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**Mesh-Free Canonical Tensor Products for
Six-Dimensional Density Matrix: Computation of
Kinetic Energy**

by

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Abstract

The computation of a six-dimensional density matrix is the crucial step for the evaluation of kinetic energy in electronic structure calculations. For molecules with heavy nuclei, one has to consider a very refined mesh in order to deal with the nuclear cusps. This leads to high computational time and needs huge memory for the computation of the density matrix. To reduce the computational complexity and avoid discretization errors in the approximation, we use mesh-free canonical tensor products in electronic structure calculations. In this paper, we approximate the six-dimensional density matrix in an efficient way and then compute the kinetic energy. Accuracy is examined by comparing our computed kinetic energy with the exact computation of the kinetic energy.

This article is dedicated to Prof. Dr. Dr. h.c. Wolfgang Hackbusch
in honour of his 65th birthday.

1 Introduction

The well known and very important example for canonical tensor products in quantum chemistry are Gaussian-type orbital (GTO) basis sets [2]. GTO basis sets have been optimized by themselves in atomic calculations. Therefore, GTO basis sets are considered as some kind of generalized tensor product approximation. In recent years, generalized tensor product decompositions without predetermined univariate components attracted considerable interest in numerical mathematics. The main interest in this subject is due to their pleasing algebraic properties and also the possibility to obtain efficient algorithms for high dimensional problems [20, 17, 18, 19, 16]. Concerning the approximation errors of GTO basis sets, rigorous results are available only for the H atom for the single-electron Schrödinger equation. It has already been shown that GTO basis sets achieve almost exponential convergence rates $\sigma_\kappa(\phi_H) \sim e^{-\mu\sqrt{\kappa}}$ for the H atom [23, 3]. Our results for the H atom [6, 9, 7] indicate that Gaussians already provide almost optimal tensor product approximations. GTO basis sets are not only used for the expansion of orbitals but also for the products of orbitals and electron densities. This requires

the so-called auxiliary GTO basis sets which attracted considerable attention within density fitting schemes, also known as resolution of the identity, in order to reduce the computational complexity for Hartree-Fock and Kohn-Sham methods in particular for the Hartree potential [13, 25, 26] and also for two-electron integrals [32, 33, 28]. These density fitting schemes have been further applied to post Hartree-Fock methods [34, 36, 29]. Recently, we have proposed a possible generalization of GTO basis sets by means of canonical tensor products [7]. It has been focussed on the application of tensor product as an alternative to conventional GTO based density fitting schemes to the products of orbitals which extended our very previous work [8], where we discussed mesh-dependent tensor product approximations of the electron density and the Hartree potential. We have used the mesh-dependent canonical tensor product approximation for the computation of the products of orbitals [7, 10]. The orbital products are required for the exchange part of Hartree-Fock and in post Hartree-Fock methods.

Usually, we use the best tensor rank κ -approximation of the orbitals and their products directly for the computation of two-electron integrals [7, 10]. They are the so-called direct orbital products and are not very efficient to treat two-electron integrals. The adaptive computation of the products of orbitals in orthogonal wavelet bases provides an important step towards efficient algorithms for two-electron integrals in tensor product format [10]. For an efficient treatment of two-electron integrals, one can have expansions of the products of orbitals that take the advantage of sparsity and can be computed in an efficient manner. Precisely, one can compute only significant contributions of the expansions and neglect the smaller contributions up to a certain threshold ϵ . Even if we take the advantage of sparsity, the number of basic products increases rapidly for more complicated molecules with heavy nuclei. For molecules with heavy nuclei, one has to consider a very refined grid in order to approximate the sharp cusps at the positions of the nuclei. This leads to high computational time and needs huge memory for the products of three-dimensional orbitals. The computational complexity becomes even worse for the six-dimensional density matrix, which is the sum of all products of orbitals with two different variables. The density matrix is used to compute the kinetic energy in electronic structure calculations and average or expectation values of some physical quantities in modern atomic physics [1].

