Theor Chim Acta (1996) 93: 49–59

Theoretica Chimica Acta

New general formulas for matrix elements of the free-particle Green's function over Cartesian Gaussians

Petr Čársky[1], Vojtěch Hrouda[1,2]*, Martin Polášek[1]

[1] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic

[2] Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, Co 80309-0215, USA

Received February 1, 1995/Accepted May 10, 1995

Summary. In this paper, we present new general analytical formulas for matrix elements of the free-particle Green's function over arbitrary Cartesian Gaussians and explicit formulas for Green's function matrix elements over *s*, *p*, *d* and *f* Gaussians. One-center matrix elements were obtained by direct integration and two-center matrix elements by differentiation of the integral formula for *s* Gaussians with respect to the position vectors of *p*, *d*, and *f* Gaussians. We also present a representative set of numerical values of the matrix elements.

Key words: Green's function – Matrix elements – Cartesian Gaussian functions

1 Introduction

Use of Gaussian basis sets in electron scattering calculations requires development of procedures for analytical evaluation of the free-particle Green's function matrix elements over Cartesian Gaussian functions. Ostlund derived formulas for the *s*-type [1] and *p*-type [2] Gaussians by direct integration. Levin and coworkers [3] derived formulas for *d*- and *f*-type Gaussians by means of the partial-wave expansion of the plane-wave function. The purpose of this paper is to show that simple and compact explicit formulas up to *f* functions may be obtained without partial-wave expansion. In their general form, the formulas may be applied to *g* and higher Cartesian Gaussians. In this paper, we also report corrections for several misprints in the published values of matrix elements [3], and list some additional data which may serve as standards for debugging new computer codes.

2 Theory

As is usual we assume the free-particle Green's function as

$$G_0^+(\boldsymbol{r}, \boldsymbol{r}'; k_0) = -\frac{1}{4\pi} \frac{e^{ik_0|\boldsymbol{r}-\boldsymbol{r}'|}}{|\boldsymbol{r}-\boldsymbol{r}'|}. \tag{1}$$

* On leave from Heyrovský Institute

and the normalized Cartesian Gaussian functions as

$$|\alpha^A_{lmn}\rangle = N_{lmn}(x - A_x)^l (y - A_y)^m (z - A_z)^n \, \mathrm{e}^{-\alpha(r-A)^2}. \tag{2}$$

Since the values of normalization constants for different types of d and f functions are different, we will derive the formulas for unnormalized Gaussian functions. Hence, we use the following formula for the Fourier transform of a Gaussian function

$$\langle \alpha^A_{lmn} | \boldsymbol{k} \rangle = \left(\frac{\pi}{\alpha}\right)^{3/2} \frac{i^{l+m+n}}{(2\sqrt{\alpha})^{l+m+n}} \mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{A}} \mathrm{e}^{-k^2/4\alpha} H_l\left(\frac{k_x}{2\sqrt{\alpha}}\right) H_m\left(\frac{k_y}{2\sqrt{\alpha}}\right) H_n\left(\frac{k_z}{2\sqrt{\alpha}}\right) \tag{3}$$

where the plane-wave function $|\boldsymbol{k}\rangle$ is also assumed to be unnormalized

$$|\boldsymbol{k}\rangle = \mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}}. \tag{4}$$

For the energy $E = k_0^2/2$ the matrix element of the Green's function is given by

$$\langle \alpha^A_{lmn} | G_0^+(E) | \beta^B_{l'm'n'} \rangle = \frac{1}{8\pi^3} \lim_{\varepsilon \to 0} \int \frac{\langle \alpha^A_{lmn} | \boldsymbol{k} \rangle \langle \boldsymbol{k} | \beta^B_{l'm'n'} \rangle}{k_0^2 - k^2 + i\varepsilon} \, \mathrm{d}\boldsymbol{k}. \tag{5}$$

We treat the one-center and two-center matrix elements separately because the former are derived by direct integration whereas the latter are derived by successive differentiation of the integral formula for s Gaussians with respect to the position vectors of p, d, and f Gaussians.

