Single-centre expansion of Gaussian basis functions and the angular decomposition of their overlap integrals

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Single-centre expansion of Gaussian basis functions and the angular decomposition of their overlap integrals

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Abstract. Single-centre partial-wave expansions are derived for several Gaussian-type functions: simple, solid harmonic and spherical Gaussians. Single-centre expansions for the most commonly used Cartesian Gaussians are obtained by expanding these functions in spherical Gaussians. Transformation matrices for expanding Cartesian in spherical Gaussians are given for s, p, d and f type functions. The single-centre expansions are used to calculate the partial-wave decomposition of overlap integrals for all Gaussian-type functions specified. The formulae given are suitable for fast numerical computation and were tested with programs developed for this purpose.

1. Introduction

Gaussian-type functions and linear combinations of them are very popular as basis set orbitals in atomic and molecular calculations. This is due to the fact that all multicentre integrals can be evaluated analytically. To do the computation, several very efficient codes have been developed, such as the widely used HONDO versions (Dupuis *et al* 1976), the GAUSSIAN (Pople *et al* 1981) and the POLYATOM (Moskowitz and Snyder 1977) program packages or the lobe programs (Ahlrichs 1974). Because of their successful use in *ab initio* quantum chemistry, Gaussian functions were also introduced in L^2 methods of molecular scattering theory (Lucchese *et al* 1986). In contrast to bound-state calculations the basis set in scattering problems is often augmented with appropriate continuum functions in order to obtain the correct asymptotic behaviour of the scattering wavefunctions. The necessary integrals with the continuum functions are evaluated using a single-centre expansion of the square-integrable basis functions about the origin of the continuum functions, which as a rule is the centre of mass or the centre of charge. This is of special importance in all R-matrix methods applied to molecular systems because the integration is carried out over a finite volume.

We showed (Kaufmann *et al* 1985), in our work on the Rydberg states of the NO molecule, that a proper idea of the angular momentum composition of the orbitals may be necessary even in bound-state calculations. In our former work we decomposed the overlap integral into contributions arising from the pure l partial waves. The corresponding overlap integrals were evaluated by numerical integration. Because of the $C_{\infty v}$ symmetry of the molecule the integration could be reduced to two dimensions.

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However, in the more complex case of a polyatomic molecule and with a large set of orbitals this procedure would be very time-consuming. Then either an analytical formula is desirable, or a formula which can be reduced to a one-dimensional quadrature. In the present work we first show that one can deduce a completely analytical formula if only Gaussian lobe functions are used as basis set orbitals. In the following part we derive a compact formula for the single-centre expansion of a general solid harmonic Gaussian function using some results of the previous part. In the sequel we describe the angular decomposition of the overlap integral by an expression which contains only geometric factors and an integral which can be evaluated numerically very easily. The reason for using solid harmonic Gaussians is the ease with which geometrical relations can be expressed by angular momentum algebra.

Finally we apply these results to the case of the Cartesian Gaussian functions commonly used in quantum chemistry. For this purpose we have completed our work with the so-called spherical Gaussian functions (Saunders 1983). These functions provide a basis for the transformation of primitive Cartesian Gaussians into spherical coordinates which also is of great interest for a number of problems besides scattering physics. A transformation of this kind and a subsequent single-centre expansion is particularly useful for the evaluation of matrix elements occurring in the calculation of certain molecular properties such as electric multipole moments, magnetic susceptibilities or spin–spin and spin–orbit couplings.

2. Simple Gaussian functions

When using an L^2 method for calculating bound or continuum orbitals the solution of the Schrödinger equation is expanded in a finite, square-integrable set of basis functions $\{\varphi_p\}$

$$\phi_i = \sum_{p=1}^{N} c_{ip}\varphi_p. \tag{1}$$

The angular momentum decomposition of the overlap integral is achieved by introducing the complete set of normalised surface spherical harmonics Y_{lm} as defined by Condon and Shortley (1970)

$$\langle\phi_i|\phi_i\rangle = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l}\langle\phi_i|Y_{lm}\rangle\langle Y_{lm}|\phi_i\rangle. \tag{2}$$

Equation (2) is equal to unity if the orbital ϕ_i is normalised. The introduction of the expansion (1) into equation (2) leads to a matrix equation of the following form

$$\langle\phi_i|\phi_i\rangle = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l}\mathrm{Tr}(\mathbf{D}_i\mathbf{S}_{lm}) = \sum_{l=0}^{\infty}|U_{il}|^2. \tag{3}$$

$\mathbf{D}_i$ is the one-particle density matrix of the orbital ϕ_i. The matrix $\mathbf{S}_{lm}$ contains the contribution of the angular momentum with quantum numbers l and m to the overlap matrix of the primitive basis set. The real quantities $|U_{il}|^2$ then give a precise measure of the partial-wave decomposiion of the orbital ϕ_i and are related to the channel mixing ratios of multichannel quantum-defect theory (Kaufmann *et al* 1985). In this paper we are concerned with the analytical evaluation of the matric elements $(\mathbf{S}_{lm})_{pq}$

which are given by

$$(\mathbf{S}_{lm})_{pq} = \int_0^\infty \varphi^*_{plm}(r)\varphi_{qlm}(r)r^2\,\mathrm{d}r \tag{4}$$

where the functions $\varphi_{plm}(r)$ are the radial functions resulting from the partial-wave decomposition of the real basis functions $\varphi_p(\boldsymbol{r})$,

$$\varphi_{plm}(r) = \int_{\Omega_r} \varphi_p(\boldsymbol{r})\, Y^*_{lm}(\Omega_r)\,\mathrm{d}\Omega_r. \tag{5}$$

