Restoration of Many Electron Wave Functions from One-Electron Density

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ABSTRACT:

General theorem describing a relation between diagonal of one-electron density matrix and a certain class of many-electron ensembles of determinant states is proved. As a corollary to this theorem a constructive proof of sufficiency of Coleman's representability conditions is obtained. It is shown that there exist rigorous schemes for construction of energy of many-electron system as functionals of one-electron density.

Key words: representability problem; density matrices; electron correlation.

Introduction

In density functional theory (DFT) approaches it is accepted that the electronic energy of many electron systems (at least for the ground state) can be presented as a functional of the first order density, or, in other words, of the diagonal of the first order density matrix. In this connection the following question seems to be pertinent: Are there rigorous schemes, that do not involve approximations and hypothesis of any kind, for construction of electronic energy as a functional of the first order density? In present paper we make an attempt to answer this question.

The second question closely related to the first one may be formulated as: Is it possible to consider electronic energy of many-electron system for some fixed basis as a function of occupation numbers? Recently orbital occupancy (OO) approach developing this idea for DFT type functionals was formulated [1-4]. In present paper we show how energy expressions involving diagonal elements of the first order density matrix may be rigorously constructed. Such energy expressions may be used only in non-gradient optimization schemes since these expressions are not differentiable in classic sense.

Basic Definitions

For a fixed basis set of n orthonormal spin-orbitals the corresponding finite-dimensional Fock space \mathcal{F}_N is spanned by determinants $|L\rangle$ where L runs over all subsets of the spin-orbital index set N. Its p-electron sector $\mathcal{F}_{N,p}$ is spanned by determinants $|L\rangle$ with |L|=p. Basis determinants will be labelled by subsets and all sign conventions connected with their representation as the Grassman product of ordered spin-orbitals will be included in the definition of the creation-annihilation operators.

The set of q-electron density operators is defined as

$$\mathcal{E}_{N,q} = \{ t_q \in \mathcal{F}_{N,q} \otimes \mathcal{F}_{N,q}^* : t_q^{\dagger} = t_q \& t_q \ge 0 \& Tr(t_q) = 1 \}$$
 (1)

The diagonal mapping over $\mathcal{F}_N \otimes \mathcal{F}_N^*$ is

$$d(t) = \sum_{L \subset N} \langle L|t|L\rangle e_L, \tag{2}$$

where $t \in \mathcal{F}_N \otimes \mathcal{F}_N^*$ and $e_L = |L\rangle\langle L|$.

The contraction operator over $\mathcal{F}_N \otimes \mathcal{F}_N^*$ is defined in terms of the standard fermion creation-annihilation operators as

$$c = \sum_{i=1}^{n} a_i \otimes a_i^{\dagger}. \tag{3}$$

Definition 1. q-electron density operator $t_q \in \mathcal{E}_{N,q}$ is called weakly p-representable if there exists p-electron density operator $t_p \in \mathcal{E}_{N,p}$ such that

$$\frac{q!}{p!}c^{p-q}(d(t_p)) = d(t_q). \tag{4}$$

This definition is correct because the contraction operator possesses the property

$$c(d(\mathcal{E}_{N,p})) \subset d(\mathcal{E}_{N,q}).$$

The set $d(\mathcal{E}_{N,p})$ is called the standard (unit) simplex of the operator space $d(\mathcal{F}_{N,p} \otimes \mathcal{F}_{N,p}^*)$ and its characterization is given by

$$\mathcal{T}_{N,p} = d(\mathcal{E}_{N,p}) = \{ \sum_{L \subset N}^{(p)} \lambda_L e_L : \lambda_L \ge 0 \& \sum_{L \subset N}^{(p)} \lambda_L = 1 \}.$$
 (5)

The combinatorial structure of $\mathcal{T}_{N,p}$ is very simple: Any part of the set of all p-element subsets of the index set N determines a face of $\mathcal{T}_{n,p}$ and its complementary part generates the opposite face. In particular, there are $\binom{n}{p}$ hyperfaces opposite to the corresponding vertices.