It is very common to evaluate the kinetic energy on a regular mesh [21, 24, 30]. In large scale calculations, numerical evaluation of both the gradient and Laplacian operators on a regular mesh can increase the computational time. It has been showed that optimization of time can be achieved if the kinetic energy is computed using the gradient operator [21]. Later, Skylaris *et al.* [30] presented a method for evaluating the kinetic energy for localized functions represented on a regular mesh using the fast Fourier transform. The localized functions are centred at atomic positions and required to be non-zero only within the spherical region. These localized functions are represented on a grid, which is usually called the real-space grid in electronic structure calculations [5, 4]. The real-space grid methods became popular in density functional calculations [4, 24]. These real-space grid methods use finite difference approaches [15] for evaluation of the kinetic energy. For well behaved functions, the second order partial derivative should converge to the exact Laplacian as the grid size tends to zero. Therefore, one needs to have a smaller grid space in order to achieve high accuracy [30]. At the same time, one has to pay a lot for that. Besides, in finite difference methods, we do not know in advance whether a particular order of finite difference approximation is sufficient to represent a particular localized function accurately. As actual physical systems are inhomogeneous, it makes really sense to use adaptive mesh which takes a refined grid near the positions of nuclei. A regular mesh can be used in curvilinear coordinates in order

to obtain an adaptive mesh in Cartesian coordinates [27]. The curvilinear coordinates are a coordinate system for the Euclidean space in which the coordinate lines may be curved. The curvilinear coordinates can be derived from a set of Cartesian coordinates by using a transformation that is locally invertible at each point. Therefore, one can convert a point given in a curvilinear coordinate system to Cartesian coordinate system and vice-versa. Such a scheme, however, has the overhead of transformation of Laplacian from Cartesian coordinates to curvilinear coordinates [27]. Therefore, the complicated molecules with heavy nuclei are much more challenging even for the adaptive mesh. Because, one has to consider a very refined mesh in order to approximate the sharp cusps at the positions of the nuclei. This leads to high computational time and needs huge memory. In order to reduce the computational overhead and avoid discretization errors in the approximation, we use mesh-free canonical tensor product approximation to the density matrix and then compute the kinetic energy in a straightforward way.

2 The density matrix

The density matrix is a six-dimensional and one of the most complicated quantities in electronic structure calculations. It can be used to compute the kinetic energy of single-, and many-electron systems. The evaluation of average or expectation values of physical quantities characterizing the many-electron systems is very difficult without use of the density matrix. Therefore, the application of the density matrix is getting more and more importance also in modern atomic physics [1]. The density matrix for N -electron system is defined as

$$\rho(\mathbf{x}, \mathbf{y}) = 2 \sum_{a=1}^{N/2} \Psi_a(\mathbf{x}) \Psi_a(\mathbf{y}), \quad (1)$$

where

$$\Psi_a(\mathbf{x}) = \sum_{i=1}^K c_i^a \prod_{\eta=1}^3 \psi_i^{(\eta)}(x_\eta) \quad (2)$$

with

$$\psi_i^{(\eta)}(x_\eta) = (x_\eta - A_{\eta,i})^{l_{\eta,i}} e^{-\alpha_i(x_\eta - A_{\eta,i})^2}. \quad (3)$$

Here, $\Psi_a(\mathbf{x})$ is a spatial orbital, i.e., a single-electron wavefunction taking only spatial coordinates, i.e., $\mathbf{x} = (x_1, x_2, x_3)$ as its parameters. $\psi_i^{(\eta)}(x_\eta)$ for $\eta = 1, 2, 3$ are univariate components of the spatial orbital $\Psi_a(\mathbf{x})$. $A_{\eta,i}$ are the centres of the Gaussians; $l_{\eta,i}$ are the polynomial degrees; c_i^a are the coefficients including normalization constants, and α_i are the exponents of the Gaussians. It should also be mentioned that K is the initial rank, i.e., the total number of Gaussians used to represent the spatial orbital $\Psi_a(\mathbf{x})$. Then the density matrix becomes

$$\rho(\mathbf{x}, \mathbf{y}) = \sum_{i=1}^K \sum_{j=1}^K d_{ij} \prod_{\eta=1}^3 \rho_{ij}^{(\eta)}(x_\eta, y_\eta), \quad (4)$$

where

$$d_{ij} = 2 \sum_{a=1}^{N/2} c_i^a c_j^a, \quad (5)$$

$$\begin{aligned}\rho_{ij}^{(\eta)}(x_\eta, y_\eta) &:= \psi_i^{(\eta)}(x_\eta) \psi_j^{(\eta)}(y_\eta) \\ &= (x_\eta - A_{\eta,i})^{l_{\eta,i}} (y_\eta - A_{\eta,j})^{l_{\eta,j}} e^{-\alpha_i(x_\eta - A_{\eta,i})^2} e^{-\alpha_j(y_\eta - A_{\eta,j})^2},\end{aligned}\quad (6)$$

