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The Multi-Centre Integrals of Derivative, Spherical GTOs

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The multi-centre integrals of the orbital system $\Delta^n \mathscr{Y}_{lm}(\nabla) \exp(-r^2)$ are evaluated using the Talmi transformation of nuclear shell theory. The integrals are simpler than those of the systems $r^{2n}\mathscr{Y}_{lm}(\boldsymbol{r}) \exp(-r^2)$, $x^l y^m z^n \exp(-r^2)$, $(\partial/\partial x)^l(\partial/\partial y)^m(\partial/\partial z)^n \exp(-r^2)$ and the spherical oscillator functions. The integral types investigated are: overlap, electric dipole transition (momentum operator), kinetic energy, three-centre nuclear attraction, four-centre electronic repulsion, three-centre spin–orbit coupling, and magnetic dipole transition (three-centre integrals of the angular momentum operator).

Key words: Multi-centre integrals – Gauss–Laguerre orbitals – Talmi-Transformation – Generalized gradient operator.

1. Introduction

In a previous paper [1] the group theoretical or tensor algebraic advantage of using spherical orbitals has been discussed and the integrals of the spherical Gauss type orbitals (GTOs) $r^{2n}\mathscr{Y}_{lm}(\boldsymbol{r}) \exp(-r^2)$ with $\mathscr{Y}_{lm}(\boldsymbol{r}) = (ir)^l Y_{lm}(\boldsymbol{r}/r)$ have been evaluated using the Talmi transformation. The same has been done by Maretis [2] for the orthonormal system of the spherical oscillator orbitals. When we now call attention to a further related orbital system, it is because of a remarkable simplification of the multi-centre integrals. The new system generated by the gradient operator $\Delta^n \mathscr{Y}_{lm}(\nabla) \exp(-r^2)$ combines the advantages of the ordinary spherical Gaussians and of the Cartesian system $(\partial/\partial x)^l(\partial/\partial y)^m(\partial/\partial z)^n \exp(-r^2)$ discussed by several authors [3]. We shall closely follow [1] in proceeding and notation and shall not repeat details already given there. The analogous entities of both orbital systems are termed by the same symbols and distinguished in this paper by an index zero.

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2. The Properties of the Orbital Functions

We define the orbitals dimensionlessly by

$$\begin{aligned}\langle \boldsymbol{r} \mid o\alpha nlm\rangle &= \alpha^{-2n-l}\Delta^n \mathscr{Y}_{lm}(\boldsymbol{\nabla}) \exp(-\alpha^2 r^2) \\ &= (\alpha^{-1}\boldsymbol{\nabla})^{2n}\mathscr{Y}_{lm}(\alpha^{-1}\boldsymbol{\nabla}) \exp(-\alpha^2 r^2). \end{aligned} \tag{2.1}$$

The generalized gradient operator $\mathscr{Y}_{lm}(\boldsymbol{\nabla})$ has been discussed in [4]. As in [1] we want to split up the orbitals in the following form:

$$\langle \boldsymbol{r} \mid o\alpha nlm\rangle = \varphi^0(\alpha, nl, r)\langle \alpha \boldsymbol{r} \mid \text{sol } lm\rangle \tag{2.2}$$

with the solid harmonic (note the phase!):

$$\langle \boldsymbol{r} \mid \text{sol } lm\rangle = (ir)^l Y_{lm}(\boldsymbol{r}/r). \tag{2.3}$$

For convenience we distinguish $\langle \boldsymbol{r} \mid \text{sol } lm\rangle$ for ordinary functions and $\mathscr{Y}_{lm}(\boldsymbol{\nabla})$ for the gradient operator.

With theorem (11) of [4] it is possible to evaluate $\varphi^0(\alpha, 0l, r)$:

$$\varphi^0(\alpha, 0l, r) = \alpha^{-2l}\left(\frac{1}{r}\cdot\frac{d}{dr}\right)^l \exp(-\alpha^2 r^2) = (-2)^l \exp(-\alpha^2 r^2). \tag{2.4}$$

From the definition (2.1) follows the recursion

$$|o\alpha n + 1lm\rangle = (1/\alpha^2)\Delta|o\alpha nlm\rangle. \tag{2.5}$$

This yields for the radial part:

$$\varphi^0(\alpha, (n+1)l, r) = (1/\alpha^2)\left(\frac{2(l+1)}{r}\cdot\frac{d}{dr} + \frac{d^2}{dr^2}\right)\varphi^0(\alpha, nl, r). \tag{2.6}$$

This latter recursion leads to the Gauss–Laguerre type functions

$$\varphi^0(\alpha, nl, r) = (-1)^{n+l}2^{2n+l}\cdot n!\cdot L_n^{l+1/2}(\alpha^2 r^2)\cdot\exp(-\alpha^2 r^2). \tag{2.7}$$

