Contents

1 Gaussian Primitive

A Cartesian Gaussian primitive is

$$g_i(\mathbf{r}|\mathbf{R}_A, \mathbf{a}) = N(\alpha_i, \mathbf{a})(x - X_A)^{a_x}(y - Y_A)^{a_y}(z - Z_A)^{a_z} \exp\left(-\alpha_i|\mathbf{r} - \mathbf{R}_A|^2\right) \tag{1}$$

where $\mathbf{r} = (x, y, z)$, $\mathbf{R}_A$ is the center of the primitive, $\mathbf{a} = (a_x, a_y, a_z)$ is the Cartesian components of the angular momentum, $\ell = a_x + a_y + a_z$, and

$$\begin{aligned} N(\alpha_i, \mathbf{a}) &= \sqrt{\left(\frac{2\alpha_i}{\pi}\right)^{\frac{3}{2}} \frac{(4\alpha_i)^{a_x+a_y+a_z}}{(2a_x - 1)!!(2a_y - 1)!!(2a_z - 1)!!}} \\ &= \sqrt{\left(\frac{2\alpha_i}{\pi}\right)^{\frac{3}{2}} (4\alpha_i)^{\ell}} \sqrt{\frac{1}{(2a_x - 1)!!(2a_y - 1)!!(2a_z - 1)!!}} \\ &= N_1(\alpha_i, \ell)N_2(\mathbf{a}) \end{aligned} \tag{2}$$

is the normalization constant of the primitive. In this module, the primitives are normalized.

A spherical Gaussian primitive is

$$g_i^s(r|\mathbf{R}_A, m, \ell) = N_s(\alpha_i, \ell)Y_{\ell m}(\phi, \theta)r^{\ell} \exp\left(-\alpha_i r^2\right) \tag{3}$$

where ℓ is the angular momentum, m is the z component of the angular momentum, $r = |\mathbf{r} - \mathbf{R}_A|$ is the distance from the center $\mathbf{R}_A$, $Y_{\ell m}$ is a spherical harmonic, and

$$N_s(\alpha_i, \ell) = \sqrt{\left(\frac{2\alpha_i}{\pi}\right)^{\frac{3}{2}} \frac{(4\alpha_i)^{\ell}}{(2\ell - 1)!!}} \tag{4}$$

In this module, we treat all spherical harmonics to be real.

The "solid harmonic" (Helgaker 6.4.2), $Y_{\ell m}(\phi, \theta)r^{\ell}$, can be transformed into the corresponding Cartesian expression, $(x - X_A)^{a_x}(y - Y_A)^{a_y}(z - Z_A)^{a_z}$. Real-valued solid harmonics are denoted with $S_{\ell m}$.

$$g_i^s(r|\mathbf{R}_A, m, \ell) = N_s(\alpha_i, \ell)S_{\ell m}(r, \phi, \theta) \exp\left(-\alpha_i r^2\right) \tag{5}$$

In this module, we strictly utilize Cartesian Gaussian primitives at the lower level and transform to the spherical form whenever needed. Therefore, primitives will refer to Cartesian primitives unless otherwise stated.

1.1 Transformation of Spherical Primitives to Cartesian Primitives

To transform the spherical primitives to Cartesian primitives, the (real) solid harmonics are first transformed into the Cartesian expressions. Using the equations from Helgaker 6.4.4,

$$S_{\ell m} = N_{\ell m}^S \sum_{t=0}^{\lfloor\frac{\ell-|m|}{2}\rfloor} \sum_{u=0}^{t} \sum_{v=0}^{\lfloor\frac{|m|}{2}\rfloor} C_{tuv}^{lm} x^{2t+|m|-2(u+v_m)} y^{2(u+v_m)} z^{\ell-2t-|m|} \tag{6}$$

where

$$v_m = \begin{cases} v & \text{if } m \geq 0 \\ v + \frac{1}{2} & \text{if } m < 0 \end{cases} \tag{7}$$

$$C^{lm}_{tuv} = (-1)^{t+v}\left(\frac{1}{4}\right)^t \binom{\ell}{t}\binom{\ell-t}{|m|+t}\binom{t}{u}\binom{|m|}{2v_m} \tag{8}$$

$$N^S_{\ell m} = \frac{1}{2^{|m|}\ell!}\sqrt{\frac{2(\ell+|m|)!(\ell-|m|)!}{2^{\delta_{0m}}}} \tag{9}$$

Then, the normalization constant of the Cartesian primitive must be replaced with the spherical primitive.

$$\begin{aligned}\frac{N(\alpha_i,\mathbf{a})}{N_s(\alpha_i,\ell)} &= \frac{\sqrt{\left(\frac{2\alpha_i}{\pi}\right)^{\frac{3}{2}}\frac{(4\alpha_i)^\ell}{(2\ell-1)!!}}}{\sqrt{\left(\frac{2\alpha_i}{\pi}\right)^{\frac{3}{2}}(4\alpha_i)^\ell}\sqrt{\frac{1}{(2a_x-1)!!(2a_y-1)!!(2a_z-1)!!}}}\\ &= \sqrt{\frac{(2a_x-1)!!(2a_y-1)!!(2a_z-1)!!}{(2\ell-1)!!}}\end{aligned} \tag{10}$$

