Integral Evaluation using the McMurchie–Davidson Scheme

Jannik P. Roth

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Abstract

This document is a short explanation of the integral evaluation scheme introduced by McMurchie and Davidson in Ref. [1]. It explains the theory and implementation of the algorithms necessary to compute the overlap, kinetic and Coulomb integrals which are necessary for many quantum chemical calculations. For a more in-depth look, the reader is referred to Ref. [2].

This document is part of a the `eduHF` repository which can be found at github.com/jannik-roth/eduHF. If you find any mistake, please contact me via mail jannikproth@gmail.com

Contents

1 Hermite Gaussians

A Hermite Gaussian function $\Lambda_{\text{tuv}}(\boldsymbol{r}, p, \boldsymbol{P})$ is defined as:[2]

$$\Lambda_{tuv}(\boldsymbol{r}, p, \boldsymbol{P}) = \left(\frac{\partial}{\partial P_x}\right)^t \left(\frac{\partial}{\partial P_y}\right)^u \left(\frac{\partial}{\partial P_z}\right)^v \exp\left(-p r_p^2\right) \tag{1}$$

with $r_{\text{P}} = |\boldsymbol{r} - \boldsymbol{P}|$. It can be separated as follows:

$$\Lambda_{tuv}(\boldsymbol{r}, p, \boldsymbol{P}) = \Lambda_t(x, p, P_x)\Lambda_u(y, p, P_y)\Lambda_v(z, p, P_z) \tag{2}$$

which allows treating the components independently.
From the definition it is obvious that:

$$\frac{\partial \Lambda_t}{\partial P_x} = -\frac{\partial \Lambda_t}{\partial x} = \Lambda_{t+1} \tag{3}$$

For later use note that:

$$\Lambda_{t+1} = \left(\frac{\partial}{\partial P_x}\right)^t \frac{\partial \Lambda_0}{\partial P_x} = 2p \left(\frac{\partial}{\partial P_x}\right)^t x_p \Lambda_0 \ . \tag{4}$$

To interchange x_P and the derivative, a commutator is being used

$$\left[\left(\frac{\partial}{\partial P_x}\right)^t, x_p\right] = -t \left(\frac{\partial}{\partial P_x}\right)^{t-1} \tag{5}$$

which leads to

$$\Lambda_{t+1} = 2p \left(x_p \Lambda_t - t\Lambda_{t-1}\right) \tag{6}$$

where the following property is used

$$\Lambda_t = 0 \text{ for } t < 0 \ . \tag{7}$$

To describe what happens by multiplying a Hermite Gaussian with x_P, simple rearrangement of eq. (6) is necessary.

$$x_p \Lambda_t = \frac{1}{2p} \Lambda_{t+1} + t\Lambda_{t-1} \tag{8}$$

The calculation of integrals over Hermite Gaussians is the next step.

$$\int_{-\infty}^{+\infty} \Lambda_t(x) \mathrm{d}x = \int_{-\infty}^{+\infty} \left(\frac{\partial}{\partial P_x}\right)^t \exp\left(-p x_p^2\right) \mathrm{d}x = \left(\frac{\partial}{\partial P_x}\right)^t \int_{-\infty}^{+\infty} \exp\left(-p x_p^2\right) \mathrm{d}x \tag{9}$$

Since the integral on the right hand side is independent of P_x, above expression can be simplified.

$$\int_{-\infty}^{+\infty} \Lambda_t(x) \mathrm{d}x = \delta_{t0} \sqrt{\frac{\pi}{p}} \tag{10}$$

The definition and description of overlap distributions is useful where the aim is to express the two-center Cartesian overlap distribution in Hermite Gaussians. Let the the first Cartesian function be of order i in x_P and the second of order j. The overlap distribution Ω_{ij} can be described by an expansion in the Hermite Gaussians up to order $t \leq i + j$.

