ANALYTIC EVALUATION OF MULTICENTER INTEGRALS FOR GAUSSIAN-TYPE ORBITALS

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Abstract

This work contains the evaluation of multicenter integrals with Cartesian Gaussian functions occurring in $\| \mathcal{H}\psi \|^2$. These integrals have to be used if it is necessary to calculate the lower bounds for eigenvalues with the method of the minimization of the variance [1]. Considering the variance $\mathcal{F}(\psi) = \| \mathcal{H}\psi \|^2 - (\mathcal{H}\psi \mid \psi)^2$, the integrals from $(\mathcal{H}\Psi, \Psi)$ are well known in contrast to those for $\| \mathcal{H}\Psi \|^2$.

1. Introduction

Almost all calculations of upper bounds for eigenvalues, using the Rayleigh–Ritz variation principle, nowadays are performed with Gaussian functions, because of the difficulties of calculating $(\mathcal{H}\Psi, \Psi)$ for Slater functions. Two methods are dominant: the use of Laplace and Fourier transform [2–4] and recurrence relations [5–8].

In contrast, there are few papers concerning the integrals for $\| \mathcal{H}\Psi \|^2$, e.g. the papers by Zimering [9] and Roberts [10]. Starting with Gaussian functions of the type

$$\chi(\alpha, l, m, n) = x_a^l\, y_a^m\, z_a^n\, \mathrm{e}^{-\alpha r_a^2}. \tag{1}$$

(x_a, y_a and z_a are the components of the vector $\boldsymbol{r}_a = \boldsymbol{r} - \boldsymbol{a}$ and l, m, n are integers ≥ 0). Four basic integrals are obtained calculating $(\mathcal{H}\Psi, \Psi)$: $J_1, \ldots, J_4$ according to the nomenclature of Huzinaga et al. [3].

In analogy, $(\mathcal{H}\Psi, \mathcal{H}\Psi)$ produces another five types of integrals $J_5, \ldots, J_9$ (see section 2). For the case $l = m = n = 0$, these integrals are given in [9, 10]. The general case $l, m, n \in \mathbb{N}$ can be treated combining the methods of Laplace and Fourier transform.

2. Basic integrals

Looking at the functions ψ in $\| \mathcal{H}\psi \|^2$ in the most general form as a linear combination of products of Gaussian functions, e.g. Slater determinants, then the products of

$$\chi_i^j = x_{q_j}^{l_i} y_{q_j}^{m_i} z_{q_j}^{n_i} \mathrm{e}^{-\alpha_i r_{q_j}^2}, \tag{2}$$

with the centers $q = a, b, c, \ldots$, can be newly centered with regard to the electrons $j = 1, 2, 3, \ldots$ [4]. Thus, one obtains linear combinations of Gaussian functions referring to just one center for each electron. With $\mathcal{H}$ as Born–Oppenheimer Hamiltonian, the following basic integrals are then needed for $\| \mathcal{H} \psi \|^2$:

$$J_5 = (r_{c_1}^{-2} \mid \chi_1),$$

$$J_6 = (\chi_1^1 \mid r_{12}^{-2} \mid \chi_2^2),$$

$$J_7 = ((r_{c_1} r_{d_1})^{-1} \mid \chi_1),$$

$$J_8 = (\chi_1^1 \mid (r_{12} r_{c_1})^{-1} \mid \chi_2^2),$$

$$J_9 = (\chi_1^1 \mid (r_{12} r_{13})^{-1} \mid \chi_2^2 \chi_3^3),$$

with

$$\chi_1^1 = x_{a_1}^{l_1} y_{a_1}^{m_1} z_{a_1}^{n_1} \mathrm{e}^{-\alpha_1 r_{a_1}^2},$$

$$\chi_2^2 = x_{b_2}^{l_2} y_{b_2}^{m_2} z_{b_2}^{n_2} \mathrm{e}^{-\alpha_2 r_{b_2}^2},$$

$$\chi_3^3 = x_{c_3}^{l_3} y_{c_3}^{m_3} z_{c_3}^{n_3} \mathrm{e}^{-\alpha_3 r_{c_3}^2}.$$

For the solution of J_5 up to J_9, the following relations are needed [3, 9, 10]:

$$\frac{1}{r} = \frac{1}{2\pi^2} \int \frac{\mathrm{d}\boldsymbol{k}}{k^2} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{r}}, \tag{3}$$

$$\frac{1}{k} = \frac{1}{\sqrt{\pi}} \int_0^\infty \frac{\mathrm{d}\eta}{\sqrt{\eta}} \mathrm{e}^{-\eta k^2} = \frac{2}{\sqrt{\pi}} \int_0^\infty \mathrm{d}\eta\, \mathrm{e}^{-\eta^2 k^2}, \tag{4}$$

$$\frac{1}{r^2} = \frac{1}{4\pi} \int \frac{\mathrm{d}\boldsymbol{k}}{k} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\boldsymbol{r}}, \tag{5}$$

