Integrals of Gaussian Type Orbitals (GTO)

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Introduction

- In computational chemistry, STOs (Slater-Type Orbitals) and GTOs (Gaussian-Type Orbitals) are fundamental for describing the electronic structure of molecules.
- These basis functions play a crucial role in methods like Hartree-Fock theory and density functional theory (DFT).

STO (Slater-Type Orbitals)

- STOs are derived from solutions of the Schrdinger equation for the hydrogen atom.
- Defined as:
$$\phi_{nlm}(\mathbf{r}) = N_{nl} r^{n-1} e^{-\zeta r} Y_{lm}(\theta, \phi)$$
- n, l, and m are quantum numbers; r is the distance from the nucleus; θ and ϕ are angles; Y_{lm} are spherical harmonics.
- STOs have limitations regarding decay properties, affecting convergence in molecular calculations.

GTO (Gaussian-Type Orbitals)

- GTOs are expressed as Gaussian functions multiplied by polynomials.
- Defined as:

$$g_{nlm}(\mathbf{r}) = N_{nl} r^n e^{-\alpha r^2} Y_{lm}(\theta, \phi)$$

- α determines the width of the Gaussian function.
- GTOs offer computational advantages due to mathematical simplicity and better decay properties.

Why We Use STO and GTO

1. Representation of Electron Wavefunctions
2. Flexibility and Accuracy
3. Computational Efficiency
4. Basis Set Expansion
5. Applicability to Various Methods
6. Adaptability to Molecular Symmetry

Introduction to Cartesian Gaussians

- Cartesian Gaussians are a type of Gaussian-type orbital (GTO) used in computational chemistry.
- They offer a convenient representation of molecular orbitals in Cartesian coordinates.
- Cartesian Gaussians are expressed in terms of x, y, and z coordinates, rather than spherical coordinates.

Form of Cartesian Gaussian

A Cartesian Gaussian takes the form:

$$C_{ijk}^{\alpha,\mathbf{x}}(\mathbf{r}) \triangleq P_{ijk}^{\mathbf{x}} \exp\left(-\alpha(\mathbf{r} - \mathbf{x})^2\right) = \langle \mathbf{r} \mid \alpha, \mathbf{x}, i, j, k \rangle$$

$$P_{ijk}^{\mathbf{x}}(\mathbf{r}) \triangleq (r_1 - x_1)^i (r_2 - x_2)^j (r_3 - x_3)^k$$

- α: This is a positive constant known as the exponent coefficient. It controls the width of the Gaussian function. Larger values of α result in a narrower peak, concentrating the function's amplitude closer to the center $\mathbf{x}$.
- $\mathbf{r}$: This is a three-dimensional vector representing the point where the function is evaluated. In Cartesian coordinates, it typically has components (r_1, r_2, r_3), corresponding to the positions along the x, y, and z axes, respectively.
- $\mathbf{x}$: This is also a three-dimensional vector representing the center of the Gaussian function. It typically has components (x_1, x_2, x_3), specifying the position of the peak along the x, y, and z axes, respectively.

Advantages of Cartesian Gaussians

- Provide a more direct representation of molecular orbitals in Cartesian coordinates.
- Well-suited for Cartesian-coordinate-based computational methods like Hartree-Fock theory and density functional theory (DFT).
- Offer computational advantages similar to other types of Gaussians, such as flexibility and ease of manipulation.

The List of Integrals

Four integrals are necessary for HF:

1. The overlap integral: $\langle p \mid q \rangle$.
2. The kinetic integral: $\langle p \left| \nabla^2 \right| q \rangle$.
3. The nuclear integral: $\langle p \left| V_{\text{nuc}} \right| q \rangle$.
4. The electron repulsion integrals (ERI): $(pq \mid rs)$ and $(pr \mid qs)$.

p, q, r, s are (contracted) Cartesian Gaussians.