2.1 One-center matrix elements

By substituting for the Fourier transforms, the one-center matrix elements may be expressed as

$$\langle \alpha^A_{lmn} | G_0^+(E) | \beta^A_{l'm'n'} \rangle = \frac{8(-1)^{l'+m'+n'} i^{l+m+n+l'+m'+n'}}{(2\sqrt{\alpha})^{l+m+n+3} (2\sqrt{\beta})^{l'+m'+n'+3}} I_{lmnl'm'n'} \tag{6}$$

where the integrals $I_{lmnl'm'n'}$ are defined as

$$I_{lmnl'm'n'} = \lim_{\varepsilon \to 0} \int \frac{H_l\left(\frac{k_x}{2\sqrt{\alpha}}\right) H_m\left(\frac{k_y}{2\sqrt{\alpha}}\right) H_n\left(\frac{k_z}{2\sqrt{\alpha}}\right) H_{l'}\left(\frac{k_x}{2\sqrt{\beta}}\right) H_{m'}\left(\frac{k_y}{2\sqrt{\beta}}\right) H_{n'}\left(\frac{k_x}{2\sqrt{\beta}}\right)}{k_0^2 - k^2 + i\varepsilon} \mathrm{e}^{-a^2k^2} \, \mathrm{d}\boldsymbol{k} \tag{7}$$

and

$$a^2 = \frac{1}{4\alpha} + \frac{1}{4\beta}. \tag{8}$$

Evaluation of these integrals through f Gaussians leads to the following formula:

$$I_{lmnl'm'n'} = \sum_{j=1}^{4} A_{2j}^{lmnl'm'n'} J_{2j}. \tag{9}$$

Table 1. Parameters $A_{2j}^{lmnl'm'n'}$ for one-center matrix elements through f Gaussians. Parameters P_j are summarized in Table 2. The *sp*, *pd*, *sf*, and *df* matrix elements are identically equal to zero by symmetry

Matrix element	A_2	A_4	A_6	A_8
ss	4π	0	0	0
pp	0	$\frac{4\pi}{3\sqrt{\alpha\beta}}P_2$	0	0
sd	$-8\pi P_1$	$\frac{4\pi}{3\beta}P_2$	0	0
dd	$16\pi P_1$	$-\frac{8\pi(\alpha+\beta)}{3\alpha\beta}P_2$	$\frac{4\pi}{5\alpha\beta}P_3$	0
pf	0	$-\frac{8\pi}{\sqrt{\alpha\beta}}P_2$	$-\frac{4\pi}{5\sqrt{\alpha\beta^3}}P_3$	0
ff	0	$\frac{48\pi}{\sqrt{\alpha\beta}}P_2$	$-\frac{24\pi(\alpha+\beta)}{5\sqrt{\alpha^3\beta^3}}P_3$	$\frac{4\pi}{7\sqrt{\alpha^3\beta^3}}P_4$

Table 2. Parameters P_j through f Gaussians for one-center matrix elements

Matrix element[a]	P_1	P_2	P_3	P_4
x–x	0	1	0	0
s–xx	1	1	0	0
xx–xx	1	1	1	0
xx–yy	1	1	1/3	0
xy–xy	0	0	1/3	0
x–xxx	0	1	1	0
x–xyy	0	1/3	1/3	0
xxx–xxx	0	1	1	1
xxx–xyy	0	1/3	1/3	1/5
xxy–xxy	0	1/9	1/9	1/5
xxy–yzz	0	1/9	1/9	1/15
xyz–xyz	0	0	0	1/15

[a] Only those types of matrix elements are listed for which the P_j parameters are nonzero

In this summation J_{2j} are integrals evaluated in Appendix A and $A_{2j}^{lmnl'm'n'}$ are parameters which are summarized in Tables 1 and 2.

The integrals $I_{lmnl'm'n'}$ can also be expressed in a general form if we realize that a product of Hermite polynomials can always be written as a power series

$$H_l\left(\frac{k_x}{2\sqrt{\alpha}}\right)H_m\left(\frac{k_y}{2\sqrt{\alpha}}\right)H_n\left(\frac{k_z}{2\sqrt{\alpha}}\right)H_{l'}\left(\frac{k_x}{2\sqrt{\beta}}\right)H_{m'}\left(\frac{k_y}{2\sqrt{\beta}}\right)H_{n'}\left(\frac{k_z}{2\sqrt{\beta}}\right)$$

$$=\sum_{L=1}^{l+l'}\sum_{M=1}^{m+m'}\sum_{N=1}^{n+n'}Q_{LMN}(k_x)^L(k_y)^M(k_z)^N \tag{10}$$

where constants $Q_{LMN}(\alpha, \beta)$ can be easily obtained. Using this expression, Eq. (7) can be rewritten as

$$I_{lmnl'm'n'} = \sum_{L=1}^{l+l'} \sum_{M=1}^{m+m'} \sum_{N=1}^{n+n'} Q_{LMN} K_{LMN}. \tag{11}$$

Here K_{LMN} are integrals given by the formula

$$K_{LMN} = \lim_{\varepsilon \to 0} \int_0^\infty \frac{(k_x)^L (k_y)^M (k_z)^N}{k_0^2 - k^2 + i\varepsilon} e^{-a^2 k^2} \, dk \tag{12}$$

which can be evaluated as shown in Appendix B.