$$\mathrm{e}^{-\delta k^2} = 2\delta k^2 \int_0^1 \frac{\mathrm{d}s}{s^3} \mathrm{e}^{-(\delta/s^2)k^2}, \tag{6}$$

$$I(n,y,a)_k = \int_{-\infty}^{+\infty} \mathrm{d}x\, x^n \mathrm{e}^{\mathrm{i}xy}\, \mathrm{e}^{-ax^2}$$

$$= (\mathrm{i})^n \sqrt{\frac{\pi}{a}}\, 2^{-n} a^{-n/2} n!\, \mathrm{e}^{-y^2/4a} \cdot \sum_{k=0}^{[n/2]} \frac{(-1)^k}{k!(n-2k)!} \left(\frac{y}{\sqrt{a}}\right)^{n-2k} . \quad (7)$$

The index k at $I(n, y, a)_k$ indicates the selected summation index.

$$J_5 = \int \mathrm{d}r r_c^{-2} x_a^l y_a^m z_a^n \mathrm{e}^{-\alpha r_a^2}.$$

With $\boldsymbol{r}_c = \boldsymbol{r} - \boldsymbol{c} = \boldsymbol{r}_a + \boldsymbol{ac}$, $\boldsymbol{ac} = \boldsymbol{a} - \boldsymbol{c}$ and the transformation of r_c^{-2} to (5), it is possible to integrate with regard to $\boldsymbol{r}$. Then, with (7) we obtain:

$$J_5 = \frac{1}{4\pi} \int \frac{\mathrm{d}\boldsymbol{k}}{k}\, I(l, -k_x, \alpha)_{i_1} I(m, -k_y, \alpha)_{i_2} I(n, -k_z, \alpha)_{i_3}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\,\boldsymbol{ac}}. \quad (8)$$

The newly produced singularity k^{-1} can be removed with (4). Thereafter, one can integrate on the $\boldsymbol{k}$-space with (7). According to the components, one obtains:

$$I\left(l-2i_1,\ -ac_x, \eta + \frac{1}{4\alpha}\right)_{j_1},$$

$$I\left(m-2i_2, -ac_y, \eta + \frac{1}{4\alpha}\right)_{j_2},$$

$$I\left(n-2i_3,\ -ac_z, \eta + \frac{1}{4\alpha}\right)_{j_3}.$$

Finally, there still remains the integration with regard to the auxiliary variable η. This results with the substitution

$$s = \sqrt{\frac{\eta}{\eta + \frac{1}{4\alpha}}}$$

in

$$\Gamma_5 = 2(4\alpha)^{\nu+1} \mathrm{e}^{-\alpha ac^2} \sum_{\lambda=0}^{\nu} \binom{\nu}{\lambda} (-1)^{\lambda} F_{\lambda}(-\alpha\, ac^2), \quad (9)$$

with $\nu = l + m + n - 2(i_1 + i_2 + i_3) - (j_1 + j_2 + j_3)$ and

$$F_\lambda(t) = \int_0^1 \mathrm{d}u\, u^{2\lambda} \mathrm{e}^{-tu^2}.$$

Summarizing the various results:

$$J_5 = 2\pi \sqrt{\frac{\pi}{\alpha}}\, \mathrm{e}^{-\alpha\, ac^2} \sum_{i_1, j_1} D_{i_1 j_1} \sum_{i_2, j_2} D_{i_2 j_2} \sum_{i_3, j_3} D_{i_3 j_3}$$

$$\times \sum_{\lambda=0}^{\nu} \binom{\nu}{\lambda} (-1)^\lambda F_\lambda(-\alpha\, ac^2), \qquad (10)$$

with

$$D_{i_1 j_1} = (-1)^l \, \frac{(-1)^{j_1} l! (4\alpha)^{-i_1 - j_1} \boldsymbol{ac}_x^{\,l - 2i_1 - 2j_1}}{i_1!\, j_1!\, (l - 2i_1 - 2j_1)!}$$

and $0 \le i_1 \le [l/2]$, $0 \le j_1 \le [(l - 2i_1)/2]$.

$$J_6 = (\chi_1^1 | r_{12}^{-2} | \chi_2^2),$$

With $\boldsymbol{r}_{12} = \boldsymbol{r}_2 - \boldsymbol{r}_1 = \boldsymbol{r}_{2b} - \boldsymbol{r}_{2a} + \boldsymbol{ba}$ and (5), (7), the space integration can be performed. The solutions

$$I(l_1, k_x, \alpha_1)_{i_1}, \quad I(m_1, k_y, \alpha_1)_{i_2}, \quad I(n_1, k_z, \alpha_1)_{i_3}$$

$$I(l_2, -k_x, \alpha_2)_{j_1}, \quad I(m_2, -k_y, \alpha_2)_{j_2}, \quad I(n_2, -k_z, \alpha_2)_{j_3},$$

can be integrated with (4) with respect to $\boldsymbol{k}$ and lead, together with (7), to

