# EVALUATION OF MOLECULAR INTEGRALS IN A MIXED GAUSSIAN AND PLANE-WAVE BASIS BY MEANS OF THE FADDEEVA FUNCTION AND ITS DERIVATIVES

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*Dedicated to Professor Rudolf Zahradnik on the occasion of his 70th birthday.*

We present formulas for two-electron free-free exchange integrals and integrals with three Gaussians and one plane-wave function that are required in calculations of electron scattering by polyatomic molecules. The formulas of integrals with p- and d-type Gaussians were obtained by differentiation of the fundamental integrals $(sk'|sk)$ and $(ss|sk)$ that contain s-type Gaussians only and that may be evaluated by means of the Faddeeva function $w$. Explicit formulas are given for the two types of integrals in the spd Gaussian basis.
**Key words:** Electron scattering; Two-electron integrals; Exchange free-free integrals; Hybrid integrals; *Ab initio* methods; Quantum chemistry.

Evaluation of hybrid two-electron integrals is still a topical problem in calculations of electron scattering by polyatomic molecules[1], particularly in applications to molecular systems which may be of chemical interest. Watson and McKoy[2] derived formulas for these integrals already a long time ago. For their method, which is based on a partial wave expansion, McKoy and collaborators advocate[1] the use of highly parallelized algorithms. Apparently, the method is computationally very demanding for treatments of polyatomic molecular targets, and therefore new ways of calculation of hybrid two-electron integrals were looked for. Recently Kuang and Lin[3] derived formulas for two-electron integrals in a mixed Slater and plane-wave basis set but, in our opinion, in applications to electron scattering by polyatomic molecules it is preferable to use Gaussian basis sets. One of the authors examined[4] therefore the use of the Rys numerical quadrature[5], developed for effective calculation of two-electron integrals in the Gaus-

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sian basis in the electronic structure theory[6,7]. In this paper we follow the suggestion by Ostlund[8] that hybrid integrals may be calculated as is usual in the electronic structure theory for calculation of two-electron integrals over Gaussians[9], except that complex arguments must be used in incomplete gamma functions[8,10]. Watson and McKoy[2] did not consider this method profitable because the formulas for p-, d-, and higher Gaussians, obtained by differentiation of the integral for s-type Gaussians, quickly become complicated and error-prone. However, our test calculations show that the method may be competitive to other methods for certain ranges of the argument of the incomplete gamma function. We considered it therefore expedient to publish the formulas we have derived for exchange free-free integrals and for integrals with three Gaussians and one plane-wave function.

## COMPUTATIONAL METHOD

A product of a Gaussian and a plane-wave function may be expressed as a product of two Gaussians, multiplied by an preeponential factor

$$\mathrm{e}^{-\alpha(\boldsymbol{r}-\boldsymbol{A})^2}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{A}}\,\mathrm{e}^{-\frac{k^2}{2\alpha}}\,\mathrm{e}^{-\frac{\alpha}{2}(\boldsymbol{r}-\boldsymbol{A})^2}\,\mathrm{e}^{-\frac{\alpha}{2}\left(\boldsymbol{r}-\boldsymbol{A}-\mathrm{i}\frac{\boldsymbol{k}}{\alpha}\right)^2}\ . \tag{1}$$

The exchange free-free integral

$$\begin{aligned}(g_ik'|g_jk) \equiv \iint \mathrm{e}^{-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}_1}\,(x_1-A_x)^{m^x}(y_1-A_y)^{m^y}\,(z_1-A_z)^{m^z}\,\mathrm{e}^{-\alpha(\boldsymbol{r}_1-\boldsymbol{A})^2}\left(\frac{1}{r_{12}}\right)\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_2}\\ \times (x_2-B_x)^{n^x}\,(y_2-B_y)^{n^y}(z_2-B_z)^{n^z}\,\mathrm{e}^{-\beta(\boldsymbol{r}_2-\boldsymbol{B})^2}\,\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\ ,\end{aligned} \tag{2}$$

and the integral with three Gaussians and one plane-wave function

$$\begin{aligned}(g_ig_j|g_kk) \equiv \iint (x_1-A_x)^{m^x}\,(y_1-A_y)^{m^y}\,(z_1-A_z)^{m^z}\,\mathrm{e}^{-\alpha(\boldsymbol{r}_1-\boldsymbol{A})^2}(x_1-B_x)^{n^x}\,(y_1-B_y)^{n^y}\,(z_1-B_z)^{n^z}\\ \times\,\mathrm{e}^{-\beta(\boldsymbol{r}_1-\boldsymbol{B})^2}\left(\frac{1}{r_{12}}\right)(x_2-C_x)^{l^x}\,(y_2-C_y)^{l^y}\,(z_2-C_z)^{l^z}\,\mathrm{e}^{-\gamma(\boldsymbol{r}_2-\boldsymbol{C})^2}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_2}\,\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\end{aligned} \tag{3}$$

may be expressed as

$$\begin{aligned}(g_ik'|g_jk) = \mathrm{e}^{-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{A}}\,\mathrm{e}^{-\frac{k'^2}{4\alpha}}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{B}}\,\mathrm{e}^{-\frac{k^2}{4\beta}}\iint (x_1-A_x)^{m^x}\,(y_1-A_y)^{m^y}\,(z_1-A_z)^{m^z}\,\mathrm{e}^{-\alpha(\boldsymbol{r}_1-\boldsymbol{A}+\frac{\mathrm{i}\boldsymbol{k}'}{2\alpha})^2}\left(\frac{1}{r_{12}}\right)\\ \times (x_2-B_x)^{n^x}\,(y_2-B_y)^{n^y}(z_2-B_z)^{n^z}\,\mathrm{e}^{-\beta(\boldsymbol{r}_2-\boldsymbol{B}-\frac{\mathrm{i}\boldsymbol{k}}{2\beta})^2}\,\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\ ,\end{aligned} \tag{4}$$

and

$$(g_i g_j | g_k k) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{C}}\,\mathrm{e}^{-\frac{k^2}{2\gamma}} \iint (x_1 - A_x)^{m^x} (y_1 - A_y)^{m^y} (z_1 - A_z)^{m^z} \mathrm{e}^{-\alpha(\boldsymbol{r}_1 - \boldsymbol{A})^2} (x_1 - B_x)^{n^x} (y_1 - B_y)^{n^y}$$
$$\times (z_1 - B_z)^{n^z} \mathrm{e}^{-\beta(\boldsymbol{r}_1 - \boldsymbol{B})^2} \left(\frac{1}{r_{12}}\right) (x_2 - C_x)^{l^x} (y_2 - C_y)^{l^y} (z_2 - C_z)^{l^z} \mathrm{e}^{-\frac{\gamma}{2}(\boldsymbol{r}_2 - \boldsymbol{C})^2} \mathrm{e}^{-\frac{\gamma}{2}(\boldsymbol{r}_2 - \boldsymbol{C} - \frac{\mathrm{i}\boldsymbol{k}}{\gamma})^2} \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \qquad (5)$$

For exchange free-free integrals define the complex vectors

$$\boldsymbol{P} = \boldsymbol{A} - \frac{\mathrm{i}}{2\alpha}\boldsymbol{k}' \ , \qquad (6)$$

$$\boldsymbol{Q} = \boldsymbol{B} + \frac{\mathrm{i}}{2\beta}\boldsymbol{k} \qquad (7)$$

and the constant

$$f = \mathrm{e}^{-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{A}}\,\mathrm{e}^{-\frac{k'^2}{4\alpha}}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{B}}\,\mathrm{e}^{-\frac{k^2}{4\beta}} \ . \qquad (8)$$