2.2 *Two-center matrix elements*

For the two-center integrals over Gaussians with nonzero l, m, n, l', m', n' we employed a method which has been used in the electronic structure theory since the early days of *ab initio* calculations [8]. This method consists of substituting the following expressions for the unnormalized p, d, and f functions

$$\begin{aligned}
|p_\lambda\rangle &= \frac{1}{2\alpha} \frac{\partial}{\partial A_\lambda} e^{-\alpha r_A^2}, \\
|d_{\lambda\mu}\rangle &= \frac{1}{4\alpha^2} \frac{\partial^2}{\partial A_\lambda \partial A_\mu} e^{-\alpha r_A^2} + \delta_{\lambda\mu} \frac{1}{2\alpha} e^{-\alpha r_A^2}, \\
|f_{\lambda\mu\nu}\rangle &= \frac{1}{8\alpha^3} \frac{\partial^3}{\partial A_\lambda \partial A_\mu \partial A_\nu} e^{-\alpha r_A^2} + \delta_{\lambda\mu} \frac{1}{4\alpha^2} \frac{\partial}{\partial A_\nu} e^{-\alpha r_A^2} \\
&\quad + \delta_{\lambda\nu} \frac{1}{4\alpha^2} \frac{\partial}{\partial A_\mu} e^{-\alpha r_A^2} + \delta_{\mu\nu} \frac{1}{4\alpha^2} \frac{\partial}{\partial A_\lambda} e^{-\alpha r_A^2}.
\end{aligned} \tag{13}$$

In these formulas we use $r_A^2 = |\boldsymbol{r} - \boldsymbol{A}|^2$ and Greek subscripts for x, y, z. To obtain a formula for two-center Green's function matrix elements we need to express these Gaussian functions in a general operator form. For this purpose we define the operator as

$$\Delta_{lmn}^A = \frac{\partial^{l+m+n}}{\partial A_x^l \partial A_y^m \partial A_z^n}. \tag{14}$$

Then the p, d, and f functions may be rewritten as

$$\begin{aligned}
|p_\lambda\rangle &= \frac{1}{2\alpha} \Delta_{lmn}^A |s\rangle, \quad l + m + n = 1, \\
|d_{\lambda\mu}\rangle &= \left[\frac{1}{4\alpha^2} \Delta_{lmn}^A + \delta_{\lambda\mu} \frac{1}{2\alpha} \Delta_{000}^A \right] |s\rangle, \quad l + m + n = 2, \\
|f_{\lambda\mu\nu}\rangle &= \left[\frac{1}{8\alpha^3} \Delta_{lmn}^A + \delta_{\lambda\mu} \frac{1}{4\alpha^2} \frac{\partial}{\partial A_\nu} \Delta_{000}^A + \delta_{\lambda\nu} \frac{1}{4\alpha^2} \frac{\partial}{\partial A_\mu} \Delta_{000}^A \right. \\
&\quad \left. + \delta_{\mu\nu} \frac{1}{4\alpha^2} \frac{\partial}{\partial A_\lambda} \Delta_{000}^A \right] |s\rangle, \quad l + m + n = 3,
\end{aligned} \tag{15}$$

where

$$\frac{\partial}{\partial A_x} \Delta^A_{000} = \Delta^A_{100}, \frac{\partial}{\partial A_y} \Delta^A_{000} = \Delta^A_{010}, \frac{\partial}{\partial A_z} \Delta^A_{000} = \Delta^A_{001}. \tag{16}$$

Formulas for g and higher functions may be obtained by means of the following recursive expression:

$$|\alpha^A_{l+1,m,n}\rangle = \frac{1}{2\alpha} \frac{\partial}{\partial A_x} |\alpha^A_{lmn}\rangle + \frac{1}{2\alpha} |\alpha_{l-1,m,n}\rangle. \tag{17}$$

Since the operators Δ^A_{lmn} (Eq. 14) do not depend on $\boldsymbol{r}$ and $\boldsymbol{r}'$, respectively, the order of differentiation with respect to Cartesian Gaussian coordinates and integration over $\boldsymbol{r}$ and $\boldsymbol{r}'$, respectively, can be interchanged. Calculation of Green's function matrix elements then reduces to the evaluation of expressions $\Delta^A_{lmn} \Delta^B_{l'm'n'} G_{ss}$, where the G_{ss} matrix element is defined as

$$\langle \alpha^A_s | G^+_0 | \beta^B_s \rangle = G_{ss}, \tag{18}$$

and its evaluation is described in Appendix C. As an example we present the matrix element for f_{xxx} and f_{zzz} functions

$$\langle \alpha^A_{300} | G^+_0 | \beta^B_{003} \rangle = G_1 + G_2 + G_3 + G_4, \tag{19}$$

where G_1, G_2, G_3, and G_4 becomes

$$G_1 = \frac{\Delta^A_{300} \Delta^B_{003}}{64\alpha^3\beta^3} G_{ss}, \quad G_2 = \frac{3\Delta^A_{300} \Delta^B_{001}}{32\alpha^3\beta^2} G_{ss},$$

$$G_3 = \frac{3\Delta^A_{100} \Delta^B_{003}}{32\alpha^2\beta^3} G_{ss}, \quad G_4 = \frac{9\Delta^A_{100} \Delta^B_{001}}{16\alpha^2\beta^2} G_{ss}. \tag{20}$$

