

# Concepts and Experiences of Density Matrix Optimization

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*Abstract: The second-order reduced density matrix is a basic tool for describing quantum mechanical systems. In addition to its numerous advantage, we meet a basic difficulty when using density matrix. Because of the so-called N-representability problem the free variation of it is not possible in quantum mechanical calculation. In this study the problem is sketched, and recent results are overviewed.*

*In our considerations second order reduced density matrix is expanded in geminal basis. First an obvious technique for optimization of density matrix is described including parameters of the underlying wave function for ensuring the exact N-representability. Then a set of necessary N-representability condition is derived in a form, which contains only the elements of density matrix, and no parameters of the wave function.*

## 1 Introduction

The basic problem of molecular physics is to solve the time independent Schrödinger equation. This is a second-order differential equation of the wave function  $\Psi$ , which is a complex function of  $4N$  real variables, where  $N$  is the number of particles in the quantum mechanical system.

$$\hat{H}\Psi = E\Psi \quad (1)$$

$\hat{H}$  is the Hamiltonian operator (s differential operator),  $E$  is an eigenvalue of  $\hat{H}$ , the energy of the system. This equation can be solved exactly only for the simplest “molecular system”, the hydrogen atom. For real molecules we have to use numerical methods for the approximation of the exact wave function. Wave function (if it is known) gives full description of the system

Generally we have to use an enormous number of parameters of the approximate wave functions making it as flexible as it is possible, and being able to taking account an acceptable amount of correlation energy. Numerical methods based on

the variational principle, so our task, in mathematical sense, is minimizing the energy as a function of many-many variables.

Second order reduced density matrix gives full description of a quantum-mechanical system involving at most two-particle interactions in the most compact form. It has more less parameter than the corresponding wave function. The idea is clear, that wave function should be relieved by second order density matrix.

Density matrices already appears in works of John von Neumann.

The first attempt of optimizing density matrix ended in failure (Hushimi, Coleman). The reason for this is the so-called N-representability problem, what proved to be a really complicated, and hard mathematical task in the last half century, and remained unsolved up till now. It means, that the mapping from the space of wave functions to density matrices is injective, and we are not able to formulate conditions for testing which density matrix is derivable from a wave function (in other words which describe a real physical system), and which does not.

The development of the concept of Contracted Schrödinger Equation opened a new method in quantum chemistry, serving results comparable with those of truncated CI methods (SDCI). At the same time the exact N-representability is not ensured by this method. Really one could almost say, that the error in energy caused by not taking into account completely of electron correlation when approximating wave function, is replaced to the error in CSE theory due to not ensuring perfect N-representability. The reader can find a good summary on density matrices and many-electron densities in reference [1].

Recently perturbation theory corrections were published for correcting the error of the energy obtained by minimizing the density matrix directly applying the known conditions of N-representability [2], and variational calculations were performed for density matrices of bosonic systems including harmonic interactions showing that two-positivity may be exact for them [3].

## **2 Second Order Reduced Density Matrix in Geminal Basis**

Our approach of the N-representability problem is an attempt to clarify the structural connection of second order reduced density matrix with the wave function from which it can be derived by definition. Of course a lot of types of approximate wave functions are used in molecular physics, our study uses the most general form. The most general approximation of the wave function of a system consisted of N fermions, in a finite dimensional subspace of the Hilbert-space is the so-called full-CI wave function:

$$\Psi = \sum_{\alpha=1}^{\mu} c_{\alpha} \Phi_{\alpha}, \quad \mu = \binom{M}{N} \quad (2)$$

where  $\Psi$  denotes the N-electron wave function, functions  $\{\Psi_{\alpha}\}_{\alpha=1,\dots,\mu}$  are Slater-determinants forming a bases of the subspace. We assume, that Slater-determinants are constructed over an M-dimensional orthonormal one-particle bases  $\{\varphi_i(1)\}_{i=1,\dots,M}$ . The number of determinants is  $\binom{M}{N}$ , determinants are orthogonal, and each of them has the norm of  $N!$  (! means factorial). The two-electron density matrix  $\left(\Gamma^{(2)}\right)$  is defined by the formula

$$\Gamma^{(2)}(1,2;1',2') = \int \Psi(1,2,3,\dots,N) \Psi^*(1',2',3,\dots,N) d3\dots dN. \quad (3)$$

