

Mathematical and computational science issues in high precision Hylleraas–configuration interaction variational calculations: II. Kinetic energy and electron–nucleus interaction integrals

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Abstract

Three-electron kinetic energy and electron–nucleus interaction integrals arising in Hylleraas–configuration interaction (Hy–CI) calculations are discussed. We show that the electron–nucleus interaction operators introduce no new integral complications and that the kinetic energy operators lead to integrals which have much in common with electron interaction integrals treated in the first paper of this series. We discuss the efficient evaluation of the kinetic energy integrals and give selected values of the integrals to 30 digit accuracy. The one new W auxiliary function which arises in treating the kinetic energy operator is discussed in appendix B. We also give a few details on accurate evaluations of the Condon and Shortley c^k s which arise in Hy–CI calculations in appendix A.

1. Introduction

In this paper, we continue the discussion, begun in the first paper of this series [1], of the three-electron integrals arising in high precision energy level calculations on few electron atoms and ions using the Hylleraas–configuration interaction (Hy–CI) formalism. The Hy–CI method uses a wavefunction consisting of a linear combination of configuration state functions multiplied by a single r_{ij} raised to some power. The basic idea is to combine the relative computational ease and orbital picture of CI with the better convergence obtained by introducing interelectronic coordinates r_{ij} directly into the wavefunction. We have recently used this technique to determine extremely accurate nonrelativistic ground-state energies of helium-like ions [2, 3]. As pointed out in the first paper of this series, the major difficulty in Hy–CI calculations as far as integrals are concerned comes from the electron interaction operators r_{ij}^{-1} in the Hamiltonian leading to two-, three- and four-electron integrals. We

postpone discussion of four-electron integrals to a future paper [4] and continue the three-electron discussion with a brief discussion of electron–nucleus interaction integrals and a detailed treatment of the remaining kinetic energy integrals. For a very thorough treatment of three-electron integrals over spherically symmetrical Slater-type orbitals (STOs), see [1–25] of the paper by Pelzl and King [5] and [16–40] in the review article by King [6]. Yan and Drake [7] treat the more general case of three-electron integrals over nonspherically symmetric STOs. Ruiz [8] also discusses kinetic energy in Hy–CI. She transforms the kinetic energy part of the Hamiltonian into the mutually independent distance coordinates r_i and r_{ij} and the polar angles θ_i and ϕ_i . Our treatment requires no transformations and leads to integrals which are special cases of integrals which we have already treated [9, 1]. The special nature of the Hy–CI expansion terms leads to much simpler integral formulae than the more general relations of Yan and Drake [7], a consequence of the restriction of at most a single r_{ij} operator in each Hy–CI term (in contrast to Hy- r_{ij} calculations where products of r_{ij} operators have to be dealt with).

Many of the details of the integrals which arise in an Hy–CI calculation of atomic systems have been discussed previously [9]. As discussed in [9], all two- and three-electron integrals can be expressed in terms of the standard Condon and Shortley coefficients (c^k s) [10] and auxiliary functions A , V and W [1, 9]. The auxiliary functions have been extensively discussed (again see the references in the paper by Pelzl and King [5] and the review article by King [6]), often under different names [11, 12]. Here we extend our paper I treatment of W -auxiliary functions to include the case of $W_{fgh}(\alpha\beta\gamma)$ for $g < 0$, $f, h \geq 0$, a case which arises in treating the kinetic energy integrals but does not arise in other three-electron interaction integrals. We also briefly discuss the three-electron integrals involving the one-electron electron–nucleus interaction operators (which present no difficulties). In this paper, we focus on the remaining untreated three-electron integrals, those involving the one-electron kinetic energy operators. Finally we give a few details on accurate evaluations of the Condon and Shortley c^k s in appendix A.

2. Kinetic energy integrals

The nonrelativistic Hamiltonian \mathcal{H} is, in atomic units (au),³

$$\mathcal{H}_{NR} = \sum_{i=1}^N \mathcal{H}_i + \sum_{i < j} r_{ij}^{-1}, \quad (1)$$

where $\mathcal{H}_i = \mathcal{T}_i + \mathcal{V}_i$ is a one-electron operator for electron i consisting of a kinetic energy part $\mathcal{T}_i = -1/2\nabla_i^2$ and a electron–nucleus interaction part $\mathcal{V}_i = -Z/r_i$.

In Hy–CI calculations, the major integral complications arise from the electron repulsion operators r_{ij}^{-1} which result in two-, three- and four-electron integrals that we have already discussed [9, 1, 4]. The other operators in the Hamiltonian are electron–nucleus interaction operators introducing no new integral complications and kinetic energy operators which lead to integrals which have much in common with the electron interaction integrals, as will be shown in this paper.

The secret to efficient calculation of the kinetic energy integrals is to avoid as much as possible differentiating r_{ij} terms arising on the right-hand side of the kinetic energy matrix elements. The method for doing this uses the Hermitian character of the kinetic energy operator. There are three cases, namely,

³ The atomic unit of energy is chosen as $\frac{\mu e^4}{\hbar^2} = 1$ au (of energy), where $\mu = m_e m_N / (m_e + m_N)$.

Case $\langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)|\mathcal{T}_1 r_{12}|\phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\rangle = \langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)r_{12}|\mathcal{T}_1|\phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\rangle$.

Case $\langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)r_{12}|\mathcal{T}_1 + \mathcal{T}_2|r_{12}\phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\rangle = \langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)|\phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\rangle + 1/2\{\langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)r_{12}^2|\mathcal{T}_1 + \mathcal{T}_2|\phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\rangle + \langle \phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)r_{12}^2|\mathcal{T}_1 + \mathcal{T}_2|\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\rangle\}$ where we have used the transformation of Kolos and Roothaan [13].

Case $\langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\phi_3(\mathbf{r}_3)r_{12}|\mathcal{T}_1 + \mathcal{T}_2 + \mathcal{T}_3|r_{13}\phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\phi'_3(\mathbf{r}_3)\rangle = \langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\phi_3(\mathbf{r}_3)|r_{12}\mathcal{T}_1 r_{13}|\phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\phi'_3(\mathbf{r}_3)\rangle + \langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\phi_3(\mathbf{r}_3)|r_{12}r_{13}|\mathcal{T}_2\phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\phi'_3(\mathbf{r}_3)\rangle + \langle \phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\phi'_3(\mathbf{r}_3)|r_{13}r_{12}|\mathcal{T}_3\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\phi_3(\mathbf{r}_3)\rangle$.