The polar angles θ and ϕ of the vector $\boldsymbol{r}$ are represented collectively by the space angle Ω_r. We will first derive an expression for the matrix elements (4) using simple Gaussian functions as primitive basis orbitals. A basis function of this type located at centre A is defined as

$$\varphi_a(\boldsymbol{r}) = N_\alpha \exp(-\alpha|\boldsymbol{r}-\boldsymbol{R}_\mathrm{A}|^2) \tag{6}$$

where $N_\alpha = (2\alpha/\pi)^{3/4}$ is a normalisation factor. The general index a comprises the characterisations of the function, $a \equiv (\alpha, \boldsymbol{R}_\mathrm{A})$. In quantum-chemical calculations the angular dependence is achieved through the combination of several slightly displaced functions (Whitten 1966). Therefore it is sufficient to consider the expansion about the origin of the coordinate system of a simple Gaussian function. This can very easily be done if a modified form of the Rayleigh expansion is introduced (Abramowitz and Stegun 1970)

$$\exp(\boldsymbol{r}_1 \cdot \boldsymbol{r}_2) = \sum_{l=0}^{\infty} (2l+1) i_l(r_1 r_2) P_l(\cos\gamma). \tag{7}$$

In this equation $i_l(x)$ denotes a modified spherical Bessel function and $P_l(\cos\gamma)$ a Legendre polynomial of order l. The angle γ is the angle between the directions $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. If we assign the vector $\boldsymbol{r}_1$ to $\boldsymbol{r}$ of equation (6) and $\boldsymbol{r}_2$ to the vector $\boldsymbol{R}_\mathrm{A}$ pointing to the centre A and combine the relations (6) and (7) we obtain, omitting the normalisation factor,

$$\exp(-\alpha|\boldsymbol{r}-\boldsymbol{R}_\mathrm{A}|^2) = \exp[-\alpha(r^2+R_\mathrm{A}^2)] \sum_{l=0}^{\infty} (2l+1) i_l(2\alpha r R_\mathrm{A}) P_l(\cos\gamma). \tag{8}$$

Application of the addition theorem for surface spherical harmonics in this equation yields the desired single-centre expansion for the functions (6)

$$\exp(-\alpha|\boldsymbol{r}-\boldsymbol{R}_\mathrm{A}|^2) = 4\pi\exp[-\alpha(r^2+R_\mathrm{A}^2)] \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} i_l(2\alpha r R_\mathrm{A})\, Y_{lm}(\Omega_r)\, Y^*_{lm}(\Omega_{\boldsymbol{R}_\mathrm{A}}). \tag{9}$$

The derivation of the analytical expression for the radial functions $\varphi_{alm}(r)$ by inserting the single-centre expansion (9) into equation (5) is now trivial. Using equations (4), (5) and (9) the partial-wave overlap integral between two functions located at centres A and B consequently can be written as follows

$$(\mathbf{S}_{lm})_{ab} = (4\pi)^2 \exp[-(\alpha R_\mathrm{A}^2 + \beta R_\mathrm{B}^2)] I_l(\alpha, R_\mathrm{A}, \beta, R_\mathrm{B})\, Y_{lm}(\Omega_{\boldsymbol{R}_\mathrm{A}})\, Y^*_{lm}(\Omega_{\boldsymbol{R}_\mathrm{B}}). \tag{10}$$

The term $I_l(\alpha, R_\mathrm{A}, \beta, R_\mathrm{B})$ denotes an integral over an exponentially damped product of two modified Bessel functions

$$I_l(\alpha, R_\mathrm{A}, \beta, R_\mathrm{B}) = \int_0^\infty \exp[-(\alpha+\beta)r^2] i_l(2\alpha r R_\mathrm{A}) i_l(2\beta r R_\mathrm{B}) r^2\,\mathrm{d}r. \tag{11}$$

This is Weber's second exponential integral which can be solved in closed form. Watson (1944) gives an analytical formula for the following integral

$$\int_0^\infty \exp(-p^2t^2)J_\nu(ut)J_\nu(vt)t\,\mathrm{d}t = \frac{1}{2p^2}I_\nu\left(\frac{uv}{2p^2}\right)\exp\left(-\frac{u^2+v^2}{4p^2}\right). \tag{12}$$

This expression is valid for $\mathrm{Re}(\nu) > -1$ and $|\arg p| < \pi/4$. J_ν is a Bessel function and I_ν is a modified Bessel function of fractional order ν. Because of the well known relations between Bessel functions, which are

$$i_l(x) = \mathrm{i}^{-l}j_l(\mathrm{i}x)$$

and

$$j_l(\mathrm{i}x) = \exp\left(-\frac{\pi}{4}\mathrm{i}\right)\left(\frac{\pi}{2x}\right)^{1/2}J_{l+1/2}(\mathrm{i}x) \tag{13}$$

the parameters u, v and p in equation (12) are set equal to

$$u = -2\mathrm{i}\alpha R_\mathrm{A} \qquad v = 2\mathrm{i}\beta R_\mathrm{B} \qquad p^2 = \alpha+\beta.$$

