

Functional N -Representability in 2-Matrix, 1-Matrix, and Density Functional Theories

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ABSTRACT

The N -representability conditions on the reduced second-order reduced density matrix (2-RDM), impose restrictions not only in the context of reduced density matrix theory (RDMT), but also on functionals advanced in one-matrix theory such as natural orbital functional theory (NOFT), and on functionals depending on the one-electron density such as those of density functional theory (DFT). We review some aspects of the applications of these N -representability conditions in these theories and present some conclusions.

Keywords: N -Representability; DFT; D1-Matrix Theory; D2-Matrix Theory

1. Introduction

Due to the fact that the Hamiltonian for a many-electron system contains at most two-particle interactions, the energy can be written solely as a functional of the reduced second-order density matrix, 2-RDM. However, minimization of the energy expression without imposing conditions on this 2-RDM leads to values of the energy below the exact ground-state value. This was denoted by Coleman as the 2-matrix N -representability problem. It emerges because constraints on the 2-matrix are necessary in order to guarantee that it comes from an N -matrix, or equivalently, from an N -particle wave function.

There has been a long history of how Density Matrix Functional Theory, DMFT, has slowly evolved in the last almost five decades and how little by little, N -representability conditions for density matrices, in particular for the 2-RDM have been discovered. This efforts, of course, have been followed by the development of practical computational schemes leading to algorithms whose levels of efficiency are nowadays competitive with those of the usual quantum chemistry programs. In fact, the present situation of DMFT looks highly promising not only in view of this computational progress but mainly because of the recent discovery of complete N -representability

conditions for the 2-RDM (for some recent reviews, see [1,2]).

An important issue having to do with RDMT (expressed in terms of the 2-RDM) is that the N -representability conditions on the energy functional are the same as those on the 2-RDM. This comes about because the energy is the trace of a known two-particle operator and an unknown 2-RDM (see Equation (8)). However, when the energy is expressed in terms of the reduced first-order density matrix, 1-RDM, the energy functional has to be reconstructed in terms of the parameters that enter into the definition of 1-RDM, namely, the occupation numbers $\{n_i\}_{i=1}^{\infty}$ and the natural-spin orbitals $\{\chi_i(r)\}_{i=1}^{\infty}$. Although the N -representability conditions on ensemble representable 1-RDM are known, the functional reconstructed in terms of $\{n_i\}$ and $\{\chi_i(r)\}$ must obey the N -representability conditions of the 2-RDM. In other words, it is through this reconstruction of the 2-RDM in terms of the 1-RDM that the functionals in NOFT are generated. Thus, the reconstructed 2-RDM entering in these functionals must satisfy the same N -representability conditions as the unreconstructed 2-RDM.

When the energy is represented as a functional of the one-particle density, again, although the N -representability conditions on the one-particle density are known,

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the energy as a functional of the one-particle density must be obtained by a reconstruction of the 2-RDM in terms of the one-particle density. Thus, in density functional theory, DFT, there arises a functional N -representability problem, namely, the requirement that the 2-RDM reconstructed in terms of the one particle density satisfy the same N -representability conditions as those imposed on the unreconstructed 2-RDM. Of course, these conditions in turn impose restrictions on the energy expressed as a functional of just the one-particle density.

The present article aims at putting in perspective the functional N -representability problem as related to the RDMT, NOFT and DFT approaches. In Section II, we briefly review RDMT with respect to the discovery of N -representability conditions for the 2-RDM. In Section III, we review advances in NOFT, placing special attention to approaches that incorporate as a basic ingredient the 2-RDM N -representability conditions for the construction of the energy functionals. In Section IV, we examine how the N -representability conditions on the 2-RDM are implicit in the definition of the universal functional generated through constrained variation. We also comment on the application of these conditions in the development of DFT functionals. Finally we review works in DFT where the problem of N -representability of the functionals has been brought into focus. Finally, in Section V, we present some conclusions.

2. N -Representability in RDM Theory

Let us start by quoting Dirac's statement of 1929 on the meaning of the Schrödinger equation for chemistry: "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed" [3]. And let us contrast it with a very recent one (2012) of Nakata *et al.*: "The goal [of chemistry] is to enable us to predict, understand, and control what happens when we mix substances. To do that, we usually do experiments, which can be explosive, poisonous, expensive, and unstable. This means that it is desirable to do chemistry without experiments. Fortunately, the basic equation of chemistry is known, and it is called the Schrödinger equation. [...] The reduced-density-matrix method is a promising next-generation electronic structure calculation method; it is equivalent to solving the Schrödinger equation for the ground state. The number of variables is the same as a four electron system and constant regardless of the number of electrons in the system. Many researchers have been hoping for a simpler method of doing quantum mechanical calculations and this one may be it" [2].