Overlap

The overlap integral is an integral over the product of two Cartesian Gaussians:

$$\langle \beta, \mathbf{y}, r, s, t \mid \alpha, \mathbf{x}, i, j, k \rangle = \int \mathrm{d}_{\mathbf{r}} \mathrm{C}_{rst}^{\beta, \mathbf{y}}(\mathbf{r}) \mathrm{C}_{ijk}^{\alpha, \mathbf{x}}(\mathbf{r})$$

Since the product of two Cartesian Gaussians is another Cartesian Gaussian, we end up integrating just a single Cartesian Gaussian. This integral relies on the observation that derivatives of a Gaussian w.r.t. its center span the vector space of Cartesian Gaussians.

$$\frac{\partial}{\partial x_1} \exp\left(-\alpha(\mathbf{r} - \mathbf{x})^2\right) = 2\alpha\left(r_1 - x_1\right) \exp\left(-\alpha(\mathbf{r} - \mathbf{x})^2\right)$$

More generally, the nth derivative defines the nth Hermite polynomial $\alpha^{n/2} H_n\left(\sqrt{\alpha}\left(r_1 - x_1\right)\right)$

$$\frac{\partial^n}{\partial x_1^n} \exp\left(-\alpha(\mathbf{r} - \mathbf{x})^2\right) = \alpha^{j/2} H_n\left(\sqrt{\alpha}\left(r_1 - x_1\right)\right) \exp\left(-\alpha(\mathbf{r} - \mathbf{x})^2\right)$$

Overlap

The Hermite polynomials form a basis set for polynomials, so we can expand the polynomial part of the Cartesian Gaussian product in terms of Hermite polynomials as

$$C_{rst}^{\beta,\mathbf{y}}(\mathbf{r})C_{ijk}^{\alpha,\mathbf{x}}(\mathbf{r}) = \exp\left(-\frac{\alpha\beta|\mathbf{x}-\mathbf{y}|^2}{\gamma}\right)\sum D_{ir}^m E_{js}^n F_{kt}^p \Lambda_{mnp}^{\gamma,\mathbf{z}}(\mathbf{r})$$

$$\Lambda_{mnp}^{\gamma,\mathbf{z}}(\mathbf{r}) = \frac{\partial^m}{\partial z_1^m}\frac{\partial^n}{\partial z_2^n}\frac{\partial^p}{\partial z_3^p}\exp\left(-\gamma(\mathbf{r}-\mathbf{z})^2\right)$$

We will call the function Λ the Hermite Gaussians. The coefficients in this basis transform can be recursively evaluated as

$$(r_1 - x_1)^i (r_1 - y_1)^r = \sum_m^{i+r} D_{i,r}^m \gamma^{m/2} H_m\left(\sqrt{\gamma}(r_1 - z_1)\right)$$

Overlap

$$(r_1 - x_1) \cdot (r_1 - x_1)^{i-1} (r_1 - y_1)^r$$

$$= \sum_{m}^{i+r-1} D_{i-1,r}^m \gamma^{m/2} \left((r_1 - z_1) + (z_1 - x_1) \right) H_m \left(\sqrt{\gamma} (r_1 - z_1) \right)$$

$$= \sum_{m}^{i+r-1} D_{i-1,r}^m \left(\gamma^{m/2} (z_1 - x_1) H_m + \gamma^{(m-1)/2} \left(m H_{m-1} - \frac{1}{2} H_{m+1} \right) \right)$$

$$= \sum_{m}^{i+r-1} D_{i-1,r}^m \gamma^{m/2} (z_1 - x_1) H_m$$

$$+ D_{i-1,r}^{m+1} \gamma^{m/2} (m+1) H_m - D_{i-r,r}^{m-1} \gamma^{(m-2)/2} \frac{1}{2} H_m,$$