Then the fundamental integral for s-type Gaussians becomes[10]

$$(sk'|sk) = \frac{2}{\sqrt{\pi}}\, a f F_0(z) \ , \qquad (9)$$

where

$$a = \frac{\pi^3}{\alpha\beta\sqrt{\alpha+\beta}} \ , \qquad (10)$$

and

$$z = \frac{\alpha\beta}{\alpha+\beta}\,\overline{PQ}^{\,2} \ . \qquad (11)$$

$PQ$ is a distance between the points P and Q. For integrals with three Gaussians and one plane-wave function we define

$$P_x = \frac{\alpha A_x + \beta B_x}{\alpha + \beta}\ ,\ P_y = \frac{\alpha A_y + \beta B_y}{\alpha + \beta}\ ,\ P_z = \frac{\alpha A_z + \beta B_z}{\alpha + \beta}\ , \qquad (12)$$

$$\boldsymbol{Q} = \boldsymbol{C} + \frac{\mathrm{i}}{2\gamma}\boldsymbol{k}\ , \qquad (13)$$

$$f = \mathrm{e}^{-\frac{\alpha\beta}{\alpha+\beta}\overline{AB}^2}\ \mathrm{e}^{-\frac{k^2}{4\gamma}}\ \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{C}}\ , \qquad (14)$$

and the fundamental integral for s-type Gaussians becomes

$$(ss|sk) = \frac{2}{\sqrt{\pi}} afF_0(z)\ , \qquad (15)$$

where

$$a = \frac{\pi^3}{(\alpha + \beta)\gamma\sqrt{\alpha + \beta + \gamma}}\ , \qquad (16)$$

and

$$z = \frac{(\alpha + \beta)\gamma}{\alpha + \beta + \gamma}\overline{PQ}^{\,2}\ . \qquad (17)$$

For both types of integrals we define a new variable

$$t = \mathrm{i}\sqrt{z}\ , \qquad (18)$$

which permits us to express the $F_0$ function by means of the $w$ function[8,11], which is also called the Faddeeva function, as

$$F_0(z) = \frac{\sqrt{\pi}}{2}\frac{\mathrm{i}}{t}\left[1 - w(t)\mathrm{e}^{t^2}\right]\ . \qquad (19)$$

The Faddeeva function $w$ may be calculated as recommended by Gautschi[12], or more conveniently by using the FORTRAN subroutine WFOZ (ref.[13]). Formulas for p-, d-, and higher Gaussians may be obtained by differentiation of the basic formulas (*9*) and (*15*). For convenience we define the function

$$W_0(t) = \frac{\mathrm{i}}{t}\left[1 - w(t)\mathrm{e}^{t^2}\right] , \tag{20}$$

where for the expression in the brackets we will use the notation

$$b(t) = 1 - w(t)\mathrm{e}^{t^2} . \tag{21}$$

For the derivatives of $W_0$ it holds

$$\frac{\mathrm{d}^n W_0(t)}{\mathrm{d}t^n} = -\frac{n}{t}\frac{\mathrm{d}^{n-1} W_0(t)}{\mathrm{d}t^{n-1}} + \frac{\mathrm{i}}{t}\frac{\mathrm{d}^n b(t)}{\mathrm{d}t^n} , \tag{22}$$

and by using the recursive expression[11] for the derivatives of the $w$ function

$$\frac{\mathrm{d}^{n+2} w(t)}{\mathrm{d}t^{n+2}} + 2t\frac{\mathrm{d}^{n+1} w(t)}{\mathrm{d}t^{n+1}} + 2(n+1)\frac{\mathrm{d}^n w(t)}{\mathrm{d}t^n} = 0 \tag{23}$$

we have

$$\frac{\mathrm{d}^n b(t)}{\mathrm{d}t^n} = \left[(n-1)!\sum_{i=0}^{[(n-1)/2]}\frac{(2t)^{n-1-2i}}{i!(n-1-2i)!}\right]\frac{\mathrm{d}b(t)}{\mathrm{d}t} . \tag{24}$$

The term in the brackets is equal to the expression for the Hermite polynomial $H_{n-1}(t)$ in which the factor for sign was dropped. For $\mathrm{d}b(t)/\mathrm{d}t$ it holds

$$\frac{\mathrm{d}b(t)}{\mathrm{d}t} = -\frac{2\mathrm{i}}{\sqrt{\pi}}\mathrm{e}^{t^2} . \tag{25}$$

For the derivatives of $W_0$ with respect to the Cartesian coordinates of the points P and Q on which the Gaussians are centered we have

$$\frac{\partial W_0}{\partial P_i} = \frac{\partial W_0}{\partial t}\frac{\partial t}{\partial P_i} , \tag{26}$$

$$\frac{\partial W_0}{\partial Q_i} = -\frac{\partial W_0}{\partial P_i} \quad , \tag{27}$$

$$\frac{\partial^2 W_0}{\partial P_i \partial P_j} = \frac{\partial^2 W_0}{\partial t^2}\frac{\partial t}{\partial P_i}\frac{\partial t}{\partial P_j} + \frac{\partial W_0}{\partial t}\frac{\partial^2 t}{\partial P_i \partial P_j} \quad , \tag{28}$$

$$\frac{\partial^2 W_0}{\partial P_i \partial P_j} = \frac{\partial^2 W_0}{\partial Q_i \partial Q_j} \quad , \tag{29}$$

$$\frac{\partial^2 W_0}{\partial P_i \partial Q_j} = -\frac{\partial^2 W_0}{\partial P_i \partial P_j} \quad , \tag{30}$$

$$\frac{\partial^3 W_0}{\partial P_i \partial P_j \partial P_k} = \frac{\partial^3 W_0}{\partial t^3}\frac{\partial t}{\partial P_i}\frac{\partial t}{\partial P_j}\frac{\partial t}{\partial P_k} + \frac{\partial^2 W_0}{\partial t^2}\left(\frac{\partial^2 t}{\partial P_i \partial P_j}\frac{\partial t}{\partial P_k} + \frac{\partial^2 t}{\partial P_i \partial P_k}\frac{\partial t}{\partial P_j} + \frac{\partial^2 t}{\partial P_j \partial P_k}\frac{\partial t}{\partial P_i}\right)$$

$$+ \frac{\partial W_0}{\partial t}\frac{\partial^3 t}{\partial P_i \partial P_j \partial P_k} \quad , \tag{31}$$

$$\frac{\partial^4 W_0}{\partial P_i \partial P_j \partial P_k \partial P_l} = \frac{\partial^4 W_0}{\partial t^4}\frac{\partial t}{\partial P_i}\frac{\partial t}{\partial P_j}\frac{\partial t}{\partial P_k}\frac{\partial t}{\partial P_l}$$

$$+ \frac{\partial^3 W_0}{\partial t^3} P_{6,ijkl}\frac{\partial^2 t}{\partial P_i \partial P_j}\frac{\partial t}{\partial P_k}\frac{\partial t}{\partial P_l} + \frac{\partial^2 W_0}{\partial t^2}\left( P_{4,ijkl}\frac{\partial^3 t}{\partial P_i \partial P_j \partial P_k}\frac{\partial t}{\partial P_l} + P_{3,ijkl}\frac{\partial^2 t}{\partial P_i \partial P_j}\frac{\partial^2 t}{\partial P_k \partial P_l}\right)$$

$$+ \frac{\partial W_0}{\partial t}\frac{\partial^4 t}{\partial P_i \partial P_j \partial P_k \partial P_l} \quad , \tag{32}$$

$$\frac{\partial^5 W_0}{\partial P_i \partial P_j \partial P_k \partial P_l \partial P_m} = \frac{\partial^5 W_0}{\partial t^5}\frac{\partial t}{\partial P_i}\frac{\partial t}{\partial P_j}\frac{\partial t}{\partial P_k}\frac{\partial t}{\partial P_l}\frac{\partial t}{\partial P_m}$$

$$+ \frac{\partial^4 W_0}{\partial t^4} P_{10,ijklm}\ \frac{\partial^2 t}{\partial P_i \partial P_j}\frac{\partial t}{\partial P_k}\frac{\partial t}{\partial P_l}\frac{\partial t}{\partial P_m}$$

$$+ \frac{\partial^3 W_0}{\partial t^3}\left( P_{10,ijklm}\ \frac{\partial^3 t}{\partial P_i \partial P_j \partial P_k}\frac{\partial t}{\partial P_l}\frac{\partial t}{\partial P_m} + P_{15,ijklm}\ \frac{\partial^2 t}{\partial P_i \partial P_j}\frac{\partial^2 t}{\partial P_k \partial P_l}\frac{\partial t}{\partial P_m}\right)$$

