Construction of a Perfectly *N*-Representable Two-Electron Density Matrix Carrying Full Information on an Interacting System

Imre Bálint,*,†,‡,§ Gergely Dezső,† and Iván Gyémánt†

Department of Theoretical Physics, University of Szeged, Szeged, Hungary, H-6720, Department of Pharmaceutical Analysis, University of Szeged, Szeged, Hungary, H-6720, and Department of Natural Sciences, Dunaújváros Polytechnic, Dunaújváros, Hungary, H-2400

The two-particle density matrix contains all information, which is "readable" by one- and two-particle operators. The report discusses the building of a two-electron density matrix, which is perfectly *N*-representable by construction. The 2-matrix of a pure quantum state is obtained without the intermediate determination of the wave function. The procedure is illustrated by computations on atomic and small molecular systems.

1. INTRODUCTION

The problems of the construction and interpretation of the structure of reduced density matrices especially in case of the two-electron density matrix have a long history in the last half of the century.[1−6] The possible characterization of quantum systems by density matrices instead of the wave function is attractive for both theoretical and computational advantages. However, the unavoidable conditions of general representability and *N*-representability proved to be difficult. The substantial efforts through the years resulted in several necessary or sufficient conditions, but none both together.[7,9,10] The papers in the proceedings of conferences held at Queen's University[8] represent well the development of the field revealing many properties and possible applications of reduced density matrices. Research interest has changed from time-to-time during past decades, and it seems to have been revived in the last few years.[11−13]

Recently a new algorithm has been developed[14] for the direct evaluation of the two-electron density matrix, which ensures the perfect *N*-representability by construction. In this report a set of structure-tensors is introduced, which determine the way of data-compression from the *N*-particle type information storage onto the two-particle type information storage. The presented method is equivalent to a full-CI procedure, but the knowledge of an optimized wave function is not assumed. The optimization of the two-electron density matrix requires M^4-scaling parameters, where M is the dimension of the one-electron function basis. The report is illustrated with examples on atomic and molecular computations, while further details will be given in ref 15.

2. THE PARAMETRIC TWO-ELECTRON DENSITY MATRIX

In the forthcoming description an *N*-electron system with nonrelativistic Hamiltonian is considered over the $\binom{M}{N}$-dimensional Hilbert space of (unnormalized) Slater-determinants

$$\left\{ \Phi_\alpha \colon \ \Phi_\alpha = \mathcal{A}(\phi_{i1}\phi_{i2}\cdots\phi_{iN}); \ \alpha = 1,..., \binom{M}{N} \right\} \quad (1)$$

where $\mathcal{A}$ is the antisymmetrization operator and

$$\{\phi_{i_k} \colon \ i_k \in \{1,...,M\}; \ \textstyle\int \phi_{i_k}^* \, \phi_{i_l} = \delta_{i_k i_l}\} \quad (2)$$

are the underlying orthonormal one-electron functions. The *N*th-order density matrix is a one-rank projector

$$\Gamma^N = \Psi\Psi^*; \quad \Psi = \sum_\alpha c_\alpha \Phi_\alpha; \quad ||\vec{c}|| = 1 \quad (3)$$

the two-particle reduced density matrix is its partly traced out image

$$\Gamma^2 = \int \Psi(\vec{1},\vec{2},\vec{3},...,\vec{N}) \, \Psi^*(\vec{1}',\vec{2}',\vec{3},...,\vec{N}) \, d\vec{3}... \, d\vec{N} \quad (4)$$

(with $\vec{1},...,\vec{N}$ as combined space and spin coordinates of the electrons), and the "mixed state" is represented by a convex sum of pure state reduced density operators

$$\tilde{\Gamma}^2 = \sum_i p_i \, \Gamma_i^2; \quad 0 \le p_i \le 1; \quad \sum_i p_i = 1 \quad (5)$$

The two-electron density matrix (2-matrix in short) will be constructed in the most general form (over the Slater-determinants), which is equivalent to one constructing it from a full-CI wave function. It is stressed however that the previous knowledge of the theoretically underlying (optimized) CI-function is not assumed.