The resulting expression for the integral (11) is consequently

$$I_l(\alpha, R_\mathrm{A}, \beta, R_\mathrm{B}) = \frac{1}{4}\left(\frac{\pi}{(\alpha+\beta)^3}\right)^{1/2} i_l\left(2\frac{\alpha\beta}{\alpha+\beta}R_\mathrm{A}R_\mathrm{B}\right)\exp\left(\frac{\alpha^2R_\mathrm{A}^2+\beta^2R_\mathrm{B}^2}{\alpha+\beta}\right). \tag{14}$$

Finally including normalisation and inserting equation (14) into equation (10) we arrive at a simple and easy-to-handle formula for the matrix elements $(\mathbf{S}_{lm})_{ab}$

$$(\mathbf{S}_{lm})_{ab} = 4\pi\left(2\frac{(\alpha\beta)^{1/2}}{\alpha+\beta}\right)^{3/2}\exp\left(-\frac{\alpha\beta}{\alpha+\beta}(R_\mathrm{A}^2+R_\mathrm{B}^2)\right)$$
$$\times i_l\left(2\frac{\alpha\beta}{\alpha+\beta}R_\mathrm{A}R_\mathrm{B}\right)Y_{lm}(\Omega_{\boldsymbol{R}_\mathrm{A}})Y_{lm}^*(\Omega_{\boldsymbol{R}_\mathrm{B}}). \tag{15}$$

Using equation (3) this formula enables us to calculate the angular momentum composition of an orbital given as an expansion in Gaussian lobe functions in a very efficient way. Similar formulae were used by Le Rouzo and Silvi (1978) for analysing the multipole components of a spatial arrangement of lobe functions. For the computation of the modified spherical Bessel functions there are standard subroutines commonly available in several numerical libraries, for instance in the CPC program library (Thompson and Barnett 1987).

3. Solid harmonic Gaussian functions

One of the main drawbacks of Gaussian lobe functions is the large number of primitives which are needed for the representation of basis functions with higher angular momenta. We will therefore now consider a more general class of functions than the simple Gaussian functions. This will be a Gaussian-type basis function, for which the angular dependence is explicitly included by multiplication with a solid harmonic r^lY_{lm} and which will be called a solid harmonic Gaussian function. Such a function located at centre A takes the form

$$\varphi_a(\boldsymbol{r}) = N_{\alpha L_\mathrm{A}}|\boldsymbol{r}-\boldsymbol{R}_\mathrm{A}|^{L_\mathrm{A}}Y_{L_\mathrm{A}M_\mathrm{A}}(\Omega_{\boldsymbol{r}-\boldsymbol{R}_\mathrm{A}})\exp(-\alpha|\boldsymbol{r}-\boldsymbol{R}_\mathrm{A}|^2) \tag{16}$$

where the normalisation factor $N_{\alpha L_A}$ is defined as

$$N_{\alpha L_A} = \left(2 \frac{(2\alpha)^{L_A+3/2}}{\Gamma(L_A+3/2)} \right)^{1/2}. \tag{17}$$

The index a stands for $a \equiv (\alpha, \boldsymbol{R}_A, L_A, M_A)$. In order to obtain a single-centre expansion of this function we need a formula for the translation of a multipole field. It was shown by Moshinsky (1959) and Seaton (1961) that the additional multipole field can be expanded in terms of multipole fields in $\boldsymbol{r}$ and $\boldsymbol{R}_A$ by the expression

$$\begin{aligned} |\boldsymbol{r}-\boldsymbol{R}_A|^{L_A} Y_{L_A M_A}(\Omega_{\boldsymbol{r}-\boldsymbol{R}_A}) \\ = \sum_{l_1,l_2=0}^{L_A} \delta_{l_1+l_2,L_A} G(l_1, l_2, L_A) \\ \times \sum_{m_1,m_2} \langle l_1 l_2 m_1 m_2 | L_A M_A \rangle r^{l_1} Y_{l_1 m_1}(\Omega_r) R_A^{l_2} Y_{l_2 m_2}(\Omega_{\boldsymbol{R}_A}). \end{aligned} \tag{18}$$

Therein the coefficient $G(l_1, l_2, L_A)$ is calculated as

$$G(l_1, l_2, L_A) = (-1)^{l_2} \left(\frac{4\pi(2L_A+1)!}{(2l_1+1)!(2l_2+1)!} \right)^{1/2} \tag{19}$$

and $\langle l_1 l_2 m_1 m_2 | L_A M_A \rangle$ is a Clebsch-Gordan coefficient. For the expansion of the exponential term we can make use of equation (9). Combining these two equations and taking into account that the product of two surface spherical harmonics can be expressed by a sum like

$$Y_{l'm'}(\Omega_r) Y_{l''m''}(\Omega_r) = \sum_{l,m} H(l', l'', l) \langle l' l'' m' m'' | lm \rangle Y_{lm}(\Omega_r) \tag{20}$$

where the summation coefficients $H(l', l'', l)$ are equal to

$$H(l', l'', l) = \left(\frac{(2l'+1)(2l''+1)}{4\pi(2l+1)} \right)^{1/2} \langle l' l'' 00 | l0 \rangle \tag{21}$$

we deduce for the single-centre expansion of a solid harmonic Gaussian

$$\begin{aligned} \varphi_a(\boldsymbol{r}) = 4\pi N_{\alpha L_A} \exp[-\alpha(r^2+R_A^2)] \sum_{l,m}^{\infty} (-1)^m i_l(2\alpha r R_A) \sum_{l_1,l_2=0}^{L_A} \delta_{l_1+l_2,L_A} G(l_1, l_2, L_A) \\ \times r^{l_1} R_A^{l_2} \sum_{m_1,m_2} \langle l_1 l_2 m_1 m_2 | L_A M_A \rangle \sum_{l',l''} H(l_1, l, l') H(l_2, l, l'') \\ \times \sum_{m',m''} \langle l_1 l m_1 m | l' m' \rangle \langle l_2 l m_2 - m | l'' m'' \rangle Y_{l'm'}(\Omega_r) Y_{l''m''}(\Omega_{\boldsymbol{R}_A}). \end{aligned} \tag{22}$$