$$\Omega_{i,j} = \sum_{t=0}^{i+j} E_t^{i,j} \Lambda_t \tag{11}$$

Here, the expansion coefficients $E_t^{i,j}$ which are constant and thereby independent of the electronic coordinates are introduced. These can be calculated using recursion relations:

$$E_t^{i+1,j} = \frac{1}{2p} E_{t-1}^{i,j} + X_{PA} E_t^{i,j} + (t+1) E_{t+1}^{i,j} \ , \tag{12}$$

$$E_t^{i,j+1} = \frac{1}{2p} E_{t-1}^{i,j} + X_{PB} E_t^{i,j} + (t+1) E_{t+1}^{i,j} \ . \tag{13}$$

where the starting value is defined by

$$E_0^{0,0} = K_{ab}^x = \exp\left(-\mu X_{AB}^2\right) \ . \tag{14}$$

The next step is to calculate the Cartesian overlap distributions that were generated from the one-center Hermite Gaussians using the expansion coefficients $E_t^{i,j}$. This can be done recursively by introducing an auxiliary distribution $\Omega_{i,j}^t$.

$$\Omega_{i,j}^t = K_{ab}^x x_\mathrm{A}^i x_\mathrm{B}^j \Lambda_t(x_\mathrm{P}) \tag{15}$$

This auxiliary distribution is equivalent to the Cartesian overlap distributions for $t = 0$. They can be evaluated using recursion relations:

$$\Omega_{i+1,j}^{t} = t\Omega_{i,j}^{t-1} + X_{PA}\Omega_{i,j}^{t} + \frac{1}{2p}\Omega_{i,j}^{t+1} \ , \tag{16}$$

$$\Omega_{i,j+1}^{t} = t\Omega_{i,j}^{t-1} + X_{PB}\Omega_{i,j}^{t} + \frac{1}{2p}\Omega_{i,j}^{t+1} \ . \tag{17}$$

2 Calculating Integrals using the McMurchie–Davidson Scheme

The McMurchie–Davidson scheme makes intensive use of the previously derived properties of Hermite Gaussians for the integral evalutation.[1,2]

2.1 Overlap Integrals

The overlap integral between two Cartesian Gaussians G_i and G_j is defined as

$$S_{ij} = \langle G_i \,|\, G_j \rangle \ . \tag{18}$$

Using the Hermite expansion the following expression is obtained

$$S_{ij} = \sum_{t=0}^{i+j} E_t^{i,j} \int_{-\infty}^{+\infty} \Lambda_t \mathrm{d}x = \sum_{t=0}^{i+j} E_t^{i,j} \delta_{t0} \sqrt{\frac{\pi}{p}} \ . \tag{19}$$

Summarizing all three dimensions (x, y and z) yields:

$$S_{ab} = E_0^{i,j} E_0^{k,l} E_0^{m,n} \left(\frac{\pi}{p}\right)^{\frac{3}{2}} \ . \tag{20}$$

2.2 Coulomb Integrals

The one-electron Coulomb integral can be written as:

$$V_{t,u,v}^{e,f,g} = \int \Lambda_{t,u,v}(\boldsymbol{r}) \left(\frac{\partial}{\partial C_x}\right)^e \left(\frac{\partial}{\partial C_y}\right)^f \left(\frac{\partial}{\partial C_z}\right)^g \frac{1}{r_C} \mathrm{d}\boldsymbol{r} \ . \tag{21}$$

