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Representation of the three-dimensional rotation operator in the anisotropic Gaussian basis

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Abstract. A method based on the generating function technique is proposed to calculate matrix elements of the three-dimensional rotation operator for anisotropic Gaussian wavefunctions.

Among the many sets of wavefunctions used in quantum mechanical calculations of atoms, molecules and atomic nuclei (see [1] for an extensive review) the Cartesian Gaussian (CG) set [2, 3] is commonly used due to its simple analytical form. The CG basis has some disadvantages, such as having the right asymptotical behaviour or not fulfulling the cusp conditions at the nuclear centres, but its simple analytical form allows for an analytical and efficient evaluation of the various matrix elements needed in the calculations [4]. Most of the CG bases used have spherical exponents but it has also been suggested [5] that using anisotropic exponents of the form $-(\alpha_x x^2 + \alpha_y y^2 \alpha_z z^2)$ could be advantageous to deal with the anisotropy of the molecular environment. In nuclear physics, where the concept of symmetry breaking at the mean-field level has been very successful in explaining collective properties of atomic nuclei such as the appearance of rotational bands, the use of an anisotropic Gaussian basis is very common [6–8].

In this paper we address the problem of finding analytical expressions for the representation of the three-dimensional rotation operator in the most general Cartesian, anisotropic Gaussian (CAG) basis in which the exponent of the Gaussian is not isotropic (this basis is also refered to as the elliptical Gaussian basis). The results obtained include as a limiting case the representation of the rotation operator for the isotropic Gaussian basis (results for isotropic Hermite–Gaussian functions and rotations along one axis can be found in [9]). The motivation for this calculation is that this representation is needed whenever one wants to include quantum mechanical effects beyond the Born–Oppenheimer approximation in dealing with the rotational bands of molecules [10], molecular collisions [11] or rotational spectra in atomic nuclei [12, 13].

The rotation matrix to be computed is defined as

$$\hat{R}(\Omega)|n\rangle = \sum_{n'} R_{nn'}(\Omega)|n'\rangle \tag{1}$$

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where $\hat{R}(\Omega)$ is the operator of active rotations written in terms of the Euler angles $\Omega = (\alpha, \beta, \gamma)$ [14]

$$\hat{R}(\Omega) = \mathrm{e}^{-\mathrm{i}\alpha\hat{J}_z}\,\mathrm{e}^{-\mathrm{i}\beta\hat{J}_y}\,\mathrm{e}^{-\mathrm{i}\gamma\hat{J}_z} \tag{2}$$

and the ket $|n\rangle$ is a shorthand notation for the CAG wavefunction

$$\langle \boldsymbol{r}|n\rangle \equiv \langle \boldsymbol{r}|n_x, n_y, n_z; b_x, b_y, b_z\rangle = \Psi_{n_x}(x/b_x)\Psi_{n_y}(y/b_y)\Psi_{n_z}(z/b_z) \tag{3}$$

where

$$\Psi_{n_i}(x_i/b_{x_i}) = \left(\frac{x_i}{b_{x_i}}\right)^{n_i}\,\mathrm{e}^{-\frac{1}{2}(x_i/b_{x_i})^2}. \tag{4}$$

Here b_{x_i} is the characteristic length along each direction and the index x_i stands for the set x, y and z. Let us note that these functions are not orthogonal:

$$\int_{-\infty}^{\infty}\mathrm{d}x_i\,\Psi_{n_i}\left(\frac{x_i}{b_{x_i}}\right)\Psi_{n_i'}\left(\frac{x_i}{b_{x_i}}\right) = \frac{\sqrt{\pi}\,b_{x_i}(n_i+n_i'-1)!!}{2^{(n_i+n_i')/2}}\delta_{n_i+n_i',\mathrm{even}}. \tag{5}$$