The first two cases involve only products of elementary one-electron integrals. In the third case, the connection with the electron interaction integrals $\langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\phi_3(\mathbf{r}_3)|r_{12}r_{13}|\phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\phi'_3(\mathbf{r}_3)\rangle$ is apparent for all except the first term. We show below that this connection also extends to this more complicated term even after the differentiations involved with \mathcal{T}_1 .

3. $I_{\mathcal{T}_1} = \langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\phi_3(\mathbf{r}_3)|r_{12}\mathcal{T}_1 r_{13}|\phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\phi'_3(\mathbf{r}_3)\rangle$

The $\phi(\mathbf{r})$ and $\phi'(\mathbf{r})$ are unnormalized, nonorthogonal Slater-type orbitals (STOs) (here, and in equations which follow, we drop parameter dependences where that would make the formulae excessively cluttered)

$$\begin{aligned}\phi(\mathbf{r}) &= \phi(r, \theta, \phi) = r^{n-1} e^{-\alpha r} Y_l^m(\theta, \phi), \\ \phi'(\mathbf{r}) &= \phi'(r, \theta, \phi) = r^{n'-1} e^{-\alpha' r} Y_{l'}^{m'}(\theta, \phi),\end{aligned}\quad (2)$$

where the radial factor depends on the orbital exponent α and the radial quantum number n . The l and m quantum numbers define the order and degree of the orthonormal spherical harmonics Y_l^m defined in the Condon and Shortley phase convention [10].⁴

We use a multipole expansion for $\nabla_i^2 \phi_1(\mathbf{r}_1)r_{13}$ and do the resulting integral in such a way that it is a special case of integrals we have already treated [1]. In the following \mathbf{I}^2 is the squared resultant one-electron orbital angular momentum operator $\mathbf{I}^2 = I_x^2 + I_y^2 + I_z^2$ which, when operating on a $\phi_i(\mathbf{r}_i)$, has the property that

$$\mathbf{I}_i^2 \phi_i(\mathbf{r}_i) = l_i(l_i + 1)\phi_i(\mathbf{r}_i). \quad (3)$$

Writing the one-electron operator \mathcal{T}_1 (equation (1)) as

$$\begin{aligned}\mathcal{T}_1 &= -\frac{1}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} \right) + \frac{\mathbf{I}^2(1)}{2r_1^2} \\ &= \mathcal{T}_1^0 + \frac{\mathbf{I}^2(1)}{2r_1^2},\end{aligned}\quad (4)$$

$I_{\mathcal{T}_1}$ can be expressed as the sum of two integrals, $I'_{\mathcal{T}_1}$ and $I''_{\mathcal{T}_1}$, given by

$$I'_{\mathcal{T}_1} = \langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\phi_3(\mathbf{r}_3)|r_{12}\mathcal{T}_1^0 r_{13}|\phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\phi'_3(\mathbf{r}_3)\rangle \quad (5)$$

and

$$I''_{\mathcal{T}_1} = \langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\phi_3(\mathbf{r}_3)|r_{12} \frac{\mathbf{I}^2(1)}{2r_1^2} r_{13}|\phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\phi'_3(\mathbf{r}_3)\rangle. \quad (6)$$

⁴ The STOs we use are defined fully in [9]. An s -type STO has $l = 0$, a p STO has $l = 1$, a d STO has $l = 2$, etc. A p_0 STO has $m = 0$.

$$3.1. I'_{T_1} = \langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\phi_3(\mathbf{r}_3) | r_{12} T_1^0 r_{13} | \phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\phi'_3(\mathbf{r}_3) \rangle$$

Consider

$$T_1^0 \phi'_1(\mathbf{r}_1) r_{13} = \left\{ -\frac{1}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} \right) \right\} \phi'_1(\mathbf{r}_1) r_{13}. \tag{7}$$

To carry out the derivatives, we use the expansion for r_{13} derived in [9],

$$\begin{aligned} r_{13} &= \sum_{n=0}^{\infty} B_n(r_{13}, 1) P_n(\cos \theta_{13}) \\ &= \sum_{n=0}^{\infty} P_n(\cos \theta_{13}) \sum_{m=0}^1 B_m^{n,1} \frac{r_{13}^{n+2-2m}}{r_{13}^{n+1-2m}}, \end{aligned} \tag{8}$$

with

$$B_0^{n,1} = \frac{1}{2n+3}, \quad B_1^{n,1} = -\frac{1}{2n-1}. \tag{9}$$

This is just a particular case of an expansion given by Perkins [14], which is a rewriting of the well-known expansion of Sack [15]. Here $r_{13<}$ and $r_{13>}$ refer to the lesser and greater of r_1 and r_3 , respectively. The term $T_1^0 \phi'_1(\mathbf{r}_1) r_{13}$ becomes, after taking the derivatives,

$$\begin{aligned} T_1^0 \phi'_1(\mathbf{r}_1) r_{13} &= \sum_{n=0}^{\infty} P_n(\cos \theta_{13}) \left\{ -\frac{1}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} \right) \right\} \phi'_1(\mathbf{r}_1) \sum_{m=0}^1 B_m^{n,1} \frac{r_{13}^{n+2-2m}}{r_{13}^{n+1-2m}} \\ &= \phi'_1(\mathbf{r}_1) \sum_{n=0}^{\infty} P_n(\cos \theta_{13}) \sum_{m=0}^1 B_m^{n,1} \\ &\quad \times \left\{ \frac{r_1^{n+2-2m}}{r_3^{n+1-2m}} \left[-\frac{(n'_1 + n + 2 - 2m)(n'_1 + n + 1 - 2m)}{2r_1^2} \right. \right. \\ &\quad \left. \left. + \frac{\alpha'_1(n'_1 + n + 2 - 2m)}{r_1} - \frac{\alpha_1'^2}{2} \right]_{r_1 < r_3} \right. \\ &\quad \left. + \frac{r_3^{n+2-2m}}{r_1^{n+1-2m}} \left[-\frac{(n'_1 - n - 1 + 2m)(n'_1 - n - 2 + 2m)}{2r_1^2} \right. \right. \\ &\quad \left. \left. + \frac{\alpha'_1(n'_1 - n - 1 + 2m)}{r_1} - \frac{\alpha_1'^2}{2} \right]_{r_3 < r_1} \right\}. \end{aligned} \tag{10}$$