This somewhat lengthy expression, which formally contains a tenfold sum, can be brought into a more convenient form as will be explained below. The summation indices, for which the limits have not been explicitly given, are restricted by the triangle relations

$$\begin{aligned} |l_1 - l| \leq l' \leq l_1 + l \\ |l_2 - l| \leq l'' \leq l_2 + l \\ m_1 + m_2 = m' + m'' = M_A. \end{aligned} \tag{23}$$

Furthermore there are only contributions from the sums with indices l' and l'' if the expressions l_1+l+l' and l_2+l+l'' are both even, because otherwise the coefficients

(21) are equal to zero. As is well known the sums of products of Clebsch-Gordan coefficients, which are called *jm* coefficients, can be transformed to 3-*nj* coefficients or products of 3-*nj* coefficients and smaller-sized *jm* coefficients. This is especially simple with the graphical methods described by Yutsis *et al* (1962). So one can show that in the present case it is possible to eliminate the sums over the twice repeated projections m_1, m_2 and m and to replace the summation of the products of the Clebsch-Gordan coefficients $\langle l_1 l_2 m_1 m_2 | L_A M_A \rangle$, $\langle l_1 l m_1 m | l' m' \rangle$ and $\langle l_2 l m_2 - m | l'' m'' \rangle$ by a product of a 6-*j* coefficient and a Wigner 3-*j* symbol. Therefore we bring equation (22) into a new simplified form, introducing a coefficient which contains all angular momentum couplings

$$\varphi_a(\boldsymbol{r}) = 4\pi N_{\alpha L_A} \exp[-\alpha(r^2 + R_A^2)] \sum_{l_1,l_2=0}^{L_A} \sum_{l=0}^{\infty} \sum_{l',l''} \sum_{m',m''} C(l_1, l_2, l, l', m', l'', m'', L_A, M_A)$$
$$\times r^{l_1} R_A^{l_2} i_l(2\alpha r R_A)\, Y_{l'm'}(\Omega_{\boldsymbol{r}})\, Y_{l''m''}(\Omega_{\boldsymbol{R}_A}) \tag{24}$$

where the coefficient $C(l_1, l_2, l, l', m', l'', m'', L_A, M_A)$ is given by

$$C(l_1, l_2, l, l', m', l'', m'', L_A, M_A)$$
$$= (-1)^{L_A + l + M_A} \delta_{l_1+l_2, L_A} G(l_1, l_2, L_A) H(l_1, l, l') H(l_2, l, l'')$$
$$\times [(2L_A+1)(2l'+1)(2l''+1)]^{1/2} \begin{Bmatrix} l' & l'' & L_A \\ l_2 & l_1 & l \end{Bmatrix} \begin{pmatrix} l' & l'' & L_A \\ m' & m'' & -M_A \end{pmatrix}. \tag{25}$$

In this form the single-centre expansion (24) of the solid harmonic Gaussians together with equation (25) is particularly suited for numerical treatment on a computer. The coupling coefficients C can be calculated in advance and stored in a database so that the sums in equation (24) can be evaluated very efficiently. This also facilitates the calculation of the matrix elements (4). For the partial-wave overlap of two solid harmonic Gaussians located at centres A and B we find

$$(\mathbf{S}_{LM})_{ab} = (4\pi)^2 \eta N_{ab} \sum_{l_1,l_2=0}^{L_A} \sum_{k_1,k_2=0}^{L_B} \sum_{l=|l_1-L|}^{l_1+L} \sum_{k=|k_1-L|}^{k_1+L} \sum_{l''=|l_2-l|}^{l_2+l} \sum_{k''=|k_2-k|}^{k_2+k}$$
$$\times C(l_1, l_2, l, L, M, l'', m'', L_A, M_A) C(k_1, k_2, k, L, M, k'', n'', L_B, M_B)$$
$$\times I(l_1, l, \alpha, R_A, k_1, k, \beta, R_B) R_A^{l_2} R_B^{k_2} (Y^*_{l''m''}(\Omega_{\boldsymbol{R}_A})\, Y_{k''n''}(\Omega_{\boldsymbol{R}_B}) \tag{26}$$