Every Slater-determinant Φ_α is expanded (through a Laplace expansion) into a sum of products of 2×2 and $(N−2) \times (N−2)$ subdeterminants

$$\Phi_\alpha = det(\phi_{i1}(\vec{1}),...,\phi_{iN}(\vec{N})) =$$
$$\sum_{r<s} {}^\alpha g_{rs}^+ (\vec{1},\vec{2})\,{}^\alpha g_{rs}^+(\vec{3},...,\vec{N}) \quad (6)$$

(standing $i1,...,iN,r,s$ for one-electron function indices), where

* Corresponding author phone/fax: 36-62-544-368; e-mail: ibalint@physx.u-szeged.hu.
† Department of Theoretical Physics, University of Szeged.
‡ Department of Pharmaceutical Analysis, University of Szeged.
§ Dunaújváros Polytechnic.

$g_{rs}(\vec{1},\vec{2})$ and $g_{rs}^+(\vec{3},...,\vec{N})$ are the associated "geminals" and "cogeminals". In this setting the 2-matrix is of the form

$$\Gamma^2 = \int \Psi\Psi^* d\vec{3}...d\vec{N} = \int \sum_\alpha c_\alpha \Phi_\alpha \sum_\beta c_\beta^* \Phi_\beta^* d\vec{3}\cdot\cdot d\vec{N} =$$

$$\sum_\alpha \sum_\beta \int c_\alpha c_\beta^* (\sum_{r<s} {}^\alpha g_{rs}(\vec{1},\vec{2}) \, {}^\alpha g_{rs}^+(\vec{3},...,\vec{N})) \times$$

$$(\sum_{u<v} {}^\beta g_{uv}(\vec{1'},\vec{2'}) {}^\beta g_{uv}^+(\vec{3},...,N)) \times d\vec{3}...d\vec{N}; \quad r,s \in I_\alpha,$$
$$u,v \in I_\beta \quad (7)$$

Here the indices of the one-electron states only run through the index (sub)sets (I_α, I_β) of the given configurations. It is advantageous to rearrange this formula into

$$\Gamma^2 = \sum_{r<s} \sum_{u<v} \sum_\alpha \sum_\beta {}^\alpha g_{rs}(\vec{1},\vec{2}) {}^\beta g_{uv}(\vec{1'},\vec{2'}) \, \Omega(\alpha,\beta,r,s,u,v)$$
$$(8)$$

where the last factor is

$$\Omega(\alpha,\beta,r,s,u,v) =$$
$$c_\alpha c_\beta \int [{}^\alpha g_{rs}^+(\vec{3},...,\vec{N}){}^\beta g_{rs}^+(\vec{3},...,\vec{N})] \, d\vec{3}...d\vec{N} =$$
$$\begin{cases} (N-2)!(-1)^{1+2+r+s} (-1)^{1+2+u+v} c_\alpha c_\beta, & if \, I_\alpha\backslash\{r,s\} = I_\beta\backslash\{u,v\}, \\ 0, & otherwise \end{cases}$$
$$(9)$$

According to (7) and (8), an (rs,uv)-indexed component of the 2-matrix is composed of those configuration coefficients, where the Slater determinants contain exclusively geminals ${}^\alpha g_{rs}$, ${}^\beta g_{uv}$ associated with identical cogeminals. If (8) is rearranged in order to free the geminals from the α,β parenthood indices, we obtain

$$\Gamma^2 = \sum_{i<j} \sum_{k<l} g_{ij}(\vec{1},\vec{2}) g_{kl}^*(\vec{1'},\vec{2'}) \Theta_{ij,kl}; \, i,j,k,l \in I \quad (10)$$

When dropping the α, β superscripts, the new subscripts i, j, k, l will run through the full index set I, and the functional Θ also has to carry the inclusion relation information previously explicitly defined by the superscripts

$$\Theta_{ij,kl} = \sum_\alpha \sum_\beta (-1)^{\pi(i)+\pi(j)+\pi(k)+\pi(l)} c_\alpha c_\beta^* \chi_{\alpha\beta}(i, j, k, l) \quad (11)$$