Although the nomination “density matrix” is widely used for this quantity, really it is the kernel of an integral operator, the so-called density operator. In the followings we call it density matrix, as it is usual. Inserting the linear combination (2) into (3), after the Laplace-expansion of the determinants the density matrix has the form:

$$\Gamma^{(2)}(1,2;1',2') = \sum_{i<j,k<l}^M g_{i,j}(1,2) \Theta_{i,j;k,l} g_{k,l}^*(1',2'), \quad (4)$$

where  $g_{i,j}(1,2) = \psi_i(1)\psi_j(2) - \psi_i(2)\psi_j(1)$ ,  $i < j$  is an anti-symmetrized two-electron function (geminal), and

$$\Theta_{i,j;k,l} = \frac{1}{N!} \sum_{\alpha,\beta=1}^{\mu} c_{\alpha} c_{\beta}^* \int {}^{\alpha} g_{i,j}^+(3,\dots,N) {}^{\beta} g_{k,l}^{+*}(3,\dots,N) d3\dots dN. \quad (5)$$

The  ${}^{\alpha} g_{i,j}^+(3,\dots,N)$  denotes the adjoint geminal of  $g_{i,j}(1,2)$  in Slater-determinant  $\Phi_{\alpha}$ . The second-order reduced density matrix is given in geminal basis by formula (4).

### 3 The Energy Expression

It is known, that the energy of the quantum-mechanical system can be expressed by the density matrix:

$$E = \frac{Tr\{K\Theta\}}{Tr\{\Theta\}} \quad (6)$$

Here  $K$  is the matrix of the co-called reduced Hamiltonian in geminal basis,  $\text{Tr}$  means trace. The formula (5) shows the functional connection between the parameters of the wave function ( $c_\alpha$ ) and the elements of density matrix in geminal basis ( $\Theta$ ). We can consider the energy as a functional of  $c_\alpha$  coefficients.

$$E(\vec{c}) = \frac{\text{Tr}\{K\Theta(\vec{c})\}}{\text{Tr}\{\Theta\}} \quad (7)$$

Eventually we can optimize the density matrix so that it minimizes the energy. Optimization of density matrices have really good convergence properties, results were published in papers [4, 5, 6, 7]. It is noted, that the optimization can be performed with any other target function.

## 4 The Structure of Density Matrix

Let us rearrange the position of coefficients  $c_\alpha$  and  $c_\beta$  in (5):

$$\Theta_{i,j;k,l} = \frac{1}{N!} \sum_{\alpha,\beta=1}^M \int c_\alpha^\alpha g_{i,j}^+(3,\dots,N) c_\beta^{*\beta} g_{k,l}^{+*}(3,\dots,N) d3\dots dN.. \quad (8)$$

While determinants  $\Phi_\alpha$  are N-electron functions, we can identify them by an index-set  $I_\alpha$  containing ordered indices of one-electron functions from which the determinant is built up. In the set  $I_\alpha$  there are N piece of integers between 1 and M,  $I_\alpha = \{\alpha_1, \alpha_2 \dots \alpha_N\}$ . Similarly, the adjoint geminals can be identified with index sets  $I_\lambda$  containing N-2 piece of integers sequentially. Really, the denomination ‘‘adjoint geminal’’ is for the relationship with the N-electron Slater determinant, but one can handle adjoint geminals as N-2-electron functions. We number adjoint geminals, and in the followings they will be noted as  $\{g_\lambda^+\}_{\lambda=1 \dots \binom{M}{N-2}}$ . Eventually, geminal  $g_{i,j}$  can be considered as a ‘‘mini-determinant’’ (2 by 2 determinant) identified by the index-set  $I_\kappa = \{i, j\}$ , so we will write  $g_\kappa$  instead of  $g_{i,j}$ .

If we have determinant  $\Phi_\alpha$ , then  $I_\kappa \subset I_\alpha$  and  $I_\lambda \subset I_\alpha$  means, that  $g_\kappa \cdot g_\lambda$  appears in the Laplace-expansion of  $\Phi_\alpha$  multiplied by + or – sign given by

expansion rules of determinants. In the followings signs of adjoint determinants are denoted as:  $\omega(\kappa, \lambda)$ . For mathematical consistency:  $\omega(\kappa, \lambda) = 0$  if  $I_\kappa \cap I_\lambda$  is not the empty set.

