function $f : \mathbb{R}^n \to \mathbb{R}$ is (globally) Lipschitz continuous if for every two points $x, y \in \mathbb{R}^n : x \neq y$ there exists a constant $L \geq 0$ such that $|f(x) - f(y)| \leq L\,|x - y|$.

Next, we focus on applying nabla to the expression under the integral.

$$\begin{aligned}
&\nabla_1 \cdot \Big(\mathbf{r}_1 \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f}\Big) \\
&= (\nabla_1 \cdot \mathbf{r}_1) \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f} \\
&+ \mathbf{r}_1 \cdot \Big(\nabla_1 \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f}\Big) \\
&= (\nabla_1 \cdot \mathbf{r}_1) \Big(\exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f}\Big) \\
&+ \mathbf{r}_1 \cdot \Big[(\nabla_1 \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4))\, r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f} \\
&+ (\nabla_1 r_1^{n_1}) \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f} \\
&+ \big(\nabla_1 r_{1,2}^{a}\big) \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f} \\
&+ \Big(\nabla_1 r_{1,3}^{b}\Big) \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f} \\
&+ \big(\nabla_1 r_{1,4}^{c}\big) \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f}\Big] .
\end{aligned} \tag{A.7}$$

Let us remind the definition of function h (as defined first in the equation (2.45))

$$\begin{aligned}
&h(a, b, c, d, e, f, n_1, n_2, n_3, n_4; w_1, w_2, w_3, w_4) = \\
&\exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f}.
\end{aligned} \tag{A.8}$$

Then, we apply rules of vector calculus[2] to obtain equation (A.7) in form

$$\begin{aligned}
&\nabla_1 \cdot \mathbf{r}_1 h(a, b, c, d, e, f, n_1, n_2, n_3, n_4; w_1, w_2, w_3, w_4) = \\
&3 \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f} + \\
&\mathbf{r}_1 \cdot \Big[-\mathbf{r}_1 w_1 \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1-1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f} \\
&+ \mathbf{r}_1 n_1 \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1-2} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f} \\
&+ (\mathbf{r}_1 - \mathbf{r}_2)\, a \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a-2} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f} \\
&+ (\mathbf{r}_1 - \mathbf{r}_3)\, b \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b-2} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f} \\
&+ (\mathbf{r}_1 - \mathbf{r}_4)\, c \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c-2} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f}\Big] ,
\end{aligned} \tag{A.9}$$

which after multiplying both sides of the equation (A.9) by 2, carrying out all vector products, and using the definition of scalar product $\mathbf{r}_i \cdot \mathbf{r}_j = (r_i^2 + r_j^2 - r_{i,j})/2$ to write the mixed products

---

[2] Such as $\nabla_i \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4) = -w_i \frac{\mathbf{r}_i}{r_i} \exp(-r_1w_1 - r_2w_2 - r_3w_3 - r_4w_4)$, $\nabla_i \cdot \mathbf{r}_i = 3$, $\nabla_i {r_i}^n = {r_i}^{n-2}\, n$ and $\nabla_i {r_{i,j}}^n = (\mathbf{r}_i - \mathbf{r}_j) {r_{i,j}}^{n-2}\, n$.

as the inter-particle distances and absorbing the results into the powers, leads to expression

$$
\begin{aligned}
&2\,\nabla_1\cdot\mathbf{r}_1 h(a,b,c,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4)\\
&= 6\,\exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{1,2}^{a}r_{1,3}^{b}r_{1,4}^{c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\\
&- 2\,w_1\exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{1+n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{1,2}^{a}r_{1,3}^{b}r_{1,4}^{c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\\
&+ 2\,n_1\exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{1,2}^{a}r_{1,3}^{b}r_{1,4}^{c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\\
&+ a\,\Bigl(\exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{2+n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{1,2}^{-2+a}r_{1,3}^{b}r_{1,4}^{c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\\
&- \exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{n_1}r_2^{2+n_2}r_3^{n_3}r_4^{n_4}r_{1,2}^{-2+a}r_{1,3}^{b}r_{1,4}^{c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\\
&+ \exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{1,2}^{a}r_{1,3}^{b}r_{1,4}^{c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\\
&+ b\,\Bigl(\exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{2+n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{1,2}^{a}r_{1,3}^{-2+b}r_{1,4}^{c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\\
&- \exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{n_1}r_2^{n_2}r_3^{2+n_3}r_4^{n_4}r_{1,2}^{a}r_{1,3}^{-2+b}r_{1,4}^{c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\\
&+ \exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{1,2}^{a}r_{1,3}^{b}r_{1,4}^{c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\Bigr)\\
&+ c\,\Bigl(\exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{2+n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{1,2}^{a}r_{1,3}^{b}r_{1,4}^{-2+c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\\
&- \exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{n_1}r_2^{n_2}r_3^{n_3}r_4^{2+n_4}r_{1,2}^{a}r_{1,3}^{b}r_{1,4}^{-2+c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\\
&+ \exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{1,2}^{a}r_{1,3}^{b}r_{1,4}^{c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\Bigr).
\end{aligned}
\tag{A.10}
$$

We observe, that we can utilise the definition of function h (equation (A.8)) and transform the right-hand side of equation (A.10) by collecting $h(a,b,c,d,e,f,n_1,n_2,n_3,n_4)$ to get the following linear combination

$$
\begin{aligned}
&2\,\nabla_1\cdot\mathbf{r}_1 h(a,b,c,d,e,f,n_1,n_2,n_3,n_4)\\
&= (6+a+b+c+2n_1)h(a,b,c,d,e,f,n_1,n_2,n_3,n_4) - 2w_1h(a,b,c,d,e,f,1+n_1,n_2,n_3,n_4)\\
&+ a\bigl[h(-2+a,b,c,d,e,f,2+n_1,n_2,n_3,n_4) - h(-2+a,b,c,d,e,f,n_1,2+n_2,n_3,n_4)\bigr]\\
&+ b\bigl[h(a,-2+b,c,d,e,f,2+n_1,n_2,n_3,n_4) - h(a,-2+b,c,d,e,f,n_1,n_2,2+n_3,n_4)\bigr]\\
&+ c\bigl[h(a,b,-2+c,d,e,f,2+n_1,n_2,n_3,n_4) - h(a,b,-2+c,d,e,f,n_1,n_2,n_3,2+n_4)\bigr]
\end{aligned}
\tag{A.11}
$$

in which we omit arguments w_i of the h for brevity. Therefore, we have obtained a result that would become the $id(1,1)$ after the integration of the both sides of the equation (A.11) over the coordinates of four electrons (multiplicative constant 2 does not change this result, since the left-hand side of equation (A.6) is zero).

Next, we proceed to calculate the expression in the mixed identity $id(1,2)$ starting with

$$
\begin{aligned}
&\nabla_1\cdot\Bigl(\mathbf{r}_2\exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{1,2}^{a}r_{1,3}^{b}r_{1,4}^{c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\Bigr)\\
&= (\nabla_1\cdot\mathbf{r}_2)\exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{1,2}^{a}r_{1,3}^{b}r_{1,4}^{c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\\
&+ \mathbf{r}_2\cdot\Bigl(\nabla_1\exp(-r_1w_1-r_2w_2-r_3w_3-r_4w_4)r_1^{n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{1,2}^{a}r_{1,3}^{b}r_{1,4}^{c}r_{2,3}^{d}r_{2,4}^{e}r_{3,4}^{f}\Bigr),
\end{aligned}
\tag{A.12}
$$

which is rather straightforwardly calculated, as the first term on the right-hand side vanishes[3]

---

[3] Since $\nabla_1\cdot\mathbf{r}_2 = 0$.

and we already calculated $\nabla_1 h$ in equation (A.9), resulting in

$$
\begin{aligned}
&\nabla_1 \cdot \Bigl(\mathbf{r}_2 \exp(-r_1 w_1 - r_2 w_2 - r_3 w_3 - r_4 w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f}\Bigr)\\
&= \mathbf{r}_2 \cdot \Bigl[\mathbf{r}_1 \Bigl(n_1 \exp(-r_1 w_1 - r_2 w_2 - r_3 w_3 - r_4 w_4) r_1^{n_1-2} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f}\\
&- \mathbf{r}_1 w_1 \exp(-r_1 w_1 - r_2 w_2 - r_3 w_3 - r_4 w_4) r_1^{n_1-1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f}\\
&+ (\mathbf{r}_1 - \mathbf{r}_2)\, a \exp(-r_1 w_1 - r_2 w_2 - r_3 w_3 - r_4 w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a-2} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f}\\
&+ (\mathbf{r}_1 - \mathbf{r}_3)\, b \exp(-r_1 w_1 - r_2 w_2 - r_3 w_3 - r_4 w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b-2} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f}\\
&+ (\mathbf{r}_1 - \mathbf{r}_4)\, c \exp(-r_1 w_1 - r_2 w_2 - r_3 w_3 - r_4 w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c-2} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f}.
\end{aligned}
\tag{A.13}
$$

Performing the same operations that lead us to $id(1,1)$ results in

$$
\begin{aligned}
&\nabla_1 \cdot \Bigl(\mathbf{r}_2 \exp(-r_1 w_1 - r_2 w_2 - r_3 w_3 - r_4 w_4) r_1^{n_1} r_2^{n_2} r_3^{n_3} r_4^{n_4} r_{1,2}^{a} r_{1,3}^{b} r_{1,4}^{c} r_{2,3}^{d} r_{2,4}^{e} r_{3,4}^{f}\Bigr)\\
&= n_1 \,[h(a,b,c,d,e,f,-2+n_1,2+n_2,n_3,n_4) + h(a,b,c,d,e,f,n_1,n_2,n_3,n_4)\\
&-\ h(2+a,b,c,d,e,f,-2+n_1,n_2,n_3,n_4)]\\
&- w_1 \,[h(a,b,c,d,e,f,-1+n_1,2+n_2,n_3,n_4) + h(a,b,c,d,e,f,1+n_1,n_2,n_3,n_4)\\
&-\ h(2+a,b,c,d,e,f,-1+n_1,n_2,n_3,n_4)]\\
&- a\,[h-2+a,b,c,d,e,f,n_1,2+n_2,n_3,n_4) - h(-2+a,b,c,d,e,f,2+n_1,n_2,n_3,n_4)\\
&+\ h(a,b,c,d,e,f,n_1,n_2,n_3,n_4)]\\
&+ b\,[-h(a,-2+b,c,d,e,f,n_1,n_2,2+n_3,n_4) + h(a,-2+b,c,d,e,f,2+n_1,n_2,n_3,n_4)\\
&+\ h(a,-2+b,c,2+d,e,f,n_1,n_2,n_3,n_4) - h(2+a,-2+b,c,d,e,f,n_1,n_2,n_3,n_4)]\\
&+ c\,[-h(a,b,-2+c,d,e,f,n_1,n_2,n_3,2+n_4) + h(a,b,-2+c,d,e,f,2+n_1,n_2,n_3,n_4)\\
&+\ h(a,b,-2+c,d,2+e,f,n_1,n_2,n_3,n_4) - h(2+a,b,-2+c,d,e,f,n_1,n_2,n_3,n_4)]\,,
\end{aligned}
\tag{A.14}
$$

which again, after integration over the spatial coordinates of all four electrons is equal to $id(1,2)$.