$N_{ab} = N_{\alpha L_A} N_{\beta L_B}$ being the normalisation and η an exponential factor which will be defined below. Because l is coupled to l_1 and l_2 we introduce the capital letters L and M to designate the angular momentum quantum numbers of the partial wave. If the generalised form of Weber's second exponential integral (11) which occurs in equation (26) is written as

$$I(l_1, l, \alpha, R_A, k_1, k, \beta, R_B) = \int_0^\infty r^{l_1+k_1+2} \exp[-(\alpha+\beta)r^2] i_l(2\alpha r R_A) i_k(2\beta r R_B)\, dr \tag{27}$$

we have for η

$$\eta = \exp[-(\alpha R_A^2 + \beta R_B^2)]. \tag{28}$$

As in the special case of equation (11) there exists an analytical expression which

allows the general integral (27) to be solved in closed form too (Erdélyi *et al* 1953):

$$\int_0^\infty \exp(-p^2t^2)J_\mu(ut)J_\nu(vt)t^{q-1}\,\mathrm{d}t$$

$$= \frac{1}{2p^q}\left(\frac{u}{2p}\right)^\mu \left(\frac{v}{2p}\right)^\nu \frac{1}{\Gamma(\nu+1)} \sum_{s=0}^{\infty} (-1)^s \frac{\Gamma(s+\frac{1}{2}\nu+\frac{1}{2}\mu+\frac{1}{2}q)}{s!\Gamma(\mu+s+1)}$$

$$\times {}_2F_1(-s, -\mu-s; \nu+1; v^2/u^2)\left(\frac{u}{2p}\right)^{2s} \tag{29}$$

where $\mathrm{Re}(\mu+\nu+q)>0$, $\mathrm{Re}(p^2)>0$. Using the relations (13) for the spherical Bessel functions equation (29) would enable us to express the integral (27) as an expansion in terms of finite Gauss hypergeometric series. However, direct numerical integration of the integral (27) is a suitable alternative to the possibly delicate evaluation of an infinite sum like (29). Therefore we rewrite equation (27) as

$$I(l_1, l, \alpha, R_A, k_1, k, \beta, R_B)$$

$$= \int_0^\infty r^{l_1+k_1+2} \exp[-(\alpha+\beta)(r-R_C)^2] f_l(2\alpha r R_A) f_k(2\beta r R_B)\,\mathrm{d}r \tag{30}$$

where

$$f_l(x) = \mathrm{e}^{-x} i_l(x) \qquad \text{and} \qquad R_C = \frac{\alpha R_A + \beta R_B}{\alpha+\beta}.$$

We have introduced in equation (30) the exponentially scaled Bessel function $f_l(x)$. This makes numerical integration feasible and prevents difficulties with the exponential increasing behaviour of the original functions $i_l(x)$ for large arguments x and high index l. The leading factor η then takes the form

$$\eta = \exp\left(-\frac{\alpha\beta}{\alpha+\beta}(R_A-R_B)^2\right). \tag{31}$$

Equation (26) proves to be useful in the calculation of partial-wave contributions according to equation (3) involving solid harmonic or Cartesian Gaussian basis functions. Equations (15) and (26) are the working equations in programs we have developed and which are used in connection with a lobe integral code and with a HONDO integral code. Whereas equation (15) can be evaluated numerically without difficulty, care has to be taken in computing the individual contributions arising from the integral (30) in equation (26) because the integrand is decreasing very slowly if moderately sized exponents are involved. For this reason we have used an adaptive numerical integration which is available in the QUADPACK subroutine package (Piessens *et al* 1983). For the fast evaluation of the functions $f_l(x)$ we use a rational approximation in small intervals similar to that described by Ahlrichs (1974). In the asymptotic region the following finite series is adequate (Abramowitz and Stegun 1970)

$$f_l(x) \sim \frac{1}{2x}\left(1 - \frac{\mu-1}{8x} + \frac{(\mu-1)(\mu-9)}{2!(8x)^2} - \frac{(\mu-1)(\mu-9)(\mu-25)}{3!(8x)^3} + \ldots\right) \tag{32}$$

with $\mu = (2l+1)^2$.

4. Spherical Gaussian functions

To express primitive Cartesian Gaussian basis functions (Dupuis *et al* 1976) completely in terms of basis functions which are defined in spherical coordinates we have to go one step further and extend our considerations to a class of functions with an additional radial dependence consisting of even powers of r. These functions are designated as spherical Gaussian functions (Saunders 1983) and are defined as

$$\varphi_a(\boldsymbol{r}) = N_{\alpha NL}|\boldsymbol{r}-\boldsymbol{R}_\mathrm{A}|^{2N+L} Y_{LM}(\Omega_{\boldsymbol{r}-\boldsymbol{R}_\mathrm{A}}) \exp(-\alpha|\boldsymbol{r}-\boldsymbol{R}_\mathrm{A}|^2) \tag{33}$$

with the normalisation factor

$$N_{\alpha NL} = \left(2\frac{(2\alpha)^{2N+L+3/2}}{\Gamma(2N+L+3/2)}\right)^{1/2}. \tag{34}$$

For the sake of notational convenience we drop in this section the capital letter A in connection with the quantum numbers N, L and M. Consequently the index a stands for $a \equiv (\alpha, R_\mathrm{A}, N, L, M)$. Again we can make use of the results of the previous sections so that the only really new task is the expansion of the even powers of the distance between two points in terms of Legendre polynomials, e.g. we have to determine radial functions $R_l^{(2N)}$ such that

$$|\boldsymbol{r}-\boldsymbol{R}_\mathrm{A}|^{2N} = \sum_l R_l^{(2N)}(r, R_\mathrm{A}) P_l(\cos\gamma) \tag{35}$$

is satisfied. For the special case of even powers this is very easy because the application of the binomial formulae is straightforward. We get

$$|\boldsymbol{r}-\boldsymbol{R}_\mathrm{A}|^{2N} = (r^2+R_\mathrm{A}^2-2rR_\mathrm{A}\cos\gamma)^N \tag{36}$$

$$= R_\mathrm{A}^{2N} \sum_{k=0}^{N} \sum_{i=k}^{N} (-2)^k \binom{N}{k} \binom{N-k}{i-k} \left(\frac{r}{R_\mathrm{A}}\right)^{2i-k} \cos^k\gamma. \tag{37}$$