Definition 2.

$$W_{N,p,q} = \frac{q!}{p!} c^{p-q} d(\mathcal{E}_{N,p}). \tag{6}$$

Weak representability problem may be formulated as the problem of description of the polyhedron $W_{N,p,q}$ with arbitrary admissible n, p, and q. Since, by definition, density operators are Hermitean, this polyhedron may be conveniently embedded into the real Euclidean space $\mathbb{R}_{N,q}$ of the dimension $\binom{n}{q}$ with its canonical basis vectors e_K labelled by q-element subsets of N. With such an embedding the tensor products of the fermion creation-annihilation operators involved in the expression (3) should be replaced by the commuting (Bose) annihilation operators

$$b_j e_J = \begin{cases} e_{J \setminus \{j\}}, & \text{if } j \in J \\ 0, & \text{if } j \notin J \end{cases} , \tag{7}$$

acting on the vector space

$$\mathbb{R}_N = \bigoplus_{q=0}^n \mathbb{R}_{N,q}.$$
 (8)

 $W_{N,p,q}$ is a polyhedron situated in the real affine hyperplane

$$\mathcal{H}_{N,q} = \{ \lambda \in \mathbb{R}_{N,q} : \sum_{J \subset N}^{(q)} \lambda_J = 1 \}.$$

$$\tag{9}$$

Let us put

$$w_{p\downarrow q}(L) = \frac{q!}{p!} c^{p-q} e_L = \frac{1}{\binom{p}{q}} \sum_{K \subset L}^{(q)} e_K.$$
 (10)

Directly from definition it follows that the polyhedron $W_{N,p,q}$ is the convex hull of $\binom{n}{p}$ vectors $w_{p\downarrow q}(L)$:

$$W_{N,p,q} = Conv(\{w_{p\downarrow q}(L)\}_{L\subset N}). \tag{11}$$

To the best of our knowledge, in contrast to the parametric description given by Eq.(11), the analytic description (that is the description in terms of the hyperfaces) of this polyhedron is obtained only for the case q=1 and is given by the following assertion that is just a consequence of the general theorem by Coleman [5-10]:

Theorem 1. Polyhedron $W_{N,p,1}$ is the set of solutions of the system

$$\begin{cases} 0 \le \lambda_k \le \frac{1}{p}, \ k \in N \\ \sum_{j \in N} \lambda_j = 1 \end{cases}$$
 (12)

This polyhedron has 2n hyperfaces with normals

$$v_k^0 = pe_k, (13a)$$

and

$$v_k^1 = -pe_k + \sum_{j \in N} e_j, (13b)$$

where $k \in \mathbb{N}$, and e_k are canonical basis vectors of the Euclidean space \mathbb{R}^n .

Restoration of p-Electron Wave Functions from One-Electron Density Matrix Diagonal

With arbitrary vector $\lambda^{(0)} \in W_{N,p,1}$ it is convenient to associate two index sets:

$$Ind(\lambda^{(0)}) = \{ i \in N : \lambda_i^{(0)} > 0 \}$$
 (14a)

$$Ind_{\frac{1}{p}}(\lambda^{(0)}) = \{i \in N : \lambda_i^{(0)} = \frac{1}{p}\}$$
 (14b)

Let us present vector $\lambda^{(0)} \in W_{N,p,1}$ as the convex combination

$$\lambda^{(0)} = p\mu^{L_0} w_{p\downarrow 1}(L_0) + (1 - p\mu^{L_0})\lambda^{(1)}$$
(15)

where (see Eq.(10))

$$w_{p\downarrow 1}(L_0) = \frac{1}{p} \sum_{i \in L_0} e_i,$$
 (16)

$$\lambda^{(1)} = \sum_{i \in L_0} \frac{\lambda_i^{(0)} - \mu^{L_0}}{1 - p\mu^{L_0}} e_i + \sum_{i \in N \setminus L_0} \frac{\lambda_i^{(0)}}{1 - p\mu^{L_0}} e_i, \tag{17}$$

and require the residual vector $\lambda^{(1)}$ to be representable. This requirement imposes the following restrictions on the admissible values of parameter μ^{L_0} :

$$\begin{cases}
0 \le \frac{\lambda_i^{(0)} - \mu^{L_0}}{1 - p\mu^{L_0}} \le \frac{1}{p}, & i \in L_0 \\
0 \le \frac{\lambda_i^{(0)}}{1 - p\mu^{L_0}} \le \frac{1}{p}, & i \in N \setminus L_0
\end{cases}$$
(18)

