Transformation Between Cartesian and Pure Spherical Harmonic Gaussians

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ABSTRACT

Spherical Gaussians can be expressed as linear combinations of the appropriate Cartesian Gaussians. General expressions for the transformation coefficients are given. Values for the transformation coefficients are tabulated up to h-type functions. © 1995 John Wiley & Sons, Inc.

Introduction

In most computer programs for molecular electronic structure calculations, molecular orbitals are expanded as linear combinations of Gaussian basis functions [1]. Although the necessary integrals over basis functions can be calculated for spherical harmonic Gaussians [2],

$$\tilde{g}(\alpha, l, m, n, \mathbf{r}) = \tilde{N}(n, \alpha) Y_m^l r^n e^{-\alpha r^2}, \quad (1)$$

most current codes rely on efficient algorithms to calculate integrals over Cartesian Gaussians [3,4]:

$$g(\alpha, l_x, l_y, l_z, \mathbf{r}) = N(l_x, l_y, l_z, \alpha) x^{l_x} y^{l_y} z^{l_z} e^{-\alpha \mathbf{r}^2}. \quad (2)$$

For a given angular momentum, $l = l_x + l_y + l_z$, the number of Cartesian Gaussians is greater than or equal to the number of pure spherical harmonic Gaussians [for fixed $n, (l+1)(l+2)/2$ Cartesian Gaussians vs. $2l+1$ spherical harmonic Gaussians]. Higher angular momentum functions are more important at correlated levels of theory than at the Hartree–Fock level. Since methods for computing electron correlation depend on the sixth, seventh, and higher powers of the number of basis functions, it is very advantageous to keep the total number of basis functions as low as possible, e.g., by using spherical Gaussians rather than Cartesians. The pure spherical harmonic Gaussians can be constructed from the appropriate Cartesian Gaussians:

$$r^{l-n}\tilde{g}(\alpha, l, m, n, \mathbf{r}) = \sum_{l_x+l_y+l_z=l} c(l, m, n, l_x, l_y, l_z) g(\alpha, l_x, l_y, l_z, \mathbf{r}). \quad (3)$$

Typically, only spherical Gaussians with $n = l$ are retained in the basis set. This reduces Eq. (3) to a simple linear transformation that is very closely re-

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lated to the transformation from Cartesian to spherical tensors [5]. The s- and p-type spherical harmonic Gaussians are equivalent to their Cartesian counterparts. The conversion of 6 d-type Cartesian Gaussians to five spherical harmonic Gaussians is fairly straightforward. The conversion of f-type functions is more complicated and the transformation for higher angular momentum functions is quite tedious. Recurrence formulas for the transformation of Cartesian to spherical Gaussians have been discussed previously [2]. In this article, we present explicit expressions for the coefficients for the conversion between normalized Cartesian and pure *spherical* harmonic Gaussians.

Theory

The normalized spherical harmonics can be generated using

$$Y_m^l = \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}}\, e^{im\phi}\, \frac{(1-\cos^2\theta)^{|m|/2}}{2^l l!} \times \frac{\partial^{l+|m|}}{\partial \cos\theta^{l+|m|}} (\cos^2\theta - 1)^l . \tag{4}$$

In terms of the spherical coordinates, the Cartesian coordinates are

$$x = r\sin\theta\cos\phi, \quad y = r\sin\theta\sin\phi, \quad z = r\cos\theta . \tag{5}$$

Substituting Eq. (5) into Eq. (4) and multiplying r^l yields normalized harmonic polynomials [4]:

$$r^l Y_m^l = \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}}\,(x \pm iy)^{|m|} \times \frac{1}{2^l l!}\frac{\partial^{l+|m|}}{\partial z^{l+|m|}} (z^2 - r^2)^l , \tag{6}$$

where + is for $m \geq 0$ and − is for $m < 0$. This can be expanded into an lth degree polynomial in x, y, z, and r. Substitution of $r^2 = x^2 + y^2 + z^2$, differentiating with respect to x, y, and z, and setting $x = y = z = 0$ yields the coefficients of $x^{l_x} y^{l_y} z^{l_z}$ in the polynomial:

$$\tilde{c}(l,m,n,l_x,l_y,l_z) = \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} \times \frac{1}{l_x!\,l_y!\,l_z!}\frac{d^l}{dx^{l_x}dx^{l_y}dx^{l_z}}\Big|_0 \times (x \pm iy)^{|m|}\frac{1}{2^l l!}\frac{\partial^{l+|m|}}{\partial z^{l+|m|}} \times (z^2 - r^2)^l , \tag{7}$$

for $n = l = l_x + l_y + l_z$. These are the coefficients for transformation of the unnormalized Gaussians. The normalization factors in Eqs. (1) and (2) are given by

$$\tilde{N}(n,\alpha) = \left[\frac{(2n+2)!\,\pi^{1/2}}{2^{2n+3}(n+1)!\,\alpha^{n+3/2}}\right]^{-1/2} \tag{8}$$

$$N(l_x,l_x,l_x,\alpha) = \left[\frac{(2l_x)!\,(2l_y)!\,(2l_z)!\,\pi^{3/2}}{2^{2l}\,l_x!\,l_y!\,l_z!\,\alpha^{l+3/2}}\right]^{-1/2} . \tag{9}$$

The coefficients for transformation of the normalized Gaussians are

$$c(l,m,n,l_x,l_y,l_z) = \frac{\tilde{N}(n,\alpha)}{N(l_x,l_x,l_x,\alpha)}\,\tilde{c}(l,m,n,l_x,l_y,l_z) . \tag{10}$$

After some simplification, this becomes

$$c(l,m,n,l_x,l_y,l_z) = \sqrt{\frac{(2l_x)!\,(2l_y)!\,(2l_z)!\,l!\,(l-|m|)!}{(2l)!\,l_x!\,l_y!\,l_z!\,(l+|m|)!}} \times \frac{1}{l_x!\,l_y!\,l_z!}\frac{d^l}{dx^{l_x}dx^{l_y}dx^{l_z}}\Big|_0 \times (x \pm iy)^{|m|}\frac{1}{2^l l!} \times \frac{\partial^{l+|m|}}{\partial z^{l+|m|}}(z^2 - r^2)^l , \tag{11}$$

for $n = l = l_x + l_y + l_z$. Equation (11) is quite suitable for evaluation with any of the symbolic algebra programs, such as Mathematica [6]. Since the angular momentum of basis functions used in electronic structure calculations is relatively small, these coefficients can be evaluated once and tabulated. The transformation from Cartesian to pure functions are listed in Table I for $l = 0$–5.

It is more desirable to have readily computable expressions for the coefficients that can be evaluated up to arbitrary order using standard computer languages. After using the binomial theorem to expand $(z^2 - r^2)^l$ and evaluating $d^{l+|m|}/dz^{l+|m|}$, Eq. (11) becomes

$$c(l,m,n,l_x,l_y,l_z) = \sqrt{\frac{(2l_x)!\,(2l_y)!\,(2l_z)!\,l!\,(l-|m|)!}{(2l)!\,l_x!\,l_y!\,l_z!\,(l+|m|)!}} \times \frac{1}{2^l l!}\frac{1}{l_x!\,l_y!\,l_z!}\frac{d^l}{dx^{l_x}dx^{l_y}dx^{l_z}}\Big|_0 \times (x \pm iy)^{|m|}\sum_{i=0}^{(l-|m|)/2}\binom{l}{i} \times \frac{(-1)^i(2l-2i)!}{(l-|m|-2i)!}\, z^{l-|m|+2i}\, r^{2i} . \tag{12}$$

TABLE I
Transformation from normalized Cartesian functions, $v(l_x, l_y, l_z)$, to normalized spherical harmonic functions, $v(l, m)^a$.

$$v(0,0) = v(0,0,0);\quad v(1,0) = v(0,0,1);\quad v(1,1) = \frac{1}{\sqrt{2}}\{v(1,0,0) + iv(0,1,0)\}$$

$$v(2,0) = v(0,0,2) - \frac{1}{2}\{v(2,0,0) + v(0,2,0)\};\quad v(2,1) = \frac{1}{\sqrt{2}}\{v(1,0,1) + iv(0,1,1)\}$$

$$v(2,2) = \sqrt{\frac{3}{8}}\{v(2,0,0) - v(0,2,0)\} + \frac{i}{\sqrt{2}}v(1,1,0)$$