$V_{t,u,v}^{0,0,0}$ describes the potential, while $V_{t,u,v}^{1,0,0}$, $V_{t,u,v}^{0,1,0}$ and $V_{t,u,v}^{0,0,1}$ are the respective components of the electric field.
The two-electron Coulomb integral can be expressed as

$$V_{t,u,v;\tau,\nu,\phi} = \iint \frac{\Lambda_{t,u,v}(\boldsymbol{r_1}) \Lambda_{\tau,\nu,\phi}(\boldsymbol{r_2})}{r_{12}} \mathrm{d}\boldsymbol{r_1} \mathrm{d}\boldsymbol{r_2} \tag{22}$$

where $\Lambda_{t,u,v}$ is the Hermite Gaussian with an exponent p centered at the point $\boldsymbol{P}$ and $\Lambda_{\tau,\nu,\phi}$ is the Hermite Gaussian with an exponent q centered at the point $\boldsymbol{Q}$.
These integrals can be evaluated using the Boys functions F_n. Taking the normalization

into account yields:

$$V_{t,u,v}^{e,f,g} = \frac{2\pi}{p}\left(\frac{\partial}{\partial P_x}\right)^t\left(\frac{\partial}{\partial P_y}\right)^u\left(\frac{\partial}{\partial P_z}\right)^v\left(\frac{\partial}{\partial C_x}\right)^e\left(\frac{\partial}{\partial C_y}\right)^f\left(\frac{\partial}{\partial C_z}\right)^g F_0(pR_{PC}^2) \tag{23}$$

$$\begin{aligned} V_{t,u,v;\tau,\nu,\phi} =& \frac{2\pi^{5/2}}{pq\sqrt{p+q}}\left(\frac{\partial}{\partial P_x}\right)^t\left(\frac{\partial}{\partial P_y}\right)^u\left(\frac{\partial}{\partial P_z}\right)^v\left(\frac{\partial}{\partial Q_x}\right)^\tau\left(\frac{\partial}{\partial Q_y}\right)^\nu\left(\frac{\partial}{\partial Q_z}\right)^\phi \\ & \times F_0(\alpha R_{PQ}^2) \end{aligned} \tag{24}$$

with $\alpha = \frac{pq}{p+q}$.
The Boys functions are defined as

$$F_n(x) = \int_0^1 \exp\left(-xt^2\right) t^{2n} \mathrm{d}t \tag{25}$$

For small values of x they can be approximated by

$$F_n(0) = \int_0^1 t^{2n}\mathrm{d}t = \frac{1}{2n+1} \tag{26}$$

and for larger values the following recursion relation is used.

$$F_{n+1}(x) = \frac{(2n+1)F_n(x) - \exp(-x)}{2x} \tag{27}$$

with the starting value

$$F_0(x) = \frac{1}{2}\sqrt{\frac{\pi}{x}}\,\mathrm{erf}\left(\sqrt{x}\right) \tag{28}$$

The Boys functions depend only on the distance between the two centers, not on their absolute position in space which allows further simplification:

$$V_{t,u,v}^{e,f,g} = (-1)^{e+f+g}\frac{2\pi}{p}R_{t+e,u+f,v+g}(p, R_{PC}) \tag{29}$$

$$V_{t,u,v;\tau,\nu,\phi} = (-1)^{\tau+\nu+\phi}\frac{2\pi^{5/2}}{pq\sqrt{p+q}}R_{t+\tau,u+\nu,v+\phi}(\alpha, R_{PQ}) \tag{30}$$

with:

$$R_{t,u,v}(p, R_{PC}) = \left(\frac{\partial}{\partial P_x}\right)^t\left(\frac{\partial}{\partial P_y}\right)^u\left(\frac{\partial}{\partial P_z}\right)^v F_0(pR_{PC}^2) \tag{31}$$

The next task is to evaluate the Hermite Coulomb integrals $R_{t,u,v}^n(p, R_{PC})$. Introducing an auxiliary function $R_{tuv}^n(p, R_{\mathrm{PC}})$:

$$R_{t,u,v}^n(p, R_{PC}) = \left(\frac{\partial}{\partial P_x}\right)^t\left(\frac{\partial}{\partial P_y}\right)^u\left(\frac{\partial}{\partial P_z}\right)^v R_{0,0,0}^n(pR_{PC}^2) \tag{32}$$