Here, $\rho_{ij}^{(\eta)}(x_\eta, y_\eta)$ for $\eta = 1, 2, 3$ are two-dimensional components of the density matrix. Usually, in our previous works [8, 7, 10], we discretized each of such components on a uniform mesh with spacing h which must be less than the standard deviation σ obtained from the largest exponent α_i of the GTO basis set. Therefore, the computational complexity to handle the density matrix $\rho(\mathbf{x}, \mathbf{y})$ is $\mathcal{O}(3N_g^2 K^2)$, where N_g^2 is the total number of grid points used to represent each two-dimensional component of the density matrix. For more complicated molecules, especially those including the heavy elements, we need to consider the very refined mesh in order to make sure that $h < \sigma$ and then approximate the cusps at the positions of the nuclei. This leads to a large number of grid points and huge computational costs. To avoid the huge computational costs and discretization errors, mesh-free canonical tensor products to approximate the density matrix would be a good alternative to the mesh-dependent approach in electronic structure calculations. The mesh-free approach requires a procedure which includes a systematic and clever way to handle the density matrix.

3 Procedure to handle the density matrix and its approximation

For handling of the density matrix, we first discuss the handling of an univariate function without discretization and then generalize it to the density matrix. In electronic structure calculations, the functions are usually normalized. But they are not orthogonal to each other. This leads to a non-diagonal overlap matrix S [31]. For a set of functions $\{\Phi_\mu\}$,

$$S_{\mu\nu} = \int \Phi_\mu(\mathbf{x}) \Phi_\nu(\mathbf{x}) d\mathbf{x} := (\Phi_\mu, \Phi_\nu) \quad (7)$$

are the entries of S . It is always possible to find a transformation matrix X such that the transformed set of functions $\{\varphi'_\mu\}$, defined by

$$\varphi'_\mu = \sum_{\nu=1}^K X_{\nu\mu} \Phi_\nu, \quad \mu = 1, \dots, K \quad (8)$$

forms an orthonormal set, i.e.,

$$\int \varphi'_\mu(\mathbf{x}) \varphi'_\nu(\mathbf{x}) d\mathbf{x} = \delta_{\mu\nu}. \quad (9)$$

The transformation matrix X is defined as

$$X = U s^{-1/2}, \quad (10)$$

where U is an orthogonal matrix and s is the diagonal matrix of the eigenvalues of S . This kind of procedure to orthogonalize the basis set is the so-called canonical orthogonalization [31]. Any given univariate function Φ_j is written as a linear combination of the orthonormal set $\{\varphi'_n\}_{n=1, \dots, K}$, i.e.,

$$\Phi_j = \sum_{n=1}^K \beta_{nj} \varphi'_n, \quad j = 1, \dots, K. \quad (11)$$

The coefficients β_{nj} can be obtained by multiplying both sides of Eq. (11) by φ_i' , then we have

$$\beta_{ij} = (\Phi_j, \varphi_i'), \quad i, j = 1, \dots, K. \quad (12)$$

Using the transformed functions (8), the coefficients β_{ij} can be obtained by

$$\beta_{ij} = \sum_{\nu=1}^K X_{\nu i} (\Phi_j, \Phi_\nu). \quad (13)$$

It is enough to approximate only the coefficients β_{ij} rather than the discrete representation of the function Φ_j in canonical tensor product format [8, 7, 10]. It means that we work directly in the function space instead of discrete representations. Now we generalize the procedure of handling the univariate functions (4). For this, we first compute the overlap integrals of the components of the density matrix, i.e.,

$$S_{ij, i'j'}^{(\eta)} = (\rho_{ij}^{(\eta)}, \rho_{i'j'}^{(\eta)}) =: \int_{\mathbb{R}} \int_{\mathbb{R}} \rho_{ij}^{(\eta)}(x_\eta, y_\eta) \rho_{i'j'}^{(\eta)}(x_\eta, y_\eta) dx_\eta dy_\eta \quad (14)$$

for $\eta = 1, 2, 3$, which are given as

$$\begin{aligned} S_{ij, i'j'}^{(\eta)} &= \int_{\mathbb{R}} \int_{\mathbb{R}} (x_\eta - A_{\eta, i})^{l_{\eta, i}} (y_\eta - A_{\eta, j})^{l_{\eta, j}} (x_\eta - A_{\eta, i'})^{l_{\eta, i'}} (y_\eta - A_{\eta, j'})^{l_{\eta, j'}} \\ &\quad \times e^{-\alpha_i (x_\eta - A_{\eta, i})^2} e^{-\alpha_j (y_\eta - A_{\eta, j})^2} e^{-\alpha_{i'} (x_\eta - A_{\eta, i'})^2} e^{-\alpha_{j'} (y_\eta - A_{\eta, j'})^2} dx_\eta dy_\eta. \end{aligned} \quad (15)$$