2 Contractions

Cartesian contractions are linear combinations of Cartesian primitives.

$$\begin{aligned}\phi(\mathbf{r}|\mathbf{R}_A,\mathbf{a},\mathbf{d},\boldsymbol{\alpha}) &= N_c(\mathbf{R}_A,\mathbf{a},\mathbf{d},\boldsymbol{\alpha})\sum_i d_i g_i(\mathbf{r}|\mathbf{R}_A,\mathbf{a})\\ &= N_c(\mathbf{R}_A,\mathbf{a},\mathbf{d},\boldsymbol{\alpha})N_2(\mathbf{a})(x-X_A)^{a_x}(y-Y_A)^{a_y}(z-Z_A)^{a_z}\sum_i N_1(\alpha_i,\ell)\exp\left(-\alpha_i|\mathbf{r}-\mathbf{R}_A|^2\right)\end{aligned} \tag{11}$$

where $\mathbf{d}$ is the contraction coefficient, $\mathbf{a}$ are the exponents of the primitive, and

$$\begin{aligned}N_c(\mathbf{R}_A,\mathbf{a},\mathbf{d},\boldsymbol{\alpha}) &= \left(\int\left(\sum_i d_i g_i(\mathbf{r}|\mathbf{R}_A,\mathbf{a})\right)\left(\sum_j d_j g_j(\mathbf{r}|\mathbf{R}_A,\mathbf{a})\right)d\mathbf{r}\right)^{-\frac{1}{2}}\\ &= \left(\sum_i\sum_j d_i d_j\int g_i(\mathbf{r}|\mathbf{R}_A,\mathbf{a})g_j(\mathbf{r}|\mathbf{R}_A,\mathbf{a})d\mathbf{r}\right)^{-\frac{1}{2}}\end{aligned} \tag{12}$$

is the normalization constant of the contraction. In this module, the contractions are normalized.

Since the Cartesian expression, $(x-X_A)^{a_x}(y-Y_A)^{a_y}(z-Z_A)^{a_z}$, separates out from the rest of the primitives, the spherical contractions can be created from Cartesian contractions in the same way that the spherical primitives are constructed. In fact, we can group together many contractions of the same angular momentum and transform the contractions at the same time. In many cases, it is economical to group together contractions that share the same properties. We will denote these groups as shells.

2.1 Segmented Contractions

In order to group transform the Cartesian contractions into spherical contractions, all of the Cartesian components are needed, i.e. all combinations of nonnegative integers a_x, a_y, and a_z that adds up to ℓ. Segmented contractions is a group of contractions with the same angular momentum (ℓ), center ($\mathbf{R}_A$), contraction coefficients ($\mathbf{b}$) and exponents ($\boldsymbol{\alpha}$):

$$\{\phi(\mathbf{r}|\mathbf{R}_A, \mathbf{a}_j, \mathbf{d}, \boldsymbol{\alpha})|(a_j)_x + (a_j)_y + (a_j)_z = \ell\} \tag{13}$$

To avoid confusion with the term contraction, we use the term "shell of segmented contractions".

2.2 Generalized Contractions

Generalized contractions are a set of contractions that have the same center ($\mathbf{R}_A$) and exponents ($\boldsymbol{\alpha}$).

$$\{\phi(\mathbf{r}|\mathbf{R}_A, \mathbf{a}_{j\ell}, \mathbf{d}_k, \boldsymbol{\alpha}_k)|(a_{j\ell})_x + (a_{j\ell})_y + (a_{j\ell})_z = \ell\} \tag{14}$$

In this module, we do not group together contractions that differ in angular momentum. We use the term "shell of generalized contractions" to refer to the set of contractions with the same center ($\mathbf{R}_A$), same angular momentum (ℓ) and exponents ($\boldsymbol{\alpha}$):

$$\{\phi(\mathbf{r}|\mathbf{R}_A, \mathbf{a}_j, \mathbf{d}_k, \boldsymbol{\alpha}_k)|(a_j)_x + (a_j)_y + (a_j)_z = \ell\} \tag{15}$$

We can think of shell of generalized contractions as a union of shells of segmented contractions that differ only by the contraction coefficients, i.e. they use the same set of primitives.

3 Basis Set

In this module, basis set is defined to be a list of shells of generalized contractions.