Comparing equation (10) with the expansion of r_{13} in equation (8) makes it clear that $\langle \dots | r_{12} T_1^0 r_{13} | \dots \rangle$ leads to the same kinds of integrals as does $\langle \dots | r_{12} r_{13} | \dots \rangle$. Indeed, our integral could be expressed as a linear combination of appropriate $\langle \dots | r_{12} r_{13} | \dots \rangle$ integrals but this is not the approach usually taken. Now introduce ‘charge distributions’

$$\Omega_i(\mathbf{r}_i) = \phi_i^*(\mathbf{r}_i)\phi'_i(\mathbf{r}_i) \tag{11}$$

which we expand in terms of STO-like functions $f_i(\mathbf{r}_i)$

$$f_i(\mathbf{r}_i) = r_i^{N_i-1} e^{-w_i r_i} Y_{L_i}^{M_i}(\theta_i, \phi_i); \tag{12}$$

the formula is

$$\Omega_i(\mathbf{r}_i) = \sum_{L_i} \left\{ \frac{(2L_i + 1)}{4\pi} \right\}^{1/2} c^{L_i}(l'_i, m'_i; l_i, m_i) f_i(\mathbf{r}_i), \tag{13}$$

where $N_i = n_i + n'_i - 1$, $w_i = \alpha_i + \alpha'_i$, and L_i satisfies the triangular inequality $|l_i - l'_i| \leq L_i \leq l_i + l'_i$ with $l_i + l'_i + L_i = 2g$ (g integral) and with the further restriction $L_i \geq |M_i|$, $M_i = m'_i - m_i$. The c^{L_i} are standard Condon and Shortley coefficients (the so-called c^k s) which we discuss in appendix A.

Using the spherical harmonic addition theorem [10] (see the Addenda)

$$P_n(\cos \theta_{13}) = \frac{4\pi}{2n+1} \sum_{m_n=-n}^n Y_n^{m_n*}(\theta_1, \phi_1) Y_n^{m_n}(\theta_3, \phi_3), \tag{14}$$

expanding r_{12} using equation (8), and expanding the products of STOs using equation (13) we get

$$I'_{T_1} = \sum_{L_1, L_2, L_3} \prod_{i=1}^3 \{(2L_i + 1)^{1/2} c^{L_i}(l'_i, m'_i; l_i, m_i)\} J'_2(L_1, L_2, L_3), \tag{15}$$

where

$$\begin{aligned} J'_2(L_1, L_2, L_3) &= \frac{1}{(4\pi)^{3/2}} \int r_{12} T_1^0 r_{13} \prod_{i=1}^3 \{f_i(\mathbf{r}_i) d\mathbf{r}_i\} \\ &= \mathcal{A}'_2(L_1, L_2, L_3) \sum_{l=0}^1 \sum_{m=0}^1 B_l^{L_2,1} B_m^{L_3,1} \\ &\quad \times \mathcal{R}'(N_1, N_2, N_3, N_{12}(l), N_{13}(m); w_1, w_2, w_3) \end{aligned} \tag{16}$$

with $N_{12}(l) = L_2 + 1 - 2l$, $N_{13}(m) = L_3 + 1 - 2m$, $N_i = n_i + n'_i - 1$, $w_i = \alpha_i + \alpha'_i$, and

$$\mathcal{A}'_2(L_1, L_2, L_3) = \delta(M_1 + M_2 + M_3, 0) (-1)^{M_2} \frac{c^{L_3}(L_2, -M_2; L_1, M_1)}{(2L_2 + 1)(2L_3 + 1)^{1/2}}. \tag{17}$$

$\mathcal{A}'_2(L_1, L_2, L_3)$ will be 0 unless the triangular inequality $|L_2 - L_1| \leq L_3 \leq L_1 + L_2$, with $L_1 + L_2 + L_3 = 2g$ (g integral), is satisfied and the sum of the M_i equals 0. $\mathcal{R}'(N_1, N_2, N_3, N_{12}(l), N_{13}(m); w_1, w_2, w_3)$ is given by

$$\begin{aligned} \mathcal{R}'(N_1, N_2, N_3, N_{12}(l), N_{13}(m); w_1, w_2, w_3) &= \int \frac{r_1^{N_{12}(l)+1}}{r_1^{N_{12}(l)}} \\ &\quad \times \left\{ \frac{r_1^{N_{13}(m)+1}}{r_3^{N_{13}(m)}} \left[-\frac{(n'_1 + N_{13}(m) + 1)(n'_1 + N_{13}(m))}{2r_1^2} + \frac{\alpha'_1(n'_1 + N_{13}(m) + 1)}{r_1} - \frac{\alpha_1'^2}{2} \right]_{r_1 < r_3} \right. \\ &\quad \left. + \frac{r_3^{N_{13}(m)+1}}{r_1^{N_{13}(m)}} \left[-\frac{(n'_1 - N_{13}(m))(n'_1 - N_{13}(m) - 1)}{2r_1^2} + \frac{\alpha'_1(n'_1 - N_{13}(m))}{r_1} - \frac{\alpha_1'^2}{2} \right]_{r_3 < r_1} \right\} \\ &\quad \times e^{-w_1 r_1 - w_2 r_2 - w_3 r_3} r_1^{N_1+1} r_2^{N_2+1} r_3^{N_3+1} dr_1 dr_2 dr_3. \end{aligned} \tag{18}$$