It may be convenient to list the explicit orbital functions for the lower main quantum numbers in terms of the Condon–Shortley spherical harmonics. Because the degree of the radial polynoms depends on n only, we can give them for arbitrary angular momentum l. From (2.1) or from (2.2/3/7) we get:

$$\begin{aligned}
\langle r \mid o\alpha 0lm\rangle &= (-2i\alpha r)^l\cdot\exp(-\alpha^2 r^2)\cdot Y_{lm}(\boldsymbol{r}/r), \\
\langle r \mid o\alpha 1lm\rangle &= -4(-2i\alpha r)^l\cdot\exp(-\alpha^2 r^2)[l + 3/2 - \alpha^2 r^2]\cdot Y_{lm}(\boldsymbol{r}/r), \\
\langle r \mid o\alpha 2lm\rangle &= 16(-2i\alpha r)^l\cdot\exp(-\alpha^2 r^2)[(l+5/2)(l+3/2) \\
&\quad - 2(l+5/2)\alpha^2 r^2 + \alpha^4 r^4]\cdot Y_{lm}(\boldsymbol{r}/r), \\
\langle r \mid o\alpha 3lm\rangle &= -64(-2i\alpha r)^l\cdot\exp(-\alpha^2 r^2)[(l+7/2)(l+5/2)(l+3/2) \\
&\quad - 3(l+7/2)(l+5/2)\alpha^2 r^2 + 3(l+7/2)\alpha^4 r^4 - \alpha^6 r^6]\cdot Y_{lm}(\boldsymbol{r}/r), \\
\langle r \mid o\alpha 4lm\rangle &= 256(-2i\alpha r)^l\cdot\exp(-\alpha^2 r^2)[(l+9/2)(l+7/2)(l+5/2)(l+3/2) \\
&\quad - 4(l+9/2)(l+7/2)(l+5/2)\alpha^2 r^2 + 6(l+9/2)(l+7/2)\alpha^4 r^4 \\
&\quad - 4(l+9/2)\alpha^6 r^6 + \alpha^8 r^8]\cdot Y_{lm}(\boldsymbol{r}/r).
\end{aligned}$$

These functions differ from the eigenfunctions of the spherical, harmonic oscillator by the factor $\exp(-\alpha^2 r^2/2)$ and therefore do not form an orthogonal system. The

same is true for the derivative, Cartesian system [3]. Instead the orbitals (2.1) and the functionals

$$\langle o'\alpha nlm \mid \boldsymbol{r}\rangle = (-1)^{n+l}2^{-2n-l+1}(\alpha^3/\Gamma(n+l+3/2))L_n^{l+1/2}(\alpha^2 r^2)\langle \mathrm{sol}\, lm \mid \beta \boldsymbol{r}\rangle \tag{2.8}$$

form a biorthogonal system. Thus an expansion theorem holds

$$|g\rangle = \sum_{nlm} \langle o'\alpha nlm \mid g\rangle \cdot |o\alpha nlm\rangle \tag{2.9}$$

provided that the integrals $\langle o'\alpha nlm \mid g\rangle$ exist.

Because of the relation to the confluent, hypergeometric function

$$L_n^{l+1/2}(x) = \left(\frac{n+l+1/2}{n}\right){}_1F_1(-n, l+3/2; x) \tag{2.10}$$

we can write

$$\varphi^0(\alpha, nl, r) = (-1)^{n+l}2^{2n+l}\cdot\frac{\Gamma(n+l+3/2)}{\Gamma(l+3/2)}\cdot{}_1F_1(-n, l+3/2; \alpha^2r^2)\exp(-\alpha^2r^2)$$

$$= (-1)^{n+l}2^{2n+l}\cdot\frac{\Gamma(n+l+3/2)}{\Gamma(l+3/2)}\cdot{}_1F_1(n+l+3/2, l+3/2; -\alpha^2r^2). \tag{2.11}$$

This representation allows the extension of the definition of φ^0 and $\langle r \mid o\alpha nlm\rangle$ to the index $n = -1$, so that

$$(1/\alpha^2)\Delta|o\alpha - 1lm\rangle = |o\alpha 0lm\rangle \tag{2.12}$$

appears as a special case of (2.5). The functions $\varphi^0(\alpha, -1l, r)$ are the higher transcendental functions always occurring in the theory of GTOs. According to (5.2) of [1] they can be expressed by the integrals

$$F_m(t) = \int_0^1 u^{2m}\exp(-tu^2)\,du \tag{2.13}$$

or the incomplete gamma functions:

$$\varphi^0(\alpha, -1l, r) = (-2)^{l-1}F_l(\alpha^2r^2)$$
$$= (-2)^{l-1}(\alpha r)^{-2l-1}\gamma(l+1/2, \alpha^2r^2)/2. \tag{2.14}$$

For more details on these functions we refer to [1] and only add a reference concerning the effective computation of the functions $F_m(t)$: [5]. The combined relation (2.5/11) will be of importance for the nuclear attraction integral.

