Problem Statement and formula constructor

The problem we want to solve is the spherically averaged exact exchange hole function. It comes down to the integration of an arbitrarily placed generalized Gaussian function over the two angles in a spherical coordinate:

$$\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\left(\vec{r}-\vec{P}\right)_x^i\left(\vec{r}-\vec{P}\right)_y^j\left(\vec{r}-\vec{P}\right)_z^k e^{-(\alpha+\beta)\left(\vec{s}+\vec{r}-\vec{P}\right)^2}\sin\theta d\theta d\varphi \qquad (1.1)$$

Where $\vec{r}$ is the position of an electron in space, $\vec{P}$ is the center of the generalized Gaussian function that describes the density of the electron and the indexes *i*, *j*, *k* are the Cartesian angular momenta of the generalized Gaussian. Vector $\vec{s}$ is the position of the second electron relative to the first electron, and θ and φ are the spherical coordinate based on $\vec{s}$.

First, we assume

$$\vec{Q}=\vec{r}-\vec{P}$$

And

$$r_Q=\vec{s}-\left(\vec{P}-\vec{r}\right)$$

So we have

$$x_Q=\left(\vec{s}+\vec{Q}\right)_x$$

$$y_Q=\left(\vec{s}+\vec{Q}\right)_y$$

$$z_Q=\left(\vec{s}+\vec{Q}\right)_z$$

$$r_Q=\vec{s}+\vec{Q}$$

So the formula (1.1) can be rewritten as

$$\int_0^{2\pi}\int_0^{\pi}x_Q^i y_Q^j z_Q^k e^{-(\alpha+\beta)r_Q^2}\sin\theta d\theta d\varphi \qquad (1.2)$$

Let’s consider the formula inside the integrate

$$x_Q^i y_Q^j z_Q^k e^{-(\alpha+\beta)r_Q^2} \qquad (1.3)$$

We suppose

$$\vec{Q}=\left(Q\sin\theta_0\cos\varphi_0 \quad Q\sin\theta_0\sin\varphi_0 \quad Q\cos\theta_0\right)^T$$

In polar coordinates.

Secondly, we fix *z* axis and rotate *XOY* plane. So we have the coordinate convert:

$$\begin{pmatrix} x_Q^{'} \\ y_Q^{'} \\ z_Q^{'} \end{pmatrix}=\begin{pmatrix} \cos\varphi_0 & \sin\varphi_0 & 0 \\ -\sin\varphi_0 & \cos\varphi_0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x_Q \\ y_Q \\ z_Q \end{pmatrix} \qquad (1.4)$$

Let

$$A_1 = \begin{pmatrix} \cos\varphi_0 & \sin\varphi_0 & 0 \\ -\sin\varphi_0 & \cos\varphi_0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Then we fix y axis and rotate the XOZ plane.

So we have the coordinate convert:

$$\begin{pmatrix} x_Q'' \\ y_Q'' \\ z_Q'' \end{pmatrix} = \begin{pmatrix} \cos\theta_0 & 0 & -\sin\theta_0 \\ 0 & 1 & 0 \\ \sin\theta_0 & 0 & \cos\theta_0 \end{pmatrix} \begin{pmatrix} x_Q' \\ y_Q' \\ z_Q' \end{pmatrix} \tag{1.5}$$

Let

$$A_2 = \begin{pmatrix} \cos\theta_0 & 0 & -\sin\theta_0 \\ 0 & 1 & 0 \\ \sin\theta_0 & 0 & \cos\theta_0 \end{pmatrix}$$

Combine (1.4) and (1.5), we have

$$\begin{pmatrix} x_Q'' \\ y_Q'' \\ z_Q'' \end{pmatrix} = A \begin{pmatrix} x_Q \\ y_Q \\ z_Q \end{pmatrix} = \begin{pmatrix} \cos\theta_0 \cos\varphi_0 & \cos\theta_0 \sin\varphi_0 & -\sin\theta_0 \\ -\sin\varphi_0 & \cos\varphi_0 & 0 \\ \sin\theta_0 \cos\varphi_0 & \sin\theta_0 \sin\varphi_0 & \cos\theta_0 \end{pmatrix} \begin{pmatrix} x_Q \\ y_Q \\ z_Q \end{pmatrix} \tag{1.6}$$