Since

$$\Delta^A_{lmn} \Delta^B_{l'm'n'} G_{ss} = (-1)^{l'+m'+n'} \Delta^A_{lmn} \Delta^A_{l'm'n'} G_{ss} \tag{21}$$

we may drop the superscripts A and B and assume only the differentiation with respect to A,

$$\Delta^A_{lmn} \equiv \Delta_{lmn}. \tag{22}$$

Differentiation of G_{ss} gives

$$\Delta_{lmn} \Delta_{l'm'n'} G_{ss} = \sum_{J=1}^{K} P^K_J G^{(J)}_{ss}, \tag{23}$$

where

$$K = l + m + n + l' + m' + n', \tag{24}$$

and $G^{(J)}_{ss}$ is the jth derivative of G_{ss} with respect to the distance $C \equiv \overline{AB}$,

$$G^{(J)}_{ss} = \frac{\partial^J G_{ss}}{\partial C^J}. \tag{25}$$

Evaluation of $G_{ss}^{(J)}$ terms is described in Appendix C. For each J and K, the coefficients P_J^K in Eq. (23) may be expressed as

$$P_J^K = \left(-\frac{1}{C}\right)^{K-J} \sum_{i=0}^{I} (-1)^i R_{J,i}^K \mathscr{P}_i(C_{\lambda_1}, C_{\lambda_2}, \ldots, C_{\lambda_K}), \; I = K/2 \text{ for } K \text{ even}$$

$$I = (K-1)/2 \text{ for } K \text{ odd}. \quad (26)$$

By $C_{\lambda_1}, C_{\lambda_2}, \ldots, C_{\lambda_K}$ we denote derivatives of C with respect to coordinates $A_{\lambda_1}, A_{\lambda_2}, \ldots, A_{\lambda_K}$

$$C_\lambda = \partial C / \partial A_\lambda. \quad (27)$$

The symbol $\mathscr{P}_i(C_{\lambda_1}, C_{\lambda_2}, \ldots, C_{\lambda_K})$ means all permutations of $C_{\lambda_1}, C_{\lambda_2}, \ldots, C_{\lambda_K}$ with respect to indices $\lambda_1, \lambda_2, \ldots, \lambda_K$ with the first i pairs $C_{\lambda_1} C_{\lambda_2}, C_{\lambda_3} C_{\lambda_4}, \ldots, C_{\lambda_{2i-1}} C_{\lambda_{2i}}$ replaced by Kronecker delta functions. For example, for $K = 4$ we have

$$\begin{aligned}
\mathscr{P}_0(C_{\lambda_1}, C_{\lambda_2}, C_{\lambda_3}, C_{\lambda_4}) &= C_{\lambda_1} C_{\lambda_2} C_{\lambda_3} C_{\lambda_4}. \\
\mathscr{P}_1(C_{\lambda_1}, C_{\lambda_2}, C_{\lambda_3}, C_{\lambda_4}) &= \mathscr{P}(\delta_{\lambda_1\lambda_2}, C_{\lambda_3}, C_{\lambda_4}) \\
\mathscr{P}_2(C_{\lambda_1}, C_{\lambda_2}, C_{\lambda_3}, C_{\lambda_4}) &= \mathscr{P}(\delta_{\lambda_1\lambda_2}, \delta_{\lambda_3\lambda_4})
\end{aligned} \quad (28)$$

and for $K = 5$

$$\begin{aligned}
\mathscr{P}_0(C_{\lambda_1}, C_{\lambda_2}, C_{\lambda_3}, C_{\lambda_4}, C_{\lambda_5}) &= C_{\lambda_1} C_{\lambda_2} C_{\lambda_3} C_{\lambda_4} C_{\lambda_5} \\
\mathscr{P}_1(C_{\lambda_1}, C_{\lambda_2}, C_{\lambda_3}, C_{\lambda_4}, C_{\lambda_5}) &= \mathscr{P}(\delta_{\lambda_1\lambda_2}, C_{\lambda_3}, C_{\lambda_4}, C_{\lambda_5}) \\
\mathscr{P}_2(C_{\lambda_1}, C_{\lambda_2}, C_{\lambda_3}, C_{\lambda_4}, C_{\lambda_5}) &= \mathscr{P}(\delta_{\lambda_1\lambda_2}, \delta_{\lambda_3\lambda_4}, C_{\lambda_5}).
\end{aligned} \quad (29)$$