Now, there are two ways to proceed. The first would be to directly attack the problem by performing the same operations for all combinations of $i, j = 1,2,3,4$ and obtain a set of sixteen linear equations of type $id(i,j) = 0$. These equations have to be solved for appropriate integrals in order to obtain useful recurrence relations. We could solve this system of equations for sixteen variables - integrals g that have the highest sum of all powers (namely $a+b+c+d+e+f+n_1+n_2+n_3+n_4$) via brute force in order to obtain sixteen expressions which increase the sum of the powers of r_i's and r_{ij}'s. However, since we are not directly interested in increasing powers of the n_i, as they can be increased via differentiation over the parameters w_i (equation (2.40)) we can proceed slightly more cleverly. For reasons explained in section 2.4.8 we only need to be able to have three recurrence relations – specifically for $a+2$, $b+2$ and $c+2$. By examining the equation (A.14) we immediately see, that $id(1,2)$ should be solved for integrals corresponding to either $h(2+a,b,c,d,e,f,-2+n_1,n_2,n_3,n_4)$ or $h(2+a,b,c,d,e,f,-1+n_1,n_2,n_3,n_4)$. After further inspection we see, that if we set $n_1 = 0$, we can eliminate the first of these two terms (along with some others) as they are multiplied by n_1. Furthermore, we can set $n_2 = n_3 = n_4 = -1$ since, as mentioned previously, we can always increase powers of r_i via differentiation over parameters.

Integrating (A.14) over the spacial coordinates of four electrons, setting $n_1 = 0, n_2 = n_3 = n_4 = 0$ and remembering the definitions of h (eq. (A.8)) and g (eq. (2.39)) leads us to the expression

$$
\begin{aligned}
&0 = id(1,2)\\
&= -w_1\left[g(a,b,c,d,e,f,-1,1,-1,-1) + g(a,b,c,d,e,f,1,-1,-1,-1)\right.\\
&\left.-\ g(2+a,b,c,d,e,f,-1,-1,-1,-1)\right]\\
&-a\left[h-2+a,b,c,d,e,f,0,1,-1,-1) - g(-2+a,b,c,d,e,f,2,-1,-1,-1)\right.\\
&\left.+\ g(a,b,c,d,e,f,0,-1,-1,-1)\right]\\
&+b\left[-g(a,-2+b,c,d,e,f,0,-1,1,-1) + g(a,-2+b,c,d,e,f,2,-1,-1,-1)\right.\\
&\left.+\ g(a,-2+b,c,2+d,e,f,0,-1,-1,-1) - g(2+a,-2+b,c,d,e,f,0,-1,-1,-1)\right]\\
&+c\left[-g(a,b,-2+c,d,e,f,0,-1,-1,1) + g(a,b,-2+c,d,e,f,2,-1,-1,-1)\right.\\
&\left.+\ g(a,b,-2+c,d,2+e,f,0,-1,-1,-1) - g(2+a,b,-2+c,d,e,f,0,-1,-1,-1)\right],
\end{aligned}
\tag{A.15}
$$

which can be solved for $g(2+a,b,c,d,e,f,-1,-1,-1,-1)$ yielding

$$
\begin{aligned}
&g(a+2,b,c,d,e,f,-1,-1,-1,-1)\\
&= g(a,b,c,d,e,f,-1,1,-1,-1) + g(a,b,c,d,e,f,1,-1,-1,-1)\\
&+\frac{1}{w_1}\Big[a\big(g(a-2,b,c,d,e,f,0,1,-1,-1) - g(a-2,b,c,d,e,f,2,-1,-1,-1)\\
&+g(a,b,c,d,e,f,0,-1,-1,-1)\big)\\
&+b\big(g(a,b-2,c,d,e,f,0,-1,1,-1) - g(a,b-2,c,d,e,f,2,-1,-1,-1)\\
&-g(a,b-2,c,d+2,e,f,0,-1,-1,-1) + g(a+2,b-2,c,d,e,f,0,-1,-1,-1)\big)\\
&+c\big(g(a,b,c-2,d,e,f,0,-1,-1,1) - g(a,b,c-2,d,e,f,2,-1,-1,-1)\\
&-g(a,b,c-2,d,e+2,f,0,-1,-1,-1) + g(a+2,b,c-2,d,e,f,0,-1,-1,-1)\big)\Big].
\end{aligned}
\tag{A.16}
$$

This expression can be further simplified. In order to do so, we solve integrated form of equation (A.11) for $g(a,b,c,d,e,f,1,-1,-1,-1)$ by setting $n_1 = 0, n_2 = n_3 = n_4 = -1$. This leads to

$$
\begin{aligned}
&g(a,b,c,d,e,f,1,-1,-1,-1) = \frac{1}{2w_1}(6+a+b+c)g(a,b,c,d,e,f,0,-1,-1,-1)\\
&+a\big[g(-2+a,b,c,d,e,f,2,-1,-1,-1) - g(-2+a,b,c,d,e,f,0,1,-1,-1)\big]\\
&+b\big[g(a,-2+b,c,d,e,f,2,-1,-1,-1) - g(a,-2+b,c,d,e,f,0,-1,1,-1)\big]\\
&+c\big[g(a,b,-2+c,d,e,f,2,-1,-1,-1) - g(a,b,-2+c,d,e,f,0,-1,-1,1)\big].
\end{aligned}
\tag{A.17}
$$

By plugging the right-hand side of equation (A.17) into the equation (A.16) (and therefore eliminating the $g(a,b,c,d,e,f,1,-1,-1,-1)$ term) and after collecting common factors together we obtain

$$
\begin{aligned}
&g(a+2,b,c,d,e,f,-1,-1,-1,-1) = g(a,b,c,d,e,f,-1,1,-1,-1)\\
&+\frac{1}{2w_1}\Big[(3a+b+c+6)g(a,b,c,d,e,f,0,-1,-1,-1)\\
&+a\big(g(a-2,b,c,d,e,f,0,1,-1,-1)-g(a-2,b,c,d,e,f,2,-1,-1,-1)\big)\\
&+b\big(g(a,b-2,c,d,e,f,0,-1,1,-1)-g(a,b-2,c,d,e,f,2,-1,-1,-1)\\
&-2g(a,b-2,c,d+2,e,f,0,-1,-1,-1)+2g(a+2,b-2,c,d,e,f,0,-1,-1,-1)\big)\\
&+c\big(g(a,b,c-2,d,e,f,0,-1,-1,1)-g(a,b,c-2,d,e,f,2,-1,-1,-1)\\
&-2g(a,b,c-2,d,e+2,f,0,-1,-1,-1)+2g(a+2,b,c-2,d,e,f,0,-1,-1,-1)\big)\Big],
\end{aligned}
\tag{A.18}
$$

which is our recurrence relation as given in equation (2.42a). We can get the recurrence relations given in equations (2.42b) and (2.42c) in analogous manner, by plugging $id(1,1)$ into $id(1,3)$ and $id(1,4)$ respectively and performing akin manipulations. Similar recurrence relations could be derived using remaining identities. This completes the derivation of four-electron recurrence relations.

A.2 Laplacian identities

We derive two identities that connect four-electron integrals to three-electron integrals, as well as lead to the differential equation that allows finding four electron integrals with powers of r_{12} equal to -1 and 1.

A.2.1 Three-dimensional Poisson equation with Dirac delta

The three dimensional Poisson equation with the right-hand side equal to $\delta^{(3)}(\mathbf{r}_1-\mathbf{r}_2)$ defines the Green's function G

$$\nabla_1^2 G(\mathbf{r}_1,\mathbf{r}_2) = \delta^{(3)}(\mathbf{r}_1-\mathbf{r}_2) \tag{A.19}$$

where $\delta^{(3)}(\mathbf{r}_1-\mathbf{r}_2)$ is the three-dimensional Dirac delta and ∇_1^2 is the Laplacian of the 1-st particle. The solution that satisfies this equation under boundary conditions $G(\mathbf{r}_1,\mathbf{r}_2)\to 0$, as $|\mathbf{r}_1-\mathbf{r}_2|\to\infty$ is

$$G(\mathbf{r}_1,\mathbf{r}_2) = -\frac{1}{4\pi\,|\mathbf{r}_1-\mathbf{r}_2|}. \tag{A.20}$$

A.2.2 Integral of Green's function

We define a specific variant of Hylleraas-type function of four electrons h_a with $\{w_1,w_2,w_3,w_4\}\in\mathbb{R}^+$ and $-1\le\{b,c,d,e,f,n_1,n_2,n_3,n_4\}\in\mathbb{Z}$ such that (we omit the parameters of h_a until further notice)

$$
\begin{aligned}
&h_a(b,c,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4)\\
&=\exp(-w_1r_1-w_2r_2-w_3r_3-w_4r_4)r_1^{n_1}r_2^{n_2}r_3^{n_3}r_4^{n_4}r_{13}^{b}r_{14}^{c}r_{23}^{d}r_{24}^{e}r_{34}^{f}.
\end{aligned}
\tag{A.21}
$$

Multiplying both sides of the equation (A.19) by h_a and writing $|\mathbf{r}_1 - \mathbf{r}_2|$ as r_{12} we get

$$h_a \delta^{(3)}(\mathbf{r}_1 - \mathbf{r}_2) = -\frac{1}{4\pi} h_a \nabla_1^2 \frac{1}{r_{12}}. \tag{A.22}$$

Next, we integrate both sides of the equation (A.22) with respect to $\mathbf{r}_1, \mathbf{r}_2$ over their whole respective spaces, $\mathbb{R}^3_{\mathbf{r}_1}, \mathbb{R}^3_{\mathbf{r}_2}$ and multiply by 4π to obtain

$$4\pi \iint \mathrm{d}^3\mathbf{r}_1 \,\mathrm{d}^3\mathbf{r}_2 h_a \delta^{(3)}(\mathbf{r}_1 - \mathbf{r}_2) = -\iint \mathrm{d}^3\mathbf{r}_1 \,\mathrm{d}^3\mathbf{r}_2 h_a \nabla_1^2 \frac{1}{r_{12}}. \tag{A.23}$$

On the left-hand side of the above equation, the integration over $\mathrm{d}^3\mathbf{r}_1$ can be straightforwardly done to yield

$$4\pi \iint \mathrm{d}^3\mathbf{r}_1 \,\mathrm{d}^3\mathbf{r}_2 h_a \delta^{(3)}(\mathbf{r}_1 - \mathbf{r}_2) = 4\pi \int \mathrm{d}^3\mathbf{r}_2 e^{(-(w_1+w_2)r_2 - w_3 r_3 - w_4 r_4)} r_2^{n1+n2} r_3^{n3} r_4^{n4} r_{23}^{b+d} r_{24}^{c+e} r_{34}^{f}. \tag{A.24}$$

In the next section, we integrate by parts the right-hand side of equation (A.23) to obtain Laplacian acting on h_a.