The overlap integrals can be computed analytically [12]. For simplicity, we rearrange the four-index overlap integrals $S_{ij, i'j'}^{(\eta)}$ to two-index overlap integrals $S_{nn'}^{(\eta)}$ and components of two-index density matrices with matrix elements $\rho_{ij}^{(\eta)}$ to univariate components $\rho_n^{(\eta)}$ for $\eta = 1, 2, 3$. Then $\rho_n^{(\eta)}$ can be written as

$$\rho_n^{(\eta)} = \sum_{i=1}^{K^2} \beta_{in}^{(\eta)} \varrho_i^{(\eta)}, \quad n = 1, \dots, K^2, \quad (16)$$

where $\{\varrho_i^{(\eta)}\}_{i=1, \dots, K^2}$ is an orthonormal set. For the tensor product approximation, the coefficients $\beta_{in}^{(\eta)}$ are obtained by using the respective overlap and transformation matrix elements, i.e.,

$$\beta_{ij}^{(\eta)} = \sum_{\nu=1}^{K^2} X_{\nu i}^{(\eta)} S_{j\nu}^{(\eta)}. \quad (17)$$

To improve the efficiency, we can also use a truncated transformation matrix $\tilde{X}^{(\eta)}$. In order to obtain $\tilde{X}^{(\eta)}$, we can consider only $K^2 - m$ eigenvectors corresponding to the significant eigenvalues of the diagonal matrix $s^{(\eta)}$. As our components of the density matrix represented in the orthonormal set (16), we now look for the best possible approximation of the density matrix $\rho(\mathbf{x}, \mathbf{y})$ in $\mathbb{R}^6$ using only the coefficient matrices $\beta^{(\eta)}$ in the sense of canonical tensor format [8, 7, 10], i.e.,

$$\rho(\mathbf{x}, \mathbf{y}) \approx \sum_{n=1}^{\kappa} \prod_{\eta=1}^3 \tilde{\rho}_n^{(\eta)}(x_\eta, y_\eta) := \tilde{\rho}(\mathbf{x}, \mathbf{y}), \quad (18)$$

for fixed separation rank κ . The approximated univariate components

$$\tilde{\rho}_n^{(\eta)} = \sum_{i=1}^{K^2-m} \tilde{\beta}_{in}^{(\eta)} \varrho_i^{(\eta)}, \quad n = 1, \dots, \kappa \quad (19)$$

for $\eta = 1, 2, 3$ have to be chosen in an “optimal” manner, where $\tilde{\beta}^{(\eta)}$ is the approximated coefficient matrix of the original coefficient matrix $\beta^{(\eta)}$. Such an approximation by a tensor product of a certain rank became known as canonical decomposition [22]. In the following we refer to κ as the tensor rank, which denotes the least possible decomposition rank of a tensor. We apply the more general notion of a separation rank to mesh-free tensor product decompositions (18) for which the rank is supposed to be suboptimal. The error of a best representation rank- κ approximation is defined via the least-squares problem

$$\sigma_\kappa(\rho) := \inf_{\tilde{\rho}_n^{(\eta)} \in L^2(\mathbb{R}^2)} \left\| \rho - \sum_{n=1}^{\kappa} \tilde{\rho}_n^{(1)} \otimes \tilde{\rho}_n^{(2)} \otimes \tilde{\rho}_n^{(3)} \right\|_{L^2(\mathbb{R}^6)}, \quad (20)$$

where the error is measured in the L^2 norm, i.e., $\|\rho\|_{L^2}^2 := \int \int |\rho(\mathbf{x}, \mathbf{y})|^2 d\mathbf{x} d\mathbf{y}$. The symbol $\otimes$ is used for an abstract tensor product among univariate components without the explicit reference to the variables. Our present algorithm for the least-squares problem (20) is the regularized Newton’s method [16] where the solution of the algorithm is a local best approximation of tensor represented in the canonical tensor format. Like for every iterative process for nonlinear optimisation, the choice of initial guess has an influence on the resulting approximation. The choice of the initial guess is very important. Therefore, there are techniques for improving the initial guess. One can choose the initial guess with different ranks for this kind of optimization problems to improve the accuracy of the resulting local best approximation. In [14, 16], a method was discussed that creates an initial guess by successive computation of the rank-one cross approximation which works fine for general cases. However, we have improved the choice of initial guesses adapted to our problem and gained a better accuracy for the resulting approximation. For this, we first construct the following auxiliary tensors