$$+\frac{\partial^2 W_0}{\partial t^2}\left(P_{5,ijklm}\ \frac{\partial^4 t}{\partial P_i \partial P_j \partial P_k \partial P_l}\frac{\partial t}{\partial P_m}+P_{10,ijklm}\ \frac{\partial^3 t}{\partial P_i \partial P_j \partial P_k}\frac{\partial^2 t}{\partial P_l \partial P_m}\right)$$

$$+\frac{\partial W_0}{\partial t}\frac{\partial^5 t}{\partial P_i \partial P_j \partial P_k \partial P_l \partial P_m}\ , \tag{33}$$

$$\frac{\partial^6 W_0}{\partial P_i \partial P_j \partial P_k \partial P_l \partial P_m \partial P_n}=\frac{\partial^6 W_0}{\partial t^6}\frac{\partial t}{\partial P_i}\frac{\partial t}{\partial P_j}\frac{\partial t}{\partial P_k}\frac{\partial t}{\partial P_l}\frac{\partial t}{\partial P_m}\frac{\partial t}{\partial P_n}$$

$$+\frac{\partial^5 W_0}{\partial t^5}P_{15,ijklmn}\ \frac{\partial^2 t}{\partial P_i \partial P_j}\frac{\partial t}{\partial P_k}\frac{\partial t}{\partial P_l}\frac{\partial t}{\partial P_m}\frac{\partial t}{\partial P_n}$$

$$+\frac{\partial^4 W_0}{\partial t^4}\left(P_{20,ijklmn}\ \frac{\partial^3 t}{\partial P_i \partial P_j \partial P_k}\frac{\partial t}{\partial P_l}\frac{\partial t}{\partial P_m}\frac{\partial t}{\partial P_n}+P_{45,ijklmn}\ \frac{\partial^2 t}{\partial P_i \partial P_j}\frac{\partial^2 t}{\partial P_k \partial P_l}\frac{\partial t}{\partial P_m}\frac{\partial t}{\partial P_n}\right)$$

$$+\frac{\partial^3 W_0}{\partial t^3}\left(P_{15,ijklmn}\ \frac{\partial^4 t}{\partial P_i \partial P_j \partial P_k \partial P_l}\frac{\partial t}{\partial P_m}\frac{\partial t}{\partial P_n}+P_{60,ijklmn}\ \frac{\partial^3 t}{\partial P_i \partial P_j \partial P_k}\frac{\partial^2 t}{\partial P_l \partial P_m}\frac{\partial t}{\partial P_n}\right.$$

$$\left.+P_{15,ijklmn}\frac{\partial^2 t}{\partial P_i \partial P_j}\frac{\partial^2 t}{\partial P_k \partial P_l}\frac{\partial^2 t}{\partial P_m \partial P_n}\right)$$

$$+\frac{\partial^2 W_0}{\partial t^2}\left(P_{6,ijklmn}\ \frac{\partial^5 t}{\partial P_i \partial P_j \partial P_k \partial P_l \partial P_m}\frac{\partial t}{\partial P_n}+P_{15,ijklmn}\ \frac{\partial^4 t}{\partial P_i \partial P_j \partial P_k \partial P_l}\frac{\partial^2 t}{\partial P_m \partial P_n}\right.$$

$$\left.+P_{10,ijklmn}\ \frac{\partial^3 t}{\partial P_i \partial P_j \partial P_k}\frac{\partial^3 t}{\partial P_l \partial P_m \partial P_n}\right)$$

$$+\frac{\partial W_0}{\partial t}\frac{\partial^5 t}{\partial P_i \partial P_j \partial P_k \partial P_l \partial P_m}\ . \tag{34}$$

The subscripts $i, j, k, l$ mean x, y, z components of the position vectors $\boldsymbol{P}$ and $\boldsymbol{Q}$, and $P_{n,ij\ldots}$ means $n$ permutations of $i, j$... As in the second derivatives, any single change of $P_i$ by $Q_i$ in the third and higher derivatives leads to the change of sign. Expressions for the derivatives of $t$ with respect to the Cartesian coordinates depend on the type of the integral. Therefore we present them separately for exchange free-free integrals and for integrals with three Gaussians and one plane-wave function.

*Special Expressions for Exchange Free-Free Integrals*

$$\frac{\partial t}{\partial A_i} = \mathrm{i}\sqrt{\frac{\alpha\beta}{\alpha+\beta}}\,\frac{P_i - Q_i}{PQ} \;, \tag{35}$$

$$\frac{\partial t}{\partial B_i} = -\frac{\partial t}{\partial A_i} \tag{36}$$

The symbols $A$, $B$, $\alpha$, $\beta$, $P$, and $Q$ have the same meaning as in Eqs (*2* ),(*6*), and (*7*). For higher derivatives we have

$$\frac{\partial^2 t}{\partial A_i \partial A_j} = -\delta_{ij}\frac{\alpha\beta}{\alpha+\beta}\frac{1}{t} - \frac{\partial t}{\partial A_i}\frac{\partial t}{\partial A_j}\frac{1}{t} \;, \tag{37}$$

$$\frac{\partial^2 t}{\partial A_i \partial B_j} = -\frac{\partial^2 t}{\partial A_i \partial A_j} \;, \tag{38}$$

$$\frac{\partial^3 t}{\partial A_i \partial A_j \partial A_k} = -\frac{1}{t}\left(\frac{\partial^2 t}{\partial A_i \partial A_j}\frac{\partial t}{\partial A_k} + \frac{\partial^2 t}{\partial A_i \partial A_k}\frac{\partial t}{\partial A_j} + \frac{\partial^2 t}{\partial A_j \partial A_k}\frac{\partial t}{\partial A_i}\right), \tag{39}$$

$$\frac{\partial^3 t}{\partial A_i \partial A_j \partial B_k} = -\frac{\partial^3 t}{\partial A_i \partial A_j \partial A_k} \;, \tag{40}$$

$$\frac{\partial^4 t}{\partial A_i \partial A_j \partial A_k \partial A_l} = -\frac{1}{t}\left(P_{4,ijkl}\frac{\partial^3 t}{\partial A_i \partial A_j \partial A_k}\frac{\partial t}{\partial A_l} + P_{3,ijkl}\frac{\partial^2 t}{\partial A_i \partial A_j}\frac{\partial^2 t}{\partial A_k \partial A_l}\right), \tag{41}$$

$$\frac{\partial^4 t}{\partial A_i \partial A_j \partial A_k \partial B_l} = -\frac{\partial^4 t}{\partial A_i \partial A_j \partial A_k \partial A_l} \;. \tag{42}$$

$P_4$ and $P_3$ mean that the terms are sums of four and three permutations in indices $i, j, k, l$, respectively. For convenience we define the following two vectors with the components

$$a_i = P_i - A_i \ , \tag{43}$$

$$b_i = Q_i - B_i \ . \tag{44}$$

Derivatives of the $W_0$ function with respect to the coordinates $A_i$ and $B_j$ are obtained readily from Eqs (*25*)–(*33*) by means of a substitution

$$\frac{\partial^n}{\partial A_i^n} = \frac{\partial^n}{\partial P_i^n} \ , \tag{45}$$

$$\frac{\partial^n}{\partial B_j^n} = \frac{\partial^n}{\partial Q_j^n} \ . \tag{46}$$

*Special Expressions for Integrals with Three Gaussians and One Plane-Wave Function*

$$\frac{\partial t}{\partial A_i} = \mathrm{i} \sqrt{\frac{(\alpha+\beta)\gamma}{\alpha+\beta+\gamma}} \frac{\alpha}{\alpha+\beta} \frac{P_i - Q_i}{\overline{PQ}} \ , \tag{47}$$

$$\frac{\partial t}{\partial B_j} = \mathrm{i} \sqrt{\frac{(\alpha+\beta)\gamma}{\alpha+\beta+\gamma}} \frac{\beta}{\alpha+\beta} \frac{P_j - Q_j}{\overline{PQ}} \ , \tag{48}$$

$$\frac{\partial t}{\partial C_k} = -\mathrm{i} \sqrt{\frac{(\alpha+\beta)\gamma}{\alpha+\beta+\gamma}} \frac{P_k - Q_k}{\overline{PQ}} \ . \tag{49}$$