Let

$$\begin{aligned} \mathcal{R}_1(N_1, N_2, N_3, N_{12}(l), N_{13}(m), p; w_1, w_2, w_3) &= W(N_1 + 3 + N_{12}(l) + N_{13}(m) + p, N_2 + 1 - N_{12}(l), N_3 + 1 - N_{13}(m); w_1, w_2, w_3) \\ &\quad + W(N_1 + 3 + N_{12}(l) + N_{13}(m) + p, N_3 + 1 - N_{13}(m), N_2 + 1 - N_{12}(l); w_1, w_3, w_2) \\ &\quad + W(N_2 + 2 + N_{12}(l), N_1 + 2 - N_{12}(l) + N_{13}(m) + p, N_3 + 1 - N_{13}(m); w_2, w_1, w_3) \end{aligned} \tag{19}$$

and

$$\begin{aligned} & \mathcal{R}_2(N_1, N_2, N_3, N_{12}(l), N_{13}(m), p; w_1, w_2, w_3) \\ &= W(N_2 + 2 + N_{12}(l), N_3 + 2 + N_{13}(m), N_1 + 1 - N_{12}(l) - N_{13}(m) + p; w_2, w_3, w_1) \\ & \quad + W(N_3 + 2 + N_{13}(m), N_1 + 2 + N_{12}(l) - N_{13}(m) + p, N_2 + 1 - N_{12}(l); w_3, w_1, w_2) \\ & \quad + W(N_3 + 2 + N_{13}(m), N_2 + 2 + N_{12}(l), N_1 + 1 - N_{12}(l) - N_{13}(m) + p; w_3, w_2, w_1), \end{aligned} \quad (20)$$

where the W integrals are defined by

$$\begin{aligned} W(fgh; \alpha\beta\gamma) \equiv W_{fgh}(\alpha\beta\gamma) &= \int_0^\infty x^f e^{-\alpha x} dx \int_x^\infty y^g e^{-\beta y} dy \int_y^\infty z^h e^{-\gamma z} dz, \\ & (f \geq 0, f + g \geq -1, f + g + h \geq -2). \end{aligned} \quad (21)$$

The W auxiliary integrals are discussed in [1]. Then

$$\begin{aligned} & \mathcal{R}'(N_1, N_2, N_3, N_{12}(l), N_{13}(m); w_1, w_2, w_3) \\ &= -1/2(n'_1 + N_{13}(m) + 1)(n'_1 + N_{13}(m))\mathcal{R}_1(N_1, N_2, N_3, N_{12}(l), N_{13}(m), -2; w_1, w_2, w_3) \\ & \quad - 1/2(n'_1 - N_{13}(m))(n'_1 - N_{13}(m) - 1)\mathcal{R}_2(N_1, N_2, N_3, N_{12}(l), N_{13}(m), -2; w_1, w_2, w_3) \\ & \quad + [\alpha'_1(n'_1 + N_{13}(m) + 1)]\mathcal{R}_1(N_1, N_2, N_3, N_{12}(l), N_{13}(m), -1; w_1, w_2, w_3) \\ & \quad + [\alpha'_1(n'_1 - N_{13}(m))]\mathcal{R}_2(N_1, N_2, N_3, N_{12}(l), N_{13}(m), -1, w_1, w_2, w_3) \\ & \quad - \frac{\alpha_1^2}{2}\{\mathcal{R}_1(N_1, N_2, N_3, N_{12}(l), N_{13}(m), 0; w_1, w_2, w_3) \\ & \quad + \mathcal{R}_2(N_1, N_2, N_3, N_{12}(l), N_{13}(m), 0; w_1, w_2, w_3)\}. \end{aligned} \quad (22)$$

Substituting equation (16) into equation (15) and rearranging terms, I'_{T_1} becomes

$$\begin{aligned} I'_{T_1} &= \delta(M_1 + M_2 + M_3, 0)(-1)^{M_2} \sum_{L_1, L_2, L_3} \mathcal{A}_2(L_1, L_2, L_3) \\ & \quad \times \sum_{l=0}^1 \sum_{m=0}^1 B_l^{L_2, 1} B_m^{L_3, 1} \mathcal{R}'(N_1, N_2, N_3, N_{12}(l), N_{13}(m); w_1, w_2, w_3), \end{aligned} \quad (23)$$

where

$$\mathcal{A}_2(L_1, L_2, L_3) = \left\{ \frac{(2L_1 + 1)}{(2L_2 + 1)} \right\}^{\frac{1}{2}} c^{L_3}(L_2, -M_2; L_1, M_1) \prod_{i=1}^3 c^{L_i}(l'_i, m'_i; l_i, m_i), \quad (24)$$

and $|L_2 - L_1| \leq L_3 \leq L_1 + L_2$, with $L_1 + L_2 + L_3 = 2g$ (g integral).

$$3.2. I''_{T_1} = \langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\phi_3(\mathbf{r}_3) | r_{12} \frac{\mathbf{I}^2(1)}{2r_1^2} r_{13} | \phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\phi'_3(\mathbf{r}_3) \rangle$$

Note that we cannot immediately expand the orbital product for electron 1 since we must first operate with $\mathbf{I}^2(1)$ on $\phi'_1(\mathbf{r}_1)r_{13}$. Expanding the charge distributions for electrons 2 and 3, I''_{T_1} becomes

$$I''_{T_1} = \sum_{L_2, L_3} \prod_{i=2}^3 \{(2L_i + 1)^{\frac{1}{2}} c^{L_i}(l'_i, m'_i; l_i, m_i)\} J''_2(L_2, L_3), \quad (25)$$

where $J''_2(L_2, L_3)$ is given by

$$J''_2(L_2, L_3) = \frac{1}{4\pi} \int \phi_1^*(\mathbf{r}_1) r_{12} \frac{\mathbf{I}^2(1)}{2r_1^2} r_{13} \phi'_1(\mathbf{r}_1) \prod_{i=2}^3 \{f_i(\mathbf{r}_i) d\mathbf{r}_i\} d\mathbf{r}_1. \quad (26)$$

To carry out the operation of $\mathbf{I}^2(1)$ on $\phi'_1(\mathbf{r}_1)r_{13}$, we again use the expansion for r_{13} (equation (8)), so that

$$\mathbf{I}^2(1)\phi'_1(\mathbf{r}_1)r_{13} = \sum_{n=0}^{\infty} B_n(r_{13}, 1)\mathbf{I}^2(1)P_n(\cos \theta_{13})\phi'_1(\mathbf{r}_1). \tag{27}$$