3.1 Ordering of basis functions

Since a shell of generalized contractions is a set of contractions, they must be unpacked. When unpacked, the basis functions are first ordered by the shells, then by the segmented contraction, and then by the angular momentum component. For example, suppose the basis set consists of three shells of generalized contractions, G_1, G_2, and G_3:

$$\begin{aligned} G_1 &= \{\phi(\mathbf{r}|\mathbf{R}_A, \mathbf{a}_{1j}, \mathbf{d}_{1k}, \boldsymbol{\alpha}_1)|(a_{1j})_x + (a_{1j})_y + (a_{1j})_z = 1\} \\ G_2 &= \{\phi(\mathbf{r}|\mathbf{R}_B, \mathbf{a}_{2j}, \mathbf{d}_{2k}, \boldsymbol{\alpha}_2)|(a_{2j})_x + (a_{2j})_y + (a_{2j})_z = 2\} \\ G_3 &= \{\phi(\mathbf{r}|\mathbf{R}_A, \mathbf{a}_{3j}, \mathbf{d}_{3k}, \boldsymbol{\alpha}_3)|(a_{3j})_x + (a_{3j})_y + (a_{3j})_z = 2\} \end{aligned} \tag{16}$$

where $\mathbf{d}_1$ corresponds to two sets of contraction coefficients, $\mathbf{d}_2$ corresponds to three sets of contraction coefficients, and $\mathbf{d}_3$ corresponds to one set of contraction coefficients. Then, the basis functions in the Cartesian form will be ordered as follows:

$$\begin{aligned}
&\phi(\mathbf{r}|\mathbf{R}_A,(1,0,0),\mathbf{d}_{11},\boldsymbol{\alpha}_1),\phi(\mathbf{r}|\mathbf{R}_A,(0,1,0),\mathbf{d}_{11},\boldsymbol{\alpha}_1),\phi(\mathbf{r}|\mathbf{R}_A,(0,0,1),\mathbf{d}_{11},\boldsymbol{\alpha}_1),\\
&-----------------------------------\\
&\phi(\mathbf{r}|\mathbf{R}_A,(1,0,0),\mathbf{d}_{12},\boldsymbol{\alpha}_1),\phi(\mathbf{r}|\mathbf{R}_A,(0,1,0),\mathbf{d}_{12},\boldsymbol{\alpha}_1),\phi(\mathbf{r}|\mathbf{R}_A,(0,0,1),\mathbf{d}_{12},\boldsymbol{\alpha}_1),\\
&===================================\\
&\phi(\mathbf{r}|\mathbf{R}_B,(2,0,0),\mathbf{d}_{21},\boldsymbol{\alpha}_2),\phi(\mathbf{r}|\mathbf{R}_B,(1,1,0),\mathbf{d}_{21},\boldsymbol{\alpha}_2),\phi(\mathbf{r}|\mathbf{R}_B,(1,0,1),\mathbf{d}_{21},\boldsymbol{\alpha}_2),\\
&\phi(\mathbf{r}|\mathbf{R}_B,(0,2,0),\mathbf{d}_{21},\boldsymbol{\alpha}_2),\phi(\mathbf{r}|\mathbf{R}_B,(0,1,1),\mathbf{d}_{21},\boldsymbol{\alpha}_2),\phi(\mathbf{r}|\mathbf{R}_B,(0,0,2),\mathbf{d}_{21},\boldsymbol{\alpha}_2),\\
&-----------------------------------\\
&\phi(\mathbf{r}|\mathbf{R}_B,(2,0,0),\mathbf{d}_{22},\boldsymbol{\alpha}_2),\phi(\mathbf{r}|\mathbf{R}_B,(1,1,0),\mathbf{d}_{22},\boldsymbol{\alpha}_2),\phi(\mathbf{r}|\mathbf{R}_B,(1,0,1),\mathbf{d}_{22},\boldsymbol{\alpha}_2),\\
&\phi(\mathbf{r}|\mathbf{R}_B,(0,2,0),\mathbf{d}_{22},\boldsymbol{\alpha}_2),\phi(\mathbf{r}|\mathbf{R}_B,(0,1,1),\mathbf{d}_{22},\boldsymbol{\alpha}_2),\phi(\mathbf{r}|\mathbf{R}_B,(0,0,2),\mathbf{d}_{22},\boldsymbol{\alpha}_2),\\
&-----------------------------------\\
&\phi(\mathbf{r}|\mathbf{R}_B,(2,0,0),\mathbf{d}_{23},\boldsymbol{\alpha}_2),\phi(\mathbf{r}|\mathbf{R}_B,(1,1,0),\mathbf{d}_{23},\boldsymbol{\alpha}_2),\phi(\mathbf{r}|\mathbf{R}_B,(1,0,1),\mathbf{d}_{23},\boldsymbol{\alpha}_2),\\
&\phi(\mathbf{r}|\mathbf{R}_B,(0,2,0),\mathbf{d}_{23},\boldsymbol{\alpha}_2),\phi(\mathbf{r}|\mathbf{R}_B,(0,1,1),\mathbf{d}_{23},\boldsymbol{\alpha}_2),\phi(\mathbf{r}|\mathbf{R}_B,(0,0,2),\mathbf{d}_{23},\boldsymbol{\alpha}_2),\\
&===================================\\
&\phi(\mathbf{r}|\mathbf{R}_A,(2,0,0),\mathbf{d}_{31},\boldsymbol{\alpha}_3),\phi(\mathbf{r}|\mathbf{R}_A,(1,1,0),\mathbf{d}_{31},\boldsymbol{\alpha}_3),\phi(\mathbf{r}|\mathbf{R}_A,(1,0,1),\mathbf{d}_{31},\boldsymbol{\alpha}_3),\\
&\phi(\mathbf{r}|\mathbf{R}_A,(0,2,0),\mathbf{d}_{31},\boldsymbol{\alpha}_3),\phi(\mathbf{r}|\mathbf{R}_A,(0,1,1),\mathbf{d}_{31},\boldsymbol{\alpha}_3),\phi(\mathbf{r}|\mathbf{R}_A,(0,0,2),\mathbf{d}_{31},\boldsymbol{\alpha}_3)
\end{aligned}\tag{17}$$