The symbols $A$, $B$, $C$, $\alpha$, $\beta$, $\gamma$, $P$, and $Q$ have the same meaning as in Eqs (*3*), (*12*), and (*13*). For the second derivatives we have

$$\frac{\partial^2 t}{\partial A_i \partial A_j} = -\delta_{ij} \frac{\alpha^2\gamma}{(\alpha+\beta+\gamma)(\alpha+\beta)} \frac{1}{t} - \frac{\partial t}{\partial A_i} \frac{\partial t}{\partial A_j} \frac{1}{t} \ , \tag{50}$$

$$\frac{\partial^2 t}{\partial A_i \partial B_j} = -\delta_{ij} \frac{\alpha\beta\gamma}{(\alpha+\beta+\gamma)(\alpha+\beta)} \frac{1}{t} - \frac{\partial t}{\partial A_i} \frac{\partial t}{\partial B_j} \frac{1}{t} \ , \tag{51}$$

$$\frac{\partial^2 t}{\partial C_i \partial C_j} = -\delta_{ij} \frac{(\alpha+\beta)\gamma}{(\alpha+\beta+\gamma)} \frac{1}{t} - \frac{\partial t}{\partial C_i} \frac{\partial t}{\partial C_j} \frac{1}{t} \ , \tag{52}$$

$$\frac{\partial^2 t}{\partial A_i \partial C_j} = \delta_{ij} \frac{\alpha\gamma}{(\alpha+\beta+\gamma)} \frac{1}{t} - \frac{\partial t}{\partial A_i} \frac{\partial t}{\partial C_j} \frac{1}{t} \ . \tag{53}$$

For higher derivatives the following general formulas hold

$$\frac{\partial^3 t}{\partial R_i \partial S_j \partial T_k} = -\frac{1}{t} \left( \frac{\partial^2 t}{\partial R_i \partial S_j} \frac{\partial t}{\partial T_k} + \frac{\partial^2 t}{\partial R_i \partial T_k} \frac{\partial t}{\partial S_j} + \frac{\partial^2 t}{\partial S_j \partial T_k} \frac{\partial t}{\partial R_i} \right) , \tag{54}$$

$$\frac{\partial^4 t}{\partial R_i \partial S_j \partial T_k \partial U_l} = -\frac{1}{t} \left( P_{4,R_iS_jT_kU_l} \frac{\partial^3 t}{\partial R_i \partial S_j \partial T_k} \frac{\partial t}{\partial U_l} + P_{3,R_iS_jT_kU_l} \frac{\partial^2 t}{\partial R_i \partial S_j} \frac{\partial^2 t}{\partial T_k \partial U_l} \right) , \tag{55}$$

$$\frac{\partial^5 t}{\partial R_i \partial S_j \partial T_k \partial U_l \partial V_m} = -\frac{1}{t} \left( P_{5,R_iS_jT_kU_lV_m} \frac{\partial^4 t}{\partial R_i \partial S_j \partial T_k \partial U_l} \frac{\partial t}{\partial V_m} \right.$$

$$\left. + P_{10,R_iS_jT_kU_lV_m} \frac{\partial^3 t}{\partial R_i \partial S_j \partial T_k} \frac{\partial^2 t}{\partial U_l \partial V_m} \right) , \tag{56}$$

$$\frac{\partial^6 t}{\partial R_i \partial S_j \partial T_k \partial U_l \partial V_m \partial W_n} = -\frac{1}{t} \left( P_{6,R_iS_jT_kU_lV_mW_n} \frac{\partial^5 t}{\partial R_i \partial S_j \partial T_k \partial U_l \partial V_m} \frac{\partial t}{\partial W_n} \right.$$

$$\left. + P_{15,R_iS_jT_kU_lV_mW_n} \frac{\partial^4 t}{\partial R_i \partial S_j \partial T_k \partial U_l} \frac{\partial^2 t}{\partial V_m \partial W_n} + P_{10,R_iS_jT_kU_lV_mW_n} \frac{\partial^3 t}{\partial R_i \partial S_j \partial T_k} \frac{\partial^3 t}{\partial U_l \partial V_m \partial W_n} \right) . \tag{57}$$

Here $R$, $S$, $T$, $U$, $V$, $W$ may represent any of the centers $A$, $B$, $C$, and $P_n$ means that the respective term is a sum of $n$ permutations in indices $R_i$, $S_j$, $T_k$, $U_l$, $V_m$, $W_n$. For convenience we define the following three vectors with the components

$$a_i = P_i - A_i \ , \tag{58}$$

$$b_i = P_i - B_i \ , \tag{59}$$

$$c_i = Q_i - C_i \ . \tag{60}$$

Derivatives of the $W_0$ function with respect to the coordinates $A_i$ , $B_j$ , and $C_k$, may be obtained from Eqs (*25*)–(*33*) by means of the following substitution

$$\frac{\partial^n}{\partial A_i^n} = \left(\frac{\alpha}{\alpha+\beta}\right)^n \frac{\partial^n}{\partial P_i^n} \ , \qquad (61)$$

$$\frac{\partial^n}{\partial B_j^n} = \left(\frac{\beta}{\alpha+\beta}\right)^n \frac{\partial^n}{\partial P_j^n} \ , \qquad (62)$$

$$\frac{\partial^n}{\partial C_k^n} = \frac{\partial^n}{\partial Q_k^n} \ . \qquad (63)$$

**FORMULAS FOR INTEGRALS IN THE spd GAUSSIAN BASIS**

*Exchange Free-Free Integrals*

In the following equations (*64*)–(*69*) $a$ is defined by Eq. (*10*), $f$ by Eq. (*8*), and the vector components $a_i$ and $b_i$ by Eqs (*43*) and (*44*). By $s$, $p$, $d$ we mean unnormalized s-, p-, and d-type Cartesian Gaussians, with exponents α (at center A) and β (at center B)

$$(sk'|sk) = afW_0 \ , \qquad (64)$$

$$(p_ik'|sk) = af\left( a_iW_0 + \frac{1}{2\alpha}\frac{\partial W_0}{\partial A_i} \right) , \qquad (65)$$

$$(p_ik'|p_jk) = af\left( a_ib_jW_0 + \frac{b_j}{2\alpha}\frac{\partial W_0}{\partial A_i} + \frac{a_i}{2\beta}\frac{\partial W_0}{\partial B_j} + \frac{1}{4\alpha\beta}\frac{\partial^2 W_0}{\partial A_i \partial B_j} \right) , \qquad (66)$$

$$(d_{ij}k'|sk) = af\left[ (a_ia_j + \delta_{ij}\frac{1}{2\alpha})W_0 + \frac{a_j}{2\alpha}\frac{\partial W_0}{\partial A_i} + \frac{a_i}{2\alpha}\frac{\partial W_0}{\partial A_j} + \frac{1}{4\alpha^2}\frac{\partial^2 W_0}{\partial A_i \partial A_j} \right] , \qquad (67)$$

$$(d_{ij}k'|p_kk) = af\left[ (a_ia_jb_k + \delta_{ij}\frac{1}{2\alpha}b_k)W_0 + \frac{a_ia_j}{2\beta}\frac{\partial W_0}{\partial B_k} + \frac{a_ib_k}{2\alpha}\frac{\partial W_0}{\partial A_j} + \frac{a_jb_k}{2\alpha}\frac{\partial W_0}{\partial A_i} + \delta_{ij}\frac{1}{4\alpha\beta}\frac{\partial W_0}{\partial B_k} \right.$$

$$\left. + a_i\frac{1}{4\alpha\beta}\frac{\partial^2 W_0}{\partial A_j \partial B_k} + a_j\frac{1}{4\alpha\beta}\frac{\partial^2 W_0}{\partial A_i \partial B_k} + b_k\frac{1}{4\alpha^2}\frac{\partial^2 W_0}{\partial A_i \partial A_j} + \frac{1}{8\alpha^2\beta}\frac{\partial^3 W_0}{\partial A_i \partial A_j \partial B_k} \right] , \qquad (68)$$

$$(d_{ij}k'|d_{kl}k) = af\Bigg[ \, (a_ia_jb_kb_l + \delta_{ij}\frac{1}{2\alpha}b_kb_l + \delta_{kl}\frac{1}{2\beta}a_ia_j + \delta_{ij}\delta_{kl}\frac{1}{4\alpha\beta})W_0$$