From the multiplication theorem of spherical harmonics follows the relation

$$\mathscr{Y}_{l_1m_1}(\nabla)\mathscr{Y}_{l_2m_2}(\nabla) = \sum_L \langle L\|l_1\|l_2\rangle\begin{pmatrix} L^+l_1l_2 \\ Mm_1m_2\end{pmatrix}\Delta^{(l_1+l_2-L)/2}\mathscr{Y}_{LM}(\nabla) \tag{2.15}$$

and therefore

$$\alpha^{-l_1}\mathscr{Y}_{l_1m_1}(\nabla)|o\alpha nl_2m_2\rangle = \sum_L \langle L\|l_1\|l_2\rangle\begin{pmatrix} L^+l_1l_2 \\ Mm_1m_2\end{pmatrix}\cdot|o\alpha, n+(l_1+l_2-L)/2, LM\rangle. \tag{2.16}$$

A special case of this relation is

$$\alpha^{-1}\nabla_\mu|o\alpha nlm\rangle = (4\pi/3)^{1/2}\sum_L \langle L\|1\|l\rangle\begin{pmatrix}L^+1l\\M\mu m\end{pmatrix}\cdot|o\alpha, n+(l+1-L)/2, LM\rangle. \tag{2.17}$$

As a final property of the orbitals $|o\alpha nlm\rangle$ we need the integral

$$\int\langle \boldsymbol{r}\mid o\alpha nlm\rangle d^3r = \delta(n,0)\,\delta(l,0)\,\delta(m,0)\cdot(\pi/2\alpha^3). \tag{2.18}$$

Together with (2.5/11) this relation yields most of the superiority of the new orbital system over the ordinary spherical GTOs and oscillator functions.

3. The Talmi Transformation

The central theorems of [1] are related to the Talmi transformation of the functions $r^{2n}\langle r\mid \text{sol } lm\rangle$ according to a special rotation in six-dimensional space:

$$\begin{aligned}\boldsymbol{r}_3 &= \boldsymbol{r}_1\cos\varphi - \boldsymbol{r}_2\sin\varphi\\ \boldsymbol{r}_4 &= \boldsymbol{r}_1\sin\varphi + \boldsymbol{r}_2\cos\varphi.\end{aligned} \tag{3.1}$$

This rotation is accompanied by

$$\begin{aligned}\boldsymbol{\nabla}_3 &= \cos\varphi\cdot\boldsymbol{\nabla}_1 - \sin\varphi\cdot\boldsymbol{\nabla}_2\\ \boldsymbol{\nabla}_4 &= \sin\varphi\cdot\boldsymbol{\nabla}_1 + \cos\varphi\cdot\boldsymbol{\nabla}_2.\end{aligned} \tag{3.2}$$

We therefore get according to (3.3) of [1]:

$$\begin{aligned}\Delta_1^{n_1}\mathscr{Y}_{l_1m_1}(\boldsymbol{\nabla}_1)\cdot\Delta_2^{n_2}\mathscr{Y}_{l_2m_2}(\boldsymbol{\nabla}_2) = \sum_{n_3l_3n_4l_4L}\sum[n_3l_3n_4l_4L\|\varphi\|n_1l_1n_2l_2L]\\ \cdot\begin{pmatrix}l_1l_2L^+\\m_1m_2M\end{pmatrix}\begin{pmatrix}l_3^+l_4^+L\\m_3m_4M\end{pmatrix}\cdot\Delta_3^{n_3}\mathscr{Y}_{l_3m_3}(\boldsymbol{\nabla}_3)\cdot\Delta_4^{n_4}\mathscr{Y}_{l_4m_4}(\boldsymbol{\nabla}_4).\end{aligned} \tag{3.3}$$

The expansion coefficients $[n_3l_3n_4l_4L\|\varphi\|n_1l_1n_2l_2L]$ are related to the Moshinsky–Smirnov coefficients of nuclear physics. For the definition, properties, evaluation, references and programs we refer to [1]. Here we only mention the condition for the non-zero coefficients: $2n_3 + l_3 + 2n_4 + l_4 = 2n_1 + l_1 + 2n_2 + l_2$. If we now apply (3.3) to the equation $\exp(-r_1^2 - r_2^2) = \exp(-r_3^2 - r_4^2)$, we get for the orbitals defined by (2.1) the same transformation as for ordinary, spherical Gaussians:

$$\begin{aligned}\langle \boldsymbol{r}_1\mid o1n_1l_1m_1\rangle\langle \boldsymbol{r}_2\mid o1n_2l_2m_2\rangle = \sum_{n_3l_3n_4l_4L}\sum[n_3l_3n_4l_4L\|\varphi\|n_1l_1n_2l_2L]\\ \cdot\begin{pmatrix}l_1l_2L^+\\m_1m_2M\end{pmatrix}\begin{pmatrix}l_3^+l_4^+L\\m_3m_4M\end{pmatrix}\langle \boldsymbol{r}_3\mid o1n_3l_3m_3\rangle\\ \cdot\langle \boldsymbol{r}_4\mid o1n_4l_4m_4\rangle.\end{aligned} \tag{3.4}$$