$$I(l_1 + l_2 - 2(i_1 + j_1), \boldsymbol{ab}_x, \delta + \eta)_{k_1},$$

$$I(m_1 + m_2 - 2(i_2 + j_2), \boldsymbol{ab}_y, \delta + \eta)_{k_2},$$

$$I(n_1 + n_2 - 2(i_3 + j_3), \boldsymbol{ab}_z, \delta + \eta)_{k_3},$$

with

$$\delta = \frac{1}{4\alpha_1} + \frac{1}{4\alpha_2}.$$

The substitution $s = \sqrt{\eta/(\delta + \eta)}$ results in the integration regarding η:

$$\Gamma_6 = 2\delta^{-\nu-1} e^{-ab^2/4\delta} \sum_{\lambda=0}^{\nu} \binom{\nu}{\lambda} (-1)^{\lambda} F_{\lambda}\left(-\frac{ab^2}{4\delta}\right), \tag{11}$$

with

$$\nu = l_1 + l_2 + m_1 + m_2 + n_1 + n_2 - 2(i_1 + i_2 + i_3 + j_1 + j_2 + j_3) - k_1 - k_2 - k_3 .$$

Finally, the solution is as follows:

$$J_6 = \frac{2\pi^2}{\alpha_1 + \alpha_2} \sqrt{\frac{\pi^2}{\alpha_1 \alpha_2}}\, e^{-ab^2/4\delta} \sum_{i_1, j_1, k_1} C_{i_1, j_1, k_1} \sum_{i_2, j_2, k_2} C_{i_2, j_2, k_2} \sum_{i_3, j_3, k_3} C_{i_3, j_3, k_3}$$
$$\times \sum_{\lambda=0}^{\nu} \binom{\nu}{\lambda} (-1)^{\lambda} F_{\lambda}\left(-\frac{ab^2}{4\delta}\right), \tag{12}$$

with

$$C_{i_1, j_1, k_1} = (-1)^{l_1} \frac{(4\alpha_1)^{i_1 - l_1} (4\alpha_2)^{j_1 - l_2} \delta^{2(i_1 + j_1) - l_1 - l_2 + k_1}}{i_1 !\, j_1 !\, (l_1 - 2i_1)! (l_2 - 2j_1)!}$$
$$\times (-1)^{k_1} \frac{l_1 !\, l_2 ! (l_1 + l_2 - 2(i_1 + j_1))!\, ab_x^{l_1 + l_2 - 2(i_1 + j_1) - 2k_1}}{k_1 ! (l_1 + l_2 - 2(i_1 + j_1) - 2k_1)!},$$
$$0 \le i_1 \le \left[\frac{l_1}{2}\right], \quad 0 \le j_1 \le \left[\frac{l_2}{2}\right], \quad 0 \le k_1 \le \left[\frac{l_1 + l_2}{2} - i_1 - j_1\right],$$

$$J_7 = \int \mathrm{d}\boldsymbol{r} \frac{1}{r_c r_d} x_a^l y_a^m z_a^n e^{-\alpha r_a^2}. \tag{13}$$

With $\boldsymbol{r}_c = \boldsymbol{r}_a + \boldsymbol{ac}$, $\boldsymbol{r}_d = \boldsymbol{r}_a + \boldsymbol{ad}$ and (3), (4), one obtains

$$\frac{1}{r_c r_d} = \pi^{-5/2} \int_0^{\infty} \mathrm{d}\eta \int \frac{\mathrm{d}\boldsymbol{k}}{k^2} e^{i\boldsymbol{k} \boldsymbol{r}_a} e^{i\boldsymbol{k}\, \boldsymbol{ad}} e^{-\eta^2 r_c^2}. \tag{14}$$

The combination of the Gaussian functions results in

$$e^{-\alpha r_a^2} e^{-\eta^2 r_c^2} = e^{-\frac{\alpha\eta^2}{\alpha + \eta^2} ac^2} e^{-(\alpha + \eta^2) r_q^2}, \tag{15}$$

with $\boldsymbol{r}_q = \boldsymbol{r} - \boldsymbol{q}$, $\boldsymbol{q} = (\alpha \boldsymbol{a} + \eta^2 \boldsymbol{c})/(\alpha + \eta^2)$. Then we have:

$$\boldsymbol{r}_a = \boldsymbol{r}_q + \boldsymbol{q}\boldsymbol{a} = \boldsymbol{r}_q - \frac{\eta^2}{\alpha+\eta^2}\,\boldsymbol{ac} \tag{16}$$

and $|\boldsymbol{qd}| = (\alpha + \eta^2)^{-1}\sqrt{P(\eta)}$, with $P(\eta) = |\alpha\boldsymbol{ad} + \eta^2\boldsymbol{cd}|^2$. With (16) we obtain

$$x_a^l = \sum_{i_0=0}^{l} (-1)^{l-i_0}\binom{l}{i_0}\left(\frac{\eta^2}{\alpha+\eta^2}\right)^{l-i_0} \boldsymbol{ac}_x^{l-i_0} x_q^{i_0}. \tag{17}$$