Apparently Dirac's request for the development of approximate methods so that the Schrödinger equation becomes a predictive tool in chemistry is in its way to being fulfilled.

In order to succinctly state the meaning of the N -representability problem in 2-RDM theory, consider the Hamiltonian for an N -electron system

$$\begin{aligned} \hat{H} &= \hat{T} + \hat{V}_{ext} + \hat{V}_{ee} \\ &= \sum_{i=1}^N \hat{t}(\mathbf{r}_i) + \sum_{i=1}^N \hat{v}_{ext}(\mathbf{r}_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \end{aligned} \quad (1)$$

where $\hat{t}(\mathbf{r}_i) = -(1/2)\nabla_{\mathbf{r}_i}^2$, $\hat{v}_{ext}(\mathbf{r}_i)$ is the interaction of the i -th electron with the external field of nuclei and $1/|\mathbf{r}_i - \mathbf{r}_j|$ represents the electron-electron repulsion. The Hamiltonian can also be written in terms of the two-particle operator $\hat{K}^N(\mathbf{r}_i, \mathbf{r}_j)$ (where its dependence on the number of electrons, N , is emphasized) as:

$$\hat{H} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{K}^N(\mathbf{r}_i, \mathbf{r}_j) \quad (2)$$

where

$$\begin{aligned} \hat{K}^N(\mathbf{r}_i, \mathbf{r}_j) &= \frac{1}{N-1} \left[\left(\hat{t}(\mathbf{r}_i) + \hat{v}_{ext}(\mathbf{r}_i) \right) + \left(\hat{t}(\mathbf{r}_j) + \hat{v}_{ext}(\mathbf{r}_j) \right) \right] \\ &+ \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \end{aligned} \quad (3)$$

The energy corresponding to a normalized wavefunction $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is:

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle \quad (4)$$

which in view of Equation (2) can be written as

$$E[\Psi] = Tr \left[\hat{K}^N D_{\Psi}^2 \right] \quad (5)$$

where $D_{\Psi}^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$ is the normalized reduced second-order density matrix obtained from the wavefunction Ψ :

$$D_{\Psi}^2 = \frac{N(N-1)}{2} \int d\mathbf{r}_3 \dots \int d\mathbf{r}_N \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \Psi(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}_3, \dots, \mathbf{r}_N)$$

Thus, the ground state energy is obtained by minimizing this functional

$$E_0 = \inf_{\Psi \in \mathcal{L}_N} \left\{ \langle \Psi | \hat{H} | \Psi \rangle \right\} \quad (7)$$

where \mathcal{L}_N is the antisymmetric Hilbert space, or equivalently through

$$E_0 = \inf_{D^2 \in \mathcal{P}_N^2} \left\{ Tr \left[\hat{K}^N D^2 \right] \right\}, \quad (8)$$

where \mathcal{P}_N^2 is the set of normalized N -representable 2-matrices. Hence, the N -representability problem in 2-RDM theory has to do with how to set up the necessary and sufficient intrinsic conditions for defining \mathcal{P}_N^2 such that it is guaranteed that the 2-RDM ($D^2 \in \mathcal{P}_N^2$) satisfies Equation (6).

The development of 2-RDM theory may be separated in the following four stages. A first stage, which is marked by the studies of the properties of reduced density matrices carried out by Löwdin (1955) [4] and McWeeny (1960) [5] (based on the pioneering works of Dirac (1930, 1931) [6,7] and Husimi (1940) [8]); by the unsuccessful attempts to obtain the energy by direct variation of the 2-RDM undertaken by Mayer in 1955 [9] and Tredgold in 1957 [10]); by the recognition and formulation of the N -representability problem by Coleman in 1963 [11] (see also [12,13]) and by the construction of a formal solution to this problem by Garrod and Percus in 1964 [14] (for a comprehensive description and bibliography of this stage, see [15-17]).