where , delimits the contractions within a shell of segmented contractions, $-$ delimits the shells of segmented contractions within a shell of generalized contractions, and $=$ delimits the shells of generalized contractions.

The basis functions in the spherical form will be ordered as follows:

$$\begin{aligned}
&\phi^s(\mathbf{r}|\mathbf{R}_A,-1,1,\mathbf{d}_{11},\boldsymbol{\alpha}_1),\phi^s(\mathbf{r}|\mathbf{R}_A,0,1,\mathbf{d}_{11},\boldsymbol{\alpha}_1),\phi^s(\mathbf{r}|\mathbf{R}_A,1,1,\mathbf{d}_{11},\boldsymbol{\alpha}_1),\\
&--------------------------------\\
&\phi^s(\mathbf{r}|\mathbf{R}_A,-1,1,\mathbf{d}_{12},\boldsymbol{\alpha}_1),\phi^s(\mathbf{r}|\mathbf{R}_A,0,1,\mathbf{d}_{12},\boldsymbol{\alpha}_1),\phi^s(\mathbf{r}|\mathbf{R}_A,1,1,\mathbf{d}_{12},\boldsymbol{\alpha}_1),\\
&================================\\
&\phi^s(\mathbf{r}|\mathbf{R}_B,-2,2,\mathbf{d}_{21},\boldsymbol{\alpha}_2),\phi^s(\mathbf{r}|\mathbf{R}_B,-1,2,\mathbf{d}_{21},\boldsymbol{\alpha}_2),\phi^s(\mathbf{r}|\mathbf{R}_B,0,2,\mathbf{d}_{21},\boldsymbol{\alpha}_2),\\
&\phi^s(\mathbf{r}|\mathbf{R}_B,1,2,\mathbf{d}_{21},\boldsymbol{\alpha}_2),\phi^s(\mathbf{r}|\mathbf{R}_B,2,2,\mathbf{d}_{21},\boldsymbol{\alpha}_2),\\
&--------------------------------\\
&\phi^s(\mathbf{r}|\mathbf{R}_B,-2,2,\mathbf{d}_{22},\boldsymbol{\alpha}_2),\phi^s(\mathbf{r}|\mathbf{R}_B,-1,2,\mathbf{d}_{22},\boldsymbol{\alpha}_2),\phi^s(\mathbf{r}|\mathbf{R}_B,0,2,\mathbf{d}_{22},\boldsymbol{\alpha}_2),\\
&\phi^s(\mathbf{r}|\mathbf{R}_B,1,2,\mathbf{d}_{22},\boldsymbol{\alpha}_2),\phi^s(\mathbf{r}|\mathbf{R}_B,2,2,\mathbf{d}_{22},\boldsymbol{\alpha}_2),\\
&--------------------------------\\
&\phi^s(\mathbf{r}|\mathbf{R}_B,-2,2,\mathbf{d}_{23},\boldsymbol{\alpha}_2),\phi^s(\mathbf{r}|\mathbf{R}_B,-1,2,\mathbf{d}_{23},\boldsymbol{\alpha}_2),\phi^s(\mathbf{r}|\mathbf{R}_B,0,2,\mathbf{d}_{23},\boldsymbol{\alpha}_2),\\
&\phi^s(\mathbf{r}|\mathbf{R}_B,1,2,\mathbf{d}_{23},\boldsymbol{\alpha}_2),\phi^s(\mathbf{r}|\mathbf{R}_B,2,2,\mathbf{d}_{23},\boldsymbol{\alpha}_2),\\
&================================\\
&\phi^s(\mathbf{r}|\mathbf{R}_A,-2,2,\mathbf{d}_{31},\boldsymbol{\alpha}_3),\phi^s(\mathbf{r}|\mathbf{R}_A,-1,2,\mathbf{d}_{31},\boldsymbol{\alpha}_3),\phi^s(\mathbf{r}|\mathbf{R}_A,0,2,\mathbf{d}_{31},\boldsymbol{\alpha}_3),\\
&\phi^s(\mathbf{r}|\mathbf{R}_A,1,2,\mathbf{d}_{31},\boldsymbol{\alpha}_3),\phi^s(\mathbf{r}|\mathbf{R}_A,2,2,\mathbf{d}_{31},\boldsymbol{\alpha}_3)
\end{aligned}\tag{18}$$

where each spherical contraction has the form $\phi^s(\mathbf{r}|\mathbf{R}_A,m,\ell,\mathbf{d},\boldsymbol{\alpha})$.