Using the spherical harmonic addition theorem (equation (14)) and the formula for expanding a product of spherical harmonics (one of which is complex conjugated),

$$Y_l^{m*}(\theta, \phi)Y_{l'}^{m'}(\theta, \phi) = \sum_L \left\{ \frac{2L+1}{4\pi} \right\}^{\frac{1}{2}} c^L(l', m'; l, m)Y_L^M(\theta, \phi), \tag{28}$$

we get

$$\begin{aligned} P_n(\cos \theta_{13})\phi'_1(\mathbf{r}_1) &= \frac{\{4\pi\}^{\frac{1}{2}}}{2n+1} r_1^{n_1-1} e^{-\alpha'_1 r_1} \sum_{m_n=-n}^n Y_n^{m_n}(\theta_3, \phi_3) \\ &\times \sum_L \{2L+1\}^{\frac{1}{2}} c^L(l'_1, m'_1; n, m_n)Y_L^M(\theta_1, \phi_1), \end{aligned} \tag{29}$$

where L satisfies the triangular inequality $|l_1 - n| \leq L \leq l_1 + n$, with $l_1 + n + L = 2g$ (g integral) and with the further restriction $L \geq |M|$, $M = m'_1 - m_n$. But

$$\mathbf{I}^2 Y_L^M(\theta, \phi) = L(L+1)Y_L^M(\theta, \phi), \tag{30}$$

so

$$\begin{aligned} \mathbf{I}^2(1)\phi'_1(\mathbf{r}_1)r_{13} &= \sum_{n=0}^{\infty} B_n(r_{13}, 1)\mathbf{I}^2(1)P_n(\cos \theta_{13})\phi'_1(\mathbf{r}_1) \\ &= \{4\pi\}^{\frac{1}{2}} r_1^{n_1-1} e^{-\alpha'_1 r_1} \sum_{n=0}^{\infty} \sum_{m_n=-n}^n \frac{1}{(2n+1)} B_n(r_{13}, 1)Y_n^{m_n}(\theta_3, \phi_3) \\ &\times \sum_L L(L+1)\{2L+1\}^{\frac{1}{2}} c^L(l'_1, m'_1; n, m_n)Y_L^M(\theta_1, \phi_1). \end{aligned} \tag{31}$$

Substituting this expression into equation (26), expanding r_{12} , and integrating over angular coordinates leads to

$$\begin{aligned} J_2''(L_2, L_3) &= \mathcal{A}''(L_2, L_3) \sum_{l=0}^1 \sum_{m=0}^1 B_l^{L_2, 1} B_m^{L_3, 1} \mathcal{R}''(N_1 - 2, N_2, N_3, N_{12}(l), \\ &N_{13}(m); w_1, w_2, w_3), \end{aligned} \tag{32}$$

where $N_{12}(l) = L_2 + 1 - 2l$ and $N_{13}(m) = L_3 + 1 - 2m$ as before and

$$\begin{aligned} \mathcal{A}_2''(L_2, L_3) &= \delta(M_1 + M_2 + M_3, 0)(-1)^{M_3} \sum_L \frac{L(L+1)(2L+1)}{2(2L_2+1)(2L_3+1)} \\ &\times c^L(l'_1, m'_1; L_3, -M_3)c^L(l_1, m_1; L_2, M_2). \end{aligned} \tag{33}$$

L needs to satisfy all of the following conditions:

- (i) $|l'_1 - L_3| \leq L \leq l'_1 + L_3, l'_1 + L_3 + L = 2g$ (g integral)
- (ii) $|l_1 - L_2| \leq L \leq l_1 + L_2, l_1 + L_2 + L = 2g'$ (g' integral)
- (iii) $L \geq |m'_1 + M_3|, L \geq |m_1 - M_2|, L > 0$

and the range of L from the first condition must overlap the range of L from the second condition. For most L_2, L_3 cases arising in practice, the range of L will be quite limited. $\mathcal{R}''(N_1 - 2, N_2, N_3, N_{12}(l), N_{13}(m); w_1, w_2, w_3)$ is given by

$$\begin{aligned} \mathcal{R}''(N_1 - 2, N_2, N_3, N_{12}(l), N_{13}(m); w_1, w_2, w_3) &= \int r_1^{N_1-1} r_2^{N_2+1} r_3^{N_3+1} \frac{r_{12<}^{N_{12}+1} r_{13<}^{N_{13}+1}}{r_{12>}^{N_{12}} r_{13>}^{N_{13}}} \\ &\times \exp(-w_1 r_1 - w_2 r_2 - w_3 r_3) dr_1 dr_2 dr_3 \\ &= W(N_1 + N_{12} + N_{13} + 1, N_2 + 1 - N_{12}, N_3 - N_{13} + 1; w_1, w_2, w_3) \\ &+ W(N_1 + N_{12} + N_{13} + 1, N_3 + 1 - N_{13}, N_2 + 1 - N_{12}; w_1, w_3, w_2) \\ &+ W(N_2 + N_{12} + 2, N_1 - N_{12} + N_{13}, N_3 - N_{13} + 1; w_2, w_1, w_3) \\ &+ W(N_2 + N_{12} + 2, N_3 + N_{13} + 2, N_1 - N_{12} - N_{13} - 1; w_2, w_3, w_1) \\ &+ W(N_3 + N_{13} + 2, N_1 + N_{12} - N_{13}, N_2 + 1 - N_{12}; w_3, w_1, w_2) \\ &+ W(N_3 + N_{13} + 2, N_2 + N_{12} + 2, N_1 - N_{12} - N_{13} - 1; w_3, w_2, w_1). \end{aligned} \quad (34)$$

\mathcal{R}'' is a special case of a more general formula for three-electron interaction radial integrals $\mathcal{R}(N_1, N_2, N_3, N_{12}, N_{13}, N_{23}, s, t, u; w_1, w_2, w_3)$ discussed elsewhere [9] which handles the operator $r_{12}^s r_{13}^t / r_{23}^u$ and reduces to equation (34) for $s = t = 1, N_{23} = 0$ and $u = 0$. Note that in $\mathcal{R}''(N_1 - 2, N_2, N_3, N_{12}(l), N_{13}(m); w_1, w_2, w_3)$ the power that r_1 is raised to is reduced by 2 due to the $\frac{1}{2r_1^2}$ factor; i.e., the radial integral is obviously the same sort of term as arises in $\langle \cdots | r_{12} r_{13} | \cdots \rangle$ except for N_1 being replaced by $N_1 - 2$. This reduction of N_1 by 2 has an effect on the $W_{fgh}(\alpha\beta\gamma)$ function evaluation, namely the case $g < 0, f, h \geq 0$ can arise now, whereas it cannot in the other three-electron interaction integrals treated in the first paper in this series [1]. In appendix B, we provide a suitable recursion scheme for this new W -function case.