In the same way as in [1] we derive by some substitutions the theorems concerning the translated orbitals

$$\langle \boldsymbol{r}\mid oA\alpha n_a am_a\rangle = \langle \boldsymbol{r}-\boldsymbol{A}\mid o\alpha n_a am_a\rangle. \tag{3.5}$$

On this occasion we introduce some functions of the orbital scaling factors:

$$\varphi_{\alpha\beta} = \arctan(\alpha/\beta), \qquad \theta_{\alpha\beta} = (\alpha^2 + \beta^2)^{1/2}, \qquad \xi_{\alpha\beta} = \alpha\beta(\alpha^2 + \beta^2)^{-1/2}.$$

For a two-centre density we thus derive

$$\langle oA\alpha n_a a m_a \mid \boldsymbol{r}\rangle\langle \boldsymbol{r} \mid oB\beta n_b b m_b\rangle = \sum_{N j n_p p L} \sum [NJn_p pL \| \varphi_{\alpha\beta} \| n_a a n_b b L] \begin{pmatrix} a^+ bL^+ \\ m_a m_b M \end{pmatrix} \cdot \begin{pmatrix} J^+ p^+ L \\ M' m_p M \end{pmatrix} \langle \boldsymbol{AB} \mid o\xi_{\alpha\beta} NJM\rangle\langle \boldsymbol{r} \mid oP\theta_{\alpha\beta} n_p p m_p\rangle \tag{3.6}$$

with $\boldsymbol{AB} = \boldsymbol{B} - \boldsymbol{A}$ and the weighed mean point $\boldsymbol{P} = (\alpha^2\boldsymbol{A} + \beta^2\boldsymbol{B})/(\alpha^2 + \beta^2)$. And for two orbitals of different particles we get:

$$\langle \boldsymbol{r}_1 \mid oP\sigma n_p p m_p\rangle\langle \boldsymbol{r}_2 \mid oQ\tau n_q q m_q\rangle = \sum_{NJn_r rL} \sum [NJn_r rL \| \varphi_{\sigma\tau} \| n_p p n_q q L] \begin{pmatrix} pqL^+ \\ m_p m_q M \end{pmatrix} \cdot \begin{pmatrix} J^+ r^+ L \\ M m_r M \end{pmatrix} \langle \boldsymbol{r}_1 - \boldsymbol{r}_2 \mid o, QP, \xi_{\sigma\tau} NJM\rangle \cdot \langle (\sigma^2 \boldsymbol{r}_1 + \tau^2 \boldsymbol{r}_2)/(\sigma^2 + \tau^2) \mid oR\theta_{\sigma\tau} n_r r m_r\rangle \tag{3.7}$$

with $\boldsymbol{R} = (\sigma^2\boldsymbol{P} + \tau^2\boldsymbol{Q})/(\sigma^2 + \tau^2)$.

We are now prepared to calculate the integrals.

4. Overlap and Related Integrals

By integration over (3.6) and using (2.18) we get immediately the overlap integral

$$\langle oA\alpha n_a a m_a \mid oB\beta n_b b m_b\rangle = \sum_L \varepsilon^0_{\alpha\beta}(n_a n_b, Lab, AB) \begin{pmatrix} a^+ bL^+ \\ m_a m_b M \end{pmatrix} \langle \xi_{\alpha\beta} \boldsymbol{AB} \mid \mathrm{sol}\, LM\rangle, \tag{4.1}$$

where the tensorial invariants of the integral are given by

$$\varepsilon^0_{\alpha\beta}(n_a n_b, Lab, AB) = [NL00L \| \varphi_{\alpha\beta} \| n_a a n_b b L](2L + 1)^{-1/2} \varphi^0(\xi_{\alpha\beta}, NL, AB) \cdot \pi/2\theta^3_{\alpha\beta} \tag{4.2}$$

with $N = n_a + n_b + (a + b - L)/2$. In comparison to [1, 2] there are two simplifications in ε^0: It contains no sum and the coefficients at the right have two zeros.

For the kinetic energy integral we derive because of (2.5):

$$\langle oA\alpha n_a a m_a | -(1/2)\Delta | oB\beta n_b b m_b\rangle = -(\beta^2/2) \sum_L \varepsilon^0_{\alpha\beta}(n_a n_b + 1, Lab, AB) \begin{pmatrix} a^+ bL^+ \\ m_a m_b M \end{pmatrix} \langle \xi_{\alpha\beta} \boldsymbol{AB} \mid \mathrm{sol}\, LM\rangle. \tag{4.3}$$

Since Δ is a Hermitian operator, we can derive from (2.5) also a useful shifting relation:

$$\begin{aligned} \varepsilon^0_{\alpha\beta}(n_a n_b, Lab, x) &= (\beta^2/\alpha^2)\varepsilon^0_{\alpha\beta}(n_a - 1, n_b + 1, Lab, x) \\ &= (\beta/\alpha)^{2n_a} \varepsilon^0_{\alpha\beta}(0, n_a + n_b, Lab, x). \end{aligned} \tag{4.4}$$