For the following treatment it is advantageous to introduce the substitution $t = 2i-k$ and to use a more compact notation for equation (37)

$$|\boldsymbol{r}-\boldsymbol{R}_\mathrm{A}|^{2N} = R_\mathrm{A}^{2N} \sum_{k=0}^{N} {\sum_{t=k}^{2N-k}}' b_{k,t}^{(2N)} \left(\frac{r}{R_\mathrm{A}}\right)^t \cos^k\gamma. \tag{38}$$

The combinatorial coefficients $b_{k,t}^{(2N)}$ are given by

$$b_{k,t}^{(2N)} = (-1)^k \frac{(2N)!!}{k!(t-k)!!(2N-k-t)!!}. \tag{39}$$

The prime at the second summation symbol indicates that the summation over t proceeds in steps of 2. From the expansion formulae given by Erdélyi *et al* (1953) we can deduce an expression for the powers of cos γ in terms of Legendre polynomials,

$$\cos^k\gamma = {\sum_{l=[0,1]}^{k}}' (2l+1) a_l^{(k)} P_l(\cos\gamma) \tag{40}$$

where the coefficients $a_l^{(k)}$ are calculated as

$$a_l^{(k)} = \frac{k!}{(k-l)!!(k+l+1)!!}. \tag{41}$$

For even k the summation starts with $l=0$ and for odd k with $l=1$. Combining equations (38) and (40) and rearranging the sums leads to

$$|\boldsymbol{r}-\boldsymbol{R}_A|^{2N} = R_A^{2N} \sum_{l=0}^{N} {\sum_{t=l}^{2N-l}}' {\sum_{k=l}^{[N]}}' (2l+1) a_l^{(k)} b_{l,t}^{(2N)} \left(\frac{r}{R_A}\right)^t P_l(\cos\gamma). \tag{42}$$

Here $[N]$ is equal to N or $N-1$ as l is even or odd, respectively. After defining a new coefficient $T_{l,t}^{(2N)}$ which combines the contributions from both the coefficients $a_l^{(k)}$ and $b_{l,t}^{(2N)}$, this equation can be brought into a very convenient form

$$|\boldsymbol{r}-\boldsymbol{R}_A|^{2N} = R_A^{2N} \sum_{l=0}^{N} {\sum_{t=l}^{2N-l}}' (2l+1) T_{l,t}^{(2N)} \left(\frac{r}{R_A}\right)^t P_l(\cos\gamma). \tag{43}$$

The combinatorial coefficients $T_{l,t}^{(2N)}$ constitute a special case of Steinborn and Filter's (1975) more generally defined coefficients $T_{l,t}^{(N)}$ with arbitrary integer N. From equations (39), (41) and (42) follows

$$T_{l,t}^{(2N)} = (-1)^l \frac{(2N+1)!}{(k-l)!!(k+l+1)!!(2N-k-l)!!(2N-k+l+1)!!}. \tag{44}$$

Comparison of (43) with equation (35) shows that the radial function $R_l^{(2N)}$ we have been looking for can be formulated as a finite sum

$$R_l^{(2N)}(r, R_A) = {\sum_{t=l}^{2N-l}}' T_{l,t}^{(2N)} \left(\frac{r}{R_A}\right)^t. \tag{45}$$

Armed with the results of the previous sections we are now able to set up the expression for the single-centre expansion of a spherical Gaussian function. We first take into consideration the additional exponential term for which the single-centre expansion has been given in equation (9). Combination of equations (8) and (35) yields

$$\begin{aligned} &|\boldsymbol{r}-\boldsymbol{R}_A|^{2N} \exp(-\alpha|\boldsymbol{r}-\boldsymbol{R}_A|^2) \\ &\quad = R_A^{2N} \exp[-\alpha(r^2+R_A^2)] \sum_{l'=0}^{\infty} \sum_{l''=0}^{N} (2l'+1) \\ &\qquad \times (2l''+1) i_{l'}(2\alpha r R_A) R_{l''}^{(2N)}(r, R_A) P_{l'}(\cos\gamma) P_{l''}(\cos\gamma). \end{aligned} \tag{46}$$

If one replaces the product of two Legendre polynomials by a sum similar to equation (20) and rearranges the sums it can be easily shown that the expansion takes the form

$$\begin{aligned} &|\boldsymbol{r}-\boldsymbol{R}_A|^{2N} \exp(-\alpha|\boldsymbol{r}-\boldsymbol{R}_A|^2) \\ &\quad = R_A^{2N} \exp[-\alpha(r^2+R_A^2)] \sum_{l=0}^{\infty} (2l+1) \zeta_l^{(2N)}(\alpha, r, R_A) P_l(\cos\gamma) \end{aligned} \tag{47}$$

where the function $\zeta_l^{(2N)}$ is defined by

$$\zeta_l^{(2N)}(\alpha, r, R_A) = 4\pi \sum_{l''=0}^{N} \sum_{l'=|l-l''|}^{l+l''} H^2(l', l'', l) i_{l'}(2\alpha r R_A) R_{l''}^{(2N)}(r, R_A). \tag{48}$$