In Eqs. (28) and (29) $\mathscr{P}$ stands for permutations of indices $\lambda_1, \lambda_2, \ldots, \lambda_K$. For example,

$$\begin{aligned}
\mathscr{P}(\delta_{\lambda_1\lambda_2} C_{\lambda_3} C_{\lambda_4}) = {} & \delta_{\lambda_1\lambda_2} C_{\lambda_3} C_{\lambda_4} + \delta_{\lambda_1\lambda_3} C_{\lambda_2} C_{\lambda_4} + \delta_{\lambda_1\lambda_4} C_{\lambda_2} C_{\lambda_3} \\
& + \delta_{\lambda_2\lambda_3} C_{\lambda_1} C_{\lambda_4} + \delta_{\lambda_2\lambda_4} C_{\lambda_1} C_{\lambda_3} + \delta_{\lambda_3\lambda_4} C_{\lambda_1} C_{\lambda_2}.
\end{aligned} \quad (30)$$

The general formulas for $R_{J,i}^K$ coefficients are the following:

$$\begin{aligned}
R_{J,i}^K &= \frac{1}{(K-J-i)!} \prod_{j=1}^{K-J-i} \left[\binom{K-i}{2} - \binom{j}{2} \right] \quad \text{for } \begin{matrix} J+i<K, \\ 2i-1<K, \end{matrix} \\
R_{J,i}^K &= 1 \quad \text{for } J+i=K,\ 2i-1<K.
\end{aligned} \quad (31)$$

If the indices J and i are outside the range given in Eq. (31), then $R_{J,i}^K = 0$. The values for $R_{J,1}^K$ coefficients needed for Green's function matrix elements through g Gaussians are listed in Table 3. The coefficients $R_{J,i}^K$ for $i > 1$ may be obtained also by means of the recursive formula

$$R_{J,i+1}^{K+1} = R_{J,i}^K \quad \text{for } \begin{matrix} J+i<K, \\ 2i<K. \end{matrix} \quad (32)$$

The explicit expressions for P_J^K coefficients needed for Green's function matrix elements through d Gaussians are presented in Table 4.

Table 3. Coefficients $R^K_{J,0}$ for $K \leqslant 8$ and $J \leqslant K$

K	$R^K_{1,0}$	$R^K_{2,0}$	$R^K_{3,0}$	$R^K_{4,0}$	$R^K_{5,0}$	$R^K_{6,0}$	$R^K_{7,0}$	$R^K_{8,0}$
1	1							
2	1	1						
3	3	3	1					
4	15	15	6	1				
5	105	105	45	10	1			
6	945	945	420	105	15	1		
7	10395	10395	4725	1260	210	21	1	
8	135135	135135	62370	17325	3150	378	28	1

3 Results and discussion

We tested the new formulas for Green's function matrix elements against the numerical data published by Levin and coworkers [3]. We also tested them by calculations in which we integrated the angular part of Eq. (5) analytically and the resulting expression was integrated numerically over k. Having calculated these integrals in two different ways, we feel confident that the data by Levin et al. [3] contains a few misprints (wrong signs of some integrals). We consider it expedient to present the corrected values, because they belong to the only data set we have found in the literature that was suitable for checking our results. The matrix elements 3–9, 3–8, and 1–6 from Table IV of Ref. [3] should read $0.334011 \times 10^{-2} + \mathrm{i}\ 0.52021 \times 10^{-6}$, $-0.182042 - \mathrm{i}\ 0.19020 \times 10^{-1}$, and $-0.255808 \times 10^{-6} - \mathrm{i}\ 0.73535 \times 10^{-9}$, and the position vector of center 9 should be $(0,0,-R)$ for $R = -1.034$ a.u.

The formulas we derived are about as complex as those by Levin and coworkers [3]. While they listed explicit formulas only for axially symmetric molecules, we present explicit formulas for a general polyatomic molecule that may be used directly for computer coding. For the purpose of checking new computer codes we present in Tables 5 and 6 a representative set of numerical matrix elements for both the one-center and two-center integrals for a set of s, p, d, and f-type Gaussian functions.