$$u = \sum_{l=1}^{K^2/2} \prod_{\eta=1}^3 \rho_l^{(\eta)} \quad \text{and} \quad v = \sum_{l=K^2/2+1}^{K^2} \prod_{\eta=1}^3 \rho_l^{(\eta)}, \quad (21)$$

and then obtain by a regularized Newton’s method their best representation rank- κ approximations

$$u \approx \tilde{u} = \sum_{l=1}^{\kappa} \prod_{\eta=1}^3 \tilde{u}_l^{(\eta)} \quad \text{and} \quad v \approx \tilde{v} = \sum_{l=1}^{\kappa} \prod_{\eta=1}^3 \tilde{v}_l^{(\eta)}. \quad (22)$$

The improved initial guess for our density matrix ρ is obtained as

$$\rho_{IG} = \sum_{l=1}^{r_1} \prod_{\eta=1}^3 \tilde{u}_l^{(\eta)} + \sum_{l=1}^{r_2} \prod_{\eta=1}^3 \tilde{v}_l^{(\eta)}, \quad r_1, r_2 \leq \kappa. \quad (23)$$

Here, the rank of the improved initial guess r_{IG} for ρ_{IG} is $r_1 + r_2$. The methods to create the initial guess to improve the quality of the approximation are explained in [14, 16].

By using the transformed set of basis functions

$$\varrho_i^{(\eta)} = \sum_{\nu=1}^{K^2} \tilde{X}_{\nu i}^{(\eta)} \rho_{\nu}^{(\eta)}, \quad i = 1, \dots, K^2 - m, \quad (24)$$

we can represent the approximated univariate components $\tilde{\rho}_n^{(\eta)}$ in terms of original univariate components $\rho_{\nu}^{(\eta)}$, i.e.,

$$\tilde{\rho}_n^{(\eta)} = \sum_{\nu=1}^{K^2} \gamma_{\nu n}^{(\eta)} \rho_{\nu}^{(\eta)}, \quad n = 1, \dots, \kappa, \quad (25)$$

where

$$\gamma_{\nu n}^{(\eta)} = \sum_{i=1}^{K^2-m} \tilde{X}_{\nu i}^{(\eta)} \tilde{\beta}_{in}^{(\eta)}, \quad \nu = 1, \dots, K^2. \quad (26)$$

In order to compute the kinetic energy, we need to have the approximated density matrix in terms of original univariate components. It is given as the following

$$\begin{aligned} \rho(\mathbf{x}, \mathbf{y}) \approx \tilde{\rho}(\mathbf{x}, \mathbf{y}) &= \sum_{n=1}^{\kappa} \left[\left(\sum_{\nu=1}^{K^2} \gamma_{\nu n}^{(1)} \rho_{\nu}^{(1)}(x_1, y_1) \right) \left(\sum_{\nu=1}^{K^2} \gamma_{\nu n}^{(2)} \rho_{\nu}^{(2)}(x_2, y_2) \right) \right. \\ &\quad \left. \times \left(\sum_{\nu=1}^{K^2} \gamma_{\nu n}^{(3)} \rho_{\nu}^{(3)}(x_3, y_3) \right) \right]. \end{aligned} \quad (27)$$

For this representation, the computational cost is $\mathcal{O}(3\kappa K^2)$, where κ is the final tensor rank which should be small. Having had the approximated density matrix in terms of the original components of the density matrix, one can compute the kinetic energy of many-electron systems in a straightforward way.

4 Computation of the kinetic energy

In quantum chemistry and quantum physics, we need to compute the kinetic energy of many-electron systems. Such a computation involves the evaluation of the Laplacian of the density matrix. As orbitals are represented as a linear combination of GTO basis functions, the analytical form of the density matrix is known in advance. Therefore, it is possible to compute the analytical or exact kinetic energy of many-electron systems. The approximated density matrix (27), can also be represented in terms of original univariate components (16), is used for the approximation of the kinetic energy of many-electron systems.