$$+\frac{1}{2\beta}\left( a_ia_jb_k + \delta_{ij}\frac{1}{2\alpha}b_k \right)\frac{\partial W_0}{\partial B_l} + \frac{1}{2\beta}\left( a_ia_jb_l + \delta_{ij}\frac{1}{2\alpha}b_l \right)\frac{\partial W_0}{\partial B_k}$$

$$+\frac{1}{2\alpha}\left( a_ib_kb_l + \delta_{kl}\frac{1}{2\beta}a_i \right)\frac{\partial W_0}{\partial A_j} + \frac{1}{2\alpha}\left( a_jb_kb_l + \delta_{kl}\frac{1}{2\beta}a_j \right)\frac{\partial W_0}{\partial A_i}$$

$$+a_ia_j\frac{1}{4\beta^2}\frac{\partial^2 W_0}{\partial B_k\partial B_l} + \frac{1}{4\alpha\beta}\left( a_ib_k\frac{\partial^2 W_0}{\partial A_j\partial B_l} + a_ib_l\frac{\partial^2 W_0}{\partial A_j\partial B_k} + a_jb_k\frac{\partial^2 W_0}{\partial A_i\partial B_l} + a_jb_l\frac{\partial^2 W_0}{\partial A_i\partial B_k} \right)$$

$$+b_kb_l\frac{1}{4\alpha^2}\frac{\partial^2 W_0}{\partial A_i\partial A_j} + \frac{1}{8\alpha\beta^2}\left( \delta_{ij}\frac{\partial^2 W_0}{\partial B_k\partial B_l} + a_i\frac{\partial^3 W_0}{\partial A_j\partial B_k\partial B_l} + a_j\frac{\partial^3 W_0}{\partial A_i\partial B_k\partial B_l} \right)$$

$$+\frac{1}{8\alpha^2\beta}\left( \delta_{kl}\frac{\partial^2 W_0}{\partial A_i\partial A_j} + b_k\frac{\partial^3 W_0}{\partial A_i\partial A_j\partial B_l} + b_l\frac{\partial^3 W_0}{\partial A_i\partial A_j\partial B_k} \right) + \frac{1}{16\alpha^2\beta^2}\frac{\partial^4 W_0}{\partial A_i\partial A_j\partial B_k\partial B_l}\Bigg] \, . \quad (69)$$

*Integrals with Three Gaussians and One Plane-Wave Function*

In the following equations (*70*)–(*102*) $a$ is defined by Eq. (*16*), $f$ by Eq. (*14*), and the vector components $a_i$, $b_i$, $c_i$, $P_i$, and $Q_i$ by Eqs (*58*)–(*60*) and (*12*)–(*13*). By *s*, *p*, *d* we mean unnormalized s-, p-, and d-type Cartesian Gaussians, with exponents α (at center A), β (at center B) and γ (at center C)

$$(ss|sk) = afW_0 \ , \quad (70)$$

$$(p_is|sk) = af\left( a_iW_0 + \frac{1}{2(\alpha+\beta)}\frac{\partial W_0}{\partial P_i} \right) , \quad (71)$$

$$(p_ip_j|sk) = af\left( D_0^{11}W_0 + D_1^{11} + D_2^{11} \right) , \quad (72)$$

$$D_0^{11} = \left( a_i b_j + \delta_{ij} \frac{1}{2(\alpha+\beta)} \right) , \tag{73}$$

$$D_1^{11} = \frac{1}{2(\alpha+\beta)} \left( b_j \frac{\partial W_0}{\partial P_i} + a_i \frac{\partial W_0}{\partial P_j} \right) , \tag{74}$$

$$D_2^{11} = \frac{1}{4(\alpha+\beta)^2} \frac{\partial^2 W_0}{\partial P_i \partial P_j} , \tag{75}$$

$$(d_{ij} s|sk) = af \left( D_0^{20} W_0 + D_1^{20} + D_2^{20} \right) , \tag{76}$$

$$D_0^{20} = \left( a_i a_j + \delta_{ij} \frac{1}{2(\alpha+\beta)} \right) , \tag{77}$$

$$D_1^{20} = \frac{1}{2(\alpha+\beta)} \left( a_j \frac{\partial W_0}{\partial P_i} + a_i \frac{\partial W_0}{\partial P_j} \right) , \tag{78}$$

$$D_2^{20} = \frac{1}{4(\alpha+\beta)^2} \frac{\partial^2 W_0}{\partial P_i \partial P_j} , \tag{79}$$

$$(d_{ij} p_k|sk) = af \left( D_0^{21} W_0 + D_1^{21} + D_2^{21} + D_3^{21} \right) , \tag{80}$$

$$D_0^{21} = \left[ a_i a_j b_k + \frac{1}{2(\alpha+\beta)} \left( \delta_{ij} b_k + \delta_{ik} a_j + \delta_{jk} a_i \right) \right] , \tag{81}$$

$$D_1^{21} = \frac{1}{2(\alpha+\beta)} \left( a_i a_j \frac{\partial W_0}{\partial P_k} + a_i b_k \frac{\partial W_0}{\partial P_j} + a_j b_k \frac{\partial W_0}{\partial P_i} \right)$$

$$+ \frac{1}{4(\alpha+\beta)^2} \left( \delta_{ij} \frac{\partial W_0}{\partial P_k} + \delta_{ik} \frac{\partial W_0}{\partial P_j} + \delta_{jk} \frac{\partial W_0}{\partial P_i} \right) , \tag{82}$$

$$D_2^{21} = \frac{1}{4(\alpha+\beta)^2} \left( a_i \frac{\partial^2 W_0}{\partial P_j \partial P_k} + a_j \frac{\partial^2 W_0}{\partial P_i \partial P_k} + b_k \frac{\partial^2 W_0}{\partial P_i \partial P_j} \right) , \tag{83}$$

$$D_3^{21} = \frac{1}{8(\alpha+\beta)^3} \frac{\partial^3 W_0}{\partial P_i \partial P_j \partial P_k} \ , \tag{84}$$

$$(d_{ij} d_{kl}|sk) = af\left( D_0^{22} W_0 + D_1^{22} + D_2^{22} + D_3^{22} + D_4^{22} \right) , \tag{85}$$

$$D_0^{22} = \Bigg[ a_i a_j b_k b_l + \frac{1}{2(\alpha+\beta)} (\delta_{ij} b_k b_l + \delta_{ik} a_j b_l + \delta_{il} a_j b_k + \delta_{jk} a_i b_l + \delta_{jl} a_i b_k + \delta_{kl} a_i a_j ) + \frac{1}{4(\alpha+\beta)^2} (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il}) \Bigg] , \tag{86}$$

$$D_1^{22} = \frac{1}{2(\alpha+\beta)} \left( a_i a_j b_k \frac{\partial W_0}{\partial P_l} + a_i a_j b_l \frac{\partial W_0}{\partial P_k} + a_i b_k b_l \frac{\partial W_0}{\partial P_j} + a_j b_k b_l \frac{\partial W_0}{\partial P_i} \right) + \frac{1}{4(\alpha+\beta)^2} \left( a_i P_{3,jkl} \delta_{jk} \frac{\partial W_0}{\partial P_l} + a_j P_{3,ikl} \delta_{ik} \frac{\partial W_0}{\partial P_l} + b_k P_{3,ijl}\, \delta_{ij} \frac{\partial W_0}{\partial P_l} + b_l P_{3,ijk}\, \delta_{ij} \frac{\partial W_0}{\partial P_k} \right) , \tag{87}$$

$$D_2^{22} = \frac{1}{4(\alpha+\beta)^2} \left( a_i a_j \frac{\partial^2 W_0}{\partial P_k \partial P_l} + a_i b_k \frac{\partial^2 W_0}{\partial P_j \partial P_l} + a_i b_l \frac{\partial^2 W_0}{\partial P_j \partial P_k} + a_j b_k \frac{\partial^2 W_0}{\partial P_i \partial P_l} + a_j b_l \frac{\partial^2 W_0}{\partial P_i \partial P_k} + b_k b_l \frac{\partial^2 W_0}{\partial P_i \partial P_j} \right) + \frac{1}{8(\alpha+\beta)^3} P_{6,ijkl} \delta_{ij} \frac{\partial^2 W_0}{\partial P_k \partial P_l} \ , \tag{88}$$

$$D_3^{22} = \frac{1}{8(\alpha+\beta)^3} \left( a_i \frac{\partial^3 W_0}{\partial P_j \partial P_k \partial P_l} + a_j \frac{\partial^3 W_0}{\partial P_i \partial P_k \partial P_l} + b_k \frac{\partial^3 W_0}{\partial P_i \partial P_j \partial P_l} + b_l \frac{\partial^3 W_0}{\partial P_i \partial P_j \partial P_k} \right) , \tag{89}$$

$$D_4^{22} = \frac{1}{16(\alpha+\beta)^4} \frac{\partial^4 W_0}{\partial P_i \partial P_j \partial P_k \partial P_l} \ , \tag{90}$$