For y_a^m, z_a^n, the summation indices will be j_0 and k_0. With (7), one can now integrate with respect to $\boldsymbol{r}_q$, obtaining

$$I(i_0, k_x, \alpha+\eta^2)_{i_1},\quad I(j_0, k_y, \alpha+\eta^2)_{i_2},\quad I(k_0, k_z, \alpha+\eta^2)_{i_3}.$$

The singularity k^{-2} can be removed with (6) according to

$$\mathrm{e}^{-\frac{k^2}{4(\alpha+\eta^2)}} = \frac{k^2}{2(\alpha+\eta^2)}\int_0^1 \mathrm{d}\mu\,\mu^{-3}\,\mathrm{e}^{-\frac{k^2}{4\mu^2(\alpha+\eta^2)}}. \tag{18}$$

Integration over $\boldsymbol{k}$ leads to the solutions

$$I(i_0, -2i_1, \boldsymbol{qd}_x, \varepsilon)_{j_1},\quad I(j_0, -2i_2, \boldsymbol{qd}_y, \varepsilon)_{j_2},\quad I(k_0, -2i_3, \boldsymbol{qd}_z, \varepsilon)_{j_3},$$

with

$$\varepsilon = \frac{1}{4\mu^2(\alpha+\eta^2)}.$$

Now one can integrate over μ, obtaining the solution

$$F_\nu[(\alpha+\eta^2)^{-1}P(\eta)] \quad \text{with} \quad \nu = i_0 + j_0 + k_0 - 2(i_1+i_2+i_3) - (j_1+j_2+j_3).$$

With

$$\boldsymbol{qd} = \frac{\eta^2}{\alpha+\eta^2}\left(\frac{\alpha}{\eta^2}\,\boldsymbol{ad} + \boldsymbol{cd}\right),$$

we obtain

$$\left(\frac{\alpha}{\eta^2}\,\boldsymbol{ad}_x + \boldsymbol{cd}_x\right)^{i_0-2(i_1+j_1)} = \sum_{k_1=0}^{i_0-2(i_1+j_1)} \binom{i_0-2(i_1+j_1)}{k_1} \alpha^{k_1}\boldsymbol{ad}_x^{k_1}\boldsymbol{cd}_x^{i_0-2(i_1+j_1)-k_1}\eta^{-2k_1}. \tag{19}$$

For qd_y, qd_z, the summation indices will be k_2 and k_3. Hence, one can integrate over η, obtaining with the substitution

$$z = \sqrt{\frac{\eta^2}{\alpha + \eta^2}},$$

$$\Gamma_7 = \frac{1}{\sqrt{\alpha}} \alpha^{\varepsilon_2} \sum_{\varepsilon_0 = 0}^{\varepsilon_2} \binom{\varepsilon_2}{\varepsilon_0} (-1)^{\varepsilon_0} \int_0^1 \frac{\mathrm{d}z}{\sqrt{1-z^2}} z^{2(\varepsilon_1 + \varepsilon_0)} \times \mathrm{e}^{-\alpha z^2 \boldsymbol{ac}^2} F_\nu [\alpha(1-z^2)^{-1} F(z)], \tag{20}$$

with $F(z) = | z^2 \boldsymbol{ca} + \boldsymbol{ad} |^2$ and

$$\varepsilon_1 = l + m + n - 2(i_1 + i_2 + i_3) - 2(j_1 + j_2 + j_3) - (k_1 + k_2 + k_3),$$

$$\varepsilon_2 = i_1 + i_2 + i_3 + j_1 + j_2 + j_3 + k_1 + k_2 + k_3 .$$

The individual results can thus be summarized:

$$J_7 = 4\sqrt{\frac{\pi}{\alpha}} \sum_{i_0, i_1, j_1, k_1} A_{i_0, i_1, j_1, k_1} \sum_{j_0, i_2, j_2, k_2} A_{j_0, i_2, j_2, k_2} \sum_{k_0, i_3, j_3, k_3} A_{k_0, i_3, j_3, k_3} \sum_{\varepsilon_0 = 0}^{\varepsilon_2} \binom{\varepsilon_2}{\varepsilon_0} (-1)^{\varepsilon_0} \times \int_0^1 \frac{\mathrm{d}z}{\sqrt{1-z^2}} z^{2(\varepsilon_1 + \varepsilon_0)} \mathrm{e}^{-\alpha z^2 \boldsymbol{ac}^2} F_\nu [\alpha(1-z^2)^{-1} F(z)], \tag{21}$$

with

$$A_{i_0, i_1, j_1, k_1} = (-1)^{l + j_1} \frac{l! (4\alpha)^{-(i_1 + j_1)} \boldsymbol{ac}_x^{l - i_0} \boldsymbol{ad}_x^{k_1} \boldsymbol{cd}_x^{i_0 - 2(i_1 + j_1) - k_1}}{(l - i_0)! i_1! j_1! k_1! (i_0 - 2(i_1 + j_1) - k_1)!}$$