Here $\pi(i)$, $\pi(j)$ and $\pi(k)$, $\pi(l)$ are the local serial numbers defining the positions of the corresponding one-electron functions inside the determinants Φ_α and Φ_β, respectively, while

$$\chi_{\alpha\beta}(i,j,k,l) =$$
$$\begin{cases} 1, & if \, (i,j \in I_\alpha) \bigwedge (k,l \in I_\beta) \bigwedge (I_\alpha\backslash\{i,j\} = I_\beta\backslash\{k,l\}) \\ 0, & otherwise \end{cases} \quad (12)$$

The $\Theta_{ij,kl}$ factors of the elementary kernels $g_{ij}(\vec{1},\vec{2}) g_{kl}^*(\vec{1'},\vec{2'})$ carry the full information about the system equipped with two-electron interactions, corresponding to the antisymmetric nature of the wave function obeying perfectly the *N*-representability requirement. Θ can be rearranged into the form

$$\Theta_{ij,kl} = Tr(C \, V^{ij,kl}) \quad (13)$$

where

$$V_{\alpha,\beta}^{ij,kl} = (-1)^{\pi(i)+\pi(j)+\pi(k)+\pi(l)} \chi_{\alpha\beta}(i,j,k,l);$$
$$C_{\alpha,\beta} = [c_\alpha c_\beta^*] \quad (14)$$

C and the structure tensors $V^{ij,kl}$ are $\binom{M}{N} \times \binom{M}{N}$-size, second-order tensors over the product space $\Phi_\alpha \times \Phi_\beta^*$, and C is of rank one, while the ranks of the Vs are higher. In the geminal basis $\{g_{ij}\}$ the matrix of Γ^2 is $\Theta_{ij,kl}$, and its components are given by the trace scalar products of the tensors C and $V^{ij,kl}$. In our setting the structure tensors $V^{ij,kl}$ play a crucial role in the construction of the 2-matrix. They carry the information on the fermionic nature of the system, and the information on the mutual orthogonality of the paired cogeminals as well as the information on the inclusion relations of the geminals and determinants. The tensorial subspace spanned by the Vs in the space of $\binom{M}{N} \times \binom{M}{N}$-size second-order tensors is necessary to define the inherently and exclusively two-particle interactions. This is the reason that some properties of the Vs are mentioned in the Appendix.

3. THE SEARCH FOR THE OPTIMUM 2-MATRIX

The direct determination of the optimum Γ^2 by varying all configuration coefficients c_α is hopeless, because of the high dimension of the configuration space. The direct optimization of the coefficients $\Theta_{ij,kl}$ without the necessary and sufficient restricting conditions violates the *N*-representability requirement. It is of paramount importance therefore to have a numerically economic procedure, which retains all interactions providing an energy optimized 2-matrix perfectly *N*-representable by construction. The presented procedure meets these requirements, straightforward optimization with respect to $\binom{M}{N}$ parameters reduces to sequential optimizations with respect to a small number of variational parameters. The exact number of variational parameters depends on the symmetries of the system and generally amounts to a fraction of $\binom{M}{2}\left(\binom{M}{2} + 1\right)/2$ the number of independent components of Γ^2.

The energy of an *N*-electron system with two-body interactions is as follows

$$E = \binom{N}{2} \frac{Tr(K^2\Gamma^2)}{Tr\Gamma^2} \quad (15)$$

where K^2 is the "reduced Hamiltonian" [7]

$$K^2 = \frac{1}{N-1} (\vec{H}_1(\vec{1}) + H_1(\vec{2})) + H_2(\vec{1},\vec{2}) \quad (16)$$

The energy is bounded from below, is a zero-degree homogeneous function of the configuration coefficients, and has several extrema where

$$0 = \partial E(\vec{c})/\partial c_\kappa$$
$$= \binom{N}{2} \frac{\partial Tr(K^2\Gamma^2)/\partial c_\kappa Tr\Gamma^2 - \partial Tr\Gamma^2/\partial c_\kappa Tr(K^2\Gamma^2)}{(Tr\Gamma^2)^2} \quad (17)$$

At a minimum, the sum of K^2-weighted elementary components of $\partial\Gamma^2/\partial c_\kappa$ (which is the gradient of the nominator) is linearly dependent on $\vec{c}$.