A.2.3 Application of Green's identity

Using the Green's first identity[4]

$$\int\limits_U dV \psi \nabla_1^2 \phi = -\int\limits_U dV \nabla_1 \psi \cdot \nabla_1 \phi + \oiint\limits_{\partial U} d\mathbf{S}_1 \cdot \psi \nabla_1 \phi, \tag{A.25}$$

on the right-hand side of equation (A.22), multiplying by -4π and taking $\psi = h_a, \phi = \frac{1}{r_{12}}$ results in

$$\int \mathrm{d}^3\mathbf{r}_1 \,\mathrm{d}^3\mathbf{r}_2 h_a \nabla_1^2 \frac{1}{r_{12}} = -\iint \mathrm{d}^3\mathbf{r}_1 \,\mathrm{d}^3\mathbf{r}_2 \nabla_1 h_a \cdot \nabla_1 \frac{1}{r_{12}} + \int \mathrm{d}^3\mathbf{r}_2 \oiint \mathrm{d}^2\hat{\mathbf{r}}_1 \cdot h_a \nabla_1 \frac{1}{r_{12}} \tag{A.26}$$

We choose the surface integral to be over the boundary of infinite sphere and it vanishes (similarly as in equation (A.4), since h_a decreases exponentially with r_1), so as a consequence of

$$\lim_{r_1 \to \infty} \oiint \mathrm{d}^2 n_{r_1} h_a \nabla_1 \frac{1}{r_{12}} \cdot \mathbf{n}_{r_1} = 0 \tag{A.27}$$

equation (A.26) takes the following form

$$\int \mathrm{d}^3\mathbf{r}_1 \,\mathrm{d}^3\mathbf{r}_2 h_a \nabla_1^2 \frac{1}{r_{12}} = -\int \mathrm{d}^3\mathbf{r}_1 \,\mathrm{d}^3\mathbf{r}_2 \nabla_1 h_a \cdot \nabla_1 \frac{1}{r_{12}}. \tag{A.28}$$

Then, we can again apply Green's identity, this time with $\psi = \frac{1}{r_{12}}, \phi = h_a$ and in the opposite way, to get the right side of (A.28) into

$$-\int \mathrm{d}^3\mathbf{r}_1 \,\mathrm{d}^3\mathbf{r}_2 \nabla_1 h_a \cdot \nabla_1 \frac{1}{r_{12}} = \int \mathrm{d}^3\mathbf{r}_1 \,\mathrm{d}^3\mathbf{r}_2 \frac{1}{r_{12}} \nabla_1^2 h_a - \int \mathrm{d}^3\mathbf{r}_2 \oiint \mathrm{d}^2\mathbf{n}_{\mathbf{r_2}} \cdot h_a \nabla_1 \frac{1}{r_{12}} \tag{A.29}$$

where, again, the surface integral vanishes yielding the result

$$\int \mathrm{d}^3\mathbf{r}_1 \,\mathrm{d}^3\mathbf{r}_2 h_a \nabla_1^2 \frac{1}{r_{12}} = \int \mathrm{d}^3\mathbf{r}_1 \,\mathrm{d}^3\mathbf{r}_2 \frac{1}{r_{12}} \nabla_1^2 h_a. \tag{A.30}$$

---

[4] Which can be straightforwardly obtained by applying divergence theorem to the field of form $\psi \nabla_1 \phi$).

A.2.4 Connection of the Green's function with integrals over the Hylleraas-type functions

Transforming equation (A.23) using equations (A.24) and (A.30) and integrating both sides w.r.t the third and fourth electron's coordinates $\mathrm{d}^3\mathbf{r}_3, \mathrm{d}^3\mathbf{r}_4$ over $\mathbb{R}^3_{\mathbf{r}_3}$ and $\mathbb{R}^3_{\mathbf{r}_4}$ of we get

$$\begin{aligned} 4\pi \iiint \mathrm{d}^3\mathbf{r}_2\, \mathrm{d}^3\mathbf{r}_3\, \mathrm{d}^3\mathbf{r}_4\; e^{(-(w_1+w_2)r_2-w_3r_3-w_4r_4)} r_2^{n_1+n_2} r_3^{n_3} r_4^{n_4} r_{23}^{b+d} r_{24}^{c+e} r_{34}^{f} \\ = \int \mathrm{d}^3\mathbf{r}_1\, \mathrm{d}^3\mathbf{r}_2\, \mathrm{d}^3\mathbf{r}_3\, \mathrm{d}^3\mathbf{r}_4 \frac{1}{r_{12}} \nabla_1^2 h_a. \end{aligned} \tag{A.31}$$

Since the three-electron Hylleraas-type integrals are defined as

$$\begin{aligned} &f(a, b, c, n_1, n_2, n_3; w_1, w_2, w_3) \\ &= \iiint \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_2}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_3}{4\pi} \exp(-w_1r_1 - w_2r_2 - w_3r_3) r_{12}^{a} r_{13}^{b} r_{23}^{c} r_1^{n_1} r_2^{n_2} r_3^{n_3}, \end{aligned} \tag{A.32}$$

by dividing the equation (A.31) by $(4\pi)^4$ we finally obtain (we now return to writing the parameters and variables of h_a explicitly)

$$\begin{aligned} &f(b+d, c+e, f, n_1+n_2, n_3, n_4, w_1+w_2, w_3, w_4) \\ &= -\int \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_2}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_4}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_4}{4\pi} \frac{1}{r_{12}} \nabla_1^2 h_a(b, c, d, e, f, n_1, n_2, n_3, n_4; w_1, w_2, w_3, w_4). \end{aligned} \tag{A.33}$$

The left-hand side of equation (A.33) is a three-electron integral, while the right-hand side corresponds to a linear combination of integrals of h_a multiplied by r_{12}^{-1}.

A.2.5 Three-dimensional Poisson equation with $2r_{12}^{-1}$

Analogous procedure can be now straightforwardly performed for the equation analogous to (A.19), but with a different right-hand side, namely

$$\nabla_1^2 H(\mathbf{r}_1, \mathbf{r}_2) = \frac{2}{r_{12}}. \tag{A.34}$$

The solution of this equation is[5]

$$H(\mathbf{r}_1, \mathbf{r}_2) = |\mathbf{r}_1 - \mathbf{r}_2| = r_{12}. \tag{A.35}$$

Following the transformations analogous to the ones in the previous paragraphs, we arrive at

$$\begin{aligned} 2\int \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_2}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_4}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_4}{4\pi} \frac{1}{r_{12}} h_a(b, c, d, e, f, n_1, n_2, n_3, n_4; w_1, w_2, w_3, w_4) = \\ \int \frac{\mathrm{d}^3\mathbf{r}_1}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_2}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_4}{4\pi} \frac{\mathrm{d}^3\mathbf{r}_4}{4\pi} r_{12} \nabla_1^2 h_a(b, c, d, e, f, n_1, n_2, n_3, n_4; w_1, w_2, w_3, w_4) \end{aligned} \tag{A.36}$$

Since the right-hand side (again) becomes a linear combination of integrals of h_a, but this time multiplied by r_{12}, it allows us to connect such expressions with the integral with $\frac{1}{r_{12}}$ that appears on the left-hand side of equation (A.36).

---

[5] It can be straightforwardly checked via the simple calculation:

$$\nabla_1^2 r_{12} = \nabla_1 \cdot \nabla_1 r_{12} = \nabla_1 \cdot \frac{\mathbf{r}_{12}}{r_{12}} = \left(\nabla_1 \frac{1}{r_{12}}\right) \mathbf{r}_{12} + \frac{1}{r_{12}} \nabla_1 \mathbf{r}_{12} = \frac{-1}{r_{12}^2} \widehat{\mathbf{r}}_{12} \cdot \mathbf{r}_{12} + \frac{3}{r_{12}} = \frac{2}{r_{12}}$$

A.2.6 Application of the Laplacian on function h_a

The final step in the derivation of the Laplacian integral identities is application of the Laplacian on the function $h_a(b, c, d, e, f, n_1, n_2, n_3, n_4; w_1, w_2, w_3, w_4)$, which appears both in the equation (A.33), as well as in the equation (A.36). Since the function h_a is spherically symmetric for any choice of the parameters, application of the the Laplacian comes down to simple (albeit tedious) differentiation applying the rules of vector calculus[6]. This results in (dependence of h_a's on w_i's is omitted for brevity)

$$\begin{aligned}
&\nabla_1^2 h_a(b,c,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4)\\
&= (b+c+n_1+1)\,(bh_a(b-2,c,d,e,f,n_1,n_2,n_3,n_4) + ch_a(b,c-2,d,e,f,n_1,n_2,n_3,n_4)\\
&+n_1 h_a(b,c,d,e,f,n_1-2,n_2,n_3,n_4)) - bch(0,b-2,c-2,d,e,f+2,n_1,n_2,n_3,n_4)\\
&- n_1\,(bh_a(b-2,c,d,e,f,n_1-2,n_2,n_3+2,n_4) + ch_a(b,c-2,d,e,f,n_1-2,n_2,n_3,n_4+2))\\
&+ w_1\,(bh_a(b-2,c,d,e,f,n_1-1,n_2,n_3+2,n_4) - bh_a(b-2,c,d,e,f,n_1+1,n_2,n_3,n_4)\\
&+ ch_a(b,c-2,d,e,f,n_1-1,n_2,n_3,n_4+2) - ch_a(b,c-2,d,e,f,n_1+1,n_2,n_3,n_4))\\
&- w_1(b+c+2n_1+2)h_a(b,c,d,e,f,n_1-1,n_2,n_3,n_4) + w_1^2 h_a(b,c,d,e,f,n_1,n_2,n_3,n_4)
\end{aligned} \tag{A.37}$$

Since higher powers of each n_i can be obtained via the differentiation of h_a over the respective w_i, we set $n_1 = 0$ and $n_2, n_3, n_4 = -1$ thus the expression (A.37) simplifies to

$$\begin{aligned}
&\nabla_1^2 h_a(b,c,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4)\\
&= (b+c+1)(bh_a(b-2,c,d,e,f,0,-1,-1,-1) + ch_a(b,c-2,d,e,f,0,-1,-1,-1))\\
&- bch_a(b-2,c-2,d,e,f+2,0,-1,-1,-1)\\
&+ w_1\big(bh_a(b-2,c,d,e,f,-1,-1,1,-1) - bh_a(b-2,c,d,e,f,1,-1,-1,-1)\\
&+ ch_a(b,c-2,d,e,f,-1,-1,-1,1) - ch_a(b,c-2,d,e,f,1,-1,-1,-1)\big)\\
&- w_1(b+c+2)h_a(b,c,d,e,f,-1,-1,-1,-1) + w_1^2 h_a(b,c,d,e,f,0,-1,-1,-1).
\end{aligned} \tag{A.38}$$

Finally, for $b, c = 0$ the equation (A.38) becomes very simple

$$\begin{aligned}
&\nabla_1^2 h_a(b,c,d,e,f,n_1,n_2,n_3,n_4;w_1,w_2,w_3,w_4)\\
&= -2w_1 h_a(b,c,d,e,f,-1,-1,-1,-1) + w_1^2 h_a(b,c,d,e,f,0,-1,-1,-1).
\end{aligned} \tag{A.39}$$

This serves as a starting point for finding the integrals of $h_a(b, c, d, e, f, -1, -1, -1, -1)$ multiplied by r_{12}^{-1} (using equation (A.33)) or by r_{12} (via equation (A.36)) by transforming this expression to the differential equation form and finding its solution.

A.3 Differential equation

A.3.1 General solution of the differential equation

Since both the equations (2.55) and (2.61) have the same form, we will solve the equation

$$-w_1^2 \frac{\partial g(w_1)}{\partial w_1} - w_1(2+b+c)g(w_1) = -r(w_1). \tag{A.40}$$

---

[6] The calculations are very similar to the ones performed in section A.1.2 of this Appendix.

After dividing its both sides by $1/w_1^2$ we get

$$\frac{\partial g(w_1)}{\partial w_1} + \frac{(2+b+c)}{w_1} g(w_1) = \frac{1}{w_1^2} r(w_1). \tag{A.41}$$

This type of equation can be solved using integration factor which takes the following form

$$\exp\left((2+b+c)\int \frac{1}{w_1}\,\mathrm{d}w_1\right) = \exp\Big((2+b+c)\ln(w_1)\Big) = w_1^{2+b+c}. \tag{A.42}$$

After multiplying both sides of the equation (A.40) by this factor we get

$$w_1^{2+b+c}\left(\frac{\partial g}{\partial w_1} + \frac{2+b+c}{w_1} g\right) = w_1^{b+c} r(w_1). \tag{A.43}$$

Noticing, that the left side can be rewritten, equation (A.43) takes form

$$\frac{\partial}{\partial w_1}\left(w_1^{2+b+c} g\right) = w_1^{b+c} r(w_1). \tag{A.44}$$

We can integrate both sides over $\mathrm{d}w_1$ giving

$$g = \frac{1}{w_1^{2+b+c}} \int w_1^{b+c} r(w_1)\,\mathrm{d}w_1 = \frac{F(w_1)}{w_1^{2+b+c}}, \tag{A.45}$$

where $F'(w_1) = w_1^{b+c} f(w_1)$. The solution is obtained up to the constant of integration. The remaining task is to find this constant. Next, we fix the constant using asymptotic analysis of g.