with

$$R_{0,0,0}^n(p, R_{PC}^2) = (-2p)^n F_n(pR_{PC}^2)\ . \tag{33}$$

the following recursion relations are obtained:[2]

$$R_{t+1,u,v}^n(p, R_{PC}) = tR_{t-1,u,v}^{n+1}(p, R_{PC}) + X_{PC}R_{t,u,v}^{n+1}(p, R_{PC})\ , \tag{34}$$

$$R_{t,u+1,v}^n(p, R_{PC}) = uR_{t,u-1,v}^{n+1}(p, R_{PC}) + Y_{PC}R_{t,u,v}^{n+1}(p, R_{PC})\ , \tag{35}$$

$$R_{t,u,v+1}^n(p, R_{PC}) = vR_{t,u,v-1}^{n+1}(p, R_{PC}) + Z_{PC}R_{t,u,v}^{n+1}(p, R_{PC})\ . \tag{36}$$

In the next step the integrals over Cartesian Gaussians are generated from the Hermite integrals.
Using the overlap distributions in the expression of the Coulomb integrals leads to:

$$V_{ab}^{e,f,g} = \int \Omega_{ab}(\boldsymbol{r}) \left(\frac{\partial}{\partial C_x}\right)^e \left(\frac{\partial}{\partial C_y}\right)^f \left(\frac{\partial}{\partial C_z}\right)^g \frac{1}{r_C} \mathrm{d}\boldsymbol{r} \tag{37}$$

$$V_{abcd} = \iint \frac{\Omega_{ab}(\boldsymbol{r_1})\Omega_{cd}(\boldsymbol{r_2})}{r_{12}} \mathrm{d}\boldsymbol{r_1}\mathrm{d}\boldsymbol{r_2} \tag{38}$$

Inserting the Hermite expansion of the overlap distribution leads to:

$$V_{ab}^{e,f,g} = \sum_{t,u,v} E_{t,u,v}^{ab} \int \Lambda_{t,u,v}(\boldsymbol{r}) \left(\frac{\partial}{\partial C_x}\right)^e \left(\frac{\partial}{\partial C_y}\right)^f \left(\frac{\partial}{\partial C_z}\right)^g \frac{1}{r_C} \mathrm{d}\boldsymbol{r} \tag{39}$$

$$V_{abcd} = \sum_{t,u,v} E_{t,u,v}^{ab} \sum_{\tau,\nu,\phi} E_{\tau,\nu,\phi}^{cd} \iint \frac{\Lambda_{t,u,v}(\boldsymbol{r_1})\Lambda_{\tau,\nu,\phi}(\boldsymbol{r_2})}{r_{12}} \mathrm{d}\boldsymbol{r_1}\mathrm{d}\boldsymbol{r_2} \tag{40}$$

where a short notation is used $E_{t,u,v}^{ab} = E_t^{i,j} E_u^{k,l} E_v^{m,n}$.
Using the Hermite integrals leads to:

$$V_{ab}^{e,f,g} = (-1)^{e+f+g} \frac{2\pi}{p} \sum_{t,u,v} E_{t,u,v}^{ab} R_{t+e,u+f,v+g}(p, R_{PC}) \ , \tag{41}$$

$$V_{abcd} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \sum_{t,u,v} E_{t,u,v}^{ab} \sum_{\tau,\nu,\phi} (-1)^{\tau+\nu+\phi} E_{\tau,\nu,\phi}^{cd} R_{t+\tau,u+\nu,v+\phi}(\alpha, R_{PQ}) \ . \tag{42}$$