The matrix elements of the rotation operator between CAG wavefunctions with different lengths can be written, in general, as

$$R_{nn'}(\Omega) \equiv \langle n_x, n_y, n_z; b_x, b_y, b_z|\hat{R}(\Omega)|n_x', n_y', n_z'; c_x, c_y, c_z\rangle = I^{n_x n_y n_z}_{n_x' n_y' n_z'} \tag{6}$$

where the quantity $I^{n_x n_y n_z}_{n_x' n_y' n_z'}$ is the following integral

$$I^{n_x n_y n_z}_{n_x' n_y' n_z'} = \int \mathrm{d}^3\boldsymbol{r}\left(\frac{x}{b_x}\right)^{n_x}\left(\frac{y}{b_y}\right)^{n_y}\left(\frac{z}{b_z}\right)^{n_z}\left(\frac{x'}{c_x}\right)^{n_x'}\left(\frac{y'}{c_y}\right)^{n_y'}\left(\frac{z'}{c_z}\right)^{n_z'}\mathrm{e}^{-\frac{1}{2}\boldsymbol{r}\mathbf{M}\boldsymbol{r}}. \tag{7}$$

Here $\boldsymbol{r}' = (x', y', z')$ are the rotated coordinates defined by $\hat{R}\,(\Omega)\,\Psi(\boldsymbol{r}) = \Psi(\boldsymbol{r}')$ and related to $\boldsymbol{r}$ according to $\boldsymbol{r}' = \mathbf{D}(\alpha\beta\gamma)\boldsymbol{r}$ with the real and unitary matrix $\mathbf{D}(\Omega)$ given by

$$\mathbf{D}(\Omega) = \begin{pmatrix}\cos\gamma & \sin\gamma & 0\\ -\sin\gamma & \cos\gamma & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}\cos\beta & 0 & -\sin\beta\\ 0 & 1 & 0\\ \sin\beta & 0 & \cos\beta\end{pmatrix}\begin{pmatrix}\cos\alpha & \sin\alpha & 0\\ -\sin\alpha & \cos\alpha & 0\\ 0 & 0 & 1\end{pmatrix}. \tag{8}$$

The matrix $\mathbf{M}$ in the exponent is

$$\mathbf{M}(\Omega) = \mathbf{B}^2 + \mathbf{D}^{\mathrm{T}}(\Omega)\mathbf{C}^2\mathbf{D}(\Omega) \tag{9}$$

with $\mathbf{B}^2$ and $\mathbf{C}^2$ given by

$$B^2 = \begin{pmatrix}1/b_x^2 & 0 & 0\\ 0 & 1/b_y^2 & 0\\ 0 & 0 & 1/b_z^2\end{pmatrix} \qquad \mathbf{C}^2 = \begin{pmatrix}1/c_x^2 & 0 & 0\\ 0 & 1/c_y^2 & 0\\ 0 & 0 & 1/c_z^2\end{pmatrix}. \tag{10}$$

From its definition it is clear that the matrix $\mathbf{M}$ is real, symmetric and definite positive.

To compute the integral we use the generating function technique. The generating function of the monomial $(x/b_x^{n_x})(y/b_y)^{n_y}(z/b_z)^{n_z}$ is defined as

$$\mathrm{e}^{2\boldsymbol{p}\mathbf{B}\boldsymbol{r}} = \sum_{n_x n_y n_z} 2^{n_x+n_y+n_z}\frac{p_x^{n_x}}{n_x!}\frac{p_y^{n_y}}{n_y!}\frac{p_z^{n_z}}{n_z!}\left(\frac{x}{b_x}\right)^{n_x}\left(\frac{y}{b_y}\right)^{n_y}\left(\frac{z}{b_z}\right)^{n_z}. \tag{11}$$

Using it, the calculation of $I^{n_x n_y n_z}_{n_x' n_y' n_z'}$ is reduced to the evaluation of the much simpler integral

$$\int \mathrm{d}^3\boldsymbol{r}\,\mathrm{e}^{-\frac{1}{2}\boldsymbol{r}\mathbf{M}\boldsymbol{r}+2\boldsymbol{a}\boldsymbol{r}} = \sum_{n_x n_y n_z n_x' n_y' n_z'} 2^{N+N'}\frac{p_x^{n_x}}{n_x!}\frac{p_y^{n_y}}{n_y!}\frac{p_z^{n_z}}{n_z!}\frac{q_x^{n_x'}}{n_x'!}\frac{q_y^{n_y'}}{n_y'!}\frac{q_z^{n_z'}}{n_z'!}I^{n_x n_y n_z}_{n_x' n_y' n_z'} \tag{12}$$

where we have introduced the column vector $\boldsymbol{a} = \mathbf{B}\boldsymbol{p} + \mathbf{D}^{\mathrm{T}}\mathbf{C}\boldsymbol{q}$ and defined $N = n_x + n_y + n_z$ and $N' = n'_x + n'_y + n'_z$. Once this integral has been computed, the result is expanded in powers of $\boldsymbol{p}$ and $\boldsymbol{q}$. Comparing this expansion with the right-hand side of equation (12) the desired result is obtained.