$$v(3,0) = v(0,0,3) - \frac{3}{2\sqrt{5}}(v(2,0,1) + v(0,2,1))$$

$$v(3,1) = \sqrt{\frac{3}{5}}\{v(1,0,2) + iv(0,1,2)\} - \frac{\sqrt{3}}{4}\{v(3,0,0) + iv(0,3,0)\} - \frac{\sqrt{3}}{4\sqrt{5}}\{v(1,2,0) + iv(2,1,0)\}$$

$$v(3,2) = \sqrt{\frac{3}{8}}\{v(2,0,1) - v(0,2,1)\} + \frac{i}{\sqrt{2}}v(1,1,1)$$

$$v(3,3) = \frac{\sqrt{5}}{4}\{v(3,0,0) - iv(0,3,0)\} - \frac{3}{4}\{v(1,2,0) - iv(2,1,0)\}$$

$$v(4,0) = v(0,0,4) + \frac{3}{8}\{v(4,0,0) + v(0,4,0)\} - \frac{3\sqrt{3}}{\sqrt{35}}\{v(2,0,2) + v(0,2,2) - \frac{1}{4}v(2,2,0)\}$$

$$v(4,1) = \sqrt{\frac{5}{7}}\{v(1,0,3) + iv(0,1,3)\} - \frac{3\sqrt{5}}{4\sqrt{7}}\{v(3,0,1) + iv(0,3,1)\} - \frac{3}{4\sqrt{7}}\{v(1,2,1) + iv(2,1,1)\}$$

$$v(4,2) = \frac{3\sqrt{3}}{2\sqrt{14}}\{v(2,0,2) - v(0,2,2)\} + \frac{3i}{\sqrt{14}}v(1,1,2) - \frac{\sqrt{5}}{4\sqrt{2}}\{v(4,0,0) - v(0,4,0)\}$$
$$- \frac{i\sqrt{5}}{2\sqrt{14}}\{v(3,1,0) + v(1,3,0)\}$$

$$v(4,3) = \frac{\sqrt{5}}{4}\{v(3,0,1) - iv(0,3,1)\} - \frac{3}{4}\{v(1,2,1) - iv(2,1,1)\}$$

$$v(4,4) = \frac{\sqrt{35}}{8\sqrt{2}}\{v(4,0,0) + v(0,4,0)\} - \frac{3\sqrt{3}}{4\sqrt{2}}v(2,2,0) + i\sqrt{\frac{5}{8}}\{v(3,1,0) - v(1,3,0)\}$$

$$v(5,0) = v(0,0,5) - \frac{5}{\sqrt{21}}\{v(2,0,3) + v(0,2,3)\} + \frac{5}{8}\{v(4,0,1) + v(0,4,1)\} + \frac{\sqrt{15}}{4\sqrt{7}}v(2,2,1)$$

$$v(5,1) = \sqrt{\frac{5}{6}}\{v(1,0,4) + iv(0,1,4)\} - \frac{3\sqrt{5}}{2\sqrt{14}}\{v(3,0,2) + iv(0,3,2)\} - \frac{3}{2\sqrt{14}}\{v(1,2,2) + iv(2,1,2)\}$$
$$+ \frac{\sqrt{15}}{8\sqrt{2}}\{v(5,0,0) + iv(0,5,0)\} + \frac{\sqrt{5}}{8\sqrt{6}}\{v(1,4,0) + iv(4,1,0)\} + \frac{\sqrt{5}}{4\sqrt{14}}\{v(3,2,0) + iv(2,3,0)\}$$

$$v(5,2) = \sqrt{\frac{5}{8}}\{v(2,0,3) - v(0,2,3)\} + i\sqrt{\frac{5}{6}}v(1,1,3) - \frac{\sqrt{35}}{4\sqrt{6}}\{v(4,0,1) - v(0,4,1)\}$$
$$- i\frac{\sqrt{5}}{2\sqrt{6}}\{v(3,1,1) + v(1,3,1)\}$$

$$v(5,3) = \frac{\sqrt{5}}{2\sqrt{3}}\{v(3,0,2) - iv(0,3,2)\} - \frac{\sqrt{3}}{2}\{v(1,2,2) - iv(2,1,2)\}$$
$$- \frac{\sqrt{35}}{16}\{v(5,0,0) - iv(0,5,0) - v(1,4,0) + iv(4,1,0)\} + \frac{\sqrt{5}}{8\sqrt{3}}\{v(3,2,0) - iv(2,3,0)\}$$