2.3 Kinetic Integral

When calculating the kinetic energy integrals the second derivative is necessary. This leads to expression (43)

$$\begin{aligned} T_{ab} = &-\frac{1}{2}\Big[j(j-1)E_0^{i,j-2}E_0^{k,l}E_0^{m,n} + l(l-1)E_0^{i,j}E_0^{k,l-2}E_0^{m,n} \\ &+n(n-1)E_0^{i,j}E_0^{k,l}E_0^{m,n-2}\Big]\left(\frac{\pi}{p}\right)^{3/2} \\ &- 2\beta^2\left[E_0^{i,j+2}E_0^{k,l}E_0^{m,n} + E_0^{i,j}E_0^{k,l+2}E_0^{m,n} + E_0^{i,j}E_0^{k,l}E_0^{m,n+2}\right]\left(\frac{\pi}{p}\right)^{3/2} \\ &+ \beta(2(j+l+n)+3)E_0^{i,j}E_0^{k,l}E_0^{m,n}\left(\frac{\pi}{p}\right)^{3/2} \end{aligned} \tag{43}$$

3 Derivatives of Integrals

The calculation of the analytical gradient of the system requires the computation of integral derivatives with respect to the atomic coordinates.
In this sub-chapter we will slightly alter the previously used naming convention. Basis functions will be denoted with arabic letter a, b, ... to be in line with the original literature.[3] The derivative with respect to an atomic coordinate is denoted with a preceding superscript, e. g. ${}^{(x)}a$ denotes the derivative of the basis function a with respect to the x-coordinate of the atomic core which a is centered at. If a is centered at a different core, its derivative is

clearly zero. For the integral this notation is expanded to also include which part of the integral to derive. E.g. ${}^{(1,x)}S_{ab}$ is the derivative of the overlap integral between the functions a and b with respect to the atomic coordinate of a certain core, which a is centered on.

$$ {}^{(1,x)}S_{ab} = \left\langle {}^{(x)}a \,\middle|\, b \right\rangle \tag{44} $$

Starting by differentiating the expansion of the overlap distribution. From its definition in eq. (11) it is clear that

$$ \frac{\partial \Omega_{i,j}}{\partial A_x} = \sum_{t=0}^{i+j+1} F_t^{i,j} \Lambda_t \tag{45} $$

with the new coefficients

$$ {}^{(1)}F_t^{i,j} = \alpha E_t^{i+1,j} - i E_t^{i-1,j} \,, \tag{46} $$

$$ {}^{(2)}F_t^{i,j} = \beta E_t^{i1,j+1} - j E_t^{i,j-1} \,. \tag{47} $$

Here the preceding superscript denotes which of the two functions that compose the overlap distribution is differentiated.
Note that in eq. (45) the limit of the sum is increased by one which means higher orders of the expansion coefficients have to be computed. All that is left to do now is to replace the summation over $E_t^{i,j}$ with the summation over $F_t^{i,j}$ in the integral evaluation.

$$ \sum_{t=0}^{i+j} E_t^{i,j} \rightarrow \sum_{t=0}^{i+j+1} {}^{(1/2)}F_t^{i,j} \tag{48} $$

For the overlap integrals S_{ab} this is straightforward. Using eq. (20) and replacing the appropriate expansion coefficient the following example is obtained:

$$ {}^{(1,x)}S_{ab} = {}^{(1)}F_0^{i,j} E_0^{k,l} E_0^{m,n} \left(\frac{\pi}{p}\right)^{\frac{3}{2}} \,. \tag{49} $$

Here the extended summation has no effect since only coefficients with $t = 0$ were considered.

For the kinetic integral, the procedure is analogous. Using eq. (43) and replacing yields:

$$ \begin{aligned} {}^{(1,x)}T_{ab} = &-\frac{1}{2}\Big[j(j-1) {}^{(1)}F_0^{i,j-2} E_0^{k,l} E_0^{m,n} + l(l-1) {}^{(1)}F_0^{i,j} E_0^{k,l-2} E_0^{m,n} \\ &+ n(n-1) {}^{(1)}F_0^{i,j} E_0^{k,l} E_0^{m,n-2} \Big] \left(\frac{\pi}{p}\right)^{3/2} \\ &- 2\beta^2 \left[{}^{(1)}F_0^{i,j+2} E_0^{k,l} E_0^{m,n} + {}^{(1)}F_0^{i,j} E_0^{k,l+2} E_0^{m,n} + {}^{(1)}F_0^{i,j} E_0^{k,l} E_0^{m,n+2} \right] \left(\frac{\pi}{p}\right)^{3/2} \\ &+ \beta(2(j+l+n)+3) {}^{(1)}F_0^{i,j} E_0^{k,l} E_0^{m,n} \left(\frac{\pi}{p}\right)^{3/2} \,. \end{aligned} \tag{50} $$

