Adaptive Gaussian basis set for quantum chemistry computation

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1. Introduction

The basis set is one of the most important building block for the quantum chemistry calculation. Two most important features to construct the basis set is the effectiveness of evaluating the integral associated with these basis functions and the expressivity of them. Classically, people have been using contracted Gaussian orbitals with polynomial factors accounting for the angular-momentum.

In this paper, we introduced the adaptive Gaussian basis, which has both the mean and covariance trainable. The flexibility of anisotropic covariance substitutes the role of the polynomial factor and enjoy more efficient evaluation of the integral due to the analytic formula of Gaussian integrals. We demonstrate this theoretically by counting the FLOPs and numerically by performing Hartree-Fock calculation over simple molecule systems.

2. Methodology

Let N, I be the number of orbitals (electrons) and the index set for the Gaussian orbital basis. Motivated by [1], each basis of this set is parametrized by a mean vector $\mu_i \in \mathbb{R}^3$ and a covariance matrix $\Sigma_i \in \mathbb{S}^3_+$. Given this basis set, the k-th orbital is given by

$$\phi_k = \sum_{i \in I} c_{ki} \mathcal{N}(\mathbf{r}; \mu_i, \Sigma_i). \tag{1}$$

The total orbital information is encoded by two sets of parameters: the coefficient matrix $\mathrm{C} \in \mathbb{C}^{|I| \times N}$ and the Gaussian basis sets $\{\mu_i, \Sigma_i\}_{i \in I}$.

We emphasize three differences between our basis set and classical basis sets such as contracted Gaussian basis functions.

1. Our basis functions do not have the angular-momentum part of the classical basis set in [2] while its covariance can be anisotropic. We use the expressivity of the covariance matrix to substitute that of the polynomial factors.

2. All the orbitals share the same set of the basis function, while classical basis set have specific basis function developed for both core and valence electrons.

3. Both the basis set function and their linear coefficients are optimizable during the problem solving, thus we call it the adaptive Gaussian basis set which can adaptively change according to the system for calculation.

Overlap matrix and energy calculation: for most calculations such as the overlap matrix and kinetic energy, the procedure is similar to classical approach as the analytic formula can be extended to Gaussian basis with anisotropic covariance.

ERI computation: to calculate the electron repulsion integrals, we consider the following decomposition of the Coulomb's kernel $\frac{1}{r} = \sum_i c_i e^{-\alpha_i r^2}$ and solve the following optimization problem

$$\begin{aligned} &\min_{c_i, \alpha_i} \int_{B_M} \left(\frac{1}{|\mathbf{r}|} - \sum_i c_i e^{-\alpha_i |\mathbf{r}|^2} \right)^2 d\mathbf{r} \\ = &\min_{c_i, \alpha_i} 4\pi \int_0^M \left(1 - \sum_i c_i r e^{-\alpha_i r^2} \right)^2 dr. \end{aligned} \tag{2}$$

After solving this optimization offline, one can evaluate the ERI as follows:

$$\begin{aligned} &\langle \mathcal{N}\left(\mathbf{r}_1 | \mu_{\mathbf{1}}, \Sigma_1\right) | \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | \mathcal{N}\left(\mathbf{r}_2 | \mu_{\mathbf{2}}, \Sigma_2\right) \rangle \\ = &\int\int d\mathbf{r} \frac{1}{\sqrt{(2\pi)^6 \det(\Sigma_1) \det(\Sigma_2)}} \sum_i c_i s(i) \\ &\exp\left[-\frac{1}{2} (\mathbf{r} - \mu(i))^T \begin{pmatrix} \Sigma_1^{-1} + 2\alpha_i \mathrm{I} & -2\alpha_i \mathrm{I} \\ -2\alpha_i \mathrm{I} & \Sigma_2^{-1} + 2\alpha_i \mathrm{I} \end{pmatrix} (\mathbf{r} - \mu(i)) \right] \\ = &\sum_i \frac{c_i s(i)}{\sqrt{\det(\Sigma_1) \det(\Sigma_2) / \det(\Sigma(i))}} \end{aligned} \tag{3}$$

Comparing to the classical algorithm for computing the ERI, e.g. MD, HPG, Rys, our framework provide a unique formula for any four-center integral with arbitrary covariance matrices, while classical methods have increasing computational cost for the integral associated with higher angular momentum.

2.1 Theoretical analysis

We optimize the computational cost of the electron repulsion integral, e.g eq. (3) which is the most expensive operations in most of the quantum chemistry calculation. Naive implementation requires solving a 6×6 linear system for each ERI, while we use the special structure of the matrix and Schur complement to reduce the computation to solve two 3×3 linear systems and calculate a 3×3 determinant, corresponding to the second, third, and fifth line of the code below. Furthermore, one of the linear system can be further reduces to a matrix vector product of size 3. The FLOPs count for a single ERI evaluation with one α is around 60, comparing to classical method: (ss|ss), (ps|ps), (pp|pp) requires 33, 58, 1326 FLOPs for a single evaluation. This demonstrate the potential effectiveness of our framework.

3. Numerical experiments

We implement our algorithm for Hartree-Fock method and compare with pyscf package [3] using different basis sets. over several simple systems. It can be conclude that our method is able to achieve similar accuracy with comparable number of basis functions.

	e_tot
OUR (H_2), 10	-1.1334
HF (STO-3G, 2)	-1.1167
HF (6-31G, 4)	-1.1267
HF (6-311G, 6)	-1.1280
OUR (CH_4), 22	-40.1225
HF (STO-3G, 9)	-39.7267
HF (6-31G, 17)	-40.1804
HF (6-311G, 25)	-40.1880
OUR (H_2O), 22	-76.0036
HF (STO-3G, 7)	-74.9630
HF (6-31G, 13)	-75.9839
HF (6-311G, 19)	-76.0094

References

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