and

$$0 \le i_0 \le l, \quad 0 \le i_1 \le \left[\frac{i_0}{2} \right], \quad 0 \le j_1 \le \left[\frac{i_0 - 2i_1}{2} \right], \quad 0 \le k_1 \le i_0 - 2(i_1 + j_1),$$

$$J_8 = (\chi_1^1 | r_{12} r_{1c})^{-1} | \chi_2^2).$$

With (3) and (4), the following can be recorded:

$$(r_{12} r_{1c})^{-1} = \pi^{-5/2} \int_0^\infty \mathrm{d}\eta \int \frac{\mathrm{d}\boldsymbol{k}}{k^2} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\,\boldsymbol{ba}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\,\boldsymbol{r}_{2b}} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\,\boldsymbol{r}_{1a}} \mathrm{e}^{-\eta^2 r_{1c}^2}, \tag{22}$$

and thus

$$\mathrm{e}^{-\alpha_1 r_{1a}^2} \mathrm{e}^{-\eta^2 r_{1c}^2} = \mathrm{e}^{-\frac{\alpha_1 \eta^2 \boldsymbol{ac}^2}{\alpha_1 + \eta^2}} \mathrm{e}^{-(\alpha_1 + \eta^2) r_{1e}^2}. \tag{23}$$

With $\boldsymbol{r}_{1e} = \boldsymbol{r}_1 - \boldsymbol{e}$, $\boldsymbol{e} = (\alpha_1\boldsymbol{a} + \eta^2\boldsymbol{c})/(\alpha_1 + \eta^2)$, we obtain

$$\boldsymbol{r}_{1a} = \boldsymbol{r}_{1e} + \boldsymbol{ea} = \boldsymbol{r}_{1e} + \frac{\eta_2}{\alpha_1 + \eta^2}\,\boldsymbol{ca} \tag{24}$$

and

$$|\boldsymbol{be}| = \frac{\sqrt{P(\eta)}}{\alpha_1 + \eta^2}\,, \tag{25}$$

with $P(\eta) = |\,\alpha_1\boldsymbol{ba} + \eta^2\boldsymbol{bc}\,|^2$. From (24), it follows:

$$x_{1a}^{l_1} = \sum_{i_0=0}^{l_1} \binom{l_1}{i_0} \left(\frac{\eta^2}{\alpha_1 + \eta^2}\right)^{l_1 - i_0} ca_x^{l_1 - i_0} x_{1e}^{i_0}\,. \tag{26}$$

For $y_{1a}^{m_1}$, $z_{1a}^{n_1}$, the summation indices will be j_0, k_0.

With (7), one can integrate over $\boldsymbol{r}_{1e}$, whereby

$$I(i_0, -k_x, \alpha_1 + \eta^2)_{i_1},\quad I(j_0, -k_y, \alpha_1 + \eta^2)_{i_2},\quad I(k_0, -k_z, \alpha_1 + \eta^2)_{i_3}$$

occur as solutions.

Direct integration over $\boldsymbol{r}_{2b}$, together with (7), leads to

$$I(l_2, k_x, \alpha_2)_{j_1},\quad I(m_2, k_y, \alpha_2)_{j_2},\quad I(n_2, k_z, \alpha_2)_{j_3}\,.$$

In order to integrate over $\boldsymbol{k}$, according to (6) we find

$$\mathrm{e}^{-\frac{k^2}{4}\gamma} = \frac{k^2}{2}\,\gamma \int_0^1 \mathrm{d}\mu\, \mu^{-3}\, \mathrm{e}^{-\frac{k^2}{4\mu^2}\gamma},$$

with

$$\gamma = \frac{\alpha_1 + \alpha_2 + \eta^2}{\alpha_2(\alpha_1 + \eta^2)}\,.$$

Thus, we obtain

$$I\left(i_0 + l_2 - 2(i_1 + j_1),\, \boldsymbol{b}e_x,\, \frac{\gamma}{4\mu^2}\right)_{k_1},$$

$$I\left(j_0 + m_2 - 2(i_2 + j_2),\, \boldsymbol{b}e_y,\, \frac{\gamma}{4\mu^2}\right)_{k_2},$$

$$I\left(k_0 + n_2 - 2(i_3 + j_3), \boldsymbol{b e}_z, \frac{\gamma}{4\mu^2}\right)_{k_3}.$$

With

$$\nu = (i_0 + j_0 + k_0) + (l_2 + m_2 + n_2) - 2(i_1 + j_1 + i_2 + j_2 + i_3 + j_3) - (k_1 + k_2 + k_3),$$