Our final expression for I''_{T_1} is thus

$$\begin{aligned} I''_{T_1} &= \delta(M_1 + M_2 + M_3, 0) (-1)^{M_3} \sum_{L_2, L_3} \mathcal{A}''_{T_1}(L_2, L_3) \\ &\times \sum_{l=0}^1 \sum_{m=0}^1 B_l^{L_2, 1} B_m^{L_3, 1} \mathcal{R}''(N_1 - 2, N_2, N_3, N_{12}(l), N_{13}(m); w_1, w_2, w_3) \end{aligned} \quad (35)$$

where

$$\begin{aligned} \mathcal{A}''_{T_1}(L_2, L_3) &= \frac{\prod_{i=2}^3 \{c^{L_i}(l'_i, m'_i; l_i, m_i)\}}{2\{(2L_2 + 1)(2L_3 + 1)\}^{\frac{1}{2}}} \\ &\times \sum_L L(L+1)(2L+1) c^L(l'_1, m'_1; L_3, -M_3) c^L(l_1, m_1; L_2, M_2) \end{aligned} \quad (36)$$

with the conditions on L given above.

I_{T_1} is the sum of two integrals, I'_{T_1} and I''_{T_1} , treated above. In table 1 we give values for the kinetic energy operator T_1 operating on r_{13} and both spherically and non-spherically symmetric STOs computed using quadruple precision (QP) arithmetic (when we refer to double, quadruple, or other precision it is with respect to a 32 bit word). In this connection, software support for a number of new data types for Fortran 90 has recently become available, including double precision with exponent (DPE) and quadruple precision with exponent (QPE) (for handling the exponent overflow problem) as well as quad-double precision (QD) and quad-double with exponent (QDE). As a check on the accuracy of the results tabulated in table 1 we computed all integrals in QD and found that the QP results agree with the QD results with an error of at most 1–2 in the last digit reported.

Table 1. Selected values of the integral $\mathbf{I}_{\mathcal{T}_1} = \langle \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\phi_3(\mathbf{r}_3) | r_{12}\mathcal{T}_1 r_{13} | \phi'_1(\mathbf{r}_1)\phi'_2(\mathbf{r}_2)\phi'_3(\mathbf{r}_3) \rangle$ computed in quadruple precision, where the s and non- s STOs $\phi_i(\mathbf{r})$ are defined in equation (2). ‘Charge distribution’ lists the orbitals used in the integrals in charge distribution form (e.g., equation (11)), the product of orbitals for electrons 1, 2 and 3, respectively, separated by commas. $\alpha = 1.4$ for orbitals labelled with ‘’, 2.86 otherwise. ω_i is the sum of the α ’s for electron i . \mathcal{T}_1 operates on both r_{13} and $\phi'_1(\mathbf{r}_1)$.

ω_1	ω_2	ω_3	Charge distribution	$\mathbf{I}_{\mathcal{T}_1}$
5.72	4.26	4.26	(1s1s,1s2s'',2s1s'')	0.13126 72235 19561 47025 67125 92522 $\times 10^{-4}$
5.72	5.72	2.8	(1s1s,1s1s,2s''2s'')	0.64207 60509 60589 25934 71629 40533 $\times 10^{-4}$
2.8	5.72	2.8	(2p'' ₀ 2p'' ₀ ,1s1s,2s''2s'')	0.57720 73518 58580 32536 07477 41306 $\times 10^{-3}$
5.72	4.26	2.8	(1s1s,1s2p'' ₀ ,2s''2p'' ₀)	0.38140 71178 87570 42824 91516 47944 $\times 10^{-5}$
5.72	5.72	4.26	(1s2p ₀ ,1s1s,1s4p'' ₀)	-0.14502 00857 39528 49418 94063 13172 $\times 10^{-6}$
5.72	5.72	4.26	(1s2p ₀ ,1s1s,1s6p'' ₀)	-0.32844 14491 49562 97251 56025 55653 $\times 10^{-6}$
4.26	5.72	4.26	(1s3d'' ₀ ,1s1s,1s3d'' ₀)	0.79465 21564 41320 36387 60727 96091 $\times 10^{-7}$
4.26	5.72	4.26	(1s3d'' ₀ ,1s1s,1s4d'' ₀)	0.12075 23527 76977 23170 64933 06356 $\times 10^{-6}$
4.26	5.72	4.26	(1s3d'' ₀ ,2p ₀ 3p ₀ ,1s4d'' ₀)	0.67304 67088 08933 49971 96261 05823 $\times 10^{-7}$
5.72	5.72	4.26	(2p ₀ 2p ₀ ,1s1s,2s2s'')	0.29871 77066 84990 94807 38892 10487 $\times 10^{-5}$
5.72	5.72	4.26	(2p ₀ 2p ₀ ,1s1s,2p ₀ 2p'' ₀)	0.29519 96062 34340 69487 85811 15133 $\times 10^{-5}$
5.72	5.72	4.26	(2p ₀ 2p ₀ ,2p ₀ 3p ₀ ,2p ₀ 3p'' ₀)	0.19213 21210 92616 69396 65303 73606 $\times 10^{-5}$
5.72	5.72	4.26	(3p ₀ 3p ₀ ,1s1s,3p ₀ 3p'' ₀)	0.40535 29068 76436 24808 08465 07749 $\times 10^{-5}$
5.72	5.72	4.26	(3d ₀ 3d ₀ ,1s1s,3d ₀ 3d'' ₀)	0.87231 87107 67592 04016 01662 18286 $\times 10^{-5}$
5.72	5.72	4.26	(3d ₀ 3d ₀ ,1s1s,3d ₀ 4d'' ₀)	0.15815 57944 02140 20530 85237 26766 $\times 10^{-4}$
5.72	5.72	4.26	(3d ₀ 3d ₀ ,1s1s,4d ₀ 4d'' ₀)	0.32596 11204 87135 13502 55123 63283 $\times 10^{-4}$
5.72	5.72	4.26	(3d ₀ 3d ₀ ,2p ₀ 3p ₀ ,4d ₀ 4d'' ₀)	0.13472 45687 15817 35201 25998 75627 $\times 10^{-4}$
5.72	5.72	4.26	(3d ₀ 3d ₀ ,3d ₀ 4d ₀ ,4d ₀ 4d'' ₀)	0.20760 58133 97401 23636 32696 31433 $\times 10^{-4}$
5.72	5.72	4.26	(2p ₁ 2p ₁ ,1s1s,2p ₁ 2p'' ₁)	0.29783 81815 72328 38477 50621 86648 $\times 10^{-5}$
5.72	5.72	4.26	(3d ₂ 3d ₂ ,1s1s,3d ₂ 3d'' ₂)	0.87337 99889 07121 70685 75959 02697 $\times 10^{-5}$
5.72	5.72	4.26	(2p ₁ 2p ₁ ,2p ₁ 2p ₁ ,2p ₁ 2p'' ₁)	0.14390 09188 74908 52676 79501 50271 $\times 10^{-5}$
5.72	5.72	4.26	(3d ₂ 3d ₂ ,3p ₁ 3p ₁ ,3d ₂ 3d'' ₂)	0.41359 57078 58469 80859 64162 38576 $\times 10^{-5}$
5.72	5.72	4.26	(2p ₀ 2p ₀ ,2p ₀ 2p ₋₁ ,2p ₀ 2p'' ₁)	-0.75104 03404 78207 96905 89118 93078 $\times 10^{-9}$
5.72	5.72	4.26	(3d ₀ 3d ₀ ,3p ₀ 3p ₋₁ ,3d ₀ 4d'' ₁)	-0.11247 28271 12214 02357 71049 25523 $\times 10^{-8}$