$$v(5,4) = \frac{\sqrt{35}}{8\sqrt{2}}\{v(4,0,1) + v(0,4,1)\} - \frac{3\sqrt{3}}{4\sqrt{2}}v(2,2,1) + i\frac{\sqrt{5}}{2\sqrt{2}}\{v(3,1,1) - v(1,3,1)\}$$

$$v(5,5) = \frac{3\sqrt{7}}{16}\{v(5,0,0) + iv(0,5,0)\} + \frac{5\sqrt{7}}{16}\{v(1,4,0) + iv(4,1,0)\} - \frac{5\sqrt{3}}{8}\{v(3,2,0) + iv(2,3,0)\}$$

[a] The transformations for $m < 0$ are the complex conjugates of the corresponding ones for $m > 0$.

Substitution of $r^{2l} = (x^2 + y^2 + z^2)^l$ and expansion gives

$$c(l,m,n,l_x,l_y,l_z) = \sqrt{\frac{(2l_x)!\,(2l_y)!\,(2l_z)!\,l!\,(l-|m|)!}{(2l)!\,l_x!\,l_y!\,l_z!\,(l+|m|)!}} \times \frac{1}{2^l l!}\frac{1}{l_x!\,l_y!\,l_z!}\frac{d^l}{dx^{l_x}dx^{l_y}dx^{l_z}}\Big|_0 \times (x \pm iy)^{|m|}\sum_{i=0}^{(l-|m|)/2}\binom{l}{i} \times \frac{(-1)^i(2l-2i)!}{(l-|m|-2i)!}z^{l-|m|+2j} \times \sum_{j=0}^{i}\binom{i}{j}(x^2+y^2)^j. \quad (13)$$

Expansion of $(x \pm iy)^{|m|}$ and $(x^2 + y^2)^j$ yields

$$c(l,m,n,l_x,l_y,l_z) = \sqrt{\frac{(2l_x)!\,(2l_y)!\,(2l_z)!\,l!\,(l-|m|)!}{(2l)!\,l_x!\,l_y!\,l_z!\,(l+|m|)!}} \times \frac{1}{2^l l!}\frac{1}{l_x!\,l_y!\,l_z!}\frac{d^l}{dx^{l_x}dx^{l_y}dx^{l_z}}\Big|_0 \times \sum_{p=0}^{|m|}(-1)^{\pm(|m|-p)/2}\binom{|m|}{p}x^p y^{|m|-p} \times \sum_{i=0}^{(l-|m|)/2}\binom{l}{i}\frac{(-1)^i(2l-2i)!}{(l-|m|-2i)!} \times z^{l-|m|+2j} \times \sum_{j=0}^{i}\binom{i}{j}\sum_{k=0}^{j}\binom{j}{k}x^{2k}y^{2j-2k}$$

$$= \sqrt{\frac{(2l_x)!\,(2l_y)!\,(2l_z)!\,l!\,(l-|m|)!}{(2l)!\,l_x!\,l_y!\,l_z!\,(l+|m|)!}} \times \frac{1}{2^l l!}\frac{1}{l_x!\,l_y!\,l_z!}\frac{d^l}{dx^{l_x}dx^{l_y}dx^{l_z}}\Big|_0 \times \sum_{p=0}^{|m|}(-1)^{\pm(|m|-p)/2}\binom{|m|}{p} \times \sum_{i=0}^{(l-|m|/2}\binom{l}{i}\frac{(-1)^i(2l-2i)!}{(l-|m|-2i)!} \times \sum_{j=0}^{i}\binom{i}{j}\sum_{k=0}^{j}\binom{j}{k}x^{p+2k} \times y^{|m|-p+2j-2k}z^{l-|m|+2j}. \quad (14)$$