Where

$$A = A_2 A_1$$

We also get the inverse of formula (1.4)

$$\begin{pmatrix} x_Q \\ y_Q \\ z_Q \end{pmatrix} = A^{-1} \begin{pmatrix} x_Q'' \\ y_Q'' \\ z_Q'' \end{pmatrix} \tag{1.7}$$

Now go back to formula (1.3) we have

$$\begin{aligned} x_Q^i y_Q^j z_Q^k e^{-(\alpha+\beta) r_Q^2} &= x_Q^i y_Q^j z_Q^k e^{-(\alpha+\beta)\left(\vec{s}+\vec{Q}\right)^2} \\ &= x_Q^i y_Q^j z_Q^k e^{-(\alpha+\beta)\left(\vec{s}^2+\vec{Q}^2+2\vec{s}\cdot\vec{Q}\right)} \end{aligned} \tag{1.8}$$

Let

$$\begin{aligned} &\gamma = \alpha + \beta \\ &s = \left|\vec{s}\right| \\ &Q = \left|\vec{Q}\right| \\ &g = e^{-(\alpha+\beta)\left(\vec{s}^2+\vec{Q}^2\right)+2(\alpha+\beta)\cdot s\cdot Q} \end{aligned}$$

And plug formula (1.7) into the formula (1.8)

$$x_Q^i y_Q^j z_Q^k e^{-(\alpha+\beta)\left(\vec{s}^2+\vec{Q}^2+2\vec{s}\cdot\vec{Q}\right)} = g\times x_Q^i y_Q^j z_Q^k e^{-2\gamma\vec{s}\cdot\vec{Q}}$$

$$= g\times\left(A_{11}^{-1}x_Q^{"} + A_{12}^{-1}y_Q^{"} + A_{13}^{-1}z_Q^{"}\right)^i \left(A_{21}^{-1}x_Q^{"} + A_{22}^{-1}y_Q^{"} + A_{23}^{-1}z_Q^{"}\right)^j$$

$$\left(A_{31}^{-1}x_Q^{"} + A_{32}^{-1}y_Q^{"} + A_{33}^{-1}z_Q^{"}\right)^k e^{-2\gamma\vec{s}\cdot\vec{Q}-2\gamma sQ}$$

Let’s we consider a simple form:

$$\left(a_1x+B_1\right)^i\left(a_2x+B_2\right)^j\left(a_3x+B_3\right)^k = \sum_{t=0}^{i+j+k} f'\left(t,i,j,k\right)x^t \tag{1.9}$$

Where

$$f'\left(t,i,j,k\right)=\sum_{l=\max\{0,t-(j+k)\}}^{\min\{i,t\}}\ \sum_{m=\max\{0,t-l-k\}}^{\min\{t-l,j\}} a_1^l a_2^m a_3^{t-l-m}\binom{i}{l}\binom{j}{m}\binom{k}{t-l-m}B_1^{i-l}B_2^{j-m}B_3^{k+l+m-t}$$

Then we can use this regression formula to construct the whole syntax since $B_s = b_s y + C_s$

So finally, the formula (1.2) can be transformed to

$$\sum_x\sum_y\sum_z f\left(l,m,n\right)\int_0^{2\pi}\int_0^{\pi} x^l y^m z^n e^{-2\gamma\vec{s}\cdot\vec{Q}-2\gamma sQ}\sin\theta d\theta d\varphi \tag{1.10}$$

Where

$$f\left(l,m,n\right)=f'\left(l,i_x,j_x,k_x\right)f'\left(m,i_y,j_y,k_y\right)f'\left(n,i_z,j_z,k_z\right)$$

And in polar coordinate, we set

$$x = s\sin\theta\cos\varphi$$
$$y = s\sin\theta\sin\varphi$$
$$z = s\cos\theta$$

Then the formula (1.10) become

$$\sum_x\sum_y\sum_z f\left(l,m,n\right)s^{l+m+n}\int_0^{2\pi}\int_0^{\pi}\sin^{l+m+1}\theta\cos^n\theta\sin^m\varphi\cos^l\varphi e^{-2\gamma sQ(\cos\theta+1)}d\theta d\varphi \tag{1.11}$$