Overlap

which yields

$$\gamma = \alpha + \beta, \mathbf{z} = \frac{\alpha \mathbf{x} + \beta \mathbf{y}}{\gamma},$$

$$D_{ir}^m = \frac{1}{2\gamma} D_{i-1,r}^{m-1} + (r_1 - x_1) D_{i-1,r}^m + (m+1) D_{i-1,r}^{m+1},$$

$$D_{0r}^m = \frac{1}{2\gamma} D_{0,r-1}^{m-1} + (r_1 - y_1) D_{0,r-1}^m + (m+1) D_{0,r-1}^{m+1},$$

$$D_{00}^0 = 1, \text{ and } D_{ir}^m = 0 \text{ if } m < 0 \text{ or } m > i + r.$$

Once we have the coefficients, the overlap integral can be performed through $\Lambda_{mnp}^{\gamma,\mathbf{z}}(\mathbf{r})$ as

$$\int d\mathbf{r} \Lambda_{mnp}^{\gamma,\mathbf{z}}(\mathbf{r}) = \frac{\partial^m}{\partial z_1^m} \frac{\partial^n}{\partial z_2^n} \frac{\partial^p}{\partial z_3^p} \int d\mathbf{r} \exp\left(-\gamma(\mathbf{r} - \mathbf{z})^2\right) = \delta_{m0} \delta_{n0} \delta_{p0} \left(\frac{\pi}{\gamma}\right)^{3/2}$$

Kinetic

The kinetic integral is also a Cartesian Gaussian integral, and it can be performed the same way as the overlap integral. We first derive the Laplacian of a Cartesian Gaussian

$$
\begin{aligned}
\nabla^2 \mathrm{C}_{ijk}^{\alpha,\mathbf{x}}(\mathbf{r}) &= \left(\nabla^2 P_{ijk}^{\mathbf{x}}(\mathbf{r})\right) \exp\left(-\alpha(\mathbf{r}-\mathbf{x})^2\right) + P_{ijk}^{\mathbf{x}}(\mathbf{r})\nabla^2 \exp\left(-\alpha(\mathbf{r}-\mathbf{x})^2\right) \\
&\quad + 2\nabla P_{ijk}^{\mathbf{x}}(\mathbf{r}) \cdot \nabla \exp\left(-\alpha(\mathbf{r}-\mathbf{x})^2\right) \\
&= \partial_{r_1}^2 P_{ijk}^{\mathbf{x}}(\mathbf{r})\big) \exp\left(-\alpha(\mathbf{r}-\mathbf{x})^2\right) + P_{ijk}^{\mathbf{x}}(\mathbf{r})\partial_{r_1}^2 \exp\left(-\alpha(\mathbf{r}-\mathbf{x})^2\right) \\
&\quad + 2\partial_{r_1} P_{ijk}^{\mathbf{x}}(\mathbf{r}) \cdot \partial_{r_1} \exp\left(-\alpha(\mathbf{r}-\mathbf{x})^2\right) + \partial_{r_2}\cdots \\
&= i(i-1)P_{i-2jk}^{\mathbf{x}}(\mathbf{r})\exp\left(-\alpha(\mathbf{r}-\mathbf{x})^2\right) \\
&\quad + 4\alpha^2 P_{i+2jk}^{\mathbf{x}}(\mathbf{r})\exp\left(-\alpha(\mathbf{r}-\mathbf{x})^2\right) - 2\alpha P_{ijk}^{\mathbf{x}}(\mathbf{r})\exp\left(-\alpha(\mathbf{r}-\mathbf{x})^2\right) \\
&\quad - 4i\alpha P_{ijk}^{\mathbf{x}}(\mathbf{r})\exp\left(-\alpha(\mathbf{r}-\mathbf{x})^2\right) + \dots \\
&= i(i-1)\mathrm{C}_{i-2jk}^{\alpha,\mathbf{x}}(\mathbf{r}) + 4\alpha^2 \mathrm{C}_{i+2jk}^{\alpha,\mathbf{x}}(\mathbf{r}) - 2\alpha(2i+1)\mathrm{C}_{ijk}^{\alpha,\mathbf{x}}(\mathbf{r}).
\end{aligned}
$$