After differentiating with respect to x, y, and z, and setting $x = y = z = 0$, $c(l, m, n, l_x, l_y, l_z) = 0$ unless $p + 2k = l_x$ and $l - |m| + 2j = l_z$. This reduces the sums over p and j to single terms. With this simplification, the formula for the transformation coefficients becomes

$$c(l,m,l_x,l_y,l_z) = \sqrt{\frac{(2l_x)!\,(2l_y)!\,(2l_z)!\,l!\,(l-|m|)!}{(2l)!\,l_x!\,l_y!\,l_z!\,(l+|m|)!}} \times \frac{1}{2^l l!}\sum_{i=0}^{(l-|m|)/2}\binom{l}{i}\binom{i}{j} \times \frac{(-1)^i(2l-2i)!}{(l-|m|-2i)!} \times \sum_{k=0}^{j}\binom{j}{k}\binom{|m|}{l_x-2k} \times (-1)^{\pm(|m|-l_x+2k)/2} \quad (15)$$

where $j = (l_x + l_y - |m|)/2$ and is an integer; $c(l, m, n, l_x, l_y, l_z) = 0$ if j is a half-integral. Note that the binomial coefficients $\binom{p}{q}$ are zero for $q < 0$ and $q > p$.

For most applications, it is more convenient to use real basis functions rather than complex ones. The $m = 0$ functions are real. For $m \neq 0$ pairs, spherical harmonics can be combined into two real functions, $(Y_m^l + Y_{-m}^l)/\sqrt{2}$ and $(Y_m^l - Y_{-m}^l)/\sqrt{-2}$. Equation (15) has been implemented in the Gaussian series of programs [7]. In connection with the Prism [4] integral package, this allows spherical harmonic Gaussians of arbitrary angular momentum to be used in electronic structure calculations.

Some manipulations, such as symmetry projection, may be easier to carry out with Cartesian functions than with spherical harmonics. The transformation from pure spherical harmonic Gaussians to Cartesians is

$$g(\alpha,l_x,l_y,l_z,\mathbf{r}) = \sum_{l\le l_x+l_y+l_z} c^{-1}(l,m,n,l_x,l_y,l_z)r^{l-n}\tilde{g}(\alpha,l,m,n,\mathbf{r}). \quad (16)$$

The back transformation has the property

$$\sum_{l_x+l_y+l_z=l} c(l_1,m_1,n,l_x,l_y,l_z)c^{-1}(l_2,m_2,n,l_x,l_y,l_z) = \delta_{l_1,l_2}\delta_{m_1,m_2}, \quad (17)$$

where $l_1, l_2 \le l$. If $\mathbf{S}$ is the overlap matrix for Cartesian Gaussians, then $\mathbf{cSc}^{\dagger} = \mathbf{I}$ is the overlap transformed to spherical harmonic Gaussian and $\mathbf{c}^{-1} = \mathbf{Sc}^{\dagger}$. For a given total angular momentum, lower angular momentum spherical harmonic Gaussians are usually not included in the basis set, making the back transformation somewhat simpler:

$$c^{-1}(l, m, n, l_{x1}, l_{y1}, l_{z1}) = \sum_{l_{x2}+l_{y2}+l_{z2}=l} S(l_{x1}, l_{y1}, l_{z1} l_{x2}, l_{y2}, l_{z2}) \times c(l, m, n, l_{x2}, l_{y2}, l_{z2})^{*}, \quad (18)$$

for $n = l = l_{x1} + l_{y1} + l_{z1} = l_{x2} + l_{y2} + l_{z2}$. The overlap between normalized Cartesian Gaussians of the same total angular momentum is

$$S(l_{x1}, l_{y1}, l_{z1}, l_{x2}, l_{y2}, l_{z2}) = \left[\frac{(l_{x1} + l_{x2})!\,(l_{y1} + l_{y2})!\,(l_{z1} + l_{z2})!}{((l_{x1} + l_{x2})/2)!\,((l_{y1} + l_{y2})/2)!\,((l_{z1} + l_{z2})/2)!}\right] \times \left[\frac{(2l_{x1})!\,(2l_{y1})!\,(2l_{z1})!\,(2l_{x2})!\,(2l_{y2})!\,(2l_{z2})!}{l_{x1}!\,l_{y1}!\,l_{z1}!\,l_{x2}!\,l_{y2}!\,l_{z2}!}\right]^{-1/2} \quad (19)$$

and $(l_{x1} + l_{x2})/2$, $(l_{y1} + l_{y2})/2$, $(l_{z1} + l_{z2})/2$ are integers; $S = 0$ otherwise.

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