Appendix

A. Evaluation of integrals J_{2j}

In this Appendix we present formulas for integrals of the following type

$$J_{2j} = \lim_{\varepsilon \to 0} \int_0^\infty \frac{k^{2j} \mathrm{e}^{-a^2k^2}}{k_0^2 - k^2 + \mathrm{i}\varepsilon} \mathrm{d}k. \tag{A.1}$$

For $j = 0$ the integral may be evaluated [4] by means of the complex error function [5] using the algorithm of Gautschi [6],

$$J_0 = -\frac{\pi}{2k_0} \mathrm{i}w(ak_0). \tag{A.2}$$

Table 4. Coefficients P_J^K for $K \leqslant 4$ and $J \leqslant K$

$l+l'$	$m+m'$	$n+n'$	K	J	P_J^K	J	P_J^K
1	0	0	1	1	C_x		
2	0	0	2	1	$-(1/C)(C_x^2-1)$	2	C_x^2
1	1	0	2	1	$-(1/C)\,C_xC_y$	2	C_xC_y
3	0	0	3	1	$(3/C^2)(C_x^3-C_x)$	2	$-(3/C)\,(C_x^3-C_x)$
				3	C_x^3		
2	1	0	3	1	$(1/C^2)\,(3C_x^2C_y-C_y)$	2	$-(1/C)\,(3C_x^2C_y-C_y)$
				3	$C_x^2C_y$		
1	1	1	3	1	$(1/C^2)\,3C_xC_yC_z$	2	$-(1/C)\,3C_xC_yC_z$
				3	$C_xC_yC_z$		
4	0	0	4	1	$-(1/C^3)(15C_x^4-18C_x^2+3)$	2	$(1/C^2)(15C_x^4-18C_x^2+3)$
				3	$-(6/C)(C_x^4-C_x^2)$	4	C_x^4
3	1	0	4	1	$-(1/C^3)(15C_x^3C_y-9C_xC_y)$	2	$(1/C^2)(15C_x^3C_y-9C_xC_y)$
				3	$-(1/C)(6C_x^3C_y-3C_xC_y)$	4	$C_x^3C_y$
2	2	0	4	1	$-(1/C^3)(15C_x^2C_y^2-3C_x^2-3C_y^2+1)$	2	$(1/C^2)(15C_x^2C_y^2-3C_x^2-3C_y^2+1)$
				3	$-(1/C)(6C_x^2C_y^2-C_x^2-C_y^2)$	4	$C_x^2C_y^2$
2	1	1	4	1	$-(1/C^3)(15C_x^2C_yC_z-3C_yC_z$	2	$(1/C^2)(15C_x^2C_yC_z-3C_yC_z)$
				3	$-(1/C)(6C_x^2C_yC_z-C_yC_z)$	4	$C_x^2C_yC_z$

Table 5. Two sets of Gaussian functions used for numerical testing of Green's function matrix elements[a, b]

Type of Gaussian	Set A		Set B	
	Number	Exponent	Number	Exponent
s	$1A$	5.0	$1B$	4.5
p_x	$2A$	3.0	$2B$	2.5
d_{xx}	$3A$	1.5	$3B$	1.0
d_{xy}	$4A$	1.5	$4B$	1.0
f_{xxx}	$5A$	1.0	$5B$	0.5
f_{xxy}	$6A$	1.0	$6B$	0.5
f_{xyz}	$7A$	1.0	$7B$	0.5

[a] Gaussians of the set A are centered at $(-0.2, -0.4, -0.1)$ a.u. and those of the set B at (1.0, 0.6, 1.6) a.u.
[b] $k = 0.85215$ a.u.

Using a decomposition,

$$\frac{k^{2j}}{k_0^2 - k^2 + i\varepsilon} = \frac{(k_0^2 + i\varepsilon)^j}{k_0^2 - k^2 + i\varepsilon} - \left[\sum_{m=0}^{j-1} k^{2(j-m-1)} (k_0^2 + i\varepsilon)^m \right], \quad j \geqslant 1, \tag{A.3}$$

a general formula for integrals J_{2j}

$$J_{2j} = k_0^{2j} J_0 - \left[\sum_{m=0}^{j-1} k_0^{2(j-m+1)} I_{2m} \right], \quad j \geqslant 1, \tag{A.4}$$

can be easily derived in which I_{2m} are Gaussian-type integrals:

$$I_{2m} = \int_0^\infty k^{2m} e^{-a^2 k^2} dk = \sqrt{\pi} \frac{|2m-1|!!}{2^{m+1} a^{2m+1}}, \quad m \geqslant 0. \tag{A.5}$$

B. Evaluation of integrals K_{LMN}

The integral K_{LMN} can be written in the form

$$K_{LMN} = R_{LM} T_{LMN} J_{L+M+N+2}, \tag{B.1}$$

where

$$R_{LM} = \int_0^{2\pi} (\cos\varphi)^L (\sin\varphi)^M d\varphi, \tag{B.2}$$

$$T_{LMN} = \int_0^{\pi} (\sin\vartheta)^{L+M+1} (\cos\vartheta)^N d\vartheta, \tag{B.3}$$

and $J_{L+M+N+2}$ is evaluated in Appendix A for $L + M + N + 2$ even. Integrals (B.2) and (B.3) may be evaluated by recursive formulas (cf. paragraph 2.51–2.52 in [7]). For $L + M + N + 2$ odd the integral K_{LMN} is zero because the product $R_{LM} \cdot T_{LMN}$ has a zero value.