$F_\nu\{\alpha_2[(\alpha_1 + \eta^2)(\alpha_1 + \alpha_2 + \eta^2)]^{-1}P(\eta)\}$ is the solution of the μ-integration. With

$$\boldsymbol{be} = \frac{\eta^2}{\alpha_1 + \eta^2}\left(\frac{\alpha_1}{\eta^2}\boldsymbol{ba} + \boldsymbol{bc}\right),$$

the result is

$$\boldsymbol{be}_x^\varepsilon = \left(\frac{\eta^2}{\alpha_1 + \eta^2}\right)^\varepsilon \sum_{\varepsilon_1 = 0}^{\varepsilon} \binom{\varepsilon}{\varepsilon_1} \alpha_1^{\varepsilon_1} \boldsymbol{ba}_x^{\varepsilon_1} \boldsymbol{bc}_x^{\varepsilon - \varepsilon_1} \eta^{-2\varepsilon_1}, \tag{27}$$

with $\varepsilon = i_0 + l_2 - 2(i_1 + j_1) - 2k_1$. The summation indices for $\boldsymbol{be}_y$, $\boldsymbol{be}_z$ will be ε_2, ε_3.

Thus, the integration with respect to η can be effected with the substitution

$$z = \sqrt{\frac{\eta^2}{\alpha_1 + \eta^2}},$$

leading to the result

$$\Gamma_8 = \sqrt{\frac{\alpha_2}{\alpha_1}}\, \alpha_2^\nu \alpha_1^{-\Omega + \nu} \sum_{\omega = 0}^{\Omega} \binom{\Omega}{\omega} (-1)^\omega \int_0^1 \frac{\mathrm{d}z}{\sqrt{\alpha_1 + (1 - z^2)\alpha_2}}\, z^{2\varepsilon_0}$$
$$\times (\alpha_1 + (1 - z^2)\alpha_2)^{-\nu} \mathrm{e}^{-\alpha_1 z^2 \boldsymbol{ac}^2} F_\nu\left\{\frac{\alpha_1 \alpha_2 F(z)}{\alpha_1 + \alpha_2(1 - z^2)}\right\}, \tag{28}$$

with

$$F(z) = |z^2 \boldsymbol{ac} + \boldsymbol{ba}|, \quad \varepsilon_0 = \lambda - (\varepsilon_1 + \varepsilon_2 + \varepsilon_3) + \omega,$$

$$\Omega = (i_0 + j_0 + k_0) - (i_1 + i_2 + i_3) + (\varepsilon_1 + \varepsilon_2 + \varepsilon_3),$$

$$\lambda = (l_1 + m_1 + n_1) + (l_2 + m_2 + n_2) - 2(i_1 + i_2 + i_3) - 2(i_0 + j_0 + k_0) - 2(k_1 + k_2 + k_3).$$

Summarizing the above, the result is as follows:

$$J_8 = \frac{4\pi^2}{\sqrt{\alpha_1}} \frac{1}{\alpha_2} \sum_{i_0,i_1,j_1,k_1,\varepsilon_1} B_{i_0,i_1,j_1,k_1,\varepsilon_1} \sum_{j_0,i_2,j_2,k_2\varepsilon_2} B_{j_0,i_2,j_2,k_2,\varepsilon_2}$$

$$\times \sum_{k_0,i_3,j_3,k_3,\varepsilon_3} B_{k_0,i_3,j_3,k_3,\varepsilon_3} \sum_{\omega=0}^{\Omega} \binom{\Omega}{\omega} (-1)^{\omega} \int_0^1 \frac{dz}{\sqrt{\alpha_1 + (1-z^2)\alpha_2}} z^{2\varepsilon_0}$$

$$\times (\alpha_1 + (1-z^2)\alpha_2)^{-\nu} e^{-\alpha_1 z^2 ac^2} F_\nu \left\{ \frac{\alpha_1 \alpha_2 F(z)}{\alpha_1 + \alpha_2(1-z^2)} \right\}, \tag{29}$$

with

$$B_{i_0,i_1,j_1,k_1,\varepsilon_1} = (-1)^{l_1+l_2+i_0+k_1} 4^{-(i_1+j_1+k_1)} \alpha_1^{l_2-i_1-2j_1-k_1}$$

$$\times \alpha_2^{i_0-2i_1-j_1-k_1} \frac{l_1!\, l_2!\, (i_0+l_2-2(i_1+j_1))!\, \boldsymbol{ac}_x^{l_1-i_0} \boldsymbol{ba}_x^{\varepsilon_1}}{(l_1-i_0)!\, j_1!\, (l_2-2j_1)!\, i_1!\, (i_0-2i_1)!}$$

$$\times \frac{\boldsymbol{bc}_x^{i_0+l_2-2(i_1+j_1)-2k_1-\varepsilon_1}}{k_1!\, \varepsilon_1!\, (i_0+l_2-2(i_1+j_1)-2k_1-\varepsilon_1)!},$$

$$0 \le i_0 \le l_1, \quad 0 \le j_1 \le l_1, \quad 0 \le i_1 \le \left[\frac{i_0}{2}\right],$$

$$0 \le k_1 \le \left[\frac{i_0+l_2-2(i_1+j_1)}{2}\right],$$

$$0 \le \varepsilon_1 \le i_0 + l_2 - 2(i_1+j_1+k_1),$$

$$J_9 = \int d\boldsymbol{r}_1\, d\boldsymbol{r}_2\, d\boldsymbol{r}_3\, (r_{12} r_{13})^{-1} \chi_1^1 \chi_2^2 \chi_3^3, \tag{30}$$

with $\boldsymbol{r}_{12} = \boldsymbol{r}_2 - \boldsymbol{r}_1$, $\boldsymbol{r}_{13} = \boldsymbol{r}_3 - \boldsymbol{r}_1$.