The specific ordering of the angular momentum components in the Cartesian and spherical form is determined by the properties gbasis.contractions.GeneralizedContractionShell.angmom_components_cart

and

gbasis.contractions.GeneralizedContractionShell.angmom_components_sph

respectively. To change the ordering, make a child of GeneralizedContractionShell and overwrite these properties with the desired ordering.

3.2 Types of coordinate systems used by basis functions

In gbasis, user can provide the coordinate system used by each shell of generalized contractions. All of the higher level functions have the keyword argument coord_type or coord_types to specify the coordinate systems used by the basis. If "spherical" is given, all of the shells are treated to be spherical. If "cartesian" is given, all of the shells are treated to be Cartesian. If different shells correspond to different coordinate system, then a list/tuple of the same length as the basis set must be provided with each entry being "spherical" or "cartesian" to specify the coordinate system of the corresponding shell.

3.3 Loading basis sets

Basis set information is often stored in text format. In gbasis, the Gaussian94 format (.gbs) and the NWChem format (.nwchem) are supported.

gbasis also interfaces to the module iodata, which handles the inputs and outputs for different quantum chemistry formats. It also interfaces to pyscf, which is an ab initio computational chemistry program.

4 Evaluations

4.1 Evaluation of contractions

The functions in module gbasis.eval return the evaluations of the contractions at different coordinates:

$$\phi(\mathbf{r}_n|\mathbf{R}_A, \mathbf{a}_j, \mathbf{d}_k, \boldsymbol{\alpha}_k) \tag{19}$$

The returned value is an array whose rows corresponds to the basis function and columns corresponds to the coordinate, $\mathbf{r}_n$.

These functions can be used to find the values of the orbitals at various points, such as a grid.

4.2 Evaluation of derivatives of contractions

In gbasis, contractions can be derivatized to arbitrary orders. The functions in module gbasis.eval_deriv return the evaluations of the given derivative of the contractions at different coordinates.

$$\frac{\partial^{m_x+m_y+m_z}}{\partial x^{m_x}\partial y^{m_y}\partial z^{m_z}}\phi(\mathbf{r}_n|\mathbf{R}_A, \mathbf{a}_j, \mathbf{d}_k, \boldsymbol{\alpha}_k) \tag{20}$$

The returned value is an array whose rows corresponds to the basis function and columns corresponds to the coordinate, $\mathbf{r}_n$.

4.3 Evaluations of density related properties

The functions in module `gbasis.density` return the evaluations of the density and its derivatives.

4.3.1 Density

$$\rho(\mathbf{r}_n) = \sum_{ij} \gamma_{ij} \phi_i(\mathbf{r}_n) \phi_j(\mathbf{r}_n) \tag{21}$$

4.3.2 Arbitrary derivatives of density

$$\frac{\partial^{L_x+L_y+L_z}}{\partial x^{L_x} \partial y^{L_y} \partial z^{L_z}} \rho(\mathbf{r}_n) = \sum_{l_x=0}^{L_x} \sum_{l_y=0}^{L_y} \sum_{l_z=0}^{L_z} \binom{L_x}{l_x} \binom{L_y}{l_y} \binom{L_z}{l_z} \sum_{ij} \gamma_{ij} \frac{\partial^{l_x+l_y+l_z} \rho(\mathbf{r}_n)}{\partial x^{l_x} \partial y^{l_y} \partial z^{l_z}} \frac{\partial^{L_x+L_y+L_z-l_x-l_y-l_z} \rho(\mathbf{r}_n)}{\partial x^{L_x-l_x} \partial y^{L_y-l_y} \partial z^{L_z-l_z}} \tag{22}$$

4.3.3 Gradient of density

$$\nabla \rho(\mathbf{r}_n) = \begin{bmatrix} \frac{\partial}{\partial x} \rho(\mathbf{r}_n) \\ \\ \frac{\partial}{\partial y} \rho(\mathbf{r}_n) \\ \\ \frac{\partial}{\partial z} \rho(\mathbf{r}_n) \end{bmatrix} \tag{23}$$

4.3.4 Laplacian of density

$$\nabla^2 \rho(\mathbf{r}_n) = \frac{\partial^2}{\partial x^2} \rho(\mathbf{r}_n) + \frac{\partial^2}{\partial y^2} \rho(\mathbf{r}_n) + \frac{\partial^2}{\partial z^2} \rho(\mathbf{r}_n) \tag{24}$$