$P_3$ in Eq. (*87*) and $P_6$ in Eq. (*88*) mean three permutations in indices $i$, $j$, $k$ and six permutations in indices $i$, $j$, $k$, $l$.

$$(ss|p_i k) = af\left( c_i W_0 + \frac{1}{2\gamma} \frac{\partial W_0}{\partial Q_i} \right) , \tag{91}$$

$$(p_i s|p_j k) = af\left( a_i c_j W_0 + a_i \frac{1}{2\gamma}\frac{\partial W_0}{\partial Q_j} + c_j \frac{1}{2(\alpha+\beta)}\frac{\partial W_0}{\partial P_i} + \frac{1}{4(\alpha+\beta)\gamma}\frac{\partial^2 W_0}{\partial P_i \partial Q_j} \right), \qquad (92)$$

$$(p_i p_j|p_k k) = af\left[ c_k(D_0^{11} W_0 + D_1^{11} + D_2^{11}) + \frac{1}{2\gamma} D_0^{11} \frac{\partial W_0}{\partial Q_k} \right.$$

$$\left. + \frac{1}{4(\alpha+\beta)\gamma}\left( a_i \frac{\partial^2 W_0}{\partial P_j \partial Q_k} + b_j \frac{\partial^2 W_0}{\partial P_i \partial Q_k} \right) + \frac{1}{8(\alpha+\beta)^2}\frac{\partial^3 W_0}{\partial P_i \partial P_j \partial Q_k} \right], \qquad (93)$$

$$(d_{ij} s|p_k k) = af\left[ c_k(D_0^{20} W_0 + D_1^{20} + D_2^{20}) + \frac{1}{2\gamma} D_0^{20} \frac{\partial W_0}{\partial Q_k} \right.$$

$$\left. + \frac{1}{4(\alpha+\beta)\gamma}\left( a_i \frac{\partial^2 W_0}{\partial P_j \partial Q_k} + a_j \frac{\partial^2 W_0}{\partial P_i \partial Q_k} \right) + \frac{1}{8(\alpha+\beta)^2\gamma}\frac{\partial^3 W_0}{\partial P_i \partial P_j \partial Q_k} \right], \qquad (94)$$

$$(d_{ij} p_k|p_l k) = af\left[ c_l(D_0^{21} W_0 + D_1^{21} + D_2^{21} + D_3^{21}) + \frac{1}{2\gamma} D_0^{21} \frac{\partial W_0}{\partial Q_l} \right.$$

$$+ \frac{1}{4(\alpha+\beta)\gamma}\left( a_i a_j \frac{\partial^2 W_0}{\partial P_k \partial Q_l} + a_i b_k \frac{\partial^2 W_0}{\partial P_j \partial Q_l} + a_j b_k \frac{\partial^2 W_0}{\partial P_i \partial Q_l} \right) + \frac{1}{8(\alpha+\beta)^2\gamma} P_{3,ijk}\delta_{ij} \frac{\partial^2 W_0}{\partial P_k \partial Q_l}$$

$$+ \frac{1}{8(\alpha+\beta)^2\gamma}\left( a_i \frac{\partial^3 W_0}{\partial P_j \partial P_k \partial Q_l} + a_j \frac{\partial^3 W_0}{\partial P_i \partial P_k \partial Q_l} + b_k \frac{\partial^3 W_0}{\partial P_i \partial P_j \partial Q_l} \right)$$

$$\left. + \frac{1}{16(\alpha+\beta)^3\gamma}\frac{\partial^4 W_0}{\partial P_i \partial P_j \partial P_k \partial Q_l} \right], \qquad (95)$$

$$(d_{ij} d_{kl}|p_m k) = af\left[ c_m(D_0^{22} W_0 + D_1^{22} + D_2^{22} + D_3^{22} + D_4^{22}) + \frac{1}{2\gamma} D_0^{22} \frac{\partial W_0}{\partial Q_m} \right.$$

$$+ \frac{1}{4(\alpha+\beta)\gamma}\left( a_i a_j b_k \frac{\partial^2 W_0}{\partial P_l \partial Q_m} + a_i a_j b_l \frac{\partial^2 W_0}{\partial P_k \partial Q_m} + a_i b_k b_l \frac{\partial^2 W_0}{\partial P_j \partial Q_m} + a_j b_k b_l \frac{\partial^2 W_0}{\partial P_i \partial Q_m} \right)$$

$$+\frac{1}{8(\alpha+\beta)^2\gamma}\left(a_iP_{3,jkl}\delta_{jk}\frac{\partial^2W_0}{\partial P_l\partial Q_m}+a_jP_{3,ikl}\delta_{ik}\frac{\partial^2W_0}{\partial P_l\partial Q_m}+b_kP_{3,ijl}\,\delta_{ij}\frac{\partial^2W_0}{\partial P_l\partial Q_m}+b_lP_{3,ijk}\delta_{ij}\frac{\partial^2W_0}{\partial P_k\partial Q_m}\right)$$

$$+\frac{1}{8(\alpha+\beta)^2\gamma}\left(a_ia_j\frac{\partial^3W_0}{\partial P_k\partial P_l\partial Q_m}+a_ib_k\frac{\partial^3W_0}{\partial P_j\partial P_l\partial Q_m}+a_ib_l\frac{\partial^3W_0}{\partial P_j\partial P_k\partial Q_m}\right.$$

$$\left.+a_jb_k\frac{\partial^3W_0}{\partial P_i\partial P_l\partial Q_m}+a_jb_l\frac{\partial^3W_0}{\partial P_i\partial P_k\partial Q_m}+b_kb_l\frac{\partial^3W_0}{\partial P_i\partial P_j\partial Q_m}\right)+\frac{1}{16(\alpha+\beta)^3\gamma}P_{6,ijkl}\delta_{ij}\frac{\partial^3W_0}{\partial P_k\partial P_l\partial Q_m}$$

$$+\frac{1}{16(\alpha+\beta)^3\gamma}\left(a_i\frac{\partial^4W_0}{\partial P_j\partial P_k\partial P_l\partial Q_m}+a_j\frac{\partial^4W_0}{\partial P_i\partial P_k\partial P_l\partial Q_m}+b_k\frac{\partial^4W_0}{\partial P_i\partial P_j\partial P_l\partial Q_m}+b_l\frac{\partial^4W_0}{\partial P_i\partial P_j\partial P_k\partial Q_m}\right)$$

$$\left.+\frac{1}{32(\alpha+\beta)^4\gamma}\frac{\partial^5W_0}{\partial P_i\partial P_j\partial P_k\partial P_l\partial Q_m}\right], \tag{96}$$

$$(ss|d_{ij}k)=af\left[\left(c_ic_j+\delta_{ij}\frac{1}{2\gamma}\right)W_0+\frac{1}{2\gamma}\left(c_i\frac{\partial W_0}{\partial Q_j}+c_j\frac{\partial W_0}{\partial Q_i}\right)+\frac{1}{4\gamma^2}\frac{\partial^2W_0}{\partial Q_i\partial Q_j}\right], \tag{97}$$

$$(p_is|d_{jk}k)=af\left[\left(c_jc_k+\delta_{jk}\frac{1}{2\gamma}\right)\left(a_iW_0+\frac{1}{2(\alpha+\beta)}\frac{\partial W_0}{\partial P_i}\right)+a_i\frac{1}{2\gamma}\left(c_j\frac{\partial W_0}{\partial Q_k}+c_k\frac{\partial W_0}{\partial Q_j}\right)\right.$$