The integral is straightforward,

$$\int \mathrm{d}^3\boldsymbol{r}\, \mathrm{e}^{-\frac{1}{2}\boldsymbol{r}\mathbf{M}\boldsymbol{r}+2\boldsymbol{a}\boldsymbol{r}} = \frac{(2\pi)^{3/2}}{\sqrt{\det \mathbf{M}}}\, \mathrm{e}^{2\boldsymbol{a}\mathbf{M}^{-1}\boldsymbol{a}} = \frac{(2\pi)^{3/2}}{\sqrt{\det \mathbf{M}}}\, \mathrm{e}^{2\boldsymbol{t}\mathbf{m}^{-1}\boldsymbol{t}} \tag{13}$$

and the result has been expressed in terms of the vector $\boldsymbol{t} = \mathbf{K}^{\mathrm{T}}\boldsymbol{a}$ where $\mathbf{K}$ is the unitary matrix that diagonalizes the Hermitian matrix $\mathbf{M}$, i.e. $\mathbf{MK} = \mathbf{Km}$, and $\mathbf{m}$ denotes the diagonal matrix of eigenvalues of $\mathbf{M}$. Now using the explicit expression of $\boldsymbol{t} = \mathbf{K}^{\mathrm{T}}\boldsymbol{a} = \mathbf{K}^{\mathrm{T}}\mathbf{B}\boldsymbol{p} + \mathbf{K}^{\mathrm{T}}\mathbf{D}^{\mathrm{T}}\mathbf{C}\boldsymbol{q}$ we can expand the right-hand side of equation (13) as

$$\sum_{f_1 f_2 f_3 g_1 g_2 g_3} \prod_{s=1,2,3} \frac{2^{f_s+g_s}(f_s+g_s-1)!!}{f_s!\, g_s!\, m_s^{(f_s+g_s)/2}} \delta_{f_s+g_s,\mathrm{even}} \left(\sum_{n=1}^{3} L_{sn}\, p_n\right)^{f_s} \left(\sum_{n=1}^{3} F_{sn} q_n\right)^{g_s} \tag{14}$$

where the following definitions have been introduced,

$$L_{ij} = (\mathbf{K}^{\mathrm{T}}\mathbf{B})_{ij} \tag{15}$$

$$F_{ij} = (\mathbf{K}^{\mathrm{T}}\mathbf{D}^{\mathrm{T}}\mathbf{C})_{ij}. \tag{16}$$

Now the quantities $(\sum_n L_{sn} p_n)^{f_s}$ and $(\sum_n F_{sn} q_n)^{g_s}$ are expanded in powers of the p_i and q_i

$$\left(\sum_{n=1}^{3} L_{sn} p_n\right)^{f_s} = f_s! L_{ss}^{f_s} \sum_{a_s=0}^{f_s} \sum_{b_s=0}^{f_s-a_s} \frac{p_s^{f_s-a_s-b_s}}{(f_s-a_s-b_s)!} \prod_{n\neq s} \left(\frac{L_{sn}}{L_{ss}}\right)^{r_n} \frac{p_n^{r_n}}{r_n!} \tag{17}$$

$$\left(\sum_{n=1}^{3} F_{sn} q_n\right)^{g_s} = g_s! F_{ss}^{g_s} \sum_{d_s=0}^{g_s} \sum_{h_s=0}^{g_s-d_s} \frac{q_s^{g_s-d_s-h_s}}{(g_s-d_s-h_s)!} \prod_{n\neq s} \left(\frac{F_{sn}}{F_{ss}}\right)^{r_n} \frac{q_n^{r_n}}{r_n!} \tag{18}$$