The frontier solution of system (18) is

$$\mu^{L_0} = \min\{\min_{i \in L_0} \{\lambda_i^{(0)}\}, \min_{i \in N \setminus L_0} \{\frac{1}{p} - \lambda_i^{(0)}\}\}.$$
 (19)

If $\mu^{L_0} \neq 0$ then we arrive at non-trivial representation of diagonal $\lambda^{(0)}$ as a convex combination of vertex $w_{p\downarrow 1}(L_0)$ and a certain representable residual vector $\lambda^{(1)}$. From Eq.(19) it is easy to see that the additional condition $\mu^{L_0} \neq 0$ holds true if and only if subset L_0 satisfies the restriction

$$Ind_{\frac{1}{n}}(\lambda^{(0)}) \subset L_0 \subset Ind(\lambda^{(0)})$$
 (20)

Iterating of Eq.(15) leads to the following expression

$$\lambda^{(0)} = \sum_{i=0}^{k-1} \left[\prod_{j=0}^{i-1} (1 - p\mu^{L_j}) \right] p\mu^{L_i} w_{p\downarrow 1}(L_i) + \left[\prod_{i=0}^{k-1} (1 - p\mu^{L_i}) \right] \lambda^{(k)}$$
 (21)

where

$$\mu^{L_i} = \min\{\min_{l \in L_i} \{\lambda_l^{(i)}\}, \min_{l \in N \setminus L_i} \{\frac{1}{p} - \lambda_l^{(i)}\}\}$$
 (22)

and

$$Ind_{\frac{1}{p}}(\lambda^{(i)}) \subset L_i \subset Ind(\lambda^{(i)})$$
 (23)

for $i = 0, 1, \dots, k - 1$.

Definition 3. Sequence $(L_0, L_1, \ldots, L_i, \ldots)$ of *p*-element subsets of *N* is called λ -admissible if for each $i = 0, 1, \ldots$ subset L_i satisfies the condition (23).

Theorem 2. For any vector $\lambda^{(0)} \in W_{N,p,1}$ the residual vector in iteration formula (21) vanishes after a finite number of steps.

Proof. First let us note that the number of nonzero components of representable residual vector $\lambda^{(k)}$ can not be less than p. If this number is equal to p then $\lambda^{(k)}$ just coincides with the vertex $w_{p\downarrow 1}(L_k)$ where $L_k =$

 $Ind(\lambda^{(k)})$, and the residual vector $\lambda^{(k+1)}$ vanishes. Let us suppose that the number of nonzero components of $\lambda^{(k)}$ is greater than p. From Eqs.(15), (17), and (19) it readily follows that there exists index $i_* \in Ind(\lambda^{(k)})$ such that $\lambda^{(k+1)}_{i_*}$ is necessarily equal either to zero or to $\frac{1}{p}$. To complete the proof it is sufficient to show that if $\lambda^{(k)}_i = \frac{1}{p}$ then $\lambda^{(k+1)}_i = \frac{1}{p}$. Condition (23) implies that all the indices $i \in N$ such that $\lambda^{(k)}_i = \frac{1}{p}$ should belong to L_k because in the opposite case the parameter μ^{L_k} would be equal to zero. If $\mu^{L_k} = \lambda^{(k)}_{i_*} > 0$ and $\lambda^{(k)}_i = \frac{1}{p}$ then $\lambda^{(k+1)}_i = \frac{\frac{1}{p} - \lambda^{(k)}_{i_*}}{1 - p \lambda^{(k)}_{i_*}} = \frac{1}{p}$. If, on the other hand, $\mu^{L_k} = \frac{1}{p} - \lambda^{(k)}_{i_*} > 0$ and $\lambda^{(k)}_i = \frac{1}{p}$ then $1 - p\mu^{L_k} = p\lambda^{(k)}_{i_*}$ and $\lambda^{(k+1)}_i = \frac{\frac{1}{p} - \mu^{L_k}}{p\lambda^{(k)}_{i_*}} = \frac{1}{p}$