4.1 Analytical kinetic energy

The kinetic energy of many-electron system is

$$T = -\frac{1}{2} \int_{\mathbb{R}^3} \left(\Delta_{\mathbf{x}} \rho(\mathbf{x}, \mathbf{y}) \right) \Big|_{\mathbf{y}=\mathbf{x}} d\mathbf{x}. \quad (28)$$

It requires the action of the Laplacian $\Delta_{\mathbf{x}}$ on the density matrix $\rho(\mathbf{x}, \mathbf{y})$. Once we have obtained the action of the Laplacian on the density matrix, we need to substitute $\mathbf{y} = \mathbf{x}$

before going to evaluate the integral. It should be mentioned here that $\mathbf{x} = (x_1, x_2, x_3)$ and $\mathbf{y} = (y_1, y_2, y_3)$. As we have the analytical form for the density matrix (4), we can compute the analytical kinetic energy

$$\begin{aligned} T &= -\frac{1}{2} \int_{\mathbb{R}^3} \left[\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) \sum_{i=1}^K \sum_{j=1}^K d_{ij} \prod_{\eta=1}^3 \rho_{ij}^{(\eta)}(x_\eta, y_\eta) \right] \Big|_{\mathbf{y}=\mathbf{x}} d\mathbf{x} \\ &= -\frac{1}{2} \sum_{i=1}^K \sum_{j=1}^K d_{ij} \left[T_{ij}^{(1)} + T_{ij}^{(2)} + T_{ij}^{(3)} \right], \end{aligned} \quad (29)$$

where

$$T_{ij}^{(\eta)} = \int_{\mathbb{R}^3} \frac{\partial^2}{\partial x_\eta^2} \left(\rho_{ij}^{(1)}(x_1, y_1) \rho_{ij}^{(2)}(x_2, y_2) \rho_{ij}^{(3)}(x_3, y_3) \right) \Big|_{\mathbf{y}=\mathbf{x}} d\mathbf{x}. \quad (30)$$

In order to compute $T_{ij}^{(\eta)}$ for $\eta = 1, 2, 3$, we need to have the partial derivatives of components of the density matrix (6). Once we have obtained the second-order partial derivative of component of the density matrix $\rho_{ij}^{(\eta)}(x_\eta, y_\eta)$ and have taken $\mathbf{y} = \mathbf{x}$, we then end up with the equation which contains the basic integrals of the following form

$$I = \int_{\mathbb{R}} (x_\eta - A_{\eta,i})^{l_{\eta,i}} (x_\eta - A_{\eta,j})^{l_{\eta,j}} e^{-\alpha_i(x_\eta - A_{\eta,i})^2} e^{-\alpha_j(x_\eta - A_{\eta,j})^2} dx_\eta. \quad (31)$$

The basic integrals can be computed analytically [12]. It should also be mentioned that the overlap integrals, i.e., Eq. (15), can also be computed analytically by taking each of them as a product of two basic integrals of the form (31) and by following the same procedure. We can compute all basic integrals and then $T_{ij}^{(\eta)}$ for $\eta = 1, 2, 3$ analytically. Finally, we can compute the analytical kinetic energy (29) of many-electron systems in a straightforward way.

4.2 Approximation of the kinetic energy

We have already discussed the procedure how we can handle and approximate the density matrix in Section 3. As kinetic energy is a very sensitive quantity, we also incorporate the mixed partial derivatives to the overlap integrals (15),

$$\begin{aligned} S_{ij,i'j'}^{(\eta)} &= \int_{\mathbb{R}} \int_{\mathbb{R}} \rho_{ij}^{(\eta)}(x_\eta, y_\eta) \rho_{i'j'}^{(\eta)}(x_\eta, y_\eta) dx_\eta dy_\eta \\ &\quad + \lambda \int_{\mathbb{R}} \int_{\mathbb{R}} \frac{\partial \rho_{ij}^{(\eta)}(x_\eta, y_\eta)}{\partial x_\eta} \frac{\partial \rho_{i'j'}^{(\eta)}(x_\eta, y_\eta)}{\partial x_\eta} dx_\eta dy_\eta \\ &\quad + \lambda \int_{\mathbb{R}} \int_{\mathbb{R}} \frac{\partial \rho_{ij}^{(\eta)}(x_\eta, y_\eta)}{\partial y_\eta} \frac{\partial \rho_{i'j'}^{(\eta)}(x_\eta, y_\eta)}{\partial y_\eta} dx_\eta dy_\eta, \end{aligned} \quad (32)$$

in order to compute the coefficients (17) of the coefficient matrix $\beta^{(\eta)}$ for $\eta = 1, 2, 3$. Here, λ is an auxiliary parameter which should be chosen small enough. Even if we take the mixed partial derivatives of the components of the density matrix, we end up with equations which contain the basic integrals of the form (31). These basic integrals can be computed analytically [12]. The kinetic energy from the approximated density matrix is