The second stage is characterized by the reduction of the Schrödinger equation to a hierarchy of equations relating RDM of different orders (Cohen and Frishberg (1976) [18], Nakatsuji (1976) [19], Alcoba and Valdemoro [20]). This reduction has received the generic name of Contracted Schrödinger Equation, CSE. These CSEs have been derived both in their Hermitian and anti-Hermitian [21,22] versions. If the RDM which are connected through the CSE are N -representable then, according to Nakatsuji's theorem [19], the CSE is equivalent to the Schrödinger equation. Harriman, however, pointed out to the difficulties of the CSE approach when the RDMs do not satisfy N -representability conditions [21].

For a number of years the CSE remained as a theoretical finding which had little possibility of being applied to solve the quantum many-body problem. However, an important development occurred when Valdemoro *et al.* advanced a way to reconstruct the higher-order RDM in terms of lower-order ones [23,24]. This effort, certainly stimulated other developments such as those of Nakatsuji and collaborators and of Mazziotti [25-28]. These advances, once again, restored the high expectations that had been previously placed on methods based on RDMs. Moreover, through these works it became evident that the N -representability conditions for the 2-RDM are intimately tied to the reconstruction of the 3- and 4-RDM in the context of the CSE formalism. As a result, the N -representability problem became a basic ingredient of the cumulant theory for RDM ensuing from these developments [27-31]. For some more recent applications and discussions of this approach, see Refs [32,33].

The third stage is related to the identification of the applied mathematical problem arising in the treatment of

RDMs as semidefinite programming. This problem had certainly attracted the attention of mathematicians and engineers (see, for example the early work of Vandenberghe and Boyd [34] plus other more recent ones [35-38]). Thus, useful tools already developed in applied mathematics were identified and adapted to the particular application at hand, namely, the direct optimization of the 2-RDM [39-47]. These efforts are still being extended to other domains of physics [48].

This third stage also comprises application of computer codes based on semidefinite programming to the actual calculation of the 2-RDM subject to N -representability conditions [49-51]. In fact, these mathematical and computational developments made it possible to systematically assess the effect that the progressive inclusion of tighter N -representability conditions had on the energy [52-56]. This has led to the possibility of approaching the accuracy of traditional and very exact quantum chemical calculations such as those based on the Coupled-Cluster method [57,58]. In fact, Nakata *et al.* [58] have obtained the following inequalities for the energies when the N -representability conditions are progressively included:

$$E_{PQ} \leq E_{PQG} \leq E_{PQGT1} \leq E_{PQGT1T2} \leq E_{PQGT1T2'} \leq E_{fullCI} \quad (9)$$

In the above expression, the energies are characterized by the imposition of a set of N -representability conditions. For example, E_{PQ} is the variational energy obtained when the conditions P and Q are imposed in the variation; similarly, $E_{PQGT1T2}$ is the variational energy obtained under conditions $P, Q, G, T1$ and $T2$. These variational energies give lower bounds because the variational 2-RDM are non- N -representable. However, the very interesting finding of these authors is that they progressively approach the upper-bound energy given by E_{fullCI} . Summing up, as in the variational upper bound calculations based on wave functions, where the accuracy is improved when the variational space is made larger, in the 2-RDM theory, the accuracy is also improved by imposition of more N -representability conditions.

Finally, we are fathoming a fourth stage marked by important mathematical developments such as Mazziotti's very recent discovery of complete N -representability conditions for the 2-RDM and higher order reduced density matrices [59,60]. No doubt, faster and more efficient computer codes will be developed to implement these new ideas. Thus, these recent developments, obviously place 2-RDM theory in a very bright perspective. To close this section, let us quote Mazziotti on these implications:

"The constructive solution of N -representability establishes 2-RDM theory as a fundamental theory for many particle quantum mechanics for particles with pairwise interactions. Lower bounds on the ground-state energy

can be computed and improved systematically within the theory. While not all of the 2-RDM conditions will be imposed in practical calculations, a complete knowledge of the conditions their form and functions can be invaluable in devising and testing approximate N -representability conditions for different types of quantum systems and interactions" [60].