4. Nuclear attraction integrals

The electron–nucleus interaction part of the one-electron operator for electron i is $\mathcal{V}_i = -Z/r_i$. The three-electron integrals involving the one-electron electron–nucleus interaction can be treated like electron interaction integrals with a modified ‘charge distribution’; i.e., a separate option in a subroutine for $\langle \cdots | r_{12}r_{13} | \cdots \rangle$ can handle the $\langle \cdots | r_{12}(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3})r_{13} | \cdots \rangle$. Alternatively, in the kinetic energy formulae the kinetic energy operator \mathcal{T}_1 can be converted into a corresponding \mathcal{H}_1 operator incorporating electron–nucleus interaction, resulting in formulae for the one-electron Hamiltonian operator \mathcal{H}_1 which reduce to the kinetic energy formulae we have given in the special case of $Z = 0$; i.e., $\mathcal{T}_1 = \mathcal{H}_1$ ($Z = 0$). In equation (18) one simply adds $-Z$ to the numerators of both r_1^{-1} terms to define a $\mathcal{R}'_Z(N_1, N_2, N_3, N_{12}(l), N_{13}(m); w_1, w_2, w_3)$. That is

$$\begin{aligned} & \mathcal{R}'_Z(N_1, N_2, N_3, N_{12}(l), N_{13}(m); w_1, w_2, w_3) \\ &= -1/2(n'_1 + N_{13}(m) + 1)(n'_1 + N_{13}(m))\mathcal{R}_1(N_1, N_2, N_3, N_{12}(l), N_{13}(m), -2; w_1, w_2, w_3) \\ & \quad - 1/2(n'_1 - N_{13}(m))(n'_1 - N_{13}(m) - 1)\mathcal{R}_2(N_1, N_2, N_3, N_{12}(l), N_{13}(m), -2; w_1, w_2, w_3) \\ & \quad + [\alpha'_1(n'_1 + N_{13}(m) + 1) - Z]\mathcal{R}_1(N_1, N_2, N_3, N_{12}(l), N_{13}(m), -1; w_1, w_2, w_3) \end{aligned}$$

$$\begin{aligned}
& + [\alpha'_1(n'_1 - N_{13}(m)) - Z]\mathcal{R}_2(N_1, N_2, N_3, N_{12}(l), N_{13}(m), -1, w_1, w_2, w_3) \\
& - \frac{\alpha_1^2}{2}\{\mathcal{R}_1(N_1, N_2, N_3, N_{12}(l), N_{13}(m), 0; w_1, w_2, w_3) \\
& + \mathcal{R}_2(N_1, N_2, N_3, N_{12}(l), N_{13}(m), 0; w_1, w_2, w_3)\}. \tag{37}
\end{aligned}$$

Using this \mathcal{R}'_Z instead of \mathcal{R}' in equation (23) yields an expression for $I'_{\mathcal{H}_1}$ which can be added to $I''_{\mathcal{H}_1}$ to form $I_{\mathcal{H}_1}$.

5. Discussion

In this paper, we have completed the discussion, begun in the first paper of this series [1], of the three-electron integrals arising in high precision energy level calculations on few electron atoms and ions using the Hylleraas–configuration interaction (Hy–CI) formalism. We provide a brief discussion of electron–nucleus interaction integrals and a detailed treatment of the remaining untreated three-electron integrals, those involving the one-electron kinetic energy operators.

The formulae we have given can be easily generalized to handle the integrals arising in a strictly Hylleraas calculation. We have deliberately chosen not to do so, since the resulting formulae are unnecessarily complicated for coding purposes when doing Hy–CI (due to the special nature of Hy–CI expansion terms). With the present formulation, the three-electron kinetic energy integrals are computed as special cases of three-electron electron repulsion integrals. We typically compute all three-electron integrals in large blocks, but for checking purposes we also have codes which allow us to calculate the needed auxiliary integrals entirely using Larsson sums. This slows down the calculation but verifies the correctness of the faster techniques.