In the case $\alpha = \beta$ thus many different overlap integrals are equal. On account of (2.16) a similar shifting of a and b is possible, but the relation involves a $6j$-symbol and is not so effective. For the two-centre integrals of the momentum operator related to the electric dipole transitions we get:

$$\langle oA\alpha n_a a m_a | \nabla_\mu | oB\beta n_b b m_b \rangle$$
$$= \sum_{Le} \lambda^0_{\alpha\beta}(n_a n_b, Labe, AB) \begin{pmatrix} a^+ eL^+ \\ m_a m_e M \end{pmatrix} \begin{pmatrix} e^+ 1b \\ m_e \mu m_b \end{pmatrix} \langle \xi_{\alpha\beta} \boldsymbol{AB} \mid \mathrm{sol}\, LM \rangle, \tag{4.5}$$

where the invariants because of (2.17) are given by

$$\lambda^0_{\alpha\beta}(n_a n_b, Labe, AB) = \langle e \| 1 \| b \rangle \cdot \varepsilon^0_{\alpha\beta}(n_a, n_b + (b + 1 - e)/2, Lab, AB). \tag{4.6}$$

There are only two possible values of e, namely $e = b \pm 1$.

With respect to our phase choice the reduced matrix elements of three spherical harmonics are

$$\langle j \| k \| l \rangle = (-1)^{j+k+l} [(2j + 1)(2k + 1)(2l + 1)/4\pi]^{1/2} \begin{pmatrix} jkl \\ 000 \end{pmatrix}. \tag{4.7}$$

5. Nuclear Attraction Integrals

As in [1] we begin with the interaction integral of a density and a point charge:

$$[1/r_C \mid oP\sigma n_p p m_p] = \tau^0_\sigma(n_p p, PC) \langle \sigma \boldsymbol{PC} \mid \mathrm{sol}\, pm_p \rangle. \tag{5.1}$$

In order to evaluate the invariant τ^0 we again use the relation

$$\begin{aligned} &[1/r_C | \Delta | oP\sigma n_p p m_p]\ [(\Delta 1/r_C) \mid oP\sigma n_p p m_p] \\ &\quad = -4\pi [\delta(\boldsymbol{r} - \boldsymbol{C}) \mid oP\sigma n_p p m_p] \\ &\quad = -4\pi \langle \boldsymbol{C} \mid oP\sigma n_p p m_p \rangle \\ &\quad = -4\pi \langle \boldsymbol{PC} \mid o\sigma n_p p m_p \rangle. \end{aligned} \tag{5.2}$$

(In [1] by a mistake the factor -4π has been omitted.) On the other hand we get because of (2.5/11):

$$[1/r_C | \Delta | oP\sigma n_p p m_p] = \sigma^2 [1/r_C \mid oP(n_p + 1) p m_p]. \tag{5.3}$$

This yields:

$$[1/r_C \mid oP\sigma n_p p m_p] = -4\pi\sigma^{-2} \langle \boldsymbol{PC} \mid o\sigma(n_p - 1) p m_p \rangle. \tag{5.4}$$

Thus the invariant is very simple:

$$\tau^0_\sigma(n_p p, PC) = -4\pi\sigma^{-2} \varphi^0(\sigma, n_p - 1p, PC). \tag{5.5}$$

Note that for $n_p \geqslant 1$ the expression involves no higher transcendental functions! This is in contrast to the cases of [1, 2] again, where the Gaussian or oscillator functions are mixed with the incomplete gamma functions for all values of n_p. Moreover Eqs. (5.1) and (5.2) imply, for large distances PC, that the integrals vanish faster than PC^{-l-1} as usual, namely according to the exponential factor in φ^0. This allows to omit terms of type (5.5) in the expansions of three- or four-centre integrals for sufficiently large distances.

The higher transcendental functions are now restricted to the case:

$$\begin{aligned}\tau^0_\sigma(0p, R) &= -4\pi\sigma^{-2}\varphi^0(\sigma, -1p, R)\\ &= -\pi\sigma^{-2}(-2)^{p+1}F_p(\sigma^2R^2)\\ &= \pi\sigma^{-2}(-2)^p(\sigma R)^{-2p-1}\gamma(p+1/2, \sigma^2R^2).\end{aligned} \tag{5.6}$$

Since the three- and four-centre integrals involve expansions in τ^0, this is a great computational advantage. The same argument applies to Cartesian GTOs.