A.3.2 Constant of integration

The constant of integration for the equation (A.45) can be found by analysing the asymptotic behaviour of the integral $g(a,b,c,d,e,f,-1,-1,-1,-1)$ at small w_1. The asymptotic analysis reveals that the Laurent expansion of both the integral $g(-1,b,c,d,e,f,0,-1,-1,-1)$ and $g(1,b,c,d,e,f,0,-1,-1,-1)$ around $w_1 = 0$ does not contain terms of order w_1^{-2-b-c}.

As proven in the section A.4.1 of the Appendix A, the lowest order of w_1 in g are

$$g(a,b,c,d,e,f,-1,-1,-1,-1) \sim \frac{1}{w_1^{2+a+b+c}} + \mathcal{O}(\frac{1}{w_1^{a+b+c}}) \tag{A.46}$$

and for $a = -1$ the lowest terms in w_1 are w_1^{-1-b-c}. Therefore, $F(w_1)$ must not have any constant terms (of order $\mathcal{O}(w_1^0)$) so the constant of integration in (A.45) is fixed by this requirement.

In the case of $a = 1$ the next order of w_1 has to be considered, since the lowest order terms of w_1 in that case are w_1^{-3-b-c}. However, the analysis of the next-to-leading order of w_1 reveals that there are no terms of order $w_1^{-1-a-b-c}$ in the integral g, as shown in section A.4.1 of the Appendix A. Consequently, also for $a = 1$ there are no terms of w_1^{-2-b-c} and the constant is fixed.

A.4 Asymptotic behaviour of integral g as a function of w_1

A.4.1 Behaviour of four-electron integral g at small w_1

In order to analyse behaviour of the integral g at small w_1, we use the following variable substitution $r_1 = R_1/w_1$. After that substitution the integral has the following form

$$\begin{aligned} &g(a, b, c, d, e, f, -1, -1, -1, -1; w_1, w_2, w_3, w_4) \\ &= \iiiint \frac{\mathrm{d}^3\mathbf{R}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi}\exp(-R_1 - w_2 r_2 - w_3 r_3 - w_4 r_4)\frac{1}{w_1^2} \\ &\times \frac{r_{23}^d r_{24}^e r_{34}^f}{R_1 r_2 r_3 r_4}\frac{|\mathbf{R}_1 - w_1\mathbf{r}_2|^a\,|\mathbf{R}_1 - w_1\mathbf{r}_3|^b\,|\mathbf{R}_1 - w_1\mathbf{r}_4|^c}{w_1^a w_1^b w_1^c}. \end{aligned} \tag{A.47}$$

Using the identity

$$|\mathbf{R}_1 - w_1\mathbf{r}_1| = \sqrt{R_1^2 + w_1^2 r_1^2 - 2w_1\mathbf{R}_1\cdot\mathbf{r}_2} = R_1\sqrt{1 - 2w_1\frac{\mathbf{R}_1\cdot\mathbf{r}_2}{R_1^2} + w_1^2\frac{r_1^2}{R_1^2}} \tag{A.48}$$

the term (A.48) can be expanded expanded in w_1 around 0 up to linear term leading to

$$|\mathbf{R}_1 - w_1\mathbf{r}_1|^a = \left(R_1\sqrt{1 - 2w_1\frac{\mathbf{R}_1\cdot\mathbf{r}_2}{R_1^2} + w_1^2\frac{r_1^2}{R_1^2}}\right)^a = R_1^a\left(1 - w_1 a\frac{\mathbf{R}_1\cdot\mathbf{r}_2}{R_1^2} + \dots\right). \tag{A.49}$$

The integrand of (A.47) can therefore be expanded for small w_1 up to the second (linear) term in w_1 to arrive at

$$\begin{aligned} &g(a, b, c, d, e, f, -1, -1, -1, -1; w_1, w_2, w_3, w_4) \\ &\approx \int \frac{\mathrm{d}^3\mathbf{R}_1}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi}\exp(-w_2 r_2 - w_3 r_3 - w_4 r_4)\frac{r_{23}^d r_{24}^e r_{34}^f}{r_2 r_3 r_4} \\ &\times e^{-R_1}\frac{R_1^{a+b+c}}{w_1^{2+a+b+c}}\left(1 - w_1\frac{\mathbf{R}_1\cdot(a\mathbf{r}_2 + b\mathbf{r}_3 + c\mathbf{r}_4)}{R_1^2}\right) \end{aligned} \tag{A.50}$$

where terms of order $\mathcal{O}(w_1^2)$ and higher were omitted. The right-hand side of the equation (A.50) can be straightforwardly integrated over $\mathbf{R}_1$ resulting in

$$\frac{\Gamma(3 + a + b + c)}{w_1^{2+a+b+c}}\int \frac{\mathrm{d}^3\mathbf{r}_2}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_3}{4\pi}\frac{\mathrm{d}^3\mathbf{r}_4}{4\pi}\exp(-w_2 r_2 - w_3 r_3 - w_4 r_4)\frac{r_{23}^d r_{24}^e r_{34}^f}{r_2 r_3 r_4}, \tag{A.51}$$

since the angular integral over $\mathbf{R}_1 \cdot \mathbf{r}_2$ is equal to 0 and thus the second term of integral (A.50) (linear in w_1) vanishes. As a consequence, $w_1^{-2-a-b-c}$ is the most negative power of w_1, and there aren't any terms of order $w_1^{-1-a-b-c}$ in the small w_1 expansion of the integral $g(a, b, c, d, e, f, -1, -1, -1, -1)$ defined in equation (A.47). Therefore, $w_1^{-2-a-b-c}$ must be the most negative power of w_1 and there are no terms of order $w_1^{-1-a-b-c}$ in the integral g.

Appendix B

Code with the implementation of the method

Below we present the code that implements the method developed in this thesis. It allows to obtain analytic formulas for singly-linked Hylleraas integrals. The code is implemented in Wolfram Language code and can be run using Wolfram Mathematica and was developed and run in Mathematica version 11.2 [137]. The four-electron integral code calculates the singly-linked Hylleraas integrals with either odd or even a and even b, c with either three d, e, f (in the case of even a) or two odd d, e, f (in case of odd a). The code given below is available as the source code from the author upon the email (tymon.kilich@pg.edu.pl) or personal request.

B.1 Three-electron integrals code

To use the code user simply has to load the file into the Mathematica. It requires the file with the three-electron code to be present in the same folder where the file is loaded. To calculate the required three-electron Hylleraas integral simply write the function `hy3el[a,b,c,n1,n2,n3]` with the ten integer arguments corresponding to the powers of the r_{ij} and r_i. The code is required to be present in the same path that the four-electron code is used in order for it to work.

```
delta[0] = 1;
delta[n_Integer] :=0/; (n!=0);
f[0,0,0,0,0,0] = l[w1,w2,w3]/(w1 w2 w3);
f[1,0,0,0,0,0] = -1/(w2^2 w3^2) Log[w1(w1+w2+w3)/(w1+w2)/(w1+w3)];
f[0,1,0,0,0,0] = -1/(w1^2 w3^2) Log[w2(w1+w2+w3)/(w2+w1)/(w2+w3)];
f[0,0,1,0,0,0] = -1/(w1^2 w2^2) Log[w3(w1+w2+w3)/(w3+w1)/(w3+w2)];
f[1,1,0,0,0,0] = 1/(w1 w2 (w1+w2) w3^2);
f[1,0,1,0,0,0] = 1/(w1 w3 (w1+w3) w2^2);
f[0,1,1,0,0,0] = 1/(w2 w3 (w2+w3) w1^2);
f[1,1,1,0,0,0] = 1/(w1^2 w2^2 w3^2);

repl = {l[w1_,w2_,w3_] -> -1/2(Log[w3/(w1+w2)] Log[1+w3/(w1+w2)]
```

```
        + PolyLog[2,-w3/(w1+w2)]+PolyLog[2,1-w3/(w1+w2)]
        + Log[w2/(w1+w3)] Log[1+w2/(w1+w3)]
        + PolyLog[2,-w2/(w1+w3)]+PolyLog[2,1-w2/(w1+w3)]
        + Log[w1/(w3+w2)] Log[1+w1/(w3+w2)]
        + PolyLog[2,-w1/(w3+w2)]+PolyLog[2,1-w1/(w3+w2)])};

f[x,n2_,n3_,n4_,n5_,n6_] = G[n5+n6-1,n4,n3+n2-1,w2+w3,w1,0];
f[n1_,x,n3_,n4_,n5_,n6_] = G[n4+n6-1,n5,n1+n3-1,w1+w3,w2,0];
f[n1_,n2_,x,n4_,n5_,n6_] = G[n4+n5-1,n6,n1+n2-1,w1+w2,w3,0];
f[n1_,n2_,n3_,x,0,0] = G[n3-1,n2-1,n1,w2,w3,0];
f[n1_,n2_,n3_,0,x,0] = G[n1-1,n3-1,n2,w3,w1,0];
f[n1_,n2_,n3_,0,0,x] = G[n2-1,n1-1,n3,w1,w2,0];

G[n1_,n2_,n3_,u1_,u2_,u3_] := ((-1)^(n1+n2+n3)
    D[1/(x1+x2)/(x2+x3)/(x1+x3),{x1,n1},{x2,n2},{x3,n3}] /. {x1->u1,
    x2->u2,x3->u3})/; (n1>-1&&n2>-1&&n3>-1);

G[-1,n2_,n3_,u1_,u2_,u3_] := ((-1)^(n2+n3)
    D[(Log[x1+x2]-Log[x1+x3])/((x2-x3)(x2+x3)),
    {x2,n2},{x3,n3}]/.{x1->u1,x2->u2,x3->u3})/; (n2>-1&&n3>-1);

G[n1_,-1,n3_,u1_,u2_,u3_] := ((-1)^(n1+n3)
    D[(Log[x2+x1]-Log[x2+x3])/((x1-x3)(x1+x3)),
    {x1,n1},{x3,n3}]/.{x1->u1,x2->u2,x3->u3})/; (n1>-1&&n3>-1);

G[n1_,n2_,-1,u1_,u2_,u3_] := ((-1)^(n1+n2)
    D[(Log[x3+x1]-Log[x3+x2])/((x1-x2)(x1+x2)),
    {x1,n1},{x2,n2}]/.{x1->u1,x2->u2,x3->u3})/; (n1>-1&&n2>-1);

rec1 = {f[n1_Integer, n2_Integer, n3_Integer, 0, 0, 0] ->
    ((-1 + n1)*((w1^2*(((3 - n1)*(-2 + n1)*f[-4 + n1, n2, 2 + n3, 0, 0, 0])/(1 + n3) +
    ((3 - n1)*(-2 + n1)*f[-4 + n1, 2 + n2, n3, 0, 0, 0])/(1 + n2)
    + (-2 - 2*(-2 + n1) - n2 - n3)*f[-2 + n1, n2, n3, 0, 0, 0] +
    delta[-2 + n1]*(G[-1, 0, 1 + n2 + n3, w2 + w3, w1, 0]/(1 + n2) +
    G[-1, 0, 1 + n2 + n3, w2 + w3, w1, 0]/(1 + n3)) -
    G[-3 + n1, 1 + n3, n2, w3, w1, 0]/(1 + n3) -
    G[1 + n2, -3 + n1, n3, w1, w2, 0]/(1 + n2)))/(w2^2*w3^2)
    + ((n1 + n2 + 2*n3)*f[-2 + n1, n2, n3, 0, 0, 0] +
    ((-1 + n3)*n3*f[-2 + n1, 2 + n2, -2 + n3, 0, 0, 0])/(1 + n2) +
    ((-1 + n3)*n3*f[n1, n2, -2 + n3, 0, 0, 0])/(-1 + n1) +
    delta[n3]*(-(G[-1, 0, -1 + n1 + n2, w1 + w2, w3, 0]/(-1 + n1)) -
    G[-1, 0, -1 + n1 + n2, w1 + w2, w3, 0]/(1 + n2)) +
```