Part 2: Now we solve the spherical integral in formula (1.11)

For any given number *i*, *j*, *k*, *l*, *α*, compute the Integral of the following function:

$$F=\int_0^{2\pi}\int_0^{\pi}\sin^i\theta\cos^j\theta\sin^k\varphi\cos^l\varphi\cdot e^{-\mu(\cos\theta+1)}d\theta d\varphi \tag{1.12}$$

First, the integral for angel θ and ϕ can be totally separated as

$$F=\int_0^{\pi}\sin^i\theta\cos^j\theta\cdot e^{-\mu(\cos\theta+1)}d\theta\cdot\int_0^{2\pi}\sin^k\varphi\cos^l\varphi d\varphi \tag{1.13}$$

Let

$$\operatorname{int}\theta = \int_0^{\pi} \sin^i \theta \cos^j \theta \cdot e^{-\mu(\cos\theta+1)} d\theta$$

$$\operatorname{int}\varphi = \int_0^{2\pi} \sin^k \varphi \cos^l \varphi d\varphi$$

So

$$F = \operatorname{int}\theta \cdot \operatorname{int}\varphi$$

i. For the intθ

$$\operatorname{int}\theta = \int_0^{\pi} \sin^i \theta \cos^j \theta \cdot e^{-\mu(\cos\theta+1)} d\theta \tag{1.14}$$

There are two cases:

Case 1: If i is an even number. Hence $i = 2i'$

$$\begin{aligned} \operatorname{int}\theta &= \int_0^{\pi} \sin^{2i'} \theta \cos^j \theta \cdot e^{-\mu(\cos\theta+1)} d\theta \\ &= \int_0^{\pi} \left(1-\cos^2\theta\right)^{i'} \cos^j \theta \cdot e^{-\mu(\cos\theta+1)} d\theta \\ &= \sum_{s=0}^{i'} (-1)^s \binom{i'}{s} \int_0^{\pi} \cos^{j+2s} \theta \cdot e^{-\mu(\cos\theta+1)} d\theta \end{aligned} \tag{1.15}$$

It can be simplified as when $t = j + 2s$

$$\int_0^{\pi} \cos^t \theta \cdot e^{-\mu(\cos\theta+1)} d\theta \tag{1.16}$$

Suppose

$$I(n,u) = \int_0^{\pi} \cos^n \theta \cdot e^{-\mu(\cos\theta+1)} d\theta$$

This one has a regression function

$$e^{-\mu}\int_0^{\pi}\cos^t\theta\cdot e^{-\mu\cos\theta}d\theta = e^{-\mu}\int_0^{\pi}\cos^{t-1}\theta\cdot e^{-\mu\cos\theta}d\sin\theta$$

$$= e^{-\mu}\cdot\left(\sin\theta\cos^{t-1}\theta\cdot e^{-\mu\cos\theta}\Big|_0^{\pi} - \int_0^{\pi}\sin\theta d\cos^{t-1}\theta\cdot e^{-\mu\cos\theta}\right)$$

$$= e^{-\mu}\left(0-\int_0^{\pi}\sin\theta\cdot\left((t-1)\cos^{t-2}\theta(-\sin\theta)e^{-\mu\cos\theta}+\cos^{t-1}\theta e^{-\mu\cos\theta}\cdot\mu\sin\theta\right)d\theta\right)$$

$$= e^{-\mu}\left(-\int_0^{\pi}(t-1)\left(-\sin^2\theta\right)\cdot\cos^{t-2}\theta e^{-\mu\cos\theta}+\mu\sin^2\theta\cos^{t-1}\theta e^{-\mu\cos\theta}d\theta\right)$$

$$= e^{-\mu}\left(\int_0^{\pi}(t-1)\left(1-\cos^2\theta\right)\cos^{t-2}\theta e^{-\mu\cos\theta}-u\left(1-\cos^2\theta\right)\cos^{t-1}\theta e^{-\mu\cos\theta}d\theta\right)$$

$$= e^{-\mu}(t-1)\int_0^{\pi}\cos^{t-2}\theta\cdot e^{-\mu\cos\theta}d\theta - e^{-\mu}(t-1)\int_0^{\pi}\cos^t\theta\cdot e^{-\mu\cos\theta}d\theta$$

$$-e^{-\mu}\mu\int_0^{\pi}\cos^{t-1}\theta\cdot e^{-\mu\cos\theta}d\theta + e^{-\mu}\mu\int_0^{\pi}\cos^{t+1}\theta\cdot e^{-\mu\cos\theta}d\theta$$