3. N -Representability in NOFT

The normalized reduced first-order density matrix or 1-RDM $D_\Psi^1(\mathbf{r}_1; \mathbf{r}'_1)$ is defined by:

$$D_\Psi^1 = N \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_N \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}'_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (10)$$

The kinetic plus the external energy are linear functionals of the 1-RDM:

$$T[\Psi] + E_{ext}[\Psi] \equiv \langle \Psi | \hat{T} + \hat{V}_{ext} | \Psi \rangle = Tr[\hat{h}_0 D^1] \quad (11)$$

where $\hat{h}_0(\mathbf{r}_i) \equiv (\hat{t}(\mathbf{r}_i) + \hat{v}_{ext}(\mathbf{r}_i))$. In view of Equation (11), the following functional of the 1-RDM can be defined: [61]

$$W[D^1] = \inf_{D^1 \in \mathcal{E}_N^1} \left\{ \langle \Psi_{D^1} | \hat{V}_{ee} | \Psi_{D^1} \rangle \right\} \\ \equiv \left\{ D^1 : 0 \leq D^1 \leq qI, D^1 \geq 0, Tr D^1 = N, (D^1)^\dagger = D^1 \right\} \quad (12)$$

$$\Psi_{D^1} \rightarrow D^1 \text{ (fixed)}$$

$\Psi_{D^1} \in \mathcal{L}_N$ (antisymmetric N -particle Hilbert space)

In this expression, \mathcal{E}_N^1 is the set containing the ensemble N -representability conditions on D^1 , [11], q is the highest eigenvalue of D^1 and I is the unit matrix.

Since \hat{V}_{ee} is a sum of 2-particle operators, we can rewrite the functional

$$W[D^1] = \inf_{D^1 \in \mathcal{E}_N^1} \left\{ Tr[\hat{v} D_{D^1}^2] \right\}, \quad (13)$$

$$D_{D^1}^2 \rightarrow D^1 \text{ (fixed)}, D_{D^1}^2 \in \mathcal{P}_N^2$$

where $\hat{v} = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$

Thus, we see that once again, the N -representability conditions $D_{D^1}^2 \in \mathcal{P}_N^2$ on the 2-RDMs that reduce to the given and fixed $D^1 \in \mathcal{E}_N^1$ also appear here in the definition of the functional $W[D^1]$ through Equation (13).

It is interesting to observe under the present perspective, *i.e.*, bearing in mind the need to impose N -representability conditions, that the initial works [62-65] attempting to obtain Euler-Lagrange equations of motion for the 1-RDM, when the 1-RDM is expressed in terms of the natural orbital expansion, namely,

$$D^1(\mathbf{r}; \mathbf{r}') = \sum_{i=1}^{\infty} n_i \chi_i(\mathbf{r}) \chi_i^*(\mathbf{r}') \quad (14)$$

led to the paradoxical situation in which all partially occupied natural spin orbitals $0 \leq n_i \leq 1$ had to belong to the same degenerate eigenvalue of a natural orbital one-particle equation:

$$\hat{h} \chi_i = \epsilon_i \chi_i \quad (15)$$

However, in the variational treatment of Nguyen-Dang, Ludeña and Tal where built-in N -representability conditions were included from the outset, this paradoxical results did not emerge [66-68].

A fairly complete historical account of the formulation and development of density matrix theory based on the 1-RDM can be found in the review article of Piris, 2007 [69].

The simplest case in which the energy can be expressed as a functional of the 1-RDM is, of course, the Hartree-Fock approximation. The exchange term is just a functional of the occupied Hartree-Fock orbitals:

$$E_x[\{\phi_i^{HF}\}] \\ = -\frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \int dx \int dx' \frac{\phi_i^{HF}(x) \phi_i^{HF}(x') \phi_j^{HF}(x) \phi_j^{HF}(x')}{|\mathbf{r} - \mathbf{r}'|} \quad (16)$$

where $x \equiv \mathbf{r}s$ denotes both the spatial and spin coordinates. In terms of natural orbitals and their occupation numbers, a generalization of this expression, for the exchange-correlation functional is given by:

$$E_x[\{n_i\}, \{\chi_i\}] \\ = -\frac{1}{2} \sum_{i=1}^m \sum_{j=1}^m f(n_i, n_j) \int dx \int dx' \frac{\chi_i(x) \chi_i(x') \chi_j(x) \chi_j(x')}{|\mathbf{r} - \mathbf{r}'|} \quad (17)$$

where $m \rightarrow \infty$

Several approximations to the function $f(n_i, n_j)$ define different types of functionals such as those of Müller, [70] Goedecker-Umrigar, [71] Csanyi and Arias, [72] Buijse and Baerends, [73,74] Gritsenko-Pernal-Baerends, [75] Sharma *et al.*, [76] and Lathiotakis *et al.* [77-80].