The kinetic integral is then easy to write down as

$$
\begin{aligned}
E_{\text{kin}} &= -\frac{1}{2} \int C_{rst}^{\beta,\mathbf{y}}(\mathbf{r}) \nabla^2 C_{ijk}^{\alpha,\mathbf{x}}(\mathbf{r}) d\mathbf{r} \\
&= -\frac{1}{2} i(i-1) \int d\mathbf{r} C_{rst}^{\beta,\mathbf{y}}(\mathbf{r}) C_{i-1jk}^{\alpha,\mathbf{x}}(\mathbf{r}) \\
&- 2\alpha^2 \int d\mathbf{r} C_{rst}^{\beta,\mathbf{y}}(\mathbf{r}) C_{i+2jk}^{\alpha,\mathbf{x}}(\mathbf{r}) + \alpha \int d\mathbf{r} C_{rst}^{\beta,\mathbf{y}}(\mathbf{r}) C_{ijk}^{\alpha,\mathbf{x}}(\mathbf{r}).
\end{aligned}
$$

The nuclear integral also involves a product of two Cartesian Gaussians. After converting the product to a sum of Hermite Gaussians, the integral boils down to evaluating:

$$\int \mathrm{d}\mathbf{r}' \Lambda_{mnp}^{\gamma,\mathbf{z}}\left(\mathbf{r}'\right) \frac{1}{|\mathbf{r}' - \mathbf{r}|}$$

This integral has a well-known analytical solution for specific cases.

The electrostatic potential of a uniformly charged sphere

For a charge distribution $\sigma\rho(\mathbf{r})$, where σ is the total charge and $\rho(\mathbf{r})$ is a normalized density, the potential energy can be evaluated as

$$V(\mathbf{r}) = \sigma \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}$$

For a uniformly charged sphere in 3D, the density is $\rho(\mathbf{r}) = \sigma\delta(r - R)$. Its potential at $\mathbf{r}$ can be analytically evaluated in the spherical coordinates.

$$= \sigma^2 \int dr' r'^2 \sin\theta d\theta d\phi \frac{\delta(r' - R)}{\sqrt{(r')^2 + r^2 - 2r'r\cos\theta}} = \sigma^2 \int \frac{R^2 \sin\theta d\theta d\phi}{\sqrt{R^2 + r^2 - 2Rr\cos\theta}}$$

$$= \frac{2\pi\sigma^2}{r} \left(\sqrt{(R+r)^2} - \sqrt{(R-r)^2} \right) = \begin{cases} \frac{R^2\sigma}{r} & \text{if } R < r \\ R\sigma & \text{if } R > r \end{cases}$$

Gaussian as stacked concentric spheres

A isotropic Gaussian distribution in 3D can be viewed as many concentric spheres stacked together and the potential is then an integral over the stacks. A isotropic Gaussian distribution in $3D \Lambda_{000}^{\gamma,0}$ can now be viewed as many concentric spheres stacked together and the potential is then an integral over the stacks

$$\rho(\mathbf{r}) = \exp\left(-\gamma r^2\right) = \int \mathrm{d}R \exp\left(-\gamma R^2\right) \delta(r - R)$$

$$V(\mathbf{r}) = 4\pi \int_0^r \mathrm{d}R \exp\left(-\gamma R^2\right) \frac{\sigma R^2}{r} + 4\pi \int_r^\infty \mathrm{d}R \exp\left(-\gamma R^2\right) \sigma R$$

$$= \frac{2\pi}{\gamma r} \int_0^r \exp\left(-\gamma R^2\right) \mathrm{d}R = \frac{2\pi}{\gamma^{3/2} r} \int_0^{\sqrt{\gamma} r} e^{-t^2} \, \mathrm{d}t = \frac{\pi^{3/2} \, \mathrm{erf}(\sqrt{\gamma} r)}{2\gamma^{3/2} r}.$$

Gaussian as stacked concentric spheres

For the purpose of differentiation it turns out to be more general to write the result in terms of $u = t/(\sqrt{\gamma}r)$ instead of the error function,

$$V(\mathbf{r}) = \frac{2\pi}{\gamma} \int_0^1 e^{-\gamma r^2 u^2} \; \mathrm{d}u \triangleq \frac{2\pi}{\gamma} F_0\left(\gamma r^2\right)$$