Table 1. Numbers of One-electron Functions, Electrons, and Configuration Functions as Well as the Hartree−Fock Electronic Energies of the Chosen Systems

	M	N	$\binom{M}{N}$	E_{HF} (au)
$C_{(STO-3G)}$	10	6	210	−37.198392546535300
$C_{(DZ)}$	18	6	18564	−37.363971882706295
$H_2O_{(STO-3G)}$	14	10	1001	−83.871812478937610
$NH_{3(STO-3G)}$	16	10	8008	−67.192777840464686

The energy $E(\vec{c})$ is at a local minimum, if the vectors $\nabla Tr(K^2\Gamma^2)$ and $\vec{c}$ are linearly dependent.

Let us turn to matrices evaluated on the geminal basis, $\bar{K}^2 := \langle g_{ij}|K^2|g_{kl}\rangle$ and $\Theta := \langle g_{ij}|\Gamma^2|g_{kl}\rangle$. If the above condition is obeyed, then

$$\binom{N}{2}\sum_{ij,kl}\bar{K}_{ij,kl}^2\ \partial\Theta_{ij,kl}/\partial c_\kappa = E(\vec{c})\sum_{ij}\partial\Theta_{ij,ij}/\partial c_\kappa =$$

$$2\binom{N}{2}E(\vec{c})c_\kappa \quad (18)$$

However using eq 19

$$\sum_{ij,kl}\bar{K}^2_{ij,kl}\partial\Theta_{ij,kl}/\partial c_\kappa = \sum_{ij,kl}\bar{K}^2_{ij,kl}\partial\left(\sum_{\alpha,\beta}V^{ij,kl}_{\alpha,\beta}c_\alpha c_\beta\right)/\partial c_\kappa \quad (19)$$

and rearranging the summations, we obtain

$$\sum_{\alpha,\beta}\partial\left(\sum_{ij,kl}K^2_{ij,kl}V^{ij,kl}_{\alpha,\beta}c_\alpha c_\beta\right)//\partial c_\kappa = \sum_{\alpha,\beta}\partial(H_{\alpha,\beta}c_\alpha c_\beta)/\partial c_\kappa \quad (20)$$

$$= \sum_\beta 2H_{\alpha,\beta}c_\beta = 2E(\vec{c})c_\kappa$$

where $H_{\alpha,\beta} := \langle\Phi_\alpha|\hat{H}|\Phi_\beta\rangle$ are the matrix elements of the Hamiltonian.

If the above linear dependency condition is met, then $\vec{c}$ is an eigenvector of the Hamiltonian matrix evaluated over the space of N-electron functions.

This result can be exploited for determining the eigenvectors by using various vector inequalitites, for instance Cauchy-Schwarz-Buniakowky's inequality.[16,17]

An eigenvector of the matrix of the Hamiltonian is obtained by minimizing the non-negative, homogeneous function $F(\vec{c})$. If $\vec{d} = \sum_{ij,kl}\bar{K}^2_{ij,kl}\ \partial\Theta_{ij,kl}/\partial c_\kappa$, then

$$\min_{\vec{c}}F(\vec{c}) = \min_{\vec{c}}F(\vec{c})\frac{\|\vec{d}\|^2\|\vec{c}\|^2 - (\vec{d}\ o\ \vec{c})^2}{(Tr\ \Gamma^2)^2} =$$

$$0 \Leftrightarrow H\vec{c} = E(\vec{c})\vec{c} \quad (21)$$

where o stands for the scalar product.

In all of the considered formulas the optimizations were expected to be done with respect to the configuration parameters. To keep the computational work under a

manageable limit the trial vector $\vec{c}$ will be sought in the form

$$\vec{\hat{c}} := \vec{c} + \sum_{ij,kl}b_{ij,kl}\nabla\Theta_{ij,kl}(\vec{c}) \Rightarrow \Theta(\vec{\hat{c}}) \equiv \Theta(\vec{b};\vec{c}) \quad (22)$$

$$\partial E(\vec{\hat{c}})/\partial b_\kappa = 0 =$$
$$\binom{N}{2}\frac{\partial Tr(\bar{K}^2\Theta(\vec{b}))/\partial b_\kappa\ Tr\Theta(\vec{b}) - \partial Tr\Theta(\vec{b})/\partial b_\kappa\ Tr(\bar{K}^2\Theta(\vec{b}))}{(Tr\Theta(\vec{b}))^2},$$
$$\kappa := (ij,kl) \quad (23)$$