The mathematical characteristics of the Müller functional, taken as a paradigmatic example, has been extensively studied [81]. The accuracy of these approximate functionals has been assessed with respect to traditional quantum chemistry methods [78]. The lack of size consistency in these functionals has been recently analyzed. [80]

We have selected to discuss separately the approach of Piris *et al.*, because although they present functionals based on occupation numbers and natural orbitals, their

approach is different in that they systematically introduce N -representability conditions. Piri's work is essentially based on the reconstruction of the 2-RDM by means of an explicit formulation of the cumulant expansion [27-30]. The particular reconstruction functional for the two-particle cumulant is presented in Ref. [82] and it is based on the introduction of some auxiliary matrices Δ , Π and Λ , expressed in terms of natural orbitals and their occupation numbers. The matrix elements of these matrices are required to satisfy some necessary conditions for the N -representability of the 2-RDM [69, 83-87].

Of course, progressive enforcement of these N -representability conditions plus some different ways of approximating the off-diagonal elements of the matrix Δ have led to the appearance of different versions of these functionals, generically denoted as Piri Natural Orbital Functional i, PNOFi. In general, the performance of these functionals is comparable to those of best quantum chemistry methods in the sense that chemical accuracy is being attained by the PNOFi, [78] in particular by PNOF5 [85].

In a recent paper, Pernal [88] has shown that PNOF5 and the natural orbital functional corresponds to the antisymmetrized product of strongly orthogonal geminal theory if the expansion of geminals is limited to two-dimensional subspaces. This result is remarkable in the sense that for the first time it is shown that top-down and bottom-up methods for generating density functionals are equivalent. The top-down method is represented by the reduction of an N -particle functional generated from an ansatz wave function such as the antisymmetrized product of strongly orthogonal geminals. In the bottom-up method a functional is generated by progressive inclusion of N -representability conditions. This example shows that perhaps the unity of quantum theory on many-particle systems can be attained by careful handling of top-down and bottom-up methods.

4. N -Representability in DFT

In the Hohenberg-Kohn-Sham version of density functional theory, HKS-DFT, there is a basic assertion concerning the existence of a universal functional $F[\rho]$, depending solely on the density which in the context of Levy's constrained-search formulation of DFT is defined as [61]:

$$F[\rho] = \inf \left\{ \langle \Psi_\rho | \hat{T} + \hat{V}_{ee} | \Psi_\rho \rangle \right\},$$

$$\rho \in \mathcal{J}_N \equiv \left\{ \rho : \rho \geq 0, \int \rho = N, \rho^{1/2} \in H^1(\mathbf{R}^3) \right\} \quad (18)$$

$$\Psi_\rho \rightarrow \rho(\text{fixed}),$$

$\Psi_\rho \in \mathcal{L}_N$ (antisymmetric N -particle Hilbert space)

Note that in this case, the wavefunction $\Psi_\rho(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is any N -particle wavefunction in \mathcal{L}_N yielding the fixed

density ρ . Now, introducing the two-particle operator

$$\hat{K}_0^N(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{N-1} \left[\hat{t}(\mathbf{r}_i) + \hat{t}(\mathbf{r}_j) \right] + \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (19)$$

and using the same arguments as those used in deriving Equation (8), the above functional can be rewritten as [89]:

$$F[\rho] = \inf_{\rho \in \mathcal{J}_N} \left\{ \text{Tr} \left[\hat{K}_0^N D_\rho^2 \right] \right\}, \quad (20)$$

$$D_\rho^2 \rightarrow \rho(\text{fixed}), D_\rho^2 \in \mathcal{P}_N^2$$

The striking similarity between Equations (8) and (20) where the latter is the definition of the *exact* functional $F[\rho]$ leads us to the conclusion that this exact functional is fully characterized only in terms of the N -representability conditions on the reduced 2-matrix.

It has been generally assumed that there is no N -representability problem in HKS-DFT as it was believed that only N -representable conditions on the one-particle densities were necessary. But, as shown by Gilbert [62] any $\rho \in \mathcal{J}_N$ is N -representable. In fact, much more effort has been dedicated to solving the one-particle density ν -representability problem. However, the existence of functional derivatives of the functionals $F[\rho]$, important for ν -representability, is not related to the N -representability of this functional [89].

By and large, the great majority of functional developments in DFT do not incorporate the N -representability conditions on approximate realizations of the functional $F[\rho]$. Some early warnings pointing out that these conditions should be relevant are given in the works of Löwdin, McWeeny, Ludeña and Keller [90-92] as well as in the local-scaling transformation version of DFT, LST-DFT [93-96].