Corollary 1. The set of solutions of the Coleman's system (12) is the convex hull of $\binom{n}{n}$ vertices $w_{p\downarrow 1}(L)$.

Corollary 2. The number of vertices in expansion of a given density diagonal obtained on the base of the recurrence formula (21) is not greater than the number of its components different from zero.

Corollary 3. λ -admissible sequence $(L_0, L_1, \ldots, L_{k_{\lambda}})$ generated recurrently on the base of the iteration formula (21) includes pairwise distinct p-element subsets and

$$\bar{\lambda}(L_0, L_1, \dots, L_{k_\lambda}) = \sum_{i=0}^{k_\lambda} \left[\prod_{j=0}^{i-1} (1 - p\mu^{L_j}) \right] p\mu^{L_i} e_{L_i}$$
 (24)

is a diagonal of p-electron density matrix such that

$$\frac{1}{p!}c^{p-1}\bar{\lambda}(L_0, L_1, \dots, L_{k_\lambda}) = \lambda. \tag{25}$$

It is to be noted that Theorem 2 is just a specification of the fundamental theorem by Carathéodory [11]:

Theorem 3. Let $X \subset \mathbb{R}^n$. Then any vector $x \in Conv(X)$ may be presented as a convex combination of no more than n+1 vectors from X. Modern proof of this result may be found in [12].

From Corollary 3 if follows that any mapping $\lambda \to s_{\lambda}$ where s_{λ} is a λ -admissible sequence compatible with the iteration formula (21) determines some global section (right inverse) $\pi_{1\uparrow p}$ of the contraction operator $\frac{1}{p!}c^{p-1}$ that is the mapping from $W_{N,p,1}$ to $\mathcal{T}_{N,p}$ such that

$$\frac{1}{p!}c^{p-1}\pi_{1\uparrow p}(\lambda) = \lambda \tag{26}$$

for any $\lambda \in W_{N,p,1}$. As it is seen from Eq.(22), sections constructed on the base of the recurrence relation (21) are not linear and even not differentiable in classic sense.

The most ambitious task arising in the frameworks of the approach outlined is to try to develop efficient methods for direct optimization of energy as a function of diagonal of the first order density matrix. General scheme embracing the whole class of such methods may be described as follows.

- 1. Some section(s) of the contraction operator should be chosen.
- 2. Using available section, it is possible of associate with some trial diagonal λ ensemble of p-electron determinant states and to determine squares of the CI coefficients:

$$|C_{L_i}|^2 = \left[\prod_{j=0}^{i-1} (1 - p\mu^{L_j})\right] p\mu^{L_i}$$
(27)

(see Eq.(24)).

3. Construct average energy

$$E_{\lambda}(\phi_0, \phi_1, \dots, \phi_{k_{\lambda}}) = \sum_{i,j=0}^{k_{\lambda}} \cos(\phi_i - \phi_j) |C_{L_i}| |C_{L_j}| < L_i |H| L_j >$$
 (28)

as a function of phases ϕ_i .

4. Minimize the function

$$E_{\pi_{1\uparrow p}}: \lambda \to \min_{\phi} E_{\lambda}(\phi)$$
 (29)

to determine optimal diagonal and its expansion via vertices $w_{p\downarrow 1}(L)$.