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    G[-1 + n1, -1 + n3, n2, w3, w1, 0]/(-1 + n1) +
    G[-1 + n3, 1 + n2, -2 + n1, w2, w3, 0]/(1 + n2))/w2^2 +
    (((-1 + n2)*n2*f[-2 + n1, -2 + n2, 2 + n3, 0, 0, 0])/(1 + n3) +
    (n1 + 2*n2 + n3)*f[-2 + n1, n2, n3, 0, 0, 0] +
    ((-1 + n2)*n2*f[n1, -2 + n2, n3, 0, 0, 0])/(-1 + n1) +
    delta[n2]*(-(G[-1, 0, -1 + n1 + n3, w1 + w3, w2, 0]/(-1 + n1)) -
    G[-1, 0, -1 + n1 + n3, w1 + w3, w2, 0]/(1 + n3)) +
    G[-1 + n2, -1 + n1, n3, w1, w2, 0]/(-1 + n1) +
    G[1 + n3, -1 + n2, -2 + n1, w2, w3, 0]/(1 + n3))/w3^2))/2};

rec2 = {f[n1_Integer, n2_Integer, n3_Integer, 0, 0, 0] ->
     ((-1 + n2)*((((-1 + n1)*n1*f[-2 + n1, -2 + n2, 2 + n3, 0, 0, 0])/(1 + n3) +
     ((-1 + n1)*n1*f[-2 + n1, n2, n3, 0, 0, 0])/(-1 + n2) +
     (2*n1 + n2 + n3)*f[n1, -2 + n2, n3, 0, 0, 0] +
     delta[n1]*(-(G[-1, 0, -1 + n2 + n3, w2 + w3, w1, 0]/(-1 + n2)) -
     G[-1, 0, -1 + n2 + n3, w2 + w3, w1, 0]/(1 + n3)) +
     G[-1 + n1, 1 + n3, -2 + n2, w3, w1, 0]/(1 + n3) +
     G[-1 + n2, -1 + n1, n3, w1, w2, 0]/(-1 + n2))/w3^2 +
     ((n1 + n2 + 2*n3)*f[n1, -2 + n2, n3, 0, 0, 0] +
     ((-1 + n3)*n3*f[n1, n2, -2 + n3, 0, 0, 0])/(-1 + n2) +
     ((-1 + n3)*n3*f[2 + n1, -2 + n2, -2 + n3, 0, 0, 0])/(1 + n1) +
     delta[n3]*(-(G[-1, 0, -1 + n1 + n2, w1 + w2, w3, 0]/(1 + n1)) -
     G[-1, 0, -1 + n1 + n2, w1 + w2, w3, 0]/(-1 + n2)) +
     G[1 + n1, -1 + n3, -2 + n2, w3, w1, 0]/(1 + n1) +
     G[-1 + n3, -1 + n2, n1, w2, w3, 0]/(-1 + n2))/w1^2 +
     (w2^2*(((3 - n2)*(-2 + n2)*f[n1, -4 + n2, 2 + n3, 0, 0, 0])/(1 + n3) +
     (-2 - n1 - 2*(-2 + n2) - n3)*f[n1, -2 + n2, n3, 0, 0, 0] -
     ((-3 + n2)*(-2 + n2)*f[2 + n1, -4 + n2, n3, 0, 0, 0])/(1 + n1) +
     delta[-2 + n2]*(G[-1, 0, 1 + n1 + n3, w1 + w3, w2, 0]/(1 + n1) +
     G[-1, 0, 1 + n1 + n3, w1 + w3, w2, 0]/(1 + n3)) -
     G[-3 + n2, 1 + n1, n3, w1, w2, 0]/(1 + n1) -
     G[1 + n3, -3 + n2, n1, w2, w3, 0]/(1 + n3)))/(w1^2*w3^2)))/2};

rec3 = {f[n1_Integer, n2_Integer, n3_Integer, 0, 0, 0] ->
    ((-1 + n3)*((((-1 + n1)*n1*f[-2 + n1, n2, n3, 0, 0, 0])/(-1 + n3) +
    ((-1 + n1)*n1*f[-2 + n1, 2 + n2, -2 + n3, 0, 0, 0])/(1 + n2) +
    (2*n1 + n2 + n3)*f[n1, n2, -2 + n3, 0, 0, 0] +
    delta[n1]*(-(G[-1, 0, -1 + n2 + n3, w2 + w3, w1, 0]/(1 + n2)) -
    G[-1, 0, -1 + n2 + n3, w2 + w3, w1, 0]/(-1 + n3)) +
    G[-1 + n1, -1 + n3, n2, w3, w1, 0]/(-1 + n3) +
    G[1 + n2, -1 + n1, -2 + n3, w1, w2, 0]/(1 + n2))/w2^2 +
    (w3^2*((-2 - n1 - n2 - 2*(-2 + n3))*f[n1, n2, -2 + n3, 0, 0, 0] -
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    ((-3 + n3)*(-2 + n3)*f[n1, 2 + n2, -4 + n3, 0, 0, 0])/(1 + n2) -
    ((-3 + n3)*(-2 + n3)*f[2 + n1, n2, -4 + n3, 0, 0, 0])/(1 + n1) +
    delta[-2 + n3]*(G[-1, 0, 1 + n1 + n2, w1 + w2, w3, 0]/(1 + n1) +
    G[-1, 0, 1 + n1 + n2, w1 + w2, w3, 0]/(1 + n2)) -
    G[1 + n1, -3 + n3, n2, w3, w1, 0]/(1 + n1) -
    G[-3 + n3, 1 + n2, n1, w2, w3, 0]/(1 + n2)))/(w1^2*w2^2) +
    (((-1 + n2)*n2*f[n1, -2 + n2, n3, 0, 0, 0])/(-1 + n3) +
    (n1 + 2*n2 + n3)*f[n1, n2, -2 + n3, 0, 0, 0] +
    ((-1 + n2)*n2*f[2 + n1, -2 + n2, -2 + n3, 0, 0, 0])/(1 + n1) +
    delta[n2]*(-(G[-1, 0, -1 + n1 + n3, w1 + w3, w2, 0]/(1 + n1)) -
    G[-1, 0, -1 + n1 + n3, w1 + w3, w2, 0]/(-1 + n3)) +
    G[-1 + n2, 1 + n1, -2 + n3, w1, w2, 0]/(1 + n1) +
    G[-1 + n3, -1 + n2, n1, w2, w3, 0]/(-1 + n3))/w1^2))/2};

rec[a_ + b_] := rec[a] + rec[b];
rec[a_] := a/; FreeQ[a,f];
rec[a_ b_] := a rec[b]/; FreeQ[a,f];
rec[f[n1_,n2_,n3_,0,0,0]] := (f[n1,n2,n3,0,0,0]/.rec1)/; (n1>=n2 && n1>=n3 && n1>1);
rec[f[n1_,n2_,n3_,0,0,0]] := (f[n1,n2,n3,0,0,0]/.rec2)/; (n2>=n1 && n2>=n3 && n2>1);
rec[f[n1_,n2_,n3_,0,0,0]] := (f[n1,n2,n3,0,0,0]/.rec3)/; (n3>=n2 && n3>=n1 && n3>1);

$RecursionLimit = 4096;

sl2tc = {Log[w1 + w2] -> Log[(w1 + w2)/w3] + Log[w3],
    Log[w2 + w3] -> Log[w1] + Log[(w2 + w3)/w1],
    Log[w1 + w3] -> Log[w2] + Log[(w1 + w3)/w2]};

sltls = a_ * Log[x_] + a_*Log[y_] -> a*Log[x*y];
sltls2 = a_ * Log[x__] + a_*Log[y__] -> a*Log[x*y];

sl3tc[1] = Log[w1 + w2 + w3] -> -Log[w1] + Log[w1 + w2] + Log[w1 + w3] +
    Log[(w1 (w1 + w2 + w3))/((w1 + w2) (w1 + w3))];

sl3tc[2] = Log[w1 + w2 + w3] -> -Log[w2] + Log[w1 + w2] + Log[w2 + w3] +
    Log[(w2 (w1 + w2 + w3))/((w1 + w2) (w2 + w3))];

sl3tc[3] = Log[w1 + w2 + w3] -> -Log[w3] + Log[w1 + w3] + Log[w2 + w3] +
    Log[(w3 (w1 + w2 + w3))/((w1 + w3) (w2 + w3))];

minapm[expr_] :=
    (mawm1 = Map[Apart[#, w3] &, expr];
    mawm1 = Map[Apart[#, w2] &, mawm1];
```

```
    mawm1 = Map[Apart[#, w1] &, mawm1];
    mawm1 = Map[Apart[#, w1] &, mawm1];
    mawm2 = Map[Apart[#, w2] &, mawm1];
    mawm3 = Map[Apart[#, w3] &, mawm1];
    mawm4 = MinimalBy[{mawm1, mawm2, mawm3}, Length];
    mawm4 = First[mawm4]);

fopt[n1_?EvenQ /; n1 >= 0, n2_?EvenQ /; n2 >= 0, n3_?EvenQ /; n3 >= 0, 0, 0, 0, f_] :=
   Collect[minapm[Expand[f /. sl2tc]], {l[w1, w2, w3], Log[(w1 + w2)/w3],
   Log[(w1 + w3)/w2], Log[(w2 + w3)/w1]}];

fopt[n1_?OddQ /; n1 >= 0, n2_?EvenQ /; n2 >= 0, n3_?EvenQ /; n3 >= 0, 0, 0, 0, f_] :=
    Collect[minapm[Expand[f /. sl3tc[1]]],
    {Log[(w1 (w1 + w2 + w3))/((w1 + w2) (w1 + w3))]}];

fopt[n1_?EvenQ /; n1 >= 0, n2_?OddQ /; n2 >= 0, n3_?EvenQ /; n3 >= 0, 0, 0, 0, f_] :=
    Collect[minapm[Expand[f /. sl3tc[2]]],
    {Log[(w2 (w1 + w2 + w3))/((w1 + w2) (w2 + w3))]}];

fopt[n1_?EvenQ /; n1 >= 0, n2_?EvenQ /; n2 >= 0, n3_?OddQ /; n3 >= 0, 0, 0, 0, f_] :=
    Collect[minapm[Expand[f /. sl3tc[3]]],
    {Log[(w3 (w1 + w2 + w3))/((w1 + w3) (w2 + w3))]}];

fopt[n1_?EvenQ /; n1 >= 0, n2_?OddQ /; n2 >= 0, n3_?OddQ /; n3 >= 0, 0, 0, 0, f_] :=
    minapm[f];

fopt[n1_?OddQ /; n1 >= 0, n2_?EvenQ /; n2 >= 0, n3_?OddQ /; n3 >= 0, 0, 0, 0, f_] :=
    minapm[f];

fopt[n1_?OddQ /; n1 >= 0, n2_?OddQ /; n2 >= 0, n3_?EvenQ /; n3 >= 0, 0, 0, 0, f_] :=
    minapm[f];

fopt[n1_?OddQ /; n1 >= 0, n2_?OddQ /; n2 >= 0, n3_?OddQ /; n3 >= 0, 0, 0, 0, f_] :=
    minapm[f];

f3el[n1_, n2_, n3_, 0, 0, 0] := f3el[n1, n2, n3, 0, 0, 0] =
fopt[n1, n2, n3, 0, 0, 0, (Expand[FixedPoint[rec, f[n1, n2, n3, 0, 0, 0]]])];