The b-dependent gradient arises from the projections of the vectors $\nabla\Theta_{ij,kl}(\vec{c})$ onto the gradient $\partial E(\vec{\hat{c}})/\partial\hat{c}_\sigma$

$$\partial E(\vec{\hat{c}})/\partial b_\kappa = \sum_\sigma \partial E(\vec{\hat{c}})/\partial\hat{c}_\sigma\ \partial\hat{c}_\sigma/\partial b_\kappa \quad (24)$$

If $\vec{b} = \vec{0}$, then $\vec{c} \equiv \vec{\hat{c}}, \vec{d} \in$ span $\{\nabla\Theta_{ij,kl}\}$ implying also $\partial E(\vec{\hat{c}})/\partial c_\sigma$ to be in the same subspace. If $\partial\hat{c}_\sigma/\partial b_\kappa = \nabla_\sigma\Theta_\kappa(\vec{c})$ are independent vectors, then

$$\partial E(\vec{\hat{c}})/\partial b_\kappa = \vec{0} \Leftrightarrow \partial E(\vec{\hat{c}})/\partial c_\sigma = \vec{0} \quad (25)$$

where the second equality is of primary importance for us. This relationship allows us to do the optimization sequentially in the local subspaces spanned by the vectors $\nabla\Theta_\kappa$.

4. NUMERICAL RESULTS

As to the computational aspects of the procedure, the algorithm is very much economical concerning the number of variational parameters, which are generally a small fraction of the number of independent components of Γ^2. This reduction is a consequence of the symmetries of the system and does not cover any approximation preserving the full exactness of the scheme. Therefore the speed of the computations may be surprisingly good. To ensure the desired speed, the V tensors must be precomputed. Although the evaluation of the Vs runs quite fast, the required time is nevertheless longer than is allowable for a built-in real-time procedure. The storage capacity demand is substantial, and also the continuous transfer of the Vs requires careful planning. The chosen examples all refer to small systems and small basis sets, where the relatively small number of configurations allows the direct comparison of the "brute-force" direct optimization with respect to all configuration parameters and the optimization in local subspaces with respect to the bs. It is shown that the minima obtained with these two differing procedures agree with any required accuracy. The price we pay for this comparison is that the obtained energies are significantly higher than the known benchmark values. To reach "chemical accuracy" with a large

Table 2. Optimized Electronic Energies, Accuracy Characterized by $\epsilon = \cos(\nabla Tr(K^2\Gamma^2)(\vec{c});\vec{c}) + 1$ and Timing Data Referring to Optimizations with Respect to All Configuration Parameters ($E(c)$) and with Respect to the bs ($E(b)$), Respectively[a]

	$E(\vec{c})$ (au)	ϵ	time (s)	$E(\vec{b})$ (au)	ϵ	time (s)
$C_{(STO-3G)}$	−37.21873353415815	<1.0−15	2.25	−37.21873353415826	<1.0−15	4.5
$C_{(DZ)}$	−37.41727298157322	<1.0−15	2057	−37.41727298157323	<1.0−15	674
$H_2O_{(STO-3G)}$	−83.93598674062193	<1.0−15	258	−83.93598674062230	<1.0−15	198
$NH_{3(STO-3G)}$	−67.27464780581809	<1.0−15	12046	−67.27464780581824	<1.0−15	2560

[a] In both cases the perfectly *N*-representable 2-matrices were constructed by the described procedure. Timing data refer to a 400 MHz single processor PC.

enough basis set, the corresponding large configuration space and the *b*-optimization represent a suitable frame. Therefore the presented energies, referenced as "Hartree−Fock electronic energy" and "electronic energy of the correlated sytem" (E(c) and E(b)) are understood as the "one-determinant electronic energy" and the "fully optimized electronic energy" in the given basis set. The optimizations of the *b*s were generally done with the BFGS algorithm, and the optimizations of the *c*s were done with the 'limited memory' BFGS[18] method.

The limited experience obtained in the presented and other pilot calculations shows that with a careful organization of the computations nonapproximate, large-scale calculations can be realistically expected well in the 10 million configuration range. On the other hand, the presented scheme provides the possibility to investigate such problems, which are directly dependent on the structure of the 2-matrix.