According to the Fourier transformation of r_{12}^{-1}, one integrates over $\boldsymbol{r}_2$ and obtains with respect to the components:

$$I(l_2, k_x, \alpha_2)_{i_1}, \quad I(m_2, k_y, \alpha_2)_{i_2}, \quad I(n_2, k_z, \alpha_2)_{i_3}.$$

The Laplace transformation of r_{13}^{-1} provides

$$e^{-\eta^2 r_{13}^2} e^{-\alpha_3 r_{c3}^2} = e^{-\frac{\alpha_3 \eta^2}{\alpha_3+\eta^2} r_{c1}^2} e^{-(\alpha_3+\eta^2)\left(\boldsymbol{r}_{c3} - \frac{\eta^2 \boldsymbol{r}_{c1}}{\alpha_3+\eta^2}\right)^2}, \tag{31}$$

the option to integrate over r_3. With

$$P = \frac{\eta^2}{\alpha_3 + \eta^2} r_{c_1}$$

and $r_{c_3} - P = r_{P_3}$ or $r_{c_3} = r_{P_3} + P$, respectively, the integration regarding r_{P_3} provides integrals of the type

$$\int dx_3 \, x_{P_3}^{2j_1} e^{-(\alpha_3 + \eta^2)x_{P_3}^2},$$

whereby the following is valid:

$$\int_{-\infty}^{\infty} dx \, x^{2n} e^{-ax^2} = (2a)^{-n} \sqrt{\frac{\pi}{a}} \, (2n-1)!! \tag{32}$$

The summation indices of the components are $0 \leq j_1 \leq [l_3/2]$, j_2, j_3. With the integration over r_1, the r-space integration can then be conluded. In this connection, the following applies:

$$e^{-\alpha_1 r_{a1}^2} e^{-\delta r_{c1}^2} = e^{-(\alpha_1 + \delta) r_{Q1}^2} e^{-\frac{\alpha_1 \delta}{\alpha_1 + \delta} ac^2}, \tag{33}$$

with

$$\delta = \frac{\alpha_3 \eta^2}{\alpha_3 + \eta^2}, \quad Q = \frac{\alpha_1 a + \delta c}{\alpha_1 + \delta}.$$

This leads to

$$I(r_1 + s_1, -k_x, \alpha_1 + \delta)_{k_1},$$

$$I(r_2 + s_2, -k_y, \alpha_1 + \delta)_{k_2},$$

$$I(r_3 + s_3, -k_z, \alpha_1 + \delta)_{k_3},$$

with $0 \leq r_1 \leq l_1$, $0 \leq s_1 \leq l_3 - 2j_1$. The singularity k^{-2} is removed by

$$e^{-\gamma k^2} = 2\gamma k^2 \int_0^1 d\mu \, \mu^{-3} e^{-\frac{\gamma}{\mu^2} k^2}, \tag{34}$$

with

$$\gamma = \frac{1}{4} \left(\frac{1}{\alpha_2} + \frac{1}{\alpha_1 + \delta} \right),$$

and one obtains

$$I(\omega_1, \boldsymbol{b}Q_x, \gamma\mu^{-2})_{t_1},\quad I(\omega_2, \boldsymbol{b}Q_y, \gamma\mu^{-2})_{t_2},\quad I(\omega_3, \boldsymbol{b}Q_z, \gamma\mu^{-2})_{t_3},$$

with $\omega_1 = l_2 - 2i_1 + r_1 + s_1 - 2k_1$, ω_2, ω_3 correspondingly.

What still remains after the integration over $\boldsymbol{r}, \boldsymbol{k}$ is the integration over the auxiliary variables η and μ. The μ-integration produces the function $F_{\omega-t}(\boldsymbol{b}Q^2/(4\gamma))$ with $t = t_1 + t_2 + t_3$, $\omega = \omega_1 + \omega_2 + \omega_3$. Finally, all η-dependent terms are collected and integrated with respect to η. The terms $\boldsymbol{b}Q_x^{\omega_1 - 2t_1}$, $\boldsymbol{b}Q_y^{\omega_2 - 2t_2}$, $\boldsymbol{b}Q_z^{\omega_3 - 2t_3}$ are multiplied and lead to summations over $0 \le u_1 \le \omega_1 - 2t_1$ and correspondingly u_2, u_3.