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Appendix A. Condon and Shortley c^k s

A Condon and Shortley coefficient [10] is defined by

$$c^k(l, m; l', m') = \sqrt{\frac{2}{2k+1}} \int_0^\pi \Theta(km - m')\Theta(lm)\Theta(l'm') \sin \theta \, d\theta. \tag{A.1}$$

This can be expressed equivalently in terms of the spherical harmonics $Y_l^m(\theta, \phi)$ as

$$c^k(l, m; l', m') = \sqrt{\frac{4\pi}{2k+1}} \int Y_k^{m-m'}(\theta, \phi) Y_l^{m*}(\theta, \phi) Y_{l'}^{m'}(\theta, \phi) \sin \theta \, d\theta \, d\phi. \tag{A.2}$$

There is a substantial body of work on the evaluation of c^k coefficients (actually on the closely related Wigner $3j$ -symbols) at the double precision level of accuracy but very little in the way of numerical results at the quadruple precision level of accuracy. Our approach is to put the c^k integral into the ‘Gaunt’ form⁵, since the Gaunt coefficient is equivalent to

⁵ [10, p 52, equation (18) and p 176, equation (11).]

the c^k coefficient except for a phase factor and is an efficient approach in terms of number of arithmetic operations. As the l, l' arguments increase; however, there can be a problem with exponent and/or mantissa overflow. This has long been known, and several recursive methods that circumvent the problem have been developed [16–18]. This work has been done at the DP level and has been particularly effective for large values (> 100) of l and l' . However, these methods are not especially efficient and in this work we are not interested in large values of the c^k arguments.

The advantage of the Gaunt formulation, using ordinary factorials, is that the calculation can be kept ‘exact’ for $l, l' \leq 7$ using DP arithmetic and for $l, l' \leq 14$ using QP arithmetic (with attention to detail in the numerics). These limits are set by mantissa overflow. A significant improvement in these l, l' limits is possible if one uses a prime factor representation (PFR) for the factorials. In this case, exact results are obtained for $l, l' \leq 15$ using DP and $l, l' \leq 30$ using QP. The reason for this is that a large common factor can be trivially factored out of each term in the Gaunt sum, thus delaying the point at which mantissa overflow occurs in the summation. Once mantissa overflow occurs the substantial differencing inherent in the Gaunt summation becomes a problem, even in the PFR case. For example, in the PFR case, for $l, l' = 14$ four digits are lost in taking the sum, while for $l, l' = 30$ over 9 digits are lost.

Emphasis in this work has been on accuracy and not execution speed. However, since the exact Gaunt formulation is a minimum operation one, the execution times turn out to be quite acceptable, namely, approximately 0.25–0.30 μs per coefficient using DP and approximately 3 μs per coefficient using QP (these times are for a generic PC (1.90 GHz Pentium III)).

Appendix B. Recurrence relationships for $W_{fgh}(\alpha\beta\gamma)$ for $f, h \geq 0, g < 0$

As explained in section 3.2, the case $g < 0, f, h \geq 0$ can arise in the three-electron kinetic energy integrals, whereas it cannot in the other three-electron interaction integrals treated in the first paper in this series [1]. A suitable recursion scheme for this new W -function case involves the V -function defined by

$$V(mn; \alpha\beta) \equiv V_{mn}(\alpha\beta) = \int_0^\infty x^m e^{-\alpha x} dx \int_x^\infty y^n e^{-\beta y} dy, \quad (m \geq 0, m+n \geq -1). \quad (\text{B.1})$$

The W -function is defined by

$$W(fgh; \alpha\beta\gamma) \equiv W_{fgh}(\alpha\beta\gamma) = \int_0^\infty x^f e^{-\alpha x} dx \int_x^\infty y^g e^{-\beta y} dy \int_y^\infty z^h e^{-\gamma z} dz, \\ (f \geq 0, f+g \geq -1, f+g+h \geq -2). \quad (\text{B.2})$$

For $h = 0$, i.e. in the f, g plane, the W 's are related to the V 's in a very simple way, namely,

$$W_{fg0}(\alpha\beta\gamma) = \gamma^{-1} V_{fg}(\alpha, \beta + \gamma), \quad (f \geq 0, f+g \geq -1). \quad (\text{B.3})$$

Then we can use

$$W_{fgh}(\alpha\beta\gamma) = \gamma^{-1} [h W_{f,g,h-1}(\alpha\beta\gamma) + V_{f,g+h}(\alpha, \beta + \gamma)], \\ (f \geq 0, f+g \geq -1, f+g+h \geq -1, h \geq 1) \quad (\text{B.4})$$

to raise h in a stable fashion. Note that we need $V_{f,g+h}(\alpha, \beta + \gamma)$ for $f = 0, f_{\max}$ and $g+h = g_{\min}, g_{\max} + h_{\max}$. The accurate calculation of this array has been discussed in the first paper in this series. The recurrence scheme is stable (the V 's are all ≥ 0 and the recurrence relation has no subtractions) and the integral accuracy will be as accurate as the calculation of the V integrals.

Addenda

In equation (23) in the first paper in this series [1] we incorrectly stated the explicit finite sum of Frolov and Smith [19] for the W_{fgh} functions for the special case of $f, g, h \geq 0$. The correct formula is

$$W_{fgh}(\alpha\beta\gamma) = \sum_{\sigma=0}^h C_h^\sigma A_\sigma(\gamma) V_{f,g+h-\sigma}(\alpha, \beta + \gamma). \quad (\text{B.5})$$

In equation (7) in [2] we gave the spherical harmonic addition theorem to be

$$P_l(\cos \theta_{12}) = \frac{4\pi}{(2l+1)} \sum_{m=-l}^l Y_l^{-m}(1) Y_l^m(2). \quad (\text{B.6})$$

That should have been

$$P_l(\cos \theta_{12}) = \frac{4\pi}{(2l+1)} \sum_{m=-l}^l (-1)^m Y_l^{-m}(1) Y_l^m(2). \quad (\text{B.7})$$

This can also be written as

$$P_l(\cos \theta_{12}) = \frac{4\pi}{(2l+1)} \sum_{m=-l}^l Y_l^{m*}(1) Y_l^m(2) \quad (\text{B.8})$$

since the Condon–Shortley phase condition is [10]

$$Y_l^{m*}(\theta, \phi) = (-1)^m Y_l^{-m}(\theta, \phi). \quad (\text{B.9})$$

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