Multiplying (3.6) by $1/r_C$ and integrating over $\boldsymbol{r}$ we derive the expression of the three-centre nuclear attraction integral:

$$\begin{aligned}\langle oA\alpha n_a a m_a|1/r_C|oB\beta n_b b m_b\rangle = \sum_{LJp}\eta^0_{\alpha\beta}(n_an_b, Lab, Jp, AB, PC)\begin{pmatrix}J^+p^+L\\ M'm_pM\end{pmatrix}\\ \cdot\begin{pmatrix}L^+a^+b\\ Mm_am_b\end{pmatrix}\langle\xi_{\alpha\beta}\boldsymbol{AB}\mid \mathrm{sol}\,JM'\rangle\langle\theta_{\alpha\beta}\boldsymbol{PC}\mid \mathrm{sol}\,pm_p\rangle,\end{aligned} \tag{5.7}$$

with the invariants

$$\begin{aligned}\eta^0_{\alpha\beta}(n_an_b, Lab, Jp, AB, PC) = -4\pi\theta^{-2}_{\alpha\beta}\sum_{Nn_p}[NJn_ppL\|\varphi_{\alpha\beta}\|n_aan_bbL]\\ \cdot\varphi^0(\xi_{\alpha\beta}, NJ, AB)\varphi^0(\theta_{\alpha\beta}, n_p-1p, PC)\end{aligned} \tag{5.8}$$

and $\boldsymbol{P} = (\alpha^2\boldsymbol{A} + \beta^2\boldsymbol{B})/(\alpha^2+\beta^2)$.

6. The Two-Electron Integrals

Again we start with the two-centre density repulsion integral:

$$\begin{aligned}[oP\sigma n_ppm_p|1/r_{12}|oQ\tau n_qqm_q] = \sum_L\mu^0_{\sigma\tau}(n_pn_q, Lpq, PQ)\begin{pmatrix}pqL^+\\ m_pm_qM\end{pmatrix}\\ \cdot\langle\xi_{\sigma\tau}\boldsymbol{PQ}\mid \mathrm{sol}\,LM\rangle.\end{aligned} \tag{6.1}$$

The invariants are now given by

$$\begin{aligned}\mu^0_{\sigma\tau}(n_pn_q, Lpq, PQ) = -(2\pi^2\xi_{\sigma\tau}/\sigma^3\tau^3)(2L+1)^{-1/2}[NL00L\|\varphi_{\sigma\tau}\|n_ppn_qqL]\\ \cdot\varphi^0(\xi_{\sigma\tau}, N-1L, PQ),\end{aligned} \tag{6.2}$$

with $N = n_p + n_q + (p+q-L)/2$. The derivation of (6.2) uses (3.7) and runs as in [1].

Note again: because of $N \geqslant n_p + n_q$ we have $N \geqslant 1$ for $n_p \geqslant 1$ or $n_g \geqslant 1$, thus no incomplete gamma functions are involved and the integral vanishes faster than any power of PQ for large distances. The contrary is true only for $n_p = n_q = 0$. But even in this case only one term of (6.1), namely $L = p + q$, requires the gamma functions. The invariants μ^0 are obviously related to the invariants of the overlap integrals:

$$\mu^0_{\sigma\tau}(n_pn_q, Lpq, x) = -4\pi\tau^{-2}\varepsilon^0_{\sigma\tau}(n_p(n_q-1), Lpq, x). \tag{6.3}$$

Thus a shifting relation like (4.4) also applies to μ^0.

Now we can calculate the four-centre electron repulsion integral. Note that the arrangement of the orbitals is according to the Dirac notation, cf. (2.14) of [1]:

$$\begin{aligned}
&\langle oA\alpha n_a am_a,\, oB\beta n_b bm_b|1/r_{12}|oC\gamma n_c cm_c,\, oD\delta n_d dm_d\rangle \\
&\quad = \sum_{LL'JJ'pql}\sum \sigma^0(n_a n_b n_c n_d, Lac, L'bd, lpq, JJ', AC, BD, PQ) \\
&\qquad \cdot \begin{pmatrix} a^+cL^+ \\ m_a m_c M \end{pmatrix}\begin{pmatrix} J^+p^+L \\ mm_p M \end{pmatrix}\begin{pmatrix} b^+dL'^+ \\ m_b m_d M' \end{pmatrix}\begin{pmatrix} J'^+q^+L' \\ m' m_q M' \end{pmatrix}\begin{pmatrix} pql^+ \\ m_p m_q n \end{pmatrix} \\
&\qquad \cdot\langle \xi_{\alpha\gamma}\boldsymbol{AC} \mid \mathrm{sol}\, Jm\rangle\langle \xi_{\beta\delta}\boldsymbol{BD} \mid \mathrm{sol}\, J'm'\rangle\langle \rho\boldsymbol{PQ} \mid \mathrm{sol}\, ln\rangle, \qquad (6.4)
\end{aligned}$$

with the abbreviations $\boldsymbol{P} = (\alpha^2\boldsymbol{A} + \gamma^2\boldsymbol{C})/(\alpha^2 + \gamma^2)$, $\boldsymbol{Q} = (\beta^2\boldsymbol{B} + \delta^2\boldsymbol{D})/(\beta^2 + \delta^2)$, and $\rho = [(\alpha^2 + \gamma^2)(\beta^2 + \delta^2)/(\alpha^2 + \beta^2 + \gamma^2 + \delta^2)]^{1/2}$.