$$T \approx \tilde{T} = -\frac{1}{2} \int_{\mathbb{R}^3} \left(\Delta_{\mathbf{x}} \tilde{\rho}(\mathbf{x}, \mathbf{y}) \right) \Big|_{\mathbf{y}=\mathbf{x}} d\mathbf{x}$$

$$\begin{aligned}
= & -\frac{1}{2} \sum_{n=1}^{\kappa} \int_{\mathbb{R}^3} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) \left[\left(\sum_{\nu=1}^{K^2} \gamma_{\nu n}^{(1)} \rho_{\nu}^{(1)}(x_1, y_1) \right) \right. \\
& \left. \times \left(\sum_{\nu=1}^{K^2} \gamma_{\nu n}^{(2)} \rho_{\nu}^{(2)}(x_2, y_2) \right) \left(\sum_{\nu=1}^{K^2} \gamma_{\nu n}^{(3)} \rho_{\nu}^{(3)}(x_3, y_3) \right) \right] \Big|_{\mathbf{y}=\mathbf{x}} d\mathbf{x}. \quad (33)
\end{aligned}$$

We rearrange the indices of univariate components of the density matrix $\{\rho_{\nu}^{(\eta)}(x_{\eta}, y_{\eta})\}_{\nu=1, \dots, K^2}$ to two-index quantity, i.e., $\{\rho_{ij}^{(\eta)}(x_{\eta}, y_{\eta})\}_{i,j=1, \dots, K}$. Then, we end up with the equation containing the integrals of the form (30). These integrals can be computed very easily. We can then compute the approximated kinetic energy of any given many-electron system.

4.3 Numerical tests

For numerical tests, we first solve the Hartree-Fock equations [31] of the LiH and CH₄ molecules by using MOLPRO [35] with valence double zeta (VDZ) basis set. MOLPRO is a standard quantum chemistry package used for electronic structure calculations. The solutions of Hartree-Fock equations are the spatial orbitals and are represented as a linear combinations of polynomials times the Cartesian Gaussian functions (2). LiH and CH₄ molecules have 2 and 5 spatial orbitals respectively. Using the spatial orbitals of any given molecule, we compute the density matrix (1). Fig. 1 shows the $x_1 y_1$ -plane of the density matrix $\rho(\mathbf{x}, \mathbf{y})$ passing through the origin for the LiH molecule. It can be seen from Fig. 1 that there is a sharp peak at the origin where the Li nucleus is sitting. As kinetic energy is considered to be a very sensitive quantity, we also incorporate the mixed partial derivatives to the overlap integrals (32) with the parameter $\lambda = 0.5$ and $\lambda = 1.0$. Once we have had the density matrix, we then obtain the best representation rank- κ approximations of the density matrix. Fig. 2 shows the absolute errors, i.e., $|T - \tilde{T}|$, in $x_1 y_1$ -plane of the density matrix passing through the origin for the LiH molecule at tensor rank $\kappa = 50$ and the parameter $\lambda = 0$ by using regularized Newton's method [16] without improved initial guess. Fig. 3 and Fig. 4 show the absolute errors in $x_1 y_1$ -plane of the density matrix passing through the origin for the LiH molecule at tensor rank $\kappa = 50$ and the parameter $\lambda = 0.5$ by using regularized Newton's method with the improved initial guess [14, 16] with rank $r_{IG} = 25$ and rank $r_{IG} = 36$ respectively. It should also be mentioned that the scale of Fig. 2 and Fig. 3 changes by three order of magnitude. Having had the best representation rank- κ approximations of the density matrix, we compute the approximation of the kinetic energy (33) in our mesh-free approach. The accuracy is examined by comparing our computed kinetic energy (33) with the exact computation of the kinetic energy (29). Table 1 shows the accuracy of the kinetic energy for the LiH molecule for improved initial guess with rank r_{IG} and the parameter λ . The accuracy of the kinetic energy for the CH₄ molecule for improved initial guess with rank r_{IG} and the parameter λ can be shown in Table 2. As we can see from Table 1 and Table 2, the parameter $\lambda = 0.5$ seems to be the "suboptimal" at higher tensor ranks. It has already been observed in our approximate correlation function calculations [11] that the parameter $\lambda = 0.5$ is almost "optimal" and the mixed partial derivatives play an important role to improve the accuracy of the approximation.

Figure 1: x_1y_1 -plane of the density matrix $\rho(\mathbf{x}, \mathbf{y})$ passing through the origin for the LiH molecule.

Figure 2: Absolute errors in x_1y_1 -plane of the density matrix $\rho(\mathbf{x}, \mathbf{y})$ passing through the origin for the LiH molecule at tensor rank $\kappa = 50$ and the parameter $\lambda = 0$ by using regularized Newton's method without improved initial guess.