That is

$$I(t,\mu)=(t-1)I(t-2,\mu)-(t-1)I(t,\mu)-\mu I(t-1,\mu)+\mu I(t+1,\mu)$$

So the regression function is

$$I(n,\mu)=\frac{1}{\mu}\left((n-1)I(n-1,\mu)+\mu I(n-2,\mu)-(n-2)I(n-3,\mu)\right) \qquad (1.17)$$

So this regression function will help us to generate the value of the function. However, we still need to know the first three items of $I(n,\mu)$

When $n=0$

$$I(0,\mu)=\int_0^{\pi}e^{-\mu(\cos\theta+1)}d\theta \qquad (1.18)$$

We do some transform here and use the expansions.

$$I(0,\mu)=\int_0^{\pi}e^{-\mu(\cos\theta+1)}d\theta$$

$$=\int_0^{\pi}e^{-2\mu\cos^2\frac{\theta}{2}}d\theta$$

Assume $\theta'=\theta/2$

$$I(0,\mu)=2\int_0^{\pi/2}e^{-2\mu\cos^2\theta'}d\theta' \qquad (1.19)$$

Let $T=\cos\theta'$ that is $\theta'=\arccos T$

$$I\left(0,\mu\right)=2\int_0^1 e^{-2\mu T^2}\frac{1}{\sqrt{1-T^2}}dT \tag{1.20}$$

Now we use binomial series to expand $1/\sqrt{1-T^2}$

$$\frac{1}{\sqrt{1-T^2}}=\sum_{n=0}^{\infty}\frac{1\cdot 3\cdot\cdots\cdot\left(2n-1\right)}{2^n n!}T^{2n}$$

So

$$I\left(0,\mu\right)=2\sum_{n=0}^{\infty}\frac{1\cdot 3\cdot\cdots\cdot\left(2n-1\right)}{2^n n!}\int_0^1 e^{-2\mu T^2}T^{2n}dT \tag{1.21}$$

Let

When $n=1$

$$I\left(1,\mu\right)=\int_0^{\pi}\cos\theta\cdot e^{-\mu\left(\cos\theta+1\right)}d\theta \tag{1.22}$$

When $n=2$

$$I\left(2,\mu\right)=\int_0^{\pi}\cos^2\theta\cdot e^{-\mu\left(\cos\theta+1\right)}d\theta \tag{1.23}$$

Case 2: *i* is an odd number. Hence $i=2i''+1$

$$\begin{aligned}\operatorname{int}\theta\left(\theta\right)&=\int_0^{\pi}\sin^{2i''+1}\theta\cos^j\theta\cdot e^{-\mu\left(\cos\theta+1\right)}d\theta\\&=e^{-\mu}\int_0^{\pi}\left(1-\cos^2\theta\right)^{i''}\cos^j\theta\cdot e^{-\mu\cos\theta}d\left(-\cos\theta\right)\\&=\sum_{s=0}^{i''}\left(-1\right)^{s+1}\cdot\binom{i''}{s}\cdot e^{-\mu}\int_0^{\pi}\cos^{j+2s}\theta\cdot e^{-\mu\cos\theta}d\cos\theta\end{aligned} \tag{1.24}$$

What we concern is

$$e^{-\mu}\int_0^{\pi}\cos^{j+2s}\theta\cdot e^{-\mu\cos\theta}d\cos\theta \tag{1.25}$$

Let $j'=j+2s$

We have

$$e^{-\mu}\int_0^{\pi}\cos^{j'}\theta\cdot e^{-\mu\cos\theta}d\cos\theta \tag{1.26}$$