The potential of $\Lambda_{mnp}^{\gamma,\mathbf{z}}$ can now be written as the derivative of F_0

$$\frac{\partial^m}{\partial z_1^m} \frac{\partial^n}{\partial z_2^n} \frac{\partial^p}{\partial z_3^p} \int \mathrm{d}\mathbf{r} \Lambda_{000}^{\gamma,\mathbf{z}}(\mathbf{r}) = \frac{2\pi}{\gamma} \frac{\partial^m}{\partial z_1^m} \frac{\partial^n}{\partial z_2^n} \frac{\partial^p}{\partial z_3^p} F_0\left(\gamma|\mathbf{r} - \mathbf{z}|^2\right) \triangleq \frac{2\pi}{\gamma} R_{mnp0}$$

Gaussian as stacked concentric spheres

Calculating R_{mnp0} is efficient with the recursive relations

$$R_{00pj} = z_3 R_{00p-1j+1} + (p-1)R_{00p-2j+1},$$
$$R_{0npj} = z_2 R_{0n-1pj+1} + (n-1)R_{0n-2}pj + 1,$$
$$R_{mnpj} = z_1 R_{m-1npj+1} + (m-1)R_{m-2npj+1},$$
$$R_{000j} = (-2\gamma)^j F_j \left(\alpha |\mathbf{r} - \mathbf{z}|^2 \right),$$
$$F_j(T) = \Gamma(m)\Gamma(m, T)/(2T^m), \text{ with } m = j + 1/2,$$
$$R_{mnpj} = 0 \text{ if } m < 0 \text{ or } n < 0 \text{ or } p < 0.$$

where $\Gamma(m)$ is the Gamma function and $\Gamma(m, T)$ is the upper incomplete Gamma function. $F_j(T)$ seemingly has a singularity at $T = 0$, which can be circumvented by Taylor expanding the expression around $T = 0$.

Given two isotropic Gaussians $\Lambda_{000}^{\alpha,\mathbf{x}}(\mathbf{r})$ and $\Lambda_{000}^{\beta,\mathbf{y}}(\mathbf{r})$, the Coulomb potential in between is

$$\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\Lambda_{000}^{\alpha,\mathbf{x}}(\mathbf{r})\Lambda_{000}^{\beta,\mathbf{y}}\left(\mathbf{r}'\right)$$

This integral is performed in the two center bipolar coordinate, where the coordinate of a point is specified by its distances to $\mathbf{x}$ and $\mathbf{y}$, which we denote p and q, and an azimuthal angle ϕ. The volume element is the shaded region, whose area is $\mathrm{d}p\ \mathrm{d}q/\sin(\theta)$ with an thickness of $h\ \mathrm{d}\phi$. h can be expressed through the area of the triangle as $h = pq\sin(\theta)/a$. Therefore, the volume element turns out to be $(pq/a)\mathrm{d}p\ \mathrm{d}q\ \mathrm{d}\phi$. Perform the integral over in the bipolar coordinates gives

$$J = \int \mathrm{d}\mathbf{r}\Lambda_{000}^{\alpha,\mathbf{x}}(\mathbf{r})V(\mathbf{r})$$

$$
= \int (pq/a) \mathrm{d}p \ \mathrm{d}q \ \mathrm{d}\phi \Lambda_{000}^{\alpha, \mathbf{x}}(\mathbf{r}) \frac{2\pi}{\alpha |\mathbf{r} - \mathbf{y}|} \int_0^{|\mathbf{r} - \mathbf{y}|} \exp\left(-\alpha R^2\right) \mathrm{d}R
$$

$$
= \frac{(2\pi)^2}{\alpha a} \int p \exp\left(-\beta p^2\right) \mathrm{d}p \ \mathrm{d}q \int_0^q \exp\left(-\alpha R^2\right) \mathrm{d}R
$$