Figure 3: Absolute errors in $x_1 y_1$ -plane of the density matrix $\rho(\mathbf{x}, \mathbf{y})$ passing through the origin for the LiH molecule at tensor rank $\kappa = 50$ and the parameter $\lambda = 0.5$ by using regularized Newton's method with the improved initial guess with rank $r_{IG} = 25$.

Figure 4: Absolute errors in $x_1 y_1$ -plane of the density matrix $\rho(\mathbf{x}, \mathbf{y})$ passing through the origin for the LiH molecule at tensor rank $\kappa = 50$ and the parameter $\lambda = 0.5$ by using regularized Newton's method with the improved initial guess with rank $r_{IG} = 36$.

Table 1: Absolute error in the kinetic energy, i.e., $|T - \tilde{T}|$, obtained from the mesh-free canonical tensor product approximation for the LiH molecule using regularized Newton’s method with the improved initial guess with rank r_{IG} and the parameter λ .

Tensor rank κ	$ T - \tilde{T} $	$ T - \tilde{T} $	$ T - \tilde{T} $	$ T - \tilde{T} $
	$r_{IG} = 25$	$r_{IG} = 25$	$r_{IG} = 36$	$r_{IG} = 36$
	$\lambda = 1.0$	$\lambda = 0.5$	$\lambda = 1.0$	$\lambda = 0.5$
	(hartree)	(hartree)	(hartree)	(hartree)
30	9.96E-02	8.27E-02		
40	8.71E-02	7.92E-02	8.25E-03	5.93E-03
50	7.10E-02	6.87E-03	5.38E-03	4.73E-03
60	1.62E-02	2.99E-03	3.17E-03	6.70E-04
70	2.50E-03	1.53E-03	9.49E-04	5.59E-04
80	9.99E-04	8.98E-04	9.13E-04	4.48E-04
90	8.31E-04	6.16E-04	7.89E-04	4.24E-04
100	6.88E-04	8.96E-05	6.15E-04	6.56E-05

Table 2: Absolute error in the kinetic energy, i.e., $|T - \tilde{T}|$, obtained from the mesh-free canonical tensor product approximation for the CH₄ molecule using regularized Newton’s method with the improved initial guess with rank r_{IG} and the parameter λ .

Tensor rank κ	$ T - \tilde{T} $	$ T - \tilde{T} $	$ T - \tilde{T} $	$ T - \tilde{T} $
	$r_{IG} = 36$	$r_{IG} = 36$	$r_{IG} = 49$	$r_{IG} = 49$
	$\lambda = 1.0$	$\lambda = 0.5$	$\lambda = 1.0$	$\lambda = 0.5$
	(hartree)	(hartree)	(hartree)	(hartree)
40	9.77E-02	8.88E-02		
50	9.19E-02	8.03E-03	8.32E-03	7.10E-03
60	7.04E-02	6.09E-03	7.00E-03	5.99E-03
70	8.76E-03	4.68E-03	5.09E-03	9.69E-04
80	4.10E-03	2.03E-03	2.79E-03	9.00E-04
90	1.54E-03	7.20E-04	7.43E-04	6.19E-04
100	8.64E-04	5.89E-04	7.00E-04	8.85E-05

5 Conclusions

The density matrix can be approximated in an efficient way for the computation of kinetic energy in electronic structure calculations by using mesh-free canonical tensor products. Mesh-free canonical tensor product approximation seems to be a good alternative to the mesh-dependent canonical tensor product approximation. Mesh-free canonical tensor products avoid the computation of the huge number of basic products on a refined grid in order to obtain the approximation of the six-dimensional density matrix. The computational complexity

of the mesh-dependent approach is $\mathcal{O}(3N_g^2K^2)$, where as in the mesh-free approach the computational complexity is $\mathcal{O}(3\kappa K^2)$. Here, the tensor rank satisfies $\kappa \ll K^2$ and $K^2 \ll N_g^2$. For heavy elements, one has to consider a very refined mesh in order to approximate the sharp cusps at the positions of the nuclei. Therefore, for molecules with heavy elements, one can benefit considerably from the mesh-free canonical tensor product approximation for the density matrix. Accuracy can be improved further by choosing the best parameter. It seems that the parameter $\lambda = 0.5$ is “suboptimal” and mixed partial derivatives play an important role to improve the accuracy of the kinetic energy which is considered to be a very sensitive quantity in electronic structure calculations.

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