However, the current situation is that the N -representability of the *exact* and approximate $F[\rho]$ has been fully recognized as a true problem in HKS-DFT [89]. In fact, formal solutions (necessary and sufficient conditions) to the N -representability problem for $F[\rho]$ have been advanced by Ayers and Liu [97] and a more practical one through a variational principle for the exchange hole, by Ayers, Cuevas-Saavedra and Chakraborty [98]. However, aside from this formal recognition, there is little that has been done to impose N -representability on the construction of commonly used functionals.

Imposition of N -representability conditions on DFT functionals is not merely an academic exercise. Its importance stems from the fact that, for example, the N -electron self-interaction error is directly related to the non- N -representability of $F[\rho]$. Also, the lack of these conditions can affect the values of vibrational frequencies as well as of dipole moments [99].

One of the most successful correlation functionals in DFT is the LYP functional developed by Lee, Yang and

Parr [100]. This functional resulted from a reconstruction of the Colle-Salvetti functional, [101] which in turn came from an approximate 2-RDM formed by the product of the Hartree-Fock 2-RDM times a correlation factor. Through this reconstruction, the functional was expressed in terms of $\rho, \nabla\rho$ and $\nabla^2\rho$. Dependence on the Laplacian was later on eliminated by integration by parts [102]. Although it was suspected that this functional was not N -representable, the mathematical proof of this fact was presented by Morrison in 1993 [103]. Also, an analysis of this functional showed that it over-correlated at high density but it did not account properly for long-range correlation [104]. Other approximations based on the Colle-Salvetti ansatz, such as the Ragot-Cortona local correlation energy model, also suffer from non- N -representability [105].

Corrections of long-range correlation by means of the introduction of “double-hybrid” functionals based on second-order Møller-Plesset perturbation theory, MP2, although quite adequate for producing reasonable values for the energy, also lead to difficulties for other variables, such as the dipole moments [99]. Again, the cause of this difficulties was traced to non-observance of N -representability conditions.

In summary, although N -representability of the DFT functionals is established as a solid mathematical fact, the actual development of functionals that satisfy these conditions has not been a general trend (we should mention, however, the exceptions cited above). This lack of compliance to these conditions not only is observed in functionals standing at all rungs of Joseph’s ladder but also in the more recent double hybrid functionals, etc.

5. Conclusions

The main purpose of reviewing from a unified perspective the somewhat disparate approaches embodied in 2-RDM, 1-RDM and DFT is to bring into focus a common problem: the N -representability conditions on the energy functionals. For a long time it had been assumed that there is no N -representability problem in DFT as all that is necessary is to enforce N -representability on the one particle densities. But, as discussed in Section 4 these conditions are trivially met by most trial densities. However, the N -representability problem of the energy functional in DFT has been finally been recognized as such and it stands nowadays on firm mathematical bases. In fact, the necessary and sufficient conditions guaranteeing the N -representability of DFT functionals are known. [97].

Also in the case of the 1-RDM theory, it has been assumed that there is no N -representability problem for the energy functional and that just the knowledge of the ensemble- N -representability conditions on the 1-RDM is sufficient. For this reason, most approximations examined

in Section 3 have been determined either through heuristic considerations or by invoking reasonable physical arguments. Only in the case of the Piris functionals does one find a systematic application of the 2-RDM N -representability conditions in the construction of the 1-RDM functional.

Of course, the full-fledged application of these N -representability conditions has been realized in the context of the 2-RDM theory. Obviously, in that case there is no need to actually construct a functional for the energy because the energy is a linear functional of the 2-RDM. In the cases of the 1-RDM theory and DFT, the functionals have to be constructed by reduction of the 2-RDM in terms of natural orbitals and their occupation numbers for the 1-RDM theory, and of the density (and other forms such as gradient, Laplacian of the density, etc.), in DFT.

A systematic construction of DFT energy functionals via a reconstruction of the 2-RDM has not been the usual way to develop these functionals. Of course, we should mention the early attempt of Colle-Salvetti of setting up a correlation functional based on the 2-RDM of the helium atom which, later on, was complemented by the reconstruction of Lee-Yang-Parr of this 2-RDM in terms of the density and its derivatives leading to the LYP correlation energy functional. Maybe it is time to devise systematic schemes for the reconstruction of 2-RDM in terms of the one-particle density (and its derivatives) taking care in applying N -representability conditions. Perhaps in this way one could incorporate the computational advantages of DFT to the strictness of a quantum mechanical approach based on the enforcement of the N -representability conditions.

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