$$
= \frac{(2\pi)^2}{\alpha a} \left(\int_0^a \mathrm{d}q \int_{a-q}^{a+q} \mathrm{d}p + \int_a^\infty \mathrm{d}q \int_{q-a}^{q+a} \mathrm{d}p \right)
$$

$$
\times \ p \exp\left(-\beta p^2\right) \int_0^q \exp\left(-\alpha R^2\right) \mathrm{d}R
$$

$$
= \frac{(2\pi)^2}{2\alpha\beta a} \left(\int_0^a \mathrm{d}q + \int_a^\infty \mathrm{d}q \right) \left(\exp\left(-\beta(a-q)^2\right) - \exp\left(-\beta(a+q)^2\right) \right)
$$

$$
\times \int_0^q \exp\left(-\alpha R^2\right) \mathrm{d}R
$$

$$
= \frac{(2\pi)^2}{2\alpha\beta a} \int_{-\infty}^\infty \mathrm{d}q \exp\left(-\beta(a-q)^2\right) \int_0^q \exp\left(-\alpha R^2\right) \mathrm{d}R
$$

To continue, we use one of those trick

$$
\begin{aligned}
J\frac{2\alpha\beta a}{(2\pi)2} &= \int_{-\infty}^{a} \mathrm{d}a' \int_{-\infty}^{\infty} \mathrm{d}q \frac{\partial}{\partial a'} \exp\left(-\beta\left(a'-q\right)^2\right) \int_{0}^{q} \exp\left(-\alpha R^2\right) \mathrm{d}R \\
&= \int_{-\infty}^{a} \mathrm{d}a' \int_{-\infty}^{\infty} \mathrm{d}q \frac{\partial}{\partial q} \exp\left(-\beta\left(a'-q\right)^2\right) \int_{0}^{q} \exp\left(-\alpha R^2\right) \mathrm{d}R \\
&= \int_{-\infty}^{a} \mathrm{d}a' \left(\exp\left(-\beta\left(a'-q\right)^2\right) \int_{0}^{q} \exp\left(-\alpha R^2\right) \mathrm{d}R \Big|_{-\infty}^{\infty} \right. \\
&\quad \left. + \int_{-\infty}^{\infty} \mathrm{d}q \exp\left(-\beta\left(a'-q\right)^2\right) \exp\left(-\alpha q^2\right) \right) \\
&= \int_{-\infty}^{a} \mathrm{d}a' \sqrt{\frac{\pi}{\alpha+\beta}} \exp\left(-\frac{\alpha\beta a'^2}{\alpha+\beta}\right)
\end{aligned}
$$

ERI

Write this in terms of F_0 yields

$$J = \frac{2\pi^{5/2}}{\alpha\beta\sqrt{\alpha+\beta}} F_0\left(\frac{|\mathbf{x}-\mathbf{y}|^2\alpha\beta}{\alpha+\beta}\right).$$

For general angular momentums, take the derivatives as before

$$\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \Lambda_{mnp}^{\alpha,\mathbf{x}}(\mathbf{r}) \Lambda_{m'n'p'}^{\beta;\mathbf{y}}(\mathbf{r}')$$

$$= \frac{\partial^m}{\partial x_1^m} \frac{\partial^n}{\partial x_2^n} \frac{\partial^p}{\partial x_3^p} \frac{\partial^{m'}}{\partial y_1^{m'}} \frac{\partial^{n'}}{\partial y_2^{n'}} \frac{\partial^{p'}}{\partial y_3^{p'}} J$$

$$= \frac{2\pi^{5/2}}{\alpha\beta\sqrt{\alpha+\beta}} (-1)^{m+n+p} R_{m+m'\,n+n'\,p+p'\,0}.$$

Conclusion

- Cartesian Gaussian-Type Orbitals provide a versatile and powerful tool for representing atomic orbitals and molecular electronic structure in quantum chemistry.
- Their ability to capture the anisotropic behavior of atomic orbitals makes them essential for accurate computational modeling of molecular systems.

Thank you