Note if both basis functions are centered at the same nucleus the derivative is equal to zero. This can be explained quite simply: if none of the basis functions are centered at the core A and we would like to differentiate with respect to one coordinate of nucleus A, then the integral is not affected by it and the derivative is thereby zero. If both are centers at A then the translational symmetry of the integrals also leads to a zero derivative.

For the derivatives of the potential integrals it is important to consider the properties of the derivatives. Using the translational symmetry and the product rule yields:

$$\left({}^{(x)}a^{(x)}b\,\middle|\,{}^{(x)}c^{(x)}d\right) = 0 = \left({}^{(x)}ab\middle|\,cd\right) + \left(a^{(x)}b\middle|\,cd\right) + \left(ab\,\middle|\,{}^{(x)}cd\right) + \left(ab\,\middle|\,c^{(x)}d\right) \tag{51}$$

Note that due to the eight-fold permutational symmetry:

$$\left(a^{(x)}b\middle|\,cd\right) = \left({}^{(x)}ba\middle|\,dc\right) \tag{52}$$

$$\left(ab\,\middle|\,{}^{(x)}cd\right) = \left({}^{(x)}cd\middle|\,ab\right) \tag{53}$$

$$\left(ab\,\middle|\,c^{(x)}d\right) = \left({}^{(x)}dc\middle|\,ab\right) \tag{54}$$

This means only one routine which is able to calculate the derivative of the two-electron integrals with respect to the atomic position of the first basis function in the integral is necessary. If the derivative is at a different position in the integral the equations above can be used to bring it into the first position.
Using eq. (42) and replacing the coefficients yields:

$${}^{(1x)}V_{abcd} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \sum_{t=0}^{i+j+1} {}^{(1)}F_t^{i,j} \sum_{u=0}^{k+l} E_u^{k,l} \sum_{v=0}^{m+n} E_v^{m,n} \sum_{\tau,\nu,\phi} (-1)^{\tau+\nu+\phi} E_{\tau,\nu,\phi}^{cd} R_{t+\tau,u+\nu,v+\phi}(\alpha, R_{PQ}) \tag{55}$$

The product rule can be used if more than one basis function is centered at the core A and the differentiation is carried out with respect to a coordinate of A.

$$\left({}^{(x)}a^{(x)}b\,\middle|\,{}^{(x)}cd\right) = -\left(ab\,\middle|\,c^{(x)}d\right) \tag{56}$$

$$\left({}^{(x)}a^{(x)}b\middle|\,cd\right) = \left({}^{(x)}ab\middle|\,cd\right) + \left(a^{(x)}b\middle|\,cd\right) \tag{57}$$

Considering the nuclei-electron potential of the form next. When computing just one addend, the translational symmetry can be used again:

$$\begin{aligned} 0 &= \left\langle {}^{(x)}a \left| {}^{(x)}\left(\frac{1}{\boldsymbol{r}-\boldsymbol{R}_A}\right) \right| {}^{(x)}b \right\rangle \\ &= \left\langle {}^{(x)}a \left| \frac{1}{\boldsymbol{r}-\boldsymbol{R}_A} \right| b \right\rangle + \left\langle a \left| {}^{(x)}\left(\frac{1}{\boldsymbol{r}-\boldsymbol{R}_A}\right) \right| b \right\rangle + \left\langle a \left| \left(\frac{1}{\boldsymbol{r}-\boldsymbol{R}_A}\right) \right| {}^{(x)}b \right\rangle \end{aligned} \tag{58}$$