The fact, that  $I_\alpha = I_\kappa \cup I_\lambda$  will be expressed by writing  $\alpha(\kappa, \lambda)$ .

Now we introduce the following notations:

$$D_\lambda^\kappa = c_{\alpha(\kappa, \lambda)} \omega(\kappa, \lambda) \quad (9)$$

$$D_{\lambda'}^{\kappa'} = c_{\alpha(\kappa', \lambda')} \omega(\kappa', \lambda') \quad (10)$$

With these notations we can write for  $\Theta$  :

$$\Theta_{\kappa, \kappa'} = \frac{1}{N!} \sum_{\lambda, \lambda'=1}^v D_\lambda^\kappa D_{\lambda'}^{\kappa'} \int \underbrace{g_\lambda^+(3, \dots, N) g_{\lambda'}^+(3, \dots, N)}_{\delta_{\lambda, \lambda'} (N-2)!} d3 \dots dN \quad (11)$$

Because of the orthogonality of N-2 electron functions (N-2 by N-2 determinant functions constructed over an orthonormal one-electron basis set) the summation indices  $\lambda$  and  $\lambda'$  can be set to be equal:

$$\Theta_{\kappa, \kappa'} = \frac{(N-2)!}{N!} \sum_{\lambda} D_\lambda^\kappa D_{\lambda'}^{\kappa'} \quad (12)$$

Quantities  $D_\lambda^\kappa$  can be considered as the  $\lambda^{\text{th}}$  element of vector  $\vec{D}^\kappa$ , so we can write the element of two-electron density matrix  $\Theta$  as a scalar product of two vectors:

$$\Theta_{\kappa, \kappa'} = \frac{(N-2)!}{N!} \vec{D}^\kappa \cdot \vec{D}^{\kappa'} \quad (13)$$

This result can be summarized in one sentence as: for an N-particle fermion system, using M-dimensional one-particle function basis, the elements of the second-order reduced density matrix in geminal basis are scalar products of  $\binom{M}{2}$

piece of  $\binom{M}{N-2}$  dimensional vectors.

The expression (13) of  $\Theta_{\kappa, \kappa'}$  gives a straightforward opportunity for continuing our considerations. We can use the most basic features of vectors, and rules of vector operations.

The norm of a vector is positive definite, so the sum of k piece of vectors  $\overline{D}_\kappa$  is positive or zero:

$$\left( \sum_{i=1}^k \overline{D}^{\kappa_i} \right)^2 \geq 0. \quad (14)$$

Here  $\kappa_i$  is an element of an index set containing k integer of possible values of geminal indices  $\kappa$ .

$$\{\kappa_1, \kappa_2 \dots \kappa_k\} \subseteq \left\{ 1, 2 \dots \binom{M}{2} \right\} \quad (15)$$

Evaluating the square of the sum of k piece of vectors for all possible value of k, a hierarchy of inequalities can be formulated:

$$\frac{1}{2} \sum_{i=1}^k \Theta_{\kappa_i, \kappa_i} \geq \sum_{i,j=1, i < j}^k \left| \Theta_{\kappa_i, \kappa_j} \right| \quad \forall k \text{ and } \forall \{\kappa_1, \kappa_2 \dots \kappa_k\}. \quad (16)$$

The number of inequalities (16) can be calculated as:

$$\binom{\binom{M}{2}}{2} + \binom{\binom{M}{2}}{3} + \dots + \binom{\binom{M}{2}}{\binom{M}{2}} = \sum_{k=2}^{\binom{M}{2}} \binom{\binom{M}{2}}{k} = 2^{\binom{M}{2}}. \quad (17)$$

Additionally, these inequalities are independent from each other, this can be directly proved by a numerical check for small values for k.

This hierarchy of inequalities is a set of necessary N-representability conditions, in the sense, that an N-representable second-order density matrix must fulfill all of them.

### Conclusions

The question, how to perform optimization of density matrices with ensuring exact N-representability is unsolved till today. Finding the answer seems to be hopeless in the opinion of many researcher. But there is a strong motivation for dealing with this problem, because if it is solved, then we get a far more natural, simple and effective tool for describing quantum mechanical systems.

Recently necessary OR sufficient conditions of N-representability are known. They are proved to be exact for special systems.

In the future, density matrix optimization may become again a highly intesively studied area of molecular physics.

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