$$\left.+\frac{1}{4(\alpha+\beta)\gamma}\left(c_j\frac{\partial^2W_0}{\partial P_i\partial Q_k}+c_k\frac{\partial^2W_0}{\partial P_i\partial Q_j}\right)+\frac{1}{4\gamma^2}a_i\frac{\partial^2W_0}{\partial Q_j\partial Q_k}+\frac{1}{8(\alpha+\beta)\gamma^2}\frac{\partial^3W_0}{\partial P_i\partial Q_j\partial Q_k}\right], \tag{98}$$

$$(p_ip_j|d_{kl}k)=af\left[\left(c_kc_l+\delta_{kl}\frac{1}{2\gamma}\right)(D_0^{11}W_0+D_1^{11}+D_2^{11})\right.$$

$$+\frac{1}{2\gamma}D_0^{11}\left(c_k\frac{\partial W_0}{\partial Q_l}+c_l\frac{\partial W_0}{\partial Q_k}+\frac{1}{2\gamma}\frac{\partial^2W_0}{\partial Q_k\partial Q_l}\right)$$

$$+\frac{1}{4(\alpha+\beta)\gamma}a_i\left(c_k\frac{\partial^2W_0}{\partial P_j\partial Q_l}+c_l\frac{\partial^2W_0}{\partial P_j\partial Q_k}\right)+\frac{1}{4(\alpha+\beta)\gamma}b_j\left(c_k\frac{\partial^2W_0}{\partial P_i\partial Q_l}+c_l\frac{\partial^2W_0}{\partial P_i\partial Q_k}\right)$$

$$+\frac{1}{8(\alpha+\beta)^2\gamma}\left(c_k\frac{\partial^3 W_0}{\partial P_i\partial P_j\partial Q_l}+c_l\frac{\partial^3 W_0}{\partial P_i\partial P_j\partial Q_k}\right)+\frac{1}{8(\alpha+\beta)\gamma^2}\left(a_i\frac{\partial^3 W_0}{\partial P_j\partial Q_k\partial Q_l}+b_j\frac{\partial^3 W_0}{\partial P_i\partial Q_k\partial Q_l}\right)$$

$$+\frac{1}{16(\alpha+\beta)^2\gamma^2}\frac{\partial^4 W_0}{\partial P_i\partial P_j\partial Q_k\partial Q_l}\Bigg], \tag{99}$$

$$(d_{ij}s|d_{kl}k)=af\Bigg[\left(c_kc_l+\delta_{kl}\frac{1}{2\gamma}\right)(D_0^{20}W_0+D_1^{20}+D_2^{20})$$

$$+\frac{1}{2\gamma}D_0^{20}\left(c_k\frac{\partial W_0}{\partial Q_l}+c_l\frac{\partial W_0}{\partial Q_k}+\frac{1}{2\gamma}\frac{\partial^2 W_0}{\partial Q_k\partial Q_l}\right)$$

$$+\frac{1}{4(\alpha+\beta)\gamma}a_i\left(c_k\frac{\partial^2 W_0}{\partial P_j\partial Q_l}+c_l\frac{\partial^2 W_0}{\partial P_j\partial Q_k}\right)+\frac{1}{4(\alpha+\beta)\gamma}a_j\left(c_k\frac{\partial^2 W_0}{\partial P_i\partial Q_l}+c_l\frac{\partial^2 W_0}{\partial P_i\partial Q_k}\right)$$

$$+\frac{1}{8(\alpha+\beta)^2\gamma}\left(c_k\frac{\partial^3 W_0}{\partial P_i\partial P_j\partial Q_l}+c_l\frac{\partial^3 W_0}{\partial P_i\partial P_j\partial Q_k}\right)+\frac{1}{8(\alpha+\beta)\gamma^2}\left(a_i\frac{\partial^3 W_0}{\partial P_j\partial Q_k\partial Q_l}+a_j\frac{\partial^3 W_0}{\partial P_i\partial Q_k\partial Q_l}\right)$$

$$+\frac{1}{16(\alpha+\beta)^2\gamma^2}\frac{\partial^4 W_0}{\partial P_i\partial P_j\partial Q_k\partial Q_l}\Bigg], \tag{100}$$

$$(d_{ij}p_k|d_{lm}k)=af\Bigg[\left(c_lc_m+\delta_{lm}\frac{1}{2\gamma}\right)(D_0^{21}W_0+D_1^{21}+D_2^{21}+D_3^{21})$$

$$+\frac{1}{2\gamma}D_0^{21}\left(c_l\frac{\partial W_0}{\partial Q_m}+c_m\frac{\partial W_0}{\partial Q_l}+\frac{1}{2\gamma}\frac{\partial^2 W_0}{\partial Q_l\partial Q_m}\right)$$

$$+\frac{1}{4(\alpha+\beta)\gamma}\left(a_ia_jP_{2,lm}c_l\frac{\partial^2 W_0}{\partial P_k\partial Q_m}+a_ib_kP_{2,lm}c_l\frac{\partial^2 W_0}{\partial P_j\partial Q_m}+a_jb_kP_{2,lm}c_l\frac{\partial^2 W_0}{\partial P_i\partial Q_m}\right)$$

$$+\frac{1}{8(\alpha+\beta)^2\gamma}\left(\delta_{ij}P_{2,lm}c_l\frac{\partial^2 W_0}{\partial P_k\partial Q_m}+\delta_{ik}P_{2,lm}c_l\frac{\partial^2 W_0}{\partial P_j\partial Q_m}+\delta_{jk}P_{2,lm}c_l\frac{\partial^2 W_0}{\partial P_i\partial Q_m}\right)$$

$$+\frac{1}{8(\alpha+\beta)\gamma^2}\left(a_i a_j \frac{\partial^3 W_0}{\partial P_k \partial Q_l \partial Q_m}+a_i b_k \frac{\partial^3 W_0}{\partial P_j \partial Q_l \partial Q_m}+a_j b_k \frac{\partial^3 W_0}{\partial P_i \partial Q_l \partial Q_m}\right)$$

$$+\frac{1}{16(\alpha+\beta)^2\gamma^2} P_{3,ijk}\delta_{ij} \frac{\partial^3 W_0}{\partial P_k \partial Q_l \partial Q_m}+\frac{1}{16(\alpha+\beta)^3\gamma} P_{2,lm} c_l \frac{\partial^4 W_0}{\partial P_i \partial P_j \partial P_k \partial Q_m}$$

$$+\frac{1}{8(\alpha+\beta)^2\gamma}\left(a_i P_{2,lm} c_l \frac{\partial^3 W_0}{\partial P_j \partial P_k \partial Q_m}+a_j P_{2,lm} \frac{\partial^3 W_0}{\partial P_i \partial P_k \partial Q_m}+b_k P_{2,lm} c_l \frac{\partial^3 W_0}{\partial P_i \partial P_j \partial Q_m}\right)$$

$$+\frac{1}{16(\alpha+\beta)^2\gamma^2}\left(a_i \frac{\partial^4 W_0}{\partial P_j \partial P_k \partial Q_l \partial Q_m}+a_j \frac{\partial^4 W_0}{\partial P_i \partial P_k \partial Q_l \partial Q_m}+b_k \frac{\partial^4 W_0}{\partial P_i \partial P_j \partial Q_l \partial Q_m}\right)$$

$$\left.+\frac{1}{32(\alpha+\beta)^3\gamma^2} \frac{\partial^5 W_0}{\partial P_i \partial P_j \partial P_k \partial Q_l \partial Q_m}\right], \tag{101}$$

$P_{2,ij}$ means two permutations in indices $i$ and $j$.