stl = {Log[w1] - Log[w1 + w2] - Log[w1 + w3] + Log[w1 + w2 + w3]
      -> Log[(w1 (w1 + w2 + w3))/((w1 + w2) (w1 + w3))],
      Log[w2] - Log[w1 + w2] - Log[w2 + w3] + Log[w1 + w2 + w3]
      -> Log[(w2 (w1 + w2 + w3))/((w1 + w2) (w2 + w3))],
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      Log[w3] - Log[w1 + w3] - Log[w2 + w3] + Log[w1 + w2 + w3]
      -> Log[(w3 (w1 + w2 + w3))/((w1 + w3) (w2 + w3))]};

lnfad = {a_Plus*Log[x__] -> HH[a]*Log[x],
         a_Plus*l[w1,w2,w3] -> HH[a]*l[w1,w2,w3],
         a_Plus*Derivative[l_,m_,n_][l][w1,w2,w3] -> HH[a]*Derivative[l,m,n][l][w1,w2,w3]};

f3el[n1_Integer /; n1 >= 0, n2_Integer /; n2 >= 0, n3_Integer /; n3 >= 0,
    n4_Integer /; n4 >= 0, n5_Integer /; n5 >= 0, n6_Integer /; n6 >=0] :=
    f3el[n1, n2, n3, n4, n5, n6] =
    If[(AnyTrue[{n1,n2,n3}, OddQ])
    ,
    ((-1)^(n4 + n5 + n6)* Collect[(Expand[(Expand[(D[PowerExpand
    [f3el[n1, n2, n3, 0, 0, 0]], {w1, n4}, {w2, n5}, {w3, n6}]
    /. stl)] /. lnfad)] /. (w1 + w2 + w3) -> s3w // minapm /. HH[x__] -> Identity[x])
    /. s3w -> (w1 + w2 + w3), Log[__]])
    ,
    ((-1)^(n4 + n5 + n6)* Collect[(Expand[(Expand[(D[
    f3el[n1, n2, n3, 0, 0, 0], {w1, n4}, {w2, n5}, {w3, n6}] /. stl)]
    /. lnfad)] // minapm /. HH[x__] -> Identity[x]),
    {l[w1,w2,w3], Log[__], Derivative[l_,m_,n_][l][w1,w2,w3]}])]

slint1 = {Log[w1 + w2] -> -Log[(w1 + w2 + w3)/(w1 + w2)] + Log[w1 + w2 + w3],
          Log[w1 + w3] -> -Log[(w1 + w2 + w3)/(w1 + w3)] + Log[w1 + w2 + w3],
          Log[w2 + w3] -> -Log[(w1 + w2 + w3)/(w2 + w3)] + Log[w1 + w2 + w3]};

slint2 = {log[w1 + w2 + w3] -> log[(w1 + w2 + w3)/w1] + log[w1],
          log[w1 + w2] -> log[(w1 + w2)/w1] + log[w1],
          log[w1 + w3] -> log[(w1 + w3)/w1] + log[w1]};

f3el[n1_?OddQ /; n1 >= 0, n2_?OddQ /; n2 >= 0, n3_?OddQ /; n3 >= 0, -1, 0, 0] :=
    f3el[n1, n2, n3, -1, 0, 0] =
    Expand[-Integrate[f3el[n1, n2, n3, 0, 0, 0], w1]
    +SeriesCoefficient[Integrate[f3el[n1, n2, n3, 0, 0, 0],w1], {w1, Infinity, 0}]];

f3el[n1_?EvenQ /; n1 >= 0, n2_?OddQ /; n2 >= 0, n3_?OddQ /; n3 >= 0, -1, 0, 0] :=
    f3el[n1, n2, n3, -1, 0, 0] =
    minapm[Expand[-Integrate[f3el[n1, n2, n3, 0, 0, 0], w1]+
    SeriesCoefficient[Integrate[f3el[n1, n2, n3, 0, 0, 0],w1], {w1, Infinity, 0}]]];

f3el[n1_?OddQ /; n1 >= 0, n2_?OddQ /; n2 >= 0, n3_?EvenQ /; n3 >= 0, -1, 0, 0] :=
    f3el[n1, n2, n3, -1, 0, 0] =
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    Collect[minapm[Expand[-Integrate[f3el[n1, n2, n3, 0, 0, 0], w1]+
    SeriesCoefficient[Integrate[f3el[n1, n2, n3, 0, 0, 0],w1],
    {w1, Infinity, 0}] /. slint2]], Log[__]];

f3el[n1_?OddQ /; n1 >= 0, n2_?EvenQ /; n2 >= 0, n3_?OddQ /; n3 >= 0, -1, 0, 0] :=
    f3el[n1, n2, n3, -1, 0, 0] =
    Collect[minapm[Expand[-Integrate[f3el[n1, n2, n3, 0, 0, 0], w1]+
    SeriesCoefficient[Integrate[f3el[n1, n2, n3, 0, 0, 0],w1],
    {w1, Infinity, 0}] /. slint2]], Log[__]];

f3el[n1_?OddQ /; n1 >= 0, n2_?EvenQ /; n2 >= 0, n3_?EvenQ /; n3 >= 0, -1, 0, 0] :=
    f3el[n1, n2, n3, -1, 0, 0] =
    Collect[Expand[Apart[-Integrate[f3el[n1, n2, n3, 0, 0, 0], w1]+
    SeriesCoefficient[Integrate[f3el[n1, n2, n3, 0, 0, 0],w1],
    {w1, Infinity, 0}], w1] /. slint1], Log[__]];

f3el[n1_?EvenQ /; n1 >= 0, n2_?OddQ /; n2 >= 0, n3_?EvenQ /; n3 >= 0, -1, 0, 0] :=
    f3el[n1, n2, n3, -1, 0, 0] =
    Collect[Expand[Apart[-Integrate[f3el[n1, n2, n3, 0, 0, 0], w1]+
    SeriesCoefficient[Integrate[f3el[n1, n2, n3, 0, 0, 0],w1],
    {w1, Infinity, 0}], w2] /. slint2], Log[__]];

f3el[n1_?EvenQ /; n1 >= 0, n2_?EvenQ /; n2 >= 0, n3_?OddQ /; n3 >= 0, -1, 0, 0] :=
    f3el[n1, n2, n3, -1, 0, 0] =
    Collect[Expand[Apart[-Integrate[f3el[n1, n2, n3, 0, 0, 0], w1] +
    SeriesCoefficient[Integrate[f3el[n1, n2, n3, 0, 0, 0],w1],
    {w1, Infinity, 0}], w3] /. slint2], Log[__]];

f3el[n1_?OddQ /; n1 >= 0, n2_?OddQ /; n2 >= 0, n3_?OddQ /; n3 >= 0,
    -1, n5_Integer /; n5 >= 0, n6_Integer /; n6 >=0] :=
    f3el[n1, n2, n3, -1, n5, n6] =
    (-1)^(n5+n6)*D[f3el[n1, n2, n3, -1, 0, 0], {w2,n5}, {w3, n6}];

f3el[n1_?EvenQ /; n1 >= 0, n2_?OddQ /; n2 >= 0, n3_?OddQ /; n3 >= 0,
    -1, n5_Integer /; n5 >= 0, n6_Integer /; n6 >=0] :=
    f3el[n1, n2, n3, -1, n5, n6] =
    (-1)^(n5+n6)*minapm[Expand[D[f3el[n1, n2, n3, -1, 0, 0], {w2,n5}, {w3, n6}]]];

f3el[n1_?OddQ /; n1 >= 0, n2_?EvenQ /; n2 >= 0, n3_?OddQ /; n3 >= 0,
    -1, n5_Integer /; n5 >= 0, n6_Integer /; n6 >=0] :=
    f3el[n1, n2, n3, -1, n5, n6] =
    Collect[(-1)^(n5+n6)*minapm[Expand[D[f3el[n1, n2, n3, -1, 0, 0],
```

```
    {w2,n5}, {w3, n6}]]], Log[__]];

f3el[n1_?OddQ /; n1 >= 0, n2_?OddQ /; n2 >= 0, n3_?EvenQ /; n3 >= 0,
    -1, n5_Integer /; n5 >= 0, n6_Integer /; n6 >=0] :=
    f3el[n1, n2, n3, -1, n5, n6] =
    Collect[(-1)^(n5+n6)*minapm[Expand[D[f3el[n1, n2, n3, -1, 0, 0],
    {w2,n5}, {w3, n6}]]], Log[__]];

scc = {Log[w1] -> Log[w1 + w2 + w3] - Log[(w1 + w2 + w3)/(w1 + w2)] -
    Log[(w1 + w2 + w3)/(w1 + w3)] + Log[(w1 (w1 + w2 + w3))/((w1 + w2) (w1 + w3))],
    Log[w2] -> Log[w1 + w2 + w3] - Log[(w1 + w2 + w3)/(w1 + w2)] -
    Log[(w1 + w2 + w3)/(w2 + w3)] + Log[(w2 (w1 + w2 + w3))/((w1 + w2) (w2 + w3))],
    Log[w3] -> Log[w1 + w2 + w3] - Log[(w1 + w2 + w3)/(w1 + w3)] -
    Log[(w1 + w2 + w3)/(w2 + w3)] + Log[(w3 (w1 + w2 + w3))/((w1 + w3) (w2 + w3))],
    Log[w1 + w2] -> Log[w1 + w2 + w3] - Log[(w1 + w2 + w3)/(w1 + w2)],
    Log[w1 + w3] -> Log[w1 + w2 + w3] - Log[(w1 + w2 + w3)/(w1 + w3)],
    Log[w2 + w3] -> Log[w1 + w2 + w3] - Log[(w1 + w2 + w3)/(w2 + w3)]};

f3el[n1_?EvenQ /; n1 >= 0, n2_?EvenQ /; n2 >= 0, n3_?OddQ /; n3 >= 0,
    -1, n5_Integer /; n5 >= 0, n6_Integer /; n6 >=0] :=
    f3el[n1, n2, n3, -1, n5, n6] =
    (-1)^(n5+n6)*D[PowerExpand[f3el[n1, n2, n3, -1, 0, 0]], {w2, n5}, {w3, n6}
    ] /. scc // Expand // Collect[#, Log[__]]&;

f3el[n1_?EvenQ /; n1 >= 0, n2_?OddQ /; n2 >= 0, n3_?EvenQ /; n3 >= 0,
    -1, n5_Integer /; n5 >= 0, n6_Integer /; n6 >=0] :=
    f3el[n1, n2, n3, -1, n5, n6] =
    (-1)^(n5+n6)*D[PowerExpand[f3el[n1, n2, n3, -1, 0, 0]
    ], {w2, n5}, {w3, n6}] /. scc // Expand // Collect[#, Log[__]]&;

f3el[n1_?OddQ /; n1 >= 0, n2_?EvenQ /; n2 >= 0, n3_?EvenQ /; n3 >= 0,
    -1, n5_Integer /; n5 >= 0, n6_Integer /; n6 >=0] :=
    f3el[n1, n2, n3, -1, n5, n6] =
    (-1)^(n5+n6)*D[PowerExpand[f3el[n1, n2, n3, -1, 0, 0]
    ], {w2, n5}, {w3, n6}] /. scc // Expand // Collect[#, Log[__]]&;

hy3el[a_?IntegerQ /; a >= -1, b_?IntegerQ /; b >= -1, c_?IntegerQ /; c>= -1,
     n1_?IntegerQ /; n1 >= -2, n2_?IntegerQ /; n2 >= -1, n3_?IntegerQ /; n3>= -1] :=
        f3el[c+1, b+1, a+1, n1+1, n2+1, n3+1];
```

B.2 Four-electron integrals code

To use the code user simply has to load the file into the Mathematica. It requires the file with the three-electron code to be present in the same folder where the file is loaded. To calculate the required four-electron singly linked integral that was obtained in this thesis, simply write the function `g4el[a,b,c,d,e,f,n1,n2,n3,n4,w1,w2,w3,w4]` with the ten integer arguments corresponding to the powers of the r_i and r_{ij} in the singly-linked Hylleraas function followed with the arguments `w1,w2,w3,w4` like the following: `g4el[0,0,0,0,0,0,0,0,0,0,w1,w2,w3,w4]`. Be aware that the calculations quickly become lengthy for the higher values of the arguments.