where for each s the couple of indices r_i and r_j $(i < j; i, j \neq s)$ stand for a_s and b_s (or d_s and h_s), respectively. The quantity $I^{n_x n_y n_z}_{n'_x n'_y n'_z}$ is proportional to the coefficient of $p_1^{n_x} p_2^{n_y} p_3^{n_z} q_1^{n'_x} q_2^{n'_y} q_3^{n'_z}$ in the expansion (14) which leads to the following systems of equations for the indices of equations (17) and (18):

$$n_x = f_1 - a_1 - b_1 + a_2 + a_3 \tag{19a}$$

$$n_y = f_2 - a_2 - b_2 + a_1 + b_3 \tag{19b}$$

$$n_z = f_3 - a_3 - b_3 + b_1 + b_2 \tag{19c}$$

and

$$n'_x = g_1 - d_1 - h_1 + d_2 + d_3 \tag{20a}$$

$$n'_y = g_2 - d_2 - h_2 + d_1 + h_3 \tag{20b}$$

$$n'_z = g_3 - d_3 - h_3 + h_1 + h_2. \tag{20c}$$

Summing up separately the three equations of equation (19) and (20) we get

$$N = n_x + n_y + n_z = f_1 + f_2 + f_3 \tag{21}$$

and

$$N' = n'_x + n'_y + n'_z = g_1 + g_2 + g_3 \tag{22}$$

respectively. These relations show that the rank of each system is two; i.e. in each system of three equations in equations (19) and (20) two out of the six unknowns can be determined in terms of the others. Taking into account the above constraints we can write

$$I^{n_x n_y n_z}_{n'_x n'_y n'_z} = \sum_{f_1+f_2+f_3=N} \sum_{g_1+g_2+g_3=N'} Q^{n_x n_y n_z}_{f_1 f_2 f_3}(\mathbf{L}) N^{f_1 f_2 f_3}_{g_1 g_2 g_3} Q^{n'_x n'_y n'_z}_{g_1 g_2 g_3}(\mathbf{F}) \tag{23}$$

with the following definitions,

$$N^{f_1 f_2 f_3}_{g_1 g_2 g_3} = \frac{(2\pi)^{3/2}}{\sqrt{\det \mathbf{M}}} \prod_{s=1,2,3} \frac{B^{f_s}_{ss}(f_s+g_s-1)!! C^{g_s}_{ss}}{m_s^{\frac{1}{2}(f_s+g_s)}} \delta_{f_s+g_s,\text{even}} \tag{24}$$

and

$$Q^{n_x n_y n_z}_{f_1 f_2 f_3}(\mathbf{L}) = n_x! n_y! n_z! \prod_{s=1,2,3} \left(\frac{L_{ss}}{B_{ss}}\right)^{f_s} \left(\sum_{a_s,b_s} \frac{1}{(f_s-a_s-b_s)!} \prod_{n\neq s} \left(\frac{L_{sn}}{L_{ss}}\right)^{r_n} \frac{1}{r_n!} \right). \tag{25}$$

Here the sum indices a_s and b_s are restricted by equation (19). The quantity $Q^{n'_x n'_y n'_z}_{g_1 g_2 g_3}(\mathbf{F})$ is defined as in equation (25) but substituting the matrix $\mathbf{L}$ by $\mathbf{F}$, the indices f_s by g_s, B_{ss} by C_{ss} and restricting the sum indices by equation (20).

In the limit $\alpha = \beta = \gamma = 0$ the rotation matrix $\mathbf{D}(0)$ is the unity matrix, $\mathbf{M}$ is diagonal and $\mathbf{K}$ is also the unity matrix. Therefore, the $\mathbf{L}$ and $\mathbf{F}$ matrices are diagonal implying that $Q^{n_x n_y n_z}_{f_1 f_2 f_3}(\mathbf{L})$ and $Q^{n'_x n'_y n'_z}_{g_1 g_2 g_3}(\mathbf{F})$ will only be different from zero when the exponents of the off diagonal elements of $\mathbf{F}$ and $\mathbf{L}$ are zero (i.e. $a_s = b_s = g_s = h_s = 0$) and then

$$Q^{n_x n_y n_z}_{f_1 f_2 f_3}(\mathbf{L}) = \delta_{f_1,n_x} \delta_{f_2,n_y} \delta_{f_3,n_z} \tag{26}$$

$$Q^{n'_x n'_y n'_z}_{g_1 g_2 g_3}(\mathbf{F}) = \delta_{g_1,n'_x} \delta_{g_2,n'_y} \delta_{g_3,n'_z}. \tag{27}$$

This result shows that the quantity $N^{f_1 f_2 f_3}_{g_1 g_2 g_3}$ is nothing but the matrix overlap of our bases.