The invariants σ^0 result from a two-fold application of (3.6) to the two-centre densities and subsequent integration using (6.1):

$$\begin{aligned}
&\sigma^0(n_a n_b n_c n_d, Lac, L'bd, lpq, JJ', x, y, z) \\
&\quad = -(2\pi^2\rho/\sigma^3\tau^3)\cdot(2l+1)^{-1/2}\cdot\sum_{Nn_pN'n_q}\sum [NJn_p pL\|\varphi_{\alpha\gamma}\|n_a an_c cL] \\
&\qquad \cdot[N'J'n_q qL'\|\varphi_{\beta\delta}\|n_b bn_d dL']\cdot[Sl00l\|\varphi_{\sigma\tau}\|n_p pn_q ql]\cdot\varphi^0(\alpha\gamma/\sigma, NJ, x) \\
&\qquad \cdot\varphi^0(\beta\delta/\tau, N'J', y)\cdot\varphi^0(\rho, S-1, l, z), \qquad (6.5)
\end{aligned}$$

with $S = n_p + n_q + (p + q - l)/2$, $\sigma = \theta_{\alpha\gamma}$, $\tau = \theta_{\beta\delta}$.

7. Spin-Orbit Coupling

As in [1] we get by partial integration the relation:

$$\begin{aligned}
&\langle oA\alpha n_a am_a|[(\nabla 1/r_C)\times\nabla]_\mu|oB\beta n_b bm_b\rangle \\
&\quad = \sqrt{3}\sum\begin{pmatrix} 1\,1^+\,1 \\ \mu_1\mu_2\mu \end{pmatrix}\langle\nabla_{\mu_1} oA\alpha n_a am_a|1/r_C\cdot\nabla_{\mu_2}|oB\beta n_b bm_b\rangle. \qquad (7.1)
\end{aligned}$$

The right side is evaluated using (2.17), which results in a sum of nuclear attraction integrals. We finally get the formula of the three-centre spin-orbit coupling integral

$$\begin{aligned}
&\langle oA\alpha n_a am_a|[(\nabla 1/r_C)\times\nabla]_\mu|oB\beta n_b bm_b\rangle \\
&\quad = \sum_{LJjp}\pi^0_{\alpha\beta}(n_a n_b, Lab, Jjp, AB, PC)\cdot\begin{pmatrix} a^+bL \\ m_a m_b M \end{pmatrix}\begin{pmatrix} J^+1L^+ \\ M\mu M \end{pmatrix}\begin{pmatrix} Jj^+p^+ \\ Mmm_p \end{pmatrix} \\
&\qquad \cdot\langle \xi_{\alpha\beta}\boldsymbol{AB} \mid \mathrm{sol}\, jm\rangle\langle \theta_{\alpha\beta}\boldsymbol{PC} \mid \mathrm{sol}\, pm_p\rangle \qquad (7.2)
\end{aligned}$$

with the invariants:

$$\begin{aligned}
&\pi^0_{\alpha\beta}(n_a n_b, Lab, Jjp, x, y) = (4\pi/\sqrt{3})(2L+1)\sum_{ef}\begin{Bmatrix} e1a \\ f1b \\ J1L \end{Bmatrix}\langle e\|1\|a\rangle\langle f\|1\|b\rangle \\
&\qquad \cdot\eta^0_{\alpha\beta}(n_a + (a+1-e)/2, n_b + (b+1-f)/2, Jef, jp, x, y). \qquad (7.3)
\end{aligned}$$

On account of the reduced matrix elements the sums run only over the values $e = a \pm 1$ and $f = b \pm 1$.

8. Angular Momentum

For the calculation of the Zeeman effect, the magnetic circular dichroism and the magnetic dipole transitions one needs the integrals of the angular momentum operator with respect to a certain centre C, probably the molecular centre:

$$\boldsymbol{L}_C = [\boldsymbol{r}_C \times \boldsymbol{p}] = \boldsymbol{L}_B + [(\boldsymbol{B} - \boldsymbol{C}) \times \boldsymbol{p}]. \tag{8.1}$$

In virtue of the second equation (8.1) one can shift the reference point of the angular momentum to an orbital centre. The integral of L_B then is evaluated using

$$L_{B\mu}|oB\beta n_b b m_b\rangle = \sum \langle b\|L^1\|b\rangle \begin{pmatrix} b^+ 1 b \\ m'_b \mu m_b \end{pmatrix} \cdot |oB\beta n_b b m'_b\rangle, \tag{8.2}$$

with the reduced matrix element

$$\langle b\|L^1\|b\rangle = \hbar[b(b+1)(2b+1)]^{1/2}. \tag{8.3}$$

By (8.2) the integral of L_B is reduced to overlap integrals. On the other hand the remaining integral is given by (4.5). Inserting all these relations into the integral of L_C we finally arrive at the formula:

$$\begin{aligned}
&\langle oA\alpha n_a a m_a|L_{C\mu}|oB\beta n_b b m_b\rangle \\
&\quad = \sum_L \omega^1_{\alpha\beta}(n_a n_b, Lab, AB) \begin{pmatrix} a^+ b L^+ \\ m_a m'_b M \end{pmatrix} \begin{pmatrix} b^+ 1 b \\ m'_b \mu m_b \end{pmatrix} \langle \xi_{\alpha\beta} AB \mid \mathrm{sol}\, LM\rangle \\
&\qquad + \sum_{Le} \omega^2_{\alpha\beta}(n_a n_b, Labe, AB) \begin{pmatrix} 1^+ 1^+ 1 \\ \mu_1 \mu_2 \mu \end{pmatrix} \begin{pmatrix} a^+ e L^+ \\ m_a m_e M \end{pmatrix} \begin{pmatrix} e^+ 1 b \\ m_e \mu_2 m_b \end{pmatrix} \\
&\qquad \cdot CB_{\mu_1} \langle \xi_{\alpha\beta} AB \mid \mathrm{sol}\, LM\rangle,
\end{aligned} \tag{8.4}$$

where both invariants are related to the invariants of the overlap integrals:

$$\omega^1_{\alpha\beta}(n_a n_b, Lab, AB) = \hbar[b(b+1)(2b+1)]^{1/2} \varepsilon^0_{\alpha\beta}(n_a n_b, Lab, AB), \tag{8.5}$$

$$\omega^2_{\alpha\beta}(n_a n_b, Labe, AB) = \sqrt{3}(\hbar/i)\langle e\|1\|b\rangle \varepsilon^0_{\alpha\beta}(n_a, n_b + (b+1-e)/2, Lab, AB). \tag{8.6}$$

9. Comparison with Cartesian Systems

Since we have already compared the new results with those for the other types of spherical Gaussians, the consideration of the Cartesian systems remains. The comparison with the derivative system of Zivkovic and Maksic [3] may suffice because it is most similar to the present one.

One main advantage of the present system is the fact that the integrals $[1/r_C \mid oP\sigma n_p p m_p]$ reduce to elementary functions for $n_p > 0$. We have derived this result from the relation $\Delta(1/r) = -4\pi\delta(r)$. If we now define the Cartesian orbitals by

$$\langle \boldsymbol{r} \mid cA\alpha pqr\rangle = (\partial/\partial x)^p (\partial/\partial y)^q (\partial/\partial z)^r \exp(-\alpha^2(r-A)^2) \tag{9.1}$$

we get the relation

$$\alpha^{-2}\Delta|cA\alpha pqr\rangle = |cA\alpha p+2qr\rangle + |cA\alpha pq+2r\rangle + |cA\alpha pqr+2\rangle \tag{9.2}$$

and the analogue of Eq. (5.4):

$$-4\pi\sigma^{-2}\langle \boldsymbol{PC} \mid c\sigma pqr\rangle = [1/r_C \mid cP\sigma p + 2qr] + [1/r_C \mid cP\sigma pq + 2r] + [1/r_C \mid cP\sigma pqr + 2]. \tag{9.3}$$

This means that only a certain sum of the integral type $[1/r_C \mid cP\sigma pqr]$ reduces to elementary functions, but the individual Cartesian integrals do not. Thus in the Cartesian system all nuclear attraction and electron-repulsion integrals involve more higher transcendental functions than in the analogous spherical system. The same applies to the system $x^p y^q z^r \exp(-\alpha^2 r^2)$.

Another advantage of all the spherical orbital systems is the orientational simplicity. Consider a three-centre nuclear attraction integral in a tetrahedral molecule like CH_4. The configuration is as follows: s-orbital at one H (point $\boldsymbol{A}$), the point charge at another H (point $\boldsymbol{C}$) and a p-orbital at the central C (point $\boldsymbol{B}$): $\langle oA000|1/r_C|oB01m\rangle$. There are at first sight 36 different integrals of this type in a tetrahedron. In the Cartesian case it is possible to show by several rotational operations that there are only two independent integrals, and it is even more laborious to express all 36 integrals explicitly as linear combinations of these two. Because the lengths of the vectors $\boldsymbol{AB}$ and $\boldsymbol{PC}$ are the same in all 36 triangles, the same result is produced automatically in the spherical system. The formula (5.7) simply gives all the integrals as linear combinations of two independent invariants:

$$\langle oA000|1/r_C|oB0lm\rangle = (72\pi)^{-1/2}(\eta^0_{11}(00, 101, 10, \boldsymbol{AB}, \boldsymbol{PC})\langle \boldsymbol{AB} \mid \text{sol } 1m\rangle + \eta_{11}(00, 101, 01, \boldsymbol{AB}, \boldsymbol{PC})\langle \boldsymbol{PC} \mid \text{sol } 1m\rangle). \tag{9.4}$$

But one must admit that in the case of the more general integrals $\langle oAn_a00|1/r_C|oBn_b1m\rangle$ there are more than two invariants, though less than 36. It is a general fact that the three- and four-centre integrals of spherical Gaussians involve a minimum of invariants if all main (but not the angular momentum) quantum numbers are zero. But since the increase of the main quantum number does not change the orbital type, it should not affect the number of independent invariants. This discrepancy is a challenge for further research.

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