```
<< ./hy3el.m

ecfld[f_] := Collect[Expand[f], {l[__], Log[__], Derivative[m_,n_,o_][l][__]}]

minapm4[expr_] := (maw4m0 = expr;
    maw4m1 = Map[Apart[#, w1] &, expr];
    maw4m1 = Map[Apart[#, w2] &, maw4m1];
    maw4m1 = Map[Apart[#, w3] &, maw4m1];
    maw4m1 = Map[Apart[#, w4] &, maw4m1];
    maw4m1 = Map[Apart[#, w1] &, maw4m1];
    maw4m2 = Map[Apart[#, w2] &, maw4m1];
    maw4m3 = Map[Apart[#, w3] &, maw4m1];
    maw4m4 = Map[Apart[#, w4] &, maw4m1];
    maw4m5 = MinimalBy[ecfld[{maw4m0, maw4m1, maw4m2, maw4m3, maw4m4}], LeafCount];
    maw4m5 = ecfld[First[maw4m5]]);

apmin[expr_] := (apm0 = expr;
    apm1 = Apart[expr, w1];
    apm2 = Apart[expr, w2];
    apm3 = Apart[expr, w3];
    apm4 = Apart[expr, w4];
    apm5 = MinimalBy[ecfld[{apm0, apm1, apm2, apm3, apm4}], Length];
    apm5 = First[apm5]);

g4el[0, 0, 0, 0, 0, 0, -1, -1, -1, -1, w1, w2, w3, w4] :=
    g4el[0, 0, 0, 0, 0, 0, -1, -1, -1, -1] = 1/(w1^2 w2^2 w3^2 w4^2);

g4el[0, 0, 0, d_Integer, e_Integer, f_Integer,
    n1_Integer, n2_Integer, n3_Integer, n4_Integer, w1, w2, w3, w4] :=
    g4el[0, 0, 0, d, e, f, n1, n2, n3, n4, w1, w2, w3, w4] =
    ecfld[(1/w1^(3 + n1)*(hy3el[f, e, d, n2, n3, n4]
    /. {w1 -> w2, w2 -> w3, w3 -> w4}))];
```

```
simpleven[fun_] :=
    minapm4[ecfld[fun] /. {a_Plus*Log[x__] -> HH[a]*Log[x],
    (w2 + w3 + w4) -> s3w}] /. {HH[x__] -> Identity[x],
    s3w -> (w2 + w3 + w4)}

g4el[a_?EvenQ /; a >= 0, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0,
    d_, e_, f_, -1, -1, -1, -1, w1, w2, w3, w4] :=
    (
    g4el[a, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4] =
    ecfld[simpleven[(1/(2 w1))(2 w1
    g4el[-2 + a, b, c, d, e, f, -1, 1, -1, -1, w1, w2, w3, w4] +
    6 g4el[-2 + a, b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    (-2 + a) (g4el[-4 + a, b, c, d, e, f, 0, 1, -1, -1, w1, w2, w3, w4] -
    g4el[-4 + a, b, c, d, e, f, 2, -1, -1, -1, w1, w2, w3, w4] +
    3 g4el[-2 + a, b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4]) +
    b (g4el[-2 + a, -2 + b, c, d, e, f, 0, -1, 1, -1, w1, w2, w3, w4] -
    g4el[-2 + a, -2 + b, c, d, e, f, 2, -1, -1, -1, w1, w2, w3, w4] -
    2 g4el[-2 + a, -2 + b, c, 2 + d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    g4el[-2 + a, b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    2 g4el[a, -2 + b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4]) +
    c (g4el[-2 + a, b, -2 + c, d, e, f, 0, -1, -1, 1, w1, w2, w3, w4] -
    g4el[-2 + a, b, -2 + c, d, e, f, 2, -1, -1, -1, w1, w2, w3, w4] -
    2 g4el[-2 + a, b, -2 + c, d, 2 + e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    g4el[-2 + a, b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    2 g4el[a, b, -2 + c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4]))]]
    ) /; (a >= b && a >= c && a > 1);

g4el[a_?EvenQ /; a >= 0, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0,
    d_, e_, f_, -1, -1, -1, -1, w1, w2, w3, w4] :=
    (
    g4el[a, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4] =
    ecfld[simpleven[(1/(2 w1))(2 w1
    g4el[a, -2 + b, c, d, e, f, -1, -1, 1, -1, w1, w2, w3, w4] +
    6 g4el[a, -2 + b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    a (g4el[-2 + a, -2 + b, c, d, e, f, 0, 1, -1, -1, w1, w2, w3, w4] -
    g4el[-2 + a, -2 + b, c, d, e, f, 2, -1, -1, -1, w1, w2, w3, w4] -
    2 g4el[-2 + a, -2 + b, c, 2 + d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    2 g4el[-2 + a, b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    g4el[a, -2 + b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4]) +
    (-2 + b) (g4el[a, -4 + b, c, d, e, f, 0, -1, 1, -1, w1, w2, w3, w4] -
    g4el[a, -4 + b, c, d, e, f, 2, -1, -1, -1, w1, w2, w3, w4] +
    3 g4el[a, -2 + b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4]) +
```

```
    c (g4el[a, -2 + b, -2 + c, d, e, f, 0, -1, -1, 1, w1, w2, w3, w4] -
    g4el[a, -2 + b, -2 + c, d, e, f, 2, -1, -1, -1, w1, w2, w3, w4] -
    2 g4el[a, -2 + b, -2 + c, d, e, 2 + f, 0, -1, -1, -1, w1, w2, w3, w4] +
    g4el[a, -2 + b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    2 g4el[a, b, -2 + c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4]))]]
    ) /; (b >= a && b >= c && b > 1);

g4el[a_?EvenQ /; a >= 0, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0,
    d_, e_, f_, -1, -1, -1, -1, w1, w2, w3, w4] :=
    (
    g4el[a, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4] =
    ecfld[simpleven[(1/(2 w1))(2 w1
    g4el[a, b, -2 + c, d, e, f, -1, -1, -1, 1, w1, w2, w3, w4] +
    6 g4el[a, b, -2 + c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    a (g4el[-2 + a, b, -2 + c, d, e, f, 0, 1, -1, -1, w1, w2, w3, w4] -
    g4el[-2 + a, b, -2 + c, d, e, f, 2, -1, -1, -1, w1, w2, w3, w4] -
    2 g4el[-2 + a, b, -2 + c, d, 2 + e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    2 g4el[-2 + a, b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    g4el[a, b, -2 + c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4]) +
    b (g4el[a, -2 + b, -2 + c, d, e, f, 0, -1, 1, -1, w1, w2, w3, w4] -
    g4el[a, -2 + b, -2 + c, d, e, f, 2, -1, -1, -1, w1, w2, w3, w4] -
    2 g4el[a, -2 + b, -2 + c, d, e, 2 + f, 0, -1, -1, -1, w1, w2, w3, w4] +
    2 g4el[a, -2 + b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    g4el[a, b, -2 + c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4]) +
    (-2 + c) (g4el[a, b, -4 + c, d, e, f, 0, -1, -1, 1, w1, w2, w3, w4] -
    g4el[a, b, -4 + c, d, e, f, 2, -1, -1, -1, w1, w2, w3, w4] +
    3 g4el[a, b, -2 + c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4]))]]
    ) /; (c >= a && c >= b && c > 1);

ssc2 = {Log[w2] -> Log[w2 + w3 + w4] - Log[(w2 + w3 + w4)/(w2 + w3)] -
    Log[(w2 + w3 + w4)/(w2 + w4)] +
    Log[(w2 (w2 + w3 + w4))/((w2 + w3) (w2 + w4))],
    Log[w3] -> Log[w2 + w3 + w4] - Log[(w2 + w3 + w4)/(w2 + w3)] -
    Log[(w2 + w3 + w4)/(w3 + w4)] +
    Log[(w3 (w2 + w3 + w4))/((w2 + w3) (w3 + w4))],
    Log[w4] -> Log[w2 + w3 + w4] - Log[(w2 + w3 + w4)/(w2 + w4)] -
    Log[(w2 + w3 + w4)/(w3 + w4)] + Log[(w4 (w2 + w3 + w4))/((w2 + w4) (w3 + w4))],
    Log[w2 + w3] -> Log[w2 + w3 + w4] - Log[(w2 + w3 + w4)/(w2 + w3)],
    Log[w2 + w4] -> Log[w2 + w3 + w4] - Log[(w2 + w3 + w4)/(w2 + w4)],
    Log[w3 + w4] -> Log[w2 + w3 + w4] - Log[(w2 + w3 + w4)/(w3 + w4)]}

g4el[a_?EvenQ, b_?EvenQ, c_?EvenQ, d_, e_, f_, n1_, n2_, n3_, n4_, w1, w2, w3, w4] :=
```

```
    ((-1)^(n1+n2+n3+n4) *
    ecfld[simpleven[PowerExpand[D[
    g4el[a, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4],
    {w1, n1+1}, {w2, n2+1}, {w3, n3+1}, {w4, n4+1}]]/. ssc2]]
    ) /; (n1 > -1 || n2 > -1 || n3 > -1 || n4 > -1);

r[-1, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_ /; d >= -1,
    e_ /; e >= -1, f_ /; f >= -1, -1, -1, -1, -1] :=
    (-hy3el[b + d, c + e, f, -1, -1, -1] /. {w1->(w1+w2), w2->w3, w3->w4}) +
    b c g4el[-1, -2 + b, -2 + c, d, e, 2 + f, 0, -1, -1, -1, w1, w2, w3, w4] -
    b w1 g4el[-1, -2 + b, c, d, e, f, -1, -1, 1, -1, w1, w2, w3, w4] +
    (-b - b^2 - b c) g4el[-1, -2 + b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    b w1 g4el[-1, -2 + b, c, d, e, f, 1, -1, -1, -1, w1, w2, w3, w4] -
    c w1 g4el[-1, b, -2 + c, d, e, f, -1, -1, -1, 1, w1, w2, w3, w4] +
    (-c - b c - c^2) g4el[-1, b, -2 + c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    c w1 g4el[-1, b, -2 + c, d, e, f, 1, -1, -1, -1, w1, w2, w3, w4]

r[1, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_ /; d >= -1,
    e_ /; e >= -1, f_ /; f >= -1, -1, -1, -1, -1] :=
    (2 g4el[-1, b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    b c g4el[1, -2 + b, -2 + c, d, e, 2 + f, 0, -1, -1, -1, w1, w2, w3, w4] -
    b w1 g4el[1, -2 + b, c, d, e, f, -1, -1, 1, -1, w1, w2, w3, w4] +
    (-b - b^2 - b c) g4el[1, -2 + b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    b w1 g4el[1, -2 + b, c, d, e, f, 1, -1, -1, -1, w1, w2, w3, w4] -
    c w1 g4el[1, b, -2 + c, d, e, f, -1, -1, -1, 1, w1, w2, w3, w4] +
    (-c - b c - c^2) g4el[1, b, -2 + c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    c w1 g4el[1, b, -2 + c, d, e, f, 1, -1, -1, -1, w1, w2, w3, w4])

frzsumw = {(w1 + w2 + w3 + w4) -> s4w, (w1 + w2 + w3) -> s3w1, (w2 + w3 + w4) -> s3w2};
unfrzsumw = {s4w -> (w1 + w2 + w3 + w4), s3w1 -> (w1 + w2 + w3), s3w2 -> (w2 + w3 + w4)};

simplodd[funct_] := ecfld[(minapm4[funct /. frzsumw /. a_Plus*Log[x__] -> HH[a*Log[x]]]
    /. HH[x__] :> minapm4[x]) /. unfrzsumw];

integ[a_Integer /; a >= -1, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_ /; d >= -1,
    e_ /; e >= -1, f_ /; f >= -1, -1, -1, -1, -1, w1, w2, w3, w4] :=
    Integrate[simplodd[ecfld[r[a, b, c, d, e, f, -1, -1, -1, -1]* w1^(b + c)]], w1,
    Assumptions -> w1 > 0 && w2 > 0 && w3 > 0 && w4 > 0] // simplodd;