The expression for the coefficients $H(l', l'', l)$ can be found in equation (21). The final form for the single-centre expansion for the spherical Gaussians is now obvious. We

have simply to replace the modified Bessel function in equation (24) by the function $\zeta_l^{(2N)}$ and multiply by R_A^{2N} to obtain

$$\varphi_a(\boldsymbol{r}) = 4\pi N_{\alpha NL} R_A^{2N} \exp[-\alpha(r^2+R_A^2)] \sum_{l_1,l_2=0}^{L} \sum_{l=0}^{\infty} \sum_{l',l''} \sum_{m',m''} \times C(l_1, l_2, l, l', m', l'', m'', L, M) r^{l_1} R_A^{l_2} \zeta_l^{(2N)}(\alpha, r, R_A) Y_{l'm'}(\Omega_r) Y_{l''m''}(\Omega_{\boldsymbol{R}A}) \tag{49}$$

where the coupling coefficients C are defined by equation (25). The expression for the overlap integral between two spherical Gaussian functions can be found in a completely analogous way by introducing the same substitutions in equation (26). So we do not give the explicit formula here.

5. Summary and discussion

We have set up formulae for the single-centre expansion of three different types of Gaussian basis functions. Formulae for the solid harmonic Gaussians were also given by Lucchese *et al* (1986) and Seeger (1982). But we believe that equation (24) is more compact and simpler to use in numerical computations. It is more efficient to calculate a 6-*j* coefficient by a closed formula than by a sum of products of three Clebsch-Gordan coefficients. We have also avoided the summation of recursively constructed terms which contain an increasing and a decreasing exponential as was suggested by the addition theorem of Seeger (1982). Such a procedure may cause serious cancellation errors. Finally the single-centre expansions (9), (24) and (49) lead us to expressions for the angular momentum decomposition of the overlap integrals which will be especially useful for an analysis of molecular, highly excited states or continuum states whose wavefunctions were calculated with an L^2 method using Gaussian basis orbitals.

The extension to spherical Gaussian functions is most important because these functions are essential for the transformation from a Gaussian basis set defined in Cartesian coordinates to a basis set defined in spherical coordinates. As was mentioned in the introduction there are a number of problems in atomic or molecular physics which can be treated more efficiently in spherical coordinates. On the other hand, Cartesian Gaussian basis sets are used very often, particularly in the large-scale variational calculations of quantum chemistry. Therefore we complete this work with an appendix which contains the corresponding transformation matrices up to an angular momentum of $l=3$.

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Appendix. Transformation of Cartesian Gaussian functions into spherical Gaussian functions

A primitive Cartesian Gaussian basis function is defined as

$$\chi_a(x, y, z) = N_{\alpha,i,j,k}(x-x_A)^i(y-y_A)^j(z-z_A)^k \exp(-\alpha|\boldsymbol{r}-\boldsymbol{R}_A|^2) \tag{A1}$$

where a stands for $a \equiv (\alpha, \boldsymbol{R}_A, i, j, k)$ and the vector $\boldsymbol{R}_A$ has the components x_A, y_A and z_A. The normalisation factor $N_{\alpha,i,j,k}$ is given by

$$N_{\alpha,i,j,k} = \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2^{2(i+j+k)}\alpha^{i+j+k}}{(2i-1)!!(2j-1)!!(2k-1)!!}\right)^{1/2}. \tag{A2}$$

The definition of the spherical Gaussian functions has been given in equation (33). The functions (A1) are connected to the functions (33) via the transformation

$$\chi_{\alpha,R_A,i,j,k}(x, y, z) = \sum_{n,l,m} A(ijk; nlm)\varphi_{\alpha,R_A,n,l,m}(\boldsymbol{r}) \tag{A3}$$

where the summation is restricted by the condition

$$i+j+k = 2n+l. \tag{A4}$$

The calculation of the matrix elements $A(ijk; nlm)$ is performed by first computing the matrix elements of the inverse transformation

$$\varphi_{\alpha,R_A,n,l,m}(\boldsymbol{r}) = \sum_{i,j,k} A(nlm; ijk)\chi_{\alpha,R_A,i,j,k}(x, y, z). \tag{A5}$$

This is very easy if one takes into account that a surface spherical harmonic takes the following form if one passes to Cartesian coordinates

$$Y_{lm}(\Omega_r) = (-1)^m \left(\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right)^{1/2} (x+\mathrm{i}y)^m \frac{\mathrm{d}^m}{\mathrm{d}z^m} P_l(z/r). \tag{A6}$$

Introducing this expression for Y_{lm} into the left-hand side of equation (A5) and comparing the result with the right-hand side yields the matrix elements $A(nlm; ijk)$ for a fixed value of $2n+l$. This matrix has to be inverted in order to give the desired matrix elements $A(ijk; nlm)$ for the transformation (A3). For the values $i+j+k = 1$, 2 and 3 these matrices are presented in tables 1 to 3. For $i+j+k = 0$ we have $A(000; 000) = 1$.