Let $x'=\cos\theta$, we can convert (1.26) to

$$e^{-\mu}\int_{1}^{-1} x'^{j'}\cdot e^{-\mu x'}dx' = e^{-\mu x'-\mu}\cdot\sum_{s=0}^{j'}(-1)^{j'-s}\frac{j'!}{s!(-\mu)^{j'-s+1}}x'^{s}\Bigg|_{1}^{-1}$$
$$= e^{-\mu x'-\mu}\cdot\sum_{s=0}^{j'}\frac{j'!}{s!\mu^{j'-s+1}}x'^{s}\Bigg|_{-1}^{1} \tag{1.27}$$

https://en.wikipedia.org/wiki/List_of_integrals_of_exponential_functions
(From https://en.wikipedia.org/wiki/List_of_integrals_of_trigonometric_functions)

ii. For the intϕ

$$\operatorname{int}\varphi = \int_0^{2\pi}\sin^k\varphi\cos^l\varphi d\varphi \tag{1.28}$$

There are two cases:
Case 1: at least one of k and l is odd.
Suppose k is odd. Hence $k = 2k'+1$
So we have

$$\sin^k\varphi = \sin^{2k'+1}\varphi = \left(\sin^2\varphi\right)^{k'}\cdot\sin\varphi$$
$$= \left(1-\cos^2\varphi\right)^{k'}\sin\varphi \tag{1.29}$$

Plug formula (1.29) to (1.28), we have

$$\operatorname{int}\varphi = \int_0^{2\pi}\left(1-\cos^2\varphi\right)^{k'}\sin\varphi\cos^l\varphi d\varphi$$
$$= \int_0^{2\pi}\left(1-\cos^2\varphi\right)^{k'}\cos^l\varphi d\left(-\cos\varphi\right) \tag{1.30}$$

Let $\nu = \cos\varphi$
So we have

$$\operatorname{int}\varphi = -\int_0^{2\pi}\left(1-\nu^2\right)^{k'}\nu^l d\nu \tag{1.31}$$

Case 2: both of k and l are even. Hence $k = 2k'', l = 2l''$

We use the relationship in double angle translate:

$$\sin^2\varphi = \frac{1-\cos(2\varphi)}{2}$$
$$\cos^2\varphi = \frac{1+\cos(2\varphi)}{2}$$

So

$$
\begin{aligned}
\operatorname{int}\varphi &= \int_0^{2\pi} \sin^k \varphi \cos^l \varphi d\varphi \\
&= \int_0^{2\pi} \sin^{2k''} \varphi \cos^{2l''} \varphi d\varphi \\
&= \int_0^{2\pi} \left(\frac{1-\cos 2\varphi}{2}\right)^{k''} \left(\frac{1+\cos 2\varphi}{2}\right)^{l''} d\varphi \\
&= 2^{-(k''+l''+1)} \int_0^{2\pi} (1-\cos 2\varphi)^{k''} (1+\cos 2\varphi)^{l''} d2\varphi \\
&= 2^{-(k''+l''+1)} \int_0^{2\pi} \sum_{i=0}^{k''} \binom{k''}{i} \cos^i 2\varphi (-1)^i \cdot \sum_{j=0}^{l''} \binom{l''}{j} \cos^j 2\varphi d2\varphi \\
&= 2^{-(k''+l''+1)} \sum_{t=0}^{k''+l''} f(t,k'',l'') \cdot \int_0^{2\pi} \cos^t 2\varphi d2\varphi
\end{aligned}
\tag{1.32}
$$

Where

$$
g(t,k'',l'') = \sum_{s=\max\{0,t-l''\}}^{\min\{k'',t\}} \binom{k''}{s} \binom{l''}{t-s} (-1)^s \tag{1.33}
$$

Let $\varphi' = 2\varphi$, then

$$
\int_0^{2\pi} \cos^t 2\varphi d2\varphi = \int_0^{\pi} \cos^t \varphi' d\varphi' \tag{1.34}
$$

For formula (1.34), there is a regression function:

$$
\int \cos^n x dx = \frac{\cos^{n-1} x \sin x}{n} + \frac{n-1}{n} \int \cos^{n-2} x dx
$$

(From https://en.wikipedia.org/wiki/List_of_integrals_of_trigonometric_functions)
(Also see http://mathworld.wolfram.com/CosineIntegral.html)