4.3.5 Hessian of density

$$H[\rho(\mathbf{r}_n)] = \begin{bmatrix} \frac{\partial^2}{\partial x^2} \rho(\mathbf{r}_n) & \frac{\partial^2}{\partial x \partial y} \rho(\mathbf{r}_n) & \frac{\partial^2}{\partial x \partial z} \rho(\mathbf{r}_n) \\ \\ \frac{\partial^2}{\partial x \partial y} \rho(\mathbf{r}_n) & \frac{\partial^2}{\partial y^2} \rho(\mathbf{r}_n) & \frac{\partial^2}{\partial y \partial z} \rho(\mathbf{r}_n) \\ \\ \frac{\partial^2}{\partial x \partial z} \rho(\mathbf{r}_n) & \frac{\partial^2}{\partial z^2} \rho(\mathbf{r}_n) & \frac{\partial^2}{\partial x \partial z} \rho(\mathbf{r}_n) \end{bmatrix} \tag{25}$$

4.4 Evaluations of density matrix related properties

Given the density matrix,

$$\gamma(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ij} \gamma_{ij} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \tag{26}$$

many properties can be defined by evaluating the derivatives of the density matrix at the same coordinate:

$$\left. \frac{\partial^{p_x+p_y+p_z}}{\partial x_1^{p_x} \partial y_1^{p_y} \partial z_1^{p_z}} \frac{\partial^{q_x+q_y+q_z}}{\partial x_2^{q_x} \partial y_2^{q_y} \partial z_2^{q_z}} \gamma(\mathbf{r}_1, \mathbf{r}_2) \right|_{\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}_n} = \sum_{ij} \gamma_{ij} \left. \frac{\partial^{p_x+p_y+p_z}}{\partial x_1^{p_x} \partial y_1^{p_y} \partial z_1^{p_z}} \phi_i(\mathbf{r}_1) \right|_{\mathbf{r}_1=\mathbf{r}_n} \left. \frac{\partial^{q_x+q_y+q_z}}{\partial x_2^{q_x} \partial y_2^{q_y} \partial z_2^{q_z}} \phi_j(\mathbf{r}_2) \right|_{\mathbf{r}_1=\mathbf{r}_n} \tag{27}$$

where $\mathbf{r}_1$ is the first coordinate, $\mathbf{r}_2$ is the second coordinate, and $\mathbf{r}_n$ is the coordinate at which the derivative is evaluated.

Since γ_{ij} is symmetric,

$$\frac{\partial^{p_x+p_y+p_z}}{\partial x_1^{p_x}\partial y_1^{p_y}\partial z_1^{p_z}}\frac{\partial^{q_x+q_y+q_z}}{\partial x_2^{q_x}\partial y_2^{q_y}\partial z_2^{q_z}}\gamma(\mathbf{r}_1,\mathbf{r}_2)\bigg|_{\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}_n} = \frac{\partial^{q_x+q_y+q_z}}{\partial x_1^{q_x}\partial y_1^{q_y}\partial z_1^{q_z}}\frac{\partial^{p_x+p_y+p_z}}{\partial x_2^{p_x}\partial y_2^{p_y}\partial z_2^{p_z}}\gamma(\mathbf{r}_1,\mathbf{r}_2)\bigg|_{\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}_n} \tag{28}$$

4.4.1 Stress tensor

$$\begin{aligned}\boldsymbol{\sigma}_{ij}(\mathbf{r}_n|\alpha,\beta) =& -\frac{1}{2}\alpha\left(\frac{\partial^2}{\partial r_i\partial r'_j}\gamma(\mathbf{r},\mathbf{r}')+\frac{\partial^2}{\partial r_j\partial r'_i}\gamma(\mathbf{r},\mathbf{r}')\right)_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n}\\ &+\frac{1}{2}(1-\alpha)\left(\frac{\partial^2}{\partial r_i\partial r_j}\gamma(\mathbf{r},\mathbf{r})+\frac{\partial^2}{\partial r'_i\partial r'_j}\gamma(\mathbf{r},\mathbf{r}')\right)_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n}\\ &-\frac{1}{2}\delta_{ij}\beta\nabla^2\rho(\mathbf{r}_n)\\ =& -\alpha\ \frac{\partial^2}{\partial r_i\partial r'_j}\gamma(\mathbf{r},\mathbf{r}')\bigg|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n}+(1-\alpha)\ \frac{\partial^2}{\partial r_i\partial r_j}\gamma(\mathbf{r},\mathbf{r})\bigg|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n}-\frac{1}{2}\delta_{ij}\beta\nabla^2\rho(\mathbf{r}_n)\end{aligned} \tag{29}$$