Table 6. Numerical values of Green's function matrix elements for Gaussians listed in Table 5

Gaussians	One-center matrix elements		Gaussians	Two-center matrix elements	
1*A*–1*A*	−0.17998D + 00	−0.95753D − 01	1*A*–1*B*	0.18798D − 01	−0.44894D − 01
1*A*–2*A*	0.00000D + 00	0.00000D + 00	1*A*–2*B*	0.14890D − 01	0.17542D − 01
1*A*–3*A*	−0.12006D + 00	−0.26073D + 00	1*A*–3*B*	0.57904D − 01	−0.12092D + 00
1*A*–4*A*	0.00000D + 00	0.00000D + 00	1*A*–4*B*	−0.29636D − 01	−0.81446D − 02
1*A*–5*A*	0.00000D + 00	0.00000D + 00	1*A*–5*B*	0.53631D − 01	0.12827D + 00
1*A*–6*A*	0.00000D + 00	0.00000D + 00	1*A*–6*B*	0.52813D − 01	0.81328D − 01
1*A*–7*A*	0.00000D + 00	0.00000D + 00	1*A*–7*B*	0.71775D − 01	0.60877D − 02
2*A*–2*A*	−0.14531D + 00	−0.18232D − 01	2*A*–2*B*	0.89301D − 03	−0.92184D − 02
2*A*–3*A*	0.00000D + 00	0.00000D + 00	2*A*–3*B*	−0.97045D − 02	−0.36164D − 01
2*A*–4*A*	0.00000D + 00	0.00000D + 00	2*A*–4*B*	0.19666D − 02	0.47151D − 02
2*A*–5*A*	−0.14769D + 00	−0.13501D + 00	2*A*–5*B*	−0.12919D − 01	−0.68011D − 01
2*A*–6*A*	0.00000D + 00	0.00000D + 00	2*A*–6*B*	−0.13385D − 02	0.10500D − 01
2*A*–7*A*	0.00000D + 00	0.00000D + 00	2*A*–7*B*	−0.11663D − 01	−0.36860D − 02
3*A*–3*A*	−0.26981D + 00	−0.63338D + 00	3*A*–3*B*	0.17096D + 00	−0.29186D + 00
3*A*–4*A*	0.00000D + 00	0.00000D + 00	3*A*–4*B*	−0.42973D − 01	−0.19049D − 01
3*A*–5*A*	0.00000D + 00	0.00000D + 00	3*A*–5*B*	0.66185D − 01	0.28483D + 00
3*A*–6*A*	0.00000D + 00	0.00000D + 00	3*A*–6*B*	0.98382D − 01	0.20489D + 00
3*A*–7*A*	0.00000D + 00	0.00000D + 00	3*A*–7*B*	0.95085D − 01	0.14637D − 01
4*A*–4*A*	−0.19601D + 00	−0.13645D − 01	4*A*–4*B*	−0.61800D − 02	−0.76198D − 02
4*A*–5*A*	0.00000D + 00	0.00000D + 00	4*A*–5*B*	−0.34555D − 01	−0.23824D − 01
4*A*–6*A*	0.00000D + 00	0.00000D + 00	4*A*–6*B*	−0.18215D − 02	−0.16832D − 01
4*A*–7*A*	0.00000D + 00	0.00000D + 00	4*A*–7*B*	0.15837D − 01	0.61563D − 02
5*A*–5*A*	−0.60989D + 00	−0.68025D + 00	5*A*–5*B*	−0.15283D − 01	−0.34206D + 00
5*A*–6*A*	0.00000D + 00	0.00000D + 00	5*A*–6*B*	0.24617D − 01	0.54280D − 01
5*A*–7*A*	0.00000D + 00	0.00000D + 00	5*A*–7*B*	−0.77152D − 01	−0.19204D − 01
6*A*–6*A*	−0.43505D + 00	−0.38269D + 00	6*A*–6*B*	−0.24533D − 01	−0.21141D + 00
6*A*–7*A*	0.00000D + 00	0.00000D + 00	6*A*–7*B*	−0.50700D − 01	−0.16308D − 01
7*A*–7*A*	−0.21650D + 00	−0.10747D − 01	7*A*–7*B*	−0.19990D − 02	−0.51694D − 02