(* chain integrals *)

chainlogs1 = {Log[w3 + w4] -> Log[w3] - Log[w1 + w2 + w3] + Log[w1 + w2 + w3 + w4]
```

```
    - Log[(w3 (w1 + w2 + w3 + w4))/((w1 + w2 + w3) (w3 + w4))],
    Log[w1 + w2] -> Log[w2] - Log[w2 + w3 + w4] + Log[w1 + w2 + w3 + w4]
    -Log[(w2 (w1 + w2 + w3 + w4))/((w1 + w2) (w2 + w3 + w4))]};

chainlogs2 = {Log[w1 + w2 + w3] -> Log[(w2 (w1 + w2 + w3))/((w1 + w2) (w2 + w3))]
    + Log[w2 + w3] + Log[w1 + w2] - Log[w2],
    Log[w2 + w3 + w4] -> -Log[(w2 (w1 + w2 + w3 + w4))/((w1 + w2) (w2 + w3 + w4))]
    + Log[w2] - Log[w1 + w2] + Log[w1 + w2 + w3 + w4]};

chainlogs3 = {Log[-(w2/w3)] -> Log[w2] - Log[w1 + w2] + Log[(-w1 - w2)/w3],
    Log[-(w2/(w3 + w4))] -> Log[w2] - Log[w1 + w2] + Log[(-w1 - w2)/(w3 + w4)],
    Log[(w1 + w2)/(w3 + w4)] -> - Log[w2] + Log[w1 + w2] +
    Log[(w1 + w2)/w3] + Log[w2 + w3] - Log[w1 + w2 + w3 + w4] +
    Log[(w2 w3 (w1 + w2 + w3 + w4))/((w1 + w2) (w2 + w3) (w3 + w4))]}

chainlogs4 = {Log[w1 (w2 w3 w4^3 + w2 w4^4)] -> Log[w1 w2 w3 w4^3 + w1 w2 w4^4]}

g4el[-1, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_?OddQ /; d >= -1,
    e_?EvenQ /; e >= -1, f_?OddQ /; f >= -1, -1, -1, -1, -1, w1, w2, w3, w4] :=
    g4el[-1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4] =
    simplodd[minapm[ecfld[((((1/w1^(2 + b + c)*
    (-integ[-1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4] +
    SeriesCoefficient[1/w1^(2 + b + c)*
    integ[-1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4], {w1, 0, -(2 + b + c)}])
    ) /. chainlogs1) /. chainlogs2) /. Log[x__] :> Log[Together[x]]) /. chainlogs3]
    ]];

g4el[-1, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_?OddQ /; d >= -1,
    e_?EvenQ /; e >= -1, f_?OddQ /; f >= -1, n1_, n2_, n3_, n4_, w1, w2, w3, w4] :=
    ((-1)^(n1+n2+n3+n4) *
    ecfld[((D[PowerExpand[g4el[-1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4]],
    {w1, n1+1}, {w2, n2+1}, {w3, n3+1}, {w4, n4+1}] /. chainlogs1) /. chainlogs2)]
    ) /; (n1 > -1 || n2 > -1 || n3 > -1 || n4 > -1);

g4el[1, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_?OddQ /; d >= -1,
    e_?EvenQ /; e >= -1, f_?OddQ /; f >= -1, -1, -1, -1, -1, w1, w2, w3, w4] :=
    g4el[1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4] =
    simplodd[minapm4[
    (((1/w1^(2 + b + c)*(-integ[1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4] +
    SeriesCoefficient[1/w1^(2 + b + c)*
    integ[1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4], {w1, 0, -(2 + b + c)}])
    ) /. chainlogs1) /. chainlogs2) /. chainlogs4]];
```

```
g4el[1, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_?OddQ /; d >= -1,
    e_?EvenQ /; e >= -1, f_?OddQ /; f >= -1, n1_, n2_, n3_, n4_, w1, w2, w3, w4] :=
    ((-1)^(n1+n2+n3+n4) *
    ecfld[((D[PowerExpand[g4el[1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4]],
    {w1, n1+1}, {w2, n2+1}, {w3, n3+1}, {w4, n4+1}] /. chainlogs1) /. chainlogs2)]
    ) /; (n1 > -1 || n2 > -1 || n3 > -1 || n4 > -1);

g4el[a_?OddQ /; a >= -1, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_?EvenQ /; d >= -1,
    e_?OddQ /; e >= -1, f_?OddQ /; f >= -1, n1_, n2_, n3_, n4_, w1, w2, w3, w4] :=
    (g4el[a, c, b, e, d, f, n1, n2, n4, n3, w1, w2, w3, w4] /. {w3 -> w4, w4 -> w3});

(* star integrals *)
starlogs1 = {Log[w1 + w2 + w3] -> Log[(w2 (w1 + w2 + w3))/((w1 + w2) (w2 + w3))]
    + Log[w2 + w3] + Log[w1 + w2] - Log[w2],
    Log[w2 + w3 + w4] -> -Log[(w2 (w1 + w2 + w3 + w4))/((w1 + w2) (w2 + w3 + w4))]
    + Log[w2] - Log[w1 + w2] + Log[w1 + w2 + w3 + w4],
    Log[w1 + w2 + w4] -> Log[(w2 (w1 + w2 + w4))/((w1 + w2) (w2 + w4))]
    + Log[w1 + w2] + Log[w2 + w4] - Log[w2]};

starlogs2 = Log[w2] -> Log[w1 + w2] + Log[w2 + w3] + Log[w2 + w4] - Log[w1 + w2 + w3 + w4]
    + Log[(w2 (w1 + w2 + w3 + w4))/((w1 + w2) (w2 + w3) (w2 + w4))];

starlogs3 = Log[w1 + w2] -> -Log[w2 + w3] - Log[w2 + w4] + Log[w1 + w2 + w3 + w4]
    -Log[(w1 + w2 + w3 + w4)/((w1 + w2) (w2 + w3) (w2 + w4))];

starlogs4 = Log[w1 + w2 + w3 + w4] ->
    Log[w2 + w3] + Log[w2 + w4] + Log[(w1 + w2 + w3 + w4)/((w2 + w3) (w2 + w4))];

g4el[-1, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_?OddQ /; d >= -1,
    e_?OddQ /; e >= -1, f_?EvenQ /; f >= -1, -1, -1, -1, -1, w1, w2, w3, w4] :=
    g4el[-1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4] =
    simplodd[minapm4[ecfld[
    ((1/w1^(2 + b + c)*(-integ[-1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4] +
    SeriesCoefficient[1/w1^(2 + b + c)*
    integ[-1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4], {w1, 0, -(2 + b + c)}]))
    /. starlogs1 /. starlogs2 /. starlogs3 /. starlogs4)]]]

g4el[-1, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_?OddQ /; d >= -1,
    e_?OddQ /; e >= -1, f_?EvenQ /; f >= -1, n1_, n2_, n3_, n4_, w1, w2, w3, w4] :=
    ((-1)^(n1+n2+n3+n4) *
    simplodd[(D[PowerExpand[g4el[-1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4]],
```

```
    {w1, n1+1}, {w2, n2+1}, {w3, n3+1}, {w4, n4+1}] /. starlogs1 /. starlogs2 /.
    starlogs3) /. starlogs4]) /; (n1 > -1 || n2 > -1 || n3 > -1 || n4 > -1);

g4el[1, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_?OddQ /; d >= -1,
    e_?OddQ /; e >= -1, f_?EvenQ /; f >= -1, -1, -1, -1, -1, w1, w2, w3, w4] :=
    g4el[1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4] =
    simplodd[ecfld[
    (((((1/w1^(2 + b + c)*(-integ[1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4] +
    SeriesCoefficient[1/w1^(2 + b + c)*
    integ[1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4], {w1, 0, -(2 + b + c)}])
    ) /. starlogs1) /. starlogs2) /. starlogs3) /. starlogs4)]];

g4el[1, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_?OddQ /; d >= -1,
    e_?OddQ /; e >= -1, f_?EvenQ /; f >= -1, n1_, n2_, n3_, n4_, w1, w2, w3, w4] :=
    ((-1)^(n1+n2+n3+n4) *
    ecfld[(D[PowerExpand[g4el[1, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4]],
    {w1, n1+1}, {w2, n2+1}, {w3, n3+1}, {w4, n4+1}] /. starlogs1 /. starlogs2 /.
    starlogs3 /. starlogs4)
    ]) /; (n1 > -1 || n2 > -1 || n3 > -1 || n4 > -1);

g4el[a_?OddQ /; a >= -1, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_?EvenQ /; d >= -1,
    e_?OddQ /; e >= -1, f_?OddQ /; f >= -1, n1_, n2_, n3_, n4_, w1, w2, w3, w4] :=
    (g4el[a, c, b, e, d, f, n1, n2, n4, n3, w1, w2, w3, w4] /. {w3 -> w4, w4 -> w3});

g4el[a_?OddQ /; a >= 3, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_ /; d >= -1,
    e_ /; e >= -1, f_ /; f >= -1, -1, -1, -1, -1, w1, w2, w3, w4] :=
    g4el[a, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4] =
    ecfld[(1/(2 w1))(2 w1 g4el[-2 + a, b, c, d, e, f, -1, 1, -1, -1, w1, w2, w3, w4] +
    6 g4el[-2 + a, b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    (-2 + a) (g4el[-4 + a, b, c, d, e, f, 0, 1, -1, -1, w1, w2, w3, w4] -
    g4el[-4 + a, b, c, d, e, f, 2, -1, -1, -1, w1, w2, w3, w4] +
    3 g4el[-2 + a, b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4]) +
    b (g4el[-2 + a, -2 + b, c, d, e, f, 0, -1, 1, -1, w1, w2, w3, w4] -
    g4el[-2 + a, -2 + b, c, d, e, f, 2, -1, -1, -1, w1, w2, w3, w4] -
    2 g4el[-2 + a, -2 + b, c, 2 + d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    g4el[-2 + a, b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    2 g4el[a, -2 + b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4]) +
    c (g4el[-2 + a, b, -2 + c, d, e, f, 0, -1, -1, 1, w1, w2, w3, w4] -
    g4el[-2 + a, b, -2 + c, d, e, f, 2, -1, -1, -1, w1, w2, w3, w4] -
    2 g4el[-2 + a, b, -2 + c, d, 2 + e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    g4el[-2 + a, b, c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4] +
    2 g4el[a, b, -2 + c, d, e, f, 0, -1, -1, -1, w1, w2, w3, w4]))]
```

```
g4el[a_?OddQ /; a >= 3, b_?EvenQ /; b >= 0, c_?EvenQ /; c >= 0, d_ /; d >= -1,
    e_ /; e >= -1, f_ /; f >= -1, n1_, n2_, n3_, n4_, w1, w2, w3, w4] :=
    ((-1)^(n1+n2+n3+n4) *
    ecfld[D[g4el[a, b, c, d, e, f, -1, -1, -1, -1, w1, w2, w3, w4], {w1, n1+1},
    {w2, n2+1}, {w3, n3+1}, {w4, n4+1}]]) /; (n1 > -1 || n2 > -1 || n3 > -1 || n4 > -1);
```