Table 1. Elements of the matrix $A(ijk; nlm)$ for $i+j+k = 1$.

	nlm		
ijk	01 −1	010	011
100	$1/\sqrt{2}$	0	$-1/\sqrt{2}$
010	$\mathrm{i}/\sqrt{2}$	0	$\mathrm{i}/\sqrt{2}$
001	0	1	0

Table 2. Elements of the matrix $A(ijk; nlm)$ for $i+j+k = 2$.

	nlm					
ijk	02 −2	02 −1	020	021	022	100
200	$1/\sqrt{6}$	0	$-1/3$	0	$1/\sqrt{6}$	$\sqrt{5}/3$
020	$-1/\sqrt{6}$	0	$-1/3$	0	$-1/\sqrt{6}$	$\sqrt{5}/3$
002	0	0	2/3	0	0	$\sqrt{5}/3$
110	$\mathrm{i}/\sqrt{2}$	0	0	0	$-\mathrm{i}/\sqrt{2}$	0
101	0	$1/\sqrt{2}$	0	$-1/\sqrt{2}$	0	0
011	0	$\mathrm{i}/\sqrt{2}$	0	$\mathrm{i}/\sqrt{2}$	0	0

Table 3. Elements of the matrix $A(ijk; nlm)$ for $i+j+k=3$.

	nlm									
ijk	03 − 3	03 − 2	03 − 1	030	031	032	033	11 − 1	110	111
300	$1/2\sqrt{5}$	0	$-\sqrt{3}/10$	0	$\sqrt{3}/10$	0	$-1/2\sqrt{5}$	$(1/5)\sqrt{(21/2)}$	0	$-(1/5)\sqrt{(21/2)}$
030	$-i/2\sqrt{5}$	0	$-i\sqrt{3}/10$	0	$-i\sqrt{3}/10$	0	$-i/2\sqrt{5}$	$(i/5)\sqrt{(21/2)}$	0	$(i/5)\sqrt{(21/2)}$
003	0	0	0	2/5	0	0	0	0	$\sqrt{21}/5$	0
210	i/2	0	$-i/2\sqrt{15}$	0	$-i2/\sqrt{15}$	0	i/2	$i\sqrt{(7/30)}$	0	$i\sqrt{(7/30)}$
201	0	$1/\sqrt{6}$	0	$-1/\sqrt{5}$	0	$1/\sqrt{6}$	0	0	$\sqrt{(7/15)}$	0
120	−1/2	0	$-1/2\sqrt{15}$	0	$1/2\sqrt{15}$	0	1/2	$\sqrt{(7/30)}$	0	$-\sqrt{(7/30)}$
102	0	0	$2/\sqrt{15}$	0	$-2/\sqrt{15}$	0	0	$\sqrt{(7/30)}$	0	$-\sqrt{(7/30)}$
021	0	$-1/\sqrt{6}$	0	$-1/\sqrt{5}$	0	$-1/\sqrt{6}$	0	0	$\sqrt{(7/15)}$	0
012	0	0	$2i/\sqrt{15}$	0	$2i/\sqrt{15}$	0	0	$i\sqrt{(7/30)}$	0	$i\sqrt{(7/30)}$
111	0	$i/\sqrt{2}$	0	0	0	$-i/\sqrt{2}$	0	0	0	0

References

Abramowitz M and Stegun I 1970 *Handbook of Mathematical Functions* (New York: Dover)

Ahlrichs R 1974 *Theor. Chim. Acta* **33** 157

Condon E U and Shortley G H 1970 *The Theory of Atomic Spectra* (Cambridge: Cambridge University Press)

Dupuis M, Rys J and King H F 1976 *J. Chem. Phys.* **65** 111

Erdélyi A, Magnus W, Oberhettinger F and Tricomi F G 1953 *Higher Transcendental Functions* vol 2 (New York: McGraw-Hill)

Kaufmann K, Nager Ch and Jungen M 1985 *Chem. Phys.* **95** 385

Le Rouzo H and Silvi B 1978 *Int. J. Quantum Chem.* **13** 311

Lucchese R R, Takatsuka K and McKoy V 1986 *Phys. Rep.* **131** 147

Moshinsky M 1959 *Nucl. Phys.* **13** 104

Moskowitz J W and Snyder L C 1977 *Methods of Electronic Structure Theory* ed H F Schaefer III (New York: Plenum) pp 387–409

Piessens R, de Doncker-Kapenga E, Ueberhuber C W and Kahaner D K 1983 *QUADPACK, A Subroutine Package for Automatic Integration* (Berlin: Springer)

Pople J A, Binkley J S, Whiteside R A, Krishnan R, Seeger R, DeFrees D J, Schlegel H B, Topiol S and Kahn L R 1981 *QCPE Catalog* vol 13 (Bloomington: Indiana University) Program 406

Saunders V R 1983 *Methods in Computational Molecular Physics* ed G H F Diercksen and S Wilson (Dordrecht: Reidel) pp 1–36

Seaton M J 1961 *Proc. Phys. Soc.* **77** 184

Seeger R 1982 *Chem. Phys. Lett.* **92** 493

Steinborn E O and Filter E 1975 *Theor. Chim. Acta* **38** 261

Thompson I J and Barnett A R 1987 *Comput. Phys. Commun.* **47** 245

Watson G N 1944 *A Treatise on the Theory of Bessel Functions* 2nd edn (Cambridge: Cambridge University Press)

Whitten J L 1966 *J. Chem. Phys.* **44** 359

Yutsis A P, Levinson J B and Vanagas V V 1962 *Mathematical Apparatus of the Theory of Angular Momentum* (Jerusalem: Israel Program for Scientific Translations)