C. Evaluation of $G_{ss}^{(J)}$ *terms*

Here, we introduce the following three auxiliary functions:

$$f^{(0)}(C) = \frac{\pi^2}{8C(\alpha\beta)^{3/2}} \exp(-C^2/4a^2), \tag{C.1}$$

$$W_{+}^{(0)}(C) = w\left(ak_0 + \frac{iC}{2a}\right) + W\left(ak_0 - \frac{iC}{2a}\right). \tag{C.2}$$

$$W_{-}^{(0)}(C) = w\left(ak_0 + \frac{iC}{2a}\right) - w\left(ak_0 - \frac{iC}{2a}\right), \tag{C.3}$$

where a is defined by Eq. (8). The fundamental integral for two s-type Gaussian is then obtained [1] as

$$\langle \alpha_s^A | G_0^+ | \beta_s^B \rangle = G_{ss} = G_{ss}^{(0)} = f^{(0)}(C) W_{-}^{(0)}(C). \tag{C.4}$$

The derivatives of this integral with respect to C are obtained from the general formula

$$G_{ss}^{(J)}(C) = \sum_{q=0}^{J} \binom{J}{q} f^{(J-q)}(C) W_{-}^{(q)}(C) \tag{C.5}$$

where $f^{(J-q)}(C)$ and $W_{-}^{(q)}(C)$ are derivatives of $f^{(0)}(C)$ and $W_{-}^{(0)}(C)$ with respect to C, respectively. The first derivatives of f, W_{+}, and W_{-} are given by the following expressions:

$$f^{(1)}(C) = -f^{(0)}(C)\,F^{(0)}(C), \tag{C.6}$$

$$W_{+}^{(1)}(C) = \frac{C}{2a^2}\,W_{+}^{(0)}(C) - ik_0\,W_{-}^{(0)}(C), \tag{C.7}$$

$$W_{-}^{(1)}(C) = \frac{C}{2a^2}\,W_{-}^{(0)}(C) - ik_0\,W_{+}^{(0)}(C) - \frac{2}{a\sqrt{\pi}}, \tag{C.8}$$

where

$$F^{(0)}(C) = \frac{1}{C} + \frac{C}{2a^2}. \tag{C.9}$$

The higher derivatives for $n \geqslant 2$ are obtained from the recursive expressions

$$f^{(n)}(C) = -\sum_{q=0}^{n-1} \binom{n-1}{q} f^{(n-q-1)}(C)\,F^{(q)}(C), \tag{C.10}$$

$$W_{+}^{(n)}(C) = (n-1)\frac{1}{2a^2}\,W_{+}^{(n-2)}(C) - ik_0\,W_{-}^{(n-1)}(C) + \frac{C}{2a^2}\,W_{+}^{(n-1)}(C), \tag{C.11}$$

$$W_{-}^{(n)}(C) = (n-1)\frac{1}{2a^2}\,W_{-}^{(n-2)}(C) - ik_0\,W_{+}^{(n-1)}(C) + \frac{C}{2a^2}\,W_{-}^{(n-1)}(C), \tag{C.12}$$

where

$$F^{(1)}(C) = -\frac{1}{C^2} + \frac{1}{2a^2}, \tag{C.13}$$

and

$$F^{(n)}(C) = (-1)^n n!\,C^{-(n+1)}. \tag{C.14}$$

Acknowledgements. This work was supported by grant No. 93018 from the US–Czechoslovak Science and Technology Program, and by grant 203/93/0044 of the Grant Agency of the Czech Republic. We wish to express our thanks to Prof. Josef Michl for valuable comments on this manuscript. In addition, one of us (V.H.) wishes to express gratitude to Prof. Michl for his generous hospitality.

References

1. Ostlund NS (1975) Chem Phys Lett 34:419
2. Ostlund NS private communication noted in Ref. [3]
3. Levin DA, Fliflet AW, Ma M, McKoy V (1978) J Comput Phys 28:416
4. Erdélyi, A, Magnus W, Oberhettinger F, Tricomi FG (1954) Tables of integral transforms, Vol 1. McGraw-Hill, New York
5. Abramowitz M, Stegun IA (eds) (1968) Handbook of mathematical functions, 7th edition. National Bureau of Standards, Washington
6. Gautschi W (1970) SIAM J Numer Anal 7:187
7. Gradshteyn IS, Ryzhik IM (1980) In: Jeffrey A (ed) Tables of integrals, series, and products, Corrected and Enlarged Edition, Chapters 8 and 9. Academic Press, New York
8. Shavitt I (1963) in: Alder B, Fernbach S, Rotenberg M (eds) Methods in computational physics, Vol 2, pp 1–45. Academic Press, New York