4.4.2 Ehrenfest force

Ehrenfest force is defined as the divergence of the stress tensor

$$\begin{aligned}F_j(\mathbf{r}_n|\alpha,\beta) =& \sum_i\frac{\partial}{\partial r_i}\boldsymbol{\sigma}_{ij}\\ =& -\alpha\sum_i\ \frac{\partial^3}{\partial r_i^2\partial r'_j}\gamma(\mathbf{r},\mathbf{r}')\bigg|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n}-\alpha\sum_i\ \frac{\partial^3}{\partial r_i\partial r'_i\partial r'_j}\gamma(\mathbf{r},\mathbf{r}')\bigg|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n}\\ &+(1-\alpha)\sum_i\ \frac{\partial^3}{\partial r_i^2\partial r_j}\gamma(\mathbf{r},\mathbf{r})\bigg|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n}+(1-\alpha)\sum_i\ \frac{\partial^3}{\partial r_i\partial r_j\partial r'_i}\gamma(\mathbf{r},\mathbf{r})\bigg|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n}-\frac{1}{2}\sum_i\delta_{ij}\beta\frac{\partial}{\partial r_i}\nabla^2\rho(\mathbf{r}_n)\\ =& -\alpha\sum_i\ \frac{\partial^3}{\partial r_i^2\partial r'_j}\gamma(\mathbf{r},\mathbf{r}')\bigg|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n}\\ &+(1-\alpha)\sum_i\ \frac{\partial^3}{\partial r_i^2\partial r_j}\gamma(\mathbf{r},\mathbf{r})\bigg|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n}+(1-2\alpha)\sum_i\ \frac{\partial^3}{\partial r_i\partial r_j\partial r'_i}\gamma(\mathbf{r},\mathbf{r})\bigg|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n}-\frac{1}{2}\sum_i\delta_{ij}\beta\frac{\partial}{\partial r_i}\nabla^2\rho(\mathbf{r}_n)\end{aligned} \tag{30}$$

4.4.3 Ehrenfest Hessian

$$
\begin{aligned}
H_{jk}(\mathbf{r}_n|\alpha,\beta) =& \frac{\partial}{\partial r_k} F_j(\mathbf{r}_n|\alpha,\beta) \\
=& -\alpha \sum_i \left(\frac{\partial^4}{\partial r_i^2 \partial r_k \partial r_j'} \gamma(\mathbf{r},\mathbf{r}') + \frac{\partial^4}{\partial r_i^2 \partial r_j' \partial r_k'} \gamma(\mathbf{r},\mathbf{r}') \right)_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n} \\
&+ (1-\alpha) \sum_i \left(\frac{\partial^4}{\partial r_i^2 \partial r_j \partial r_k} \gamma(\mathbf{r},\mathbf{r}) + \frac{\partial^4}{\partial r_i^2 \partial r_j \partial r_k'} \gamma(\mathbf{r},\mathbf{r}) \right)_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n} \\
&+ (1-2\alpha) \sum_i \left(\frac{\partial^4}{\partial r_i \partial r_j \partial r_k \partial r_i'} \gamma(\mathbf{r},\mathbf{r}) + \frac{\partial^4}{\partial r_i \partial r_j \partial r_i' \partial r_k'} \gamma(\mathbf{r},\mathbf{r}) \right)_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n} \\
&- \frac{1}{2} \sum_i \delta_{ij} \beta \frac{\partial^2}{\partial r_i \partial r_k} \nabla^2 \rho(\mathbf{r}_n)
\end{aligned} \tag{31}
$$

4.4.4 Positive-definite kinetic energy density

$$
\begin{aligned}
t_+(\mathbf{r}_n) &= \frac{1}{2} \left. \nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{r}'} \gamma(\mathbf{r},\mathbf{r}') \right|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n} \\
&= \frac{1}{2} \left(\frac{\partial^2}{\partial x \partial x'} \gamma(\mathbf{r},\mathbf{r}') + \frac{\partial^2}{\partial y \partial y'} \gamma(\mathbf{r},\mathbf{r}') + \frac{\partial^2}{\partial z \partial z'} \gamma(\mathbf{r},\mathbf{r}') \right)_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_n}
\end{aligned} \tag{32}
$$

4.4.5 General form of kinetic energy density

$$
t_\alpha(\mathbf{r}_n) = t_+(\mathbf{r}_n) + \alpha \nabla^2 \rho(\mathbf{r}_n) \tag{33}
$$

5 Integrals

5.1 Multipole moment integral

Multipole moment integral can be obtained for arbitrary moments.

$$
\int \phi_a(\mathbf{r})(x-X_C)^{c_x}(y-Y_C)^{c_y}(z-Z_C)^{c_z}\phi_b(\mathbf{r})d\mathbf{r} \tag{34}
$$

5.2 Overlap integral

Overlap integrals can be thought of as multipole moment integrals with zero moments.

$$
\int \phi_a(\mathbf{r})\phi_b(\mathbf{r})d\mathbf{r} \tag{35}
$$

5.2.1 Overlap integral between two different basis sets

Overlap integrals between two different basis sets are supported i.e. ϕ_a belongs to one basis set and ϕ_b belongs to another.