Another interesting limit corresponds to the isotropic case where the matrices $\mathbf{B}$ and $\mathbf{C}$ are proportional to the unity matrix. In this case $\mathbf{M}$ is also diagonal and $\mathbf{K}$ is again the unity matrix. Then $\mathbf{L} = \mathbf{B}$ implying $Q^{n_x n_y n_z}_{f_1 f_2 f_3}(\mathbf{L}) = \delta_{f_1,n_x} \delta_{f_2,n_y} \delta_{f_3,n_z}$. On the other hand, $\mathbf{F} = \mathbf{D}^{\mathrm{T}}\mathbf{C}$ and therefore

$$\begin{aligned} Q^{n'_x n'_y n'_z}_{g_1 g_2 g_3}(\mathbf{F}) = n'_x! n'_y! n'_z! \sum_{h_1 h_2 h_3 d_1 d_2 d_3} & \frac{D^{g_1-d_1-h_1}_{11} D^{d_1}_{21} D^{h_1}_{31}}{(g_1-d_1-h_1)! d_1! h_1!} \frac{D^{g_2-d_2-h_2}_{22} D^{d_2}_{12} D^{h_2}_{32}}{(g_2-d_2-h_2)! d_2! h_2!} \\ & \times \frac{D^{g_3-d_3-h_3}_{33} D^{d_3}_{13} D^{h_3}_{23}}{(g_3-d_3-h_3)! d_3! h_3!} \end{aligned} \tag{28}$$

where the summation indices are again restricted by equation (20).

In conclusion, we have obtained an analytical expression for the rotation matrix in the Gaussian anisotropic basis that is well suited for practical applications as in, for instance, the full quantal treatment of the rotational motion in molecules or atomic nuclei.

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References

[1] Burden F R and Wilson R M 1972 *Adv. Phys.* **21** 825
[2] Boys S F 1950 *Proc. R. Soc.* A **200** 542
Boys S F 1950 *Proc. R. Soc.* A **201** 125
[3] McWeeny R 1950 *Nature* **166** 21
[4] Shavitt I 1963 *Math. Comput. Phys.* **2** 1
[5] Katriel J 1969 *Chem. Phys. Lett.* **3** 642
Katriel J and Adam G 1970 *Chem. Phys. Lett.* **4** 596
Katriel J and Adam G 1970 *Chem. Phys. Lett.* **5** 302
Zivkovic T and Maksic Z B 1968 *J. Chem. Phys.* **49** 3083
[6] Nilsson S G 1955 *Mat. Fys. Medd. Dan. Vid. Selsk.* **29** 1
Rassey A J 1958 *Phys. Rev.* **109** 949
Chi B 1966 *Nucl. Phys.* **83** 97
[7] Vautherin D 1972 *Phys. Rev.* C **7** 296
[8] Girod M and Grammaticos B 1983 *Phys. Rev.* C **27** 2317
[9] Kivkovic T 1971 *J. Chem. Phys.* **55** 1672
[10] Lathouwers L and Van Leuven P 1982 *Adv. Chem. Phys.* **49** 115
Woolley R G and Sutcliffe B T 1977 *Chem. Phys. Lett.* **45** 393
[11] Child M S 1974 *Molecular Collision Theory* (London and New York: Academic)
[12] Ring P and Shuck P 1980 *The Nuclear Many Body Problem* (Berlin: Springer)
[13] Schmid K W and Gruemmer F 1987 *Rep. Prog. Phys.* **50** 731
[14] Varshalovich D A, Moskalev A N and Khersonskii V K 1988 *Quantum Theory of Angular Momentum* (Singapore: World Scientific)