There are no serious problems in implementation of steps 2-4 of this scheme and the only complicated step is reasonable selection of mapping(s) $\pi_{1\uparrow p}$ (note that in general several different sections may be employed in the course of the energy optimization). It is rather difficult to estimate a priori the quality of some chosen concrete section $\pi_{1\uparrow p}$. There are two readily coming to mind general algorithms to construct such sections. Both of them involve full sorting of p-electron subsets of the spin-orbital index set.

1. Maximization of parameter (22) on each iteration: On the k-th step current L_k may be determined from the condition

$$\mu^{L_k} = \max_{L} \left\{ \min\{ \min_{l \in L} \{\lambda_l^{(k)}\}, \min_{l \in N \setminus L} \{\frac{1}{p} - \lambda_l^{(k)}\} \} \right\}.$$
 (30)

In this case it is not necessary to take into account Eq.(23) explicitly.

This section is probably optimal from formal mathematical viewpoint but has no physical idea behind it. Computer experiments show that in restoration process of such type high order excitations from the HF state contribute mostly. Even if exact FCI occupancies for the ground state are chosen, the restoration produces ensemble of determinant states that involves HF determinant and excited determinants that practically do not interact with the HF one.

2. Energy minimization: On the k-th iteration among subsets satisfying the condition (23) it is chosen the subset L_k such that the lowest eigenvalue of p-electron Hamiltonian in the basis $\{|L_0\rangle, |L_1\rangle, \ldots, |L_k\rangle\}$ is minimal.

This is undoubtedly the best possible section of the contraction operator. Unfortunately, the use of this section for the energy minimization is of no sense because it is equivalent to a certain CI scheme that can be described as follows.

- 1. First it is necessary to fix the maximal number mdet of determinants in wave function expansion and put k = 0;
 - 2. Put k = k + 1;
- 3. Sort all determinants different from the already chosen and select the one that corresponds to the lowest eigenvalue of the Hamiltonian in the basis of k determinants $\{|L_1>, |L_2>, \ldots, |L_k>\}$. If k < mdet, return to step 2.

Finally in a certain sense optimal basis involving not greater than *mdet* determinants will be obtained. This scheme is based on the well-known bracketing theorem of matrix algebra (see, e.g.,[13]) and is used in quantum chemistry for years in different modifications to select initial determinant space for multi-reference CI calculations [14, 15]. In our opinion this scheme is interesting in its own right as a self-sufficient one when a relatively small number of leading determinants should be constructed from active orbitals with close orbital energies (the case that occurs extensively in transition metal complexes) because

- (1) CI spaces of huge dimensions can be efficiently handled and disk memory usage is minimal;
 - (2) Calculations can be easily restarted;
- (3) Algorithms are trivially parallelized and if, say, PC clusters are used, data transfer via local net is minimal;
- (4) It is easy to handle both single excited state and a group of successive states.

For the restoration purpose the above scheme can be considered as a

certain benchmark one because it gives the best possible occupancies and energy that can be obtained on the basis of the restoration routine described by Theorem 2.

Conclusion

General theorem establishing a connection between diagonal of the first order density matrix and a certain set of many-electron wave functions is proved. It is shown that rigorous energy expression involving only oneelectron density becomes well-defined as soon as a certain right inverse of the contraction operator is chosen. For a fixed representable diagonal of the first order density matrix there exist quite a number of ways to restore pelectron determinant ensembles that are contracted to the diagonal under consideration. Each such way is in fact a path of a rather complicated graph with its vertices labelled by admissible (in sense of definition 3) p-element spin-orbital index sets. The main problem arising in implementation of optimization schemes based on such energy expressions is the lack of general simple algorithms for selection of admissible paths for restoration of wave functions from one-electron densities. Such algorithms, besides requirement being simple, should generate paths close in a certain sense to ones obtained by the benchmark calculations based on the bracketing theorem. Search for such algorithms is in progress now. Note in conclusion that the recurrence formula (21) can be easily generalized to treat densities of higher order and the only obstacle here is the lack of the complete set of inequalities for analytic description of the polyhedron $W_{N,p,q}$ in the case q>1.

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