5.3 Integrals over differential operator

Integrals over arbitrary differential operator (for Cartesian coordinates) are supported.

$$\int \phi_a(\mathbf{r}) \frac{\partial^{e+f+g}}{\partial x^e \partial y^f \partial z^g} \phi_b(\mathbf{r}) d\mathbf{r} \tag{36}$$

5.3.1 Kinetic energy integral

$$\begin{aligned}\left\langle \hat{T} \right\rangle &= \int \phi_a(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \phi_b(\mathbf{r}) d\mathbf{r} \\ &= -\frac{1}{2}\left(\int \phi_a(\mathbf{r}) \frac{\partial^2}{\partial x^2} \phi_b(\mathbf{r}) d\mathbf{r} + \int \phi_a(\mathbf{r}) \frac{\partial^2}{\partial y^2} \phi_b(\mathbf{r}) d\mathbf{r} + \int \phi_a(\mathbf{r}) \frac{\partial^2}{\partial z^2} \phi_b(\mathbf{r}) d\mathbf{r}\right)\end{aligned} \tag{37}$$

5.3.2 Momentum integral

$$\begin{aligned}\langle \hat{\mathbf{p}} \rangle &= \int \phi_a(\mathbf{r}) \left(-i\nabla\right) \phi_b(\mathbf{r}) d\mathbf{r} \\ &= -i \begin{bmatrix} \int \phi_a(\mathbf{r}) \frac{\partial}{\partial x} \phi_b(\mathbf{r}) d\mathbf{r} \\ \int \phi_a(\mathbf{r}) \frac{\partial}{\partial y} \phi_b(\mathbf{r}) d\mathbf{r} \\ \int \phi_a(\mathbf{r}) \frac{\partial}{\partial z} \phi_b(\mathbf{r}) d\mathbf{r} \end{bmatrix}\end{aligned} \tag{38}$$

5.3.3 Angular momentum integral

$$\begin{aligned}\left\langle \hat{\mathbf{L}} \right\rangle &= \int \phi_a(\mathbf{r}) \left(-i\mathbf{r} \times \nabla\right) \phi_b(\mathbf{r}) d\mathbf{r} \\ &= -i \begin{bmatrix} \int \phi_a(\mathbf{r}) y \frac{\partial}{\partial z} \phi_b(\mathbf{r}) d\mathbf{r} - \int \phi_a(\mathbf{r}) z \frac{\partial}{\partial y} \phi_b(\mathbf{r}) d\mathbf{r} \\ \int \phi_a(\mathbf{r}) z \frac{\partial}{\partial x} \phi_b(\mathbf{r}) d\mathbf{r} - \int \phi_a(\mathbf{r}) x \frac{\partial}{\partial z} \phi_b(\mathbf{r}) d\mathbf{r} \\ \int \phi_a(\mathbf{r}) x \frac{\partial}{\partial y} \phi_b(\mathbf{r}) d\mathbf{r} - \int \phi_a(\mathbf{r}) y \frac{\partial}{\partial x} \phi_b(\mathbf{r}) d\mathbf{r} \\ \end{bmatrix}\end{aligned} \tag{39}$$

5.4 Integral for interaction with point-charge

$$\int \phi_a(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{R}_C|} \phi_b(\mathbf{r}) d\mathbf{r} \tag{40}$$

5.4.1 Nuclear-electron attraction integral

$$\int \phi_a(\mathbf{r}) \frac{-Z_c}{|\mathbf{r} - \mathbf{R}_C|} \phi_b(\mathbf{r}) d\mathbf{r} = -Z_C \int \phi_a(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{R}_C|} \phi_b(\mathbf{r}) d\mathbf{r} \tag{41}$$

5.4.2 Electrostatic potential

$$-\left(-\sum_A \frac{Z_A}{|\mathbf{R}_C - \mathbf{R}_A|} + \sum_{ab} \gamma_{ab} \int \phi_a(\mathbf{r}) \frac{-1}{|\mathbf{r} - \mathbf{R}_C|} \phi_b(\mathbf{r}) d\mathbf{r}\right) = \sum_A \frac{Z_A}{|\mathbf{R}_C - \mathbf{R}_A|} - \sum_{ab} \gamma_{ab} \int \phi_a(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{R}_C|} \phi_b(\mathbf{r}) d\mathbf{r} \tag{42}$$

5.5 Electron-electron repulsion integral

In the Chemists' notation,

$$\int \phi_a^*(\mathbf{r}_1) \phi_b(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_c^*(\mathbf{r}_2) \phi_d(\mathbf{r}_2) d\mathbf{r} \tag{43}$$

In the Physicists' notation

$$\int \phi_a^*(\mathbf{r}_1) \phi_b^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_c(\mathbf{r}_1) \phi_d(\mathbf{r}_2) d\mathbf{r} \tag{44}$$

Though both conventions are supported at the higher level, lower level code uses the Chemists' notation.