Then the substitution $z = \sqrt{\eta^2/(\alpha_3 + \eta^2)}$ leads to the following result:

$$\begin{aligned} J_9 = {} & \frac{4\pi^2}{\alpha_3}\left(\frac{\pi}{\alpha_2}\right)^{3/2} \sum_{i_1,j_1,r_1,s_1,k_1,t_1,u_1} N_{i_1,j_1,r_1,s_1,k_1,t_1,u_1} \\ & \times \sum_{i_2,j_2,r_2,s_2,k_2,t_2,u_2} N_{i_2,j_2,r_2,s_2,k_2,t_2,u_2} \sum_{i_3,j_3,r_3,s_3,k_3,t_3,u_3} N_{i_3,j_3,r_3,s_3,k_3,t_3,u_3} \\ & \times \int_0^1 \mathrm{d}z\, z^{2\varepsilon_1}(1-z^2)^j(\alpha_1 + \alpha_3 z^2)^{\varepsilon_2 - 3/2}\left[\frac{\alpha_1\alpha_2 + \alpha_2\alpha_3 z^2}{\alpha_1 + \alpha_2 + \alpha_3 z^2}\right]^{\omega - t + 1/2} \\ & \times \mathrm{e}^{-\frac{\alpha_1\alpha_3 z^2}{\alpha_1 + \alpha_3 z^2}\boldsymbol{ac}^2} F_{\omega - t}\left[\frac{\alpha_2 F(z)}{(\alpha_1 + \alpha_2 + \alpha_3 z^2)(\alpha_1 + \alpha_3 z^2)}\right], \end{aligned} \tag{35}$$

with

$$F(z) = |\alpha_3 z^2 \boldsymbol{bc} - \alpha_1 \boldsymbol{ab}|^2,$$

$$\varepsilon_1 = l - 2j + u + l_0 - r, \quad \varepsilon_2 = k - \omega + 2t - l_0 - l + 2j,$$

$$l = l_3 + m_3 + n_3, \quad l_0 = l_1 + m_1 + n_1,$$

$$\lambda = \sum_{i=1}^{3} \lambda_i, \qquad \lambda = u, j, r, k, t, \omega$$

and

$$\begin{aligned} N_{i_1,j_1,r_1,s_1,k_1,t_1,u_1} = {} & (-1)^{l_1 + t_1 + i_1 + r_1 + u_1} 2^{-j_1} 4^{-(i_1 + k_1 + t_1)} \alpha_1^{\omega_1 - 2t_1 - u_1 + l_3 - 2j_1 - s_1} \alpha_2^{-l_2 + i_1} \\ & \times \alpha_3^{u_1 + l_1 - r_1} \binom{l_3}{2j_1}\binom{l_1}{r_1}\binom{l_3 - 2j_1}{s_1} \frac{l_2!(2j_1 - 1)!!(r_1 - s_1)!\omega_1!}{i_1!(l_2 - 2i_1)!k_1!} \\ & \times \frac{\boldsymbol{ab}_x^{\omega_1 - 2t_1 - u_1} \boldsymbol{ac}_x^{l_1 - r_1 + l_3 - 2j_1 - s_1} \boldsymbol{bc}_x^{u_1}}{(r_1 + s_1 - 2k_1)!t_1!u_1!(\omega_1 - 2t_1 - u_1)!}, \end{aligned}$$

with

$$0 \le i_1 \le \left[\frac{l_2}{2} \right], \quad 0 \le j_1 \le \left[\frac{l_3}{2} \right], \; 0 \le r_1 \le l_1,$$

$$0 \le s_1 \le l_3 - 2j_1, \; 0 \le k_1 \le \left[\frac{r_1 + s_1}{2} \right],$$

$$0 \le t_1 \le \left[\frac{\omega_1}{2} \right], \quad 0 \le u_1 \le \omega_1 - 2t_1 .$$

References

[1] H. Kleindienst and W. Müller, Theor. Chim. Acta (Berl.) 56(1980)183.
[2] S.F. Boys, Proc. Roy. Soc. A200(1950)542.
[3] S. Huzinaga, H. Taketa and K.O. Ohata, J. Phys. Soc. (Japan) 21(1966)2313.
[4] V.R. Saunders, Molecular integrals for Gaussian type functions, NATO ASI Ser. C113(1983) 1–36, in: *Methods in Computational Molecular Physics*, ed. G.H.F. Diercksen and S. Wilson (Reidel, Dordrecht, 1983).
[5] S. Obara and A. Saika, J. Chem. Phys. 84(1986)3963.
[6] S. Obara and A. Saika, J. Chem. Phys. 89(1988)1540.
[7] M. Head-Gordon and J.A. Pople, J. Chem. Phys. 89(1988)5777.
[8] H.F. King and Th.R. Furlani, J. Comput. Chem. 9(1988)771.
[9] S. Zimering, J. Math. Phys. 8(1967)1266.
[10] P.J. Roberts, Proc. Phys. Soc. 89(1966)67.