Differentiating the basis functions is simple. Using eq. (41) yields:

$${}^{(1x)}V_{ab}^{e,f,g} = (-1)^{e+f+g} \frac{2\pi}{p} \sum_{t=0}^{i+j+1} {}^{(1)}F_t^{i,j} \sum_{u=0}^{k+l} E_u^{k,l} \sum_{v=0}^{m+n} E_v^{m,n} R_{t+e,u+f,v+g}(p, R_{PC}) \tag{59}$$

4 implementation

At the core of the McMurchie–Davidson scheme is the calculation of the coefficients $E_t^{i,j}$. For this a recursion relation can be used.

Result: Compute the coefficient $E_t^{i,j}$
if $t < 0$ *or* $t > i + j$ **then**
  return 0
end
else if $t = i = j = 0$ **then**
  return $\exp\left(-\frac{\alpha\beta}{\alpha+\beta}R_{\mathrm{AB}}^2\right)$
end
else if $i = 0$ **then**
  return $\frac{1}{2(\alpha+\beta)}E_{t-1}^{i,j-1} + \alpha\frac{R_{\mathrm{AB}}}{\alpha+\beta}E_t^{i,j-1} + (t+1)E_{t+1}^{i,j-1}$
end
else
  return $\frac{1}{2(\alpha+\beta)}E_{t-1}^{i-1,j} - \beta\frac{R_{\mathrm{AB}}}{\alpha+\beta}E_t^{i-1,j} + (t+1)E_{t+1}^{i-1,j}$
end

Algorithm 1: Computation of the coefficient $E_t^{i,j}$ within the McMurchie–Davidson scheme.

Result: Compute the coefficient $R_{t,u,v}^n$
if $t = u = v = 0$ **then**
  return $(-2p)^n F_n(pR_{PC}^2)$
end
else if $t = u = 0$ *and* $v > 0$ **then**
  return $(v-1)R_{t,u,v-2}^{n+1}(p, R_{PC}) + Z_{PC}R_{t,u,v-1}^{n+1}(p, R_{PC})$
end
else if $t = 0$ *and* $u > 0$ **then**
  return $(u-1)R_{t,u-2,v}^{n+1}(p, R_{PC}) + Y_{PC}R_{t,u-1,v}^{n+1}(p, R_{PC})$
end
else
  return $(t-1)R_{t-2,u,v}^{n+1}(p, R_{PC}) + X_{PC}R_{t-1,u,v}^{n+1}(p, R_{PC})$
end

Algorithm 2: Computation of the coefficient $R_{t,u,v}^n$ within the McMurchie–Davidson scheme.

The Boys funtions can be calculated as follows.

Result: Compute the boys function $F_n(x)$
if $x < 10^{-11}$ **then**
  return $\frac{1}{2n+1}$
end
else if $n = 0$ **then**
  return $\frac{1}{2}\sqrt{\frac{\pi}{x}}\,\mathrm{erf}\,(\sqrt{x})$
end
else
  return $\frac{(2n-1)F_{n-1}(x)-\exp(-x)}{2x}$
end

Algorithm 3: Computation of the boys function $F_n(x)$.

For the calculation of the integrals, the eqs. (20), (43), (41) and (42) can be used.

For the calculation of derivative of the integrals, the eqs. (49), (50), (59) and (55) can be used.

To compute all possibilities one must use the chain rule and the translational symmetry of the integrals as described in section 3.

References

(1) McMurchie, L. E.; Davidson, E. R. *J. Comput. Phys.* **1978**, *26*, 218–231.

(2) Helgaker, T.; Jorgensen, P.; Olsen, J., *Molecular Electronic-Structure Theory*, 2013.

(3) Helgaker, T.; Taylor, P. R. *Theor. Chim. Acta* **1992**, *83*, 177–183.