APPENDIX

Some Properties of Structure Tensors $V^{ij,kl}$. The $V^{ij,kl}$ tensors can be classified into three types by the differences in the one-electron function contents of the underlying pairing Slater determinants. Since the cogeminals are identical in all terms, the $V^{ij,ij}(i \neq j)$-type tensors are associated with geminals $g_{ij}(\vec{1},\vec{2})g_{ij}^*(\vec{1}',\vec{2}')$ containing the same one-electron functions, therefore the associated determinants are said to be nonexcited with respect to each other. The $V^{ij,jl}(i \neq j, i \neq l, j \neq l)$ are said to be 1-fold excited and the $V^{ij,kl}$-type tensors are said to be 2-fold excited with respect to each other. The Vs are nonsymmetrical, sparse tensors with either full zeros or only one ± 1 component and further zeros in every row/column. The components are all distinct, therefore the rank depends on the number of acceptable $(N−2)$-tuples among the $M−4$, $M−3$, and $M−2$ one-electron functions remaining after the selection of the geminals assigned to the V in question.

The rank of the tensor $V^\gamma_{\alpha,\beta}$, $\gamma : \{(ij,ij),(ij,jl),(ij,kl)\}$ is equal to the number of the nonzero elements, which are $\binom{M-2}{N-2}$, $\binom{M-3}{N-2}$, and $\binom{M-4}{N-2}$, in the nonexcited, 1-fold and 2-fold excited classes, respectively.

If an (α,β) index pair is assigned to a nonzero tensor component ($V^\gamma_{\alpha,\beta} \neq 0$, γ defined above), then this index pair may be associated with a nonzero component in another tensor ($V^{\gamma'}_{\alpha,\beta} \neq 0$, $\gamma \neq \gamma'$), only if the tensors γ, γ' pairwise belong either to the nonexcited or to the 1-fold excited class.

An (α,β)-index pair, which is associated with a nonzero tensor component appears in $\binom{N}{2}$ members of the nonexcited class, in N-1 members of the 1-fold excited class and in a single member of the 2-fold excited class.

As a consequence of the above, common index pairs assigned to nonzero tensor components appear only in the nonexcited and 1-fold excited classes. In pairs of tensors in these classes the common indices belong to those pairs of determinants, which contain the *V*-defining geminals.

In two tensors, the number of common indices assigned to nonzero components is $\binom{M-4}{N-4}$ in the nonexcited class, $\binom{M-4}{N-3}$ in the 1-fold excited class and zero in the 2-fold excited class.

The *V*s are nonsymmetrical, but two tensors associated with transposed supersripts are transposed to each other.

Those Vs, which are associated with transposed components of Γ^2 are transposed to each other, i.e., $(V^{kl,ij})^T = V^{ij,kl}$.

The members of the nonexcited, 1-fold excited and 2-fold excited classes behave differently with respect to the trace scalar product. Tensors in the nonexcited class have only nonzero components in the main diagonal. Their self-products provide the rank, their mutual product provides the number of common elements. The tensors in the one- and 2-fold excited classes have only off-diagonal nonzero components. Their trace scalar self-product yields zero, their mutual product yields zero if both componets of the product belong either to the upper- or lower triangular part of the $[ij,kl]_{ij,kl}$ index matrix. However the trace scalar product of transposed pairs $\mathrm{Tr}(V^{ij,kl}V^{kl,ij})$ provides the (identical) ranks of both tensors.

Members of the nonexcited, 1-fold excited and 2-fold excited classes span orthogonal subspaces with respect to the trace scalar product.

Those *V* tensors, which are associated with superscripts belonging to the upper- or the lower triangular part of Γ^2 span a vector space of dimension equal to the number of elements in the corresponding triangular part of Γ^2.

The dimensions of span$\{V^{ij,ij}\}$, span$\{V^{ij,jl}\}$ and span$\{V^{ij,kl}\}$- are equal to the number of independent tensor components of types $\Theta_{ij,ij}, \Theta_{ij,jl}$ and $\Theta_{ij,kl}$.

This short account on the structure-related properties of the *V* tensors hopefully helps to clarify the way of contraction of the *N*-particle information to two-particle one.

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