$$(d_{ij}d_{kl}|d_{mn}k) = af\left[\left(c_m c_n + \delta_{mn}\frac{1}{2\gamma}\right)(D_0^{22}W_0 + D_1^{22} + D_2^{22} + D_3^{22} + D_4^{22})\right.$$

$$+\frac{1}{2\gamma} D_0^{22}\left(c_m \frac{\partial W_0}{\partial Q_n}+c_n \frac{\partial W_0}{\partial Q_m}+\frac{1}{2\gamma} \frac{\partial^2 W_0}{\partial Q_m \partial Q_n}\right)$$

$$+\frac{1}{4(\alpha+\beta)\gamma}\left(a_i a_j P_{2,kl} P_{2,mn} b_k c_m \frac{\partial^2 W_0}{\partial P_l \partial Q_n}+b_k b_l P_{2,ij} P_{2,mn} a_i c_m \frac{\partial^2 W_0}{\partial P_j \partial Q_n}\right)$$

$$+\frac{1}{8(\alpha+\beta)^2\gamma}\left(a_i P_{3,jkl} P_{2,mn} \delta_{jk} c_m \frac{\partial^2 W_0}{\partial P_l \partial Q_n}+a_j P_{3,ikl} P_{2,mn} \delta_{ik} c_m \frac{\partial^2 W_0}{\partial P_l \partial Q_n}\right.$$

$$\left.+b_k P_{3,ijl} P_{2,mn} \delta_{ij} c_m \frac{\partial^2 W_0}{\partial P_l \partial Q_n}+b_l P_{3,ijk} P_{2,mn} \delta_{ij} c_m \frac{\partial^2 W_0}{\partial P_k \partial Q_n}\right)$$

$$+\frac{1}{8(\alpha+\beta)\gamma^2}\left(P_{2,kl} a_i a_j b_k \frac{\partial^3 W_0}{\partial P_l \partial Q_m \partial Q_n}+P_{2,ij} a_i b_k b_l \frac{\partial^3 W_0}{\partial P_j \partial Q_m \partial Q_n}\right)$$

$$+\frac{1}{16(\alpha+\beta)^2\gamma^2}\left(P_{2,kl}\,(\delta_{ij}b_k+\delta_{ik}a_j+\delta_{jk}a_i)\,\frac{\partial^3 W_0}{\partial P_l\partial Q_m\partial Q_n}\right.$$

$$\left.+P_{2,ij}(\delta_{ik}b_l+\delta_{il}b_k+\delta_{kl}a_i)\,\frac{\partial^3 W_0}{\partial P_j\partial Q_m\partial Q_n}\right)$$

$$+\frac{1}{8(\alpha+\beta)^2\gamma}\left(a_i a_j P_{2,mn}c_m\,\frac{\partial^3 W_0}{\partial P_k\partial P_l\partial Q_n}+b_k b_l P_{2,mn}c_m\,\frac{\partial^3 W_0}{\partial P_i\partial P_j\partial Q_n}\right.$$

$$\left.+P_{2,ij}P_{2,kl}a_i b_k P_{2,mn}c_m\,\frac{\partial^3 W_0}{\partial P_j\partial P_l\partial Q_n}\right)+\frac{1}{16(\alpha+\beta)^3\gamma}\,P_{6,ijkl}\delta_{ij}P_{2,mn}c_m\,\frac{\partial^3 W_0}{\partial P_k\partial P_l\partial Q_n}$$

$$+\frac{1}{16(\alpha+\beta)^2\gamma^2}\left(a_i a_j\,\frac{\partial^4 W_0}{\partial P_k\partial P_l\partial Q_m\partial Q_n}+b_k b_l\,\frac{\partial^4 W_0}{\partial P_i\partial P_j\partial Q_m\partial Q_n}+P_{2,ij}P_{2,kl}a_i b_k\,\frac{\partial^4 W_0}{\partial P_j\partial P_l\partial Q_m\partial Q_n}\right)$$

$$+\frac{1}{32(\alpha+\beta)^3\gamma^2}\,P_{6,ijkl}\delta_{ij}\,\frac{\partial^4 W_0}{\partial P_k\partial P_l\partial Q_m\partial Q_n}$$

$$+\frac{1}{16(\alpha+\beta)^3\gamma}\left(P_{2,ij}a_i P_{2,mn}c_m\,\frac{\partial^4 W_0}{\partial P_j\partial P_k\partial P_l\partial Q_n}+P_{2,kl}b_k P_{2,mn}c_m\,\frac{\partial^4 W_0}{\partial P_i\partial P_j\partial P_l\partial Q_n}\right)$$

$$+\frac{1}{32(\alpha+\beta)^3\gamma^2}\left(P_{2,ij}a_i\,\frac{\partial^5 W_0}{\partial P_j\partial P_k\partial P_l\partial Q_m\partial Q_n}+P_{2,kl}b_k\,\frac{\partial^5 W_0}{\partial P_i\partial P_j\partial P_l\partial Q_m\partial Q_n}\right)$$

$$\frac{1}{32(\alpha+\beta)^4\gamma}\,P_{2,mn}c_m\,\frac{\partial^5 W_0}{\partial P_i\partial P_j\partial P_k\partial P_l\partial Q_n}+\frac{1}{64(\alpha+\beta)^4\gamma^2}\,\frac{\partial^6 W_0}{\partial P_i\partial P_j\partial P_k\partial P_l\partial Q_m\partial Q_n}\Bigg]\,, \qquad (102)$$

$P_{2,ij}$ means two permumations in indices $i$ and $j$, and $P_{6,ijkl}$ six permutations in indices $i$, $j$, $k$, $l$.

Use of complicated formulas for $(g_1g_2|p_ik)$ and $(g_1g_2|d_{ij}k)$ integrals may be avoided by means of the following expressions

$$(g_1g_2|p_ik)=c_i(g_1g_2|sk)+(g_1g_2|s_ik)\;, \qquad (103)$$

$$(g_1g_2|d_{ij}k) = \left( c_ic_j + \delta_{ij}\frac{1}{2\gamma}\right)(g_1g_2|sk) + c_i(g_1g_2|s_ik) + c_j(g_1g_2|s_jk) + (g_1g_2|s_{ij}k) \ , \qquad (104)$$

where $(g_1g_2|s_ik)$ is obtained by the formula for $(g_1g_2|sk)$ integrals but each derivative of $W_0$ is substituted by a higher derivative according to the pattern

$$W_0 \to \frac{1}{2\gamma}\frac{\partial W_0}{\partial Q_i} \ ,$$

$$\frac{\partial W_0}{\partial P_j} \to \frac{1}{2\gamma}\frac{\partial^2 W_0}{\partial Q_i \partial P_j} \ ,$$

$$\frac{\partial^n W_0}{\partial P_j \ldots \partial P_m} \to \frac{1}{2\gamma}\frac{\partial^{n+1} W_0}{\partial Q_i \partial P_j \ldots \partial P_m} \ .$$

Integral $(g_1g_2|s_{ij}k)$ is also obtained by the formula for $(g_1g_2|sk)$ but each derivative of $W_0$ is substituted by a higher derivative according to the pattern

$$W_0 \to \frac{1}{4\gamma^2}\frac{\partial^2 W_0}{\partial Q_i \partial Q_j} \ ,$$

$$\frac{\partial W_0}{\partial P_k} \to \frac{1}{4\gamma^2}\frac{\partial^3 W_0}{\partial Q_i \partial Q_j \partial P_k} \ ,$$

$$\frac{\partial^n W_0}{\partial P_k \ldots \partial P_m} \to \frac{1}{4\gamma^2}\frac{\partial^{n+2} W_0}{\partial Q_i \partial Q_j \partial P_k \ldots \partial P_m} \ .$$

## CONCLUSIONS

We have derived formulas for two-electron free-free exchange integrals in a Gaussian basis and two-electron hybrid integrals with three Gaussians and one plane-wave function. For integrals with p- and d-type Gaussians we used a traditional method of differentiation of the fundamental integrals containing s-type Gaussians only. Since the fundamental integrals may be evaluated by means of the Faddeeva function *w*, their differentiation leads to expressions containg derivatives of *w* with respect to Cartesian coordinates of points on which the Gaussians are centered. The formula for $(dd|dk)$ integrals given by Eq. (*102*) supports the opinion of Watson and McKoy[2] that the method becomes quickly cumbersome as it is applied to Gaussians with higher quantum numbers of the angular momentum. However, we still believe that the method may be useful for electron-molecule scattering calculations in the spd Gaussian basis set. A work is now in progress in which we test the efficiency of different methods for the evaluation of two electron integrals in a mixed plane-wave and Gaussian basis.

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