Chapter 22
The role of the N-representability in one-particle functional theories

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22.1 Introduction

The purpose of this chapter is to analyze the role of the N-representability in one-particle functional theories, that is, in theories where the ground-state energy is represented in terms of the first-order reduced density matrix (1RDM) Γ or simply its diagonal part: the density ρ. I have chosen to write on this topic to honor Norman H. March since he has always been interested on the subject. Throughout these years during his visits to the Donostia International Physics Center, Professor March has encouraged me to emphasize the importance of the *functional N-representability*, an issue that has not received enough attention in the literature. This has led us to recently write several articles together [1, 2, 3, 4, 5] using what is so far the only known natural orbital functional, namely PNOF5 [6, 7], which even including the electronic correlation, maintains a one-to-one correspondence with the energy obtained from an N-particle wavefunction [8, 9].

The term N-representability was coined by John Coleman in 1963 [10]. Already in the 1940s [11] it was known that for an N-particle quantum system with a Hamiltonian involving not more than two-body interactions, the energy is an exact functional $E[D]$ of the second-order reduced density matrix (2RDM) D. Therefore, it was frequently pointed out that the N-particle wavefunction tells us more than we need to know and its role can be assumed by the 2RDM in the discussion of physical systems. Coleman attempted this in 1951 [12] and realized that it is necessary to impose some limitations on the allowed two-matrices, in addition to general properties, to ensure a physical value of ground-state energy. The needed conditions [10] were that the two-matrix be derived from an N-particle wavefunction that is symmetric or

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antisymmetric with respect to the interchange of similar bosons or fermions, respectively. From that moment on, the search for the necessary and sufficient conditions for ensuring that D corresponds to an N-particle wavefunction became known as the N-representability problem of the 2RDM. In what follows, I will limit our attention to the case of electrons.

Many necessary conditions on the N-representability of the 2RDM were obtained in the last half-century [13], and in principle the problem was formally solved [14]. Recently, the so called $(2, q)$-positivity conditions have been proposed by Mazziotti [15], where the number q corresponds to the higher qRDM that serves as the starting point for the derivation of the condition. The (2,2)- and (2,3)-positivity conditions correspond to the already known D, Q, G, $T1$, and $T2$ conditions [10, 16, 17], whereas when $q = r$, being r the rank of the one-electron basis set, the positivity conditions are complete. Unfortunately, a complete set of N-representability conditions that do not depend on higher-order RDMs remains unknown, so a tractable solution to the N-representability problem of the 2RDM has been not found.

On the contrary, the necessary and sufficient conditions that guarantee the ensemble N-representability of Γ and ρ are well established and are very easy to implement [10, 18, 19], hence an alternative would be to develop a functional theory based on them. Like D, Γ and ρ are simpler objects than the N-particle wavefunction and further reduce the number of coordinates on which the fundamental variable depends, namely, only six or three coordinates, respectively. Hence one-particle theories are very attractive, but can we achieve exact functionals of Γ and ρ?

Starting with the Thomas-Fermi theory [20, 21], extended later by Dirac [22], the beginnings of one-particle theories go back to the time of the appearance of quantum mechanics. Important developments were made in the Thomas-Fermi theory, including those of Professor March [23], until it reached the status of density functional theory (DFT) in 1964 [24]. That year, Hohenberg and Kohn (HK) showed that the ground-state electron density for some external potential determines every property of an electronic system. An extension of the original HK theorem that eliminates the v-representability requirement on ρ was later given by Levy [25], and extensively mathematically treated by Lieb [26].

A decade after the appearance of the HK theorem, Gilbert [18] proved its analog for Γ. This work together with those of Donnelly and Parr [27], Levy [25] and Valone [28] laid the groundwork for the 1RDM functional theory (1RDMFT). However, the computational schemes based on these formulations of DFT and 1RDMFT are several times more expensive than solving directly the Schrödinger equation. Accordingly, the answer to the previous question about the existence of exact functionals is affirmative, but not in a practical sense because these exact functionals do not have an appropriate form for computation. Practical applications of one-particle theories require another approach in the construction of functionals $E[\Gamma]$ or $E[\rho]$ for the ground-state energy.

In 1967 [29], Rosina had already demonstrated that there is a one-to-one mapping from the 2RDM to the N-particle wavefunction in the case of the ground state of a Hamiltonian with at most two-body interactions. Taking advantage of the Rosina's theorem, Mazziotti defined [30] the universal functionals of Levy [25] and Valone

[28] restricting the 2RDM to be pure or ensemble *N*-representable, respectively. Therefore, the existence theorems of one-particle functionals implicitly establish a one-to-one correspondence between the ground-state D and ground-state Γ and ρ, respectively. Consequently, functionals $E[\Gamma]$ and $E[\rho]$ must match the above-mentioned exact functional $E[D]$ as expected.

It is important to note that $E[D]$ reconstructions in DFT require greater effort than in 1RDMFT, since the non-interacting part of the Hamiltonian is actually a single-particle operator, so it has an explicit dependence on Γ. The unknown functional in a Γ-based theory only needs to reconstruct the electron-electron potential energy. This reflects an undeniable advantage of 1RDMFT with respect to DFT in reconstructing the exact functional $E[D]$, and it is not surprising that the main source of problems in DFT is related to the construction of kinetic energy functional.

It is evident that if we have the exact reconstruction of $E[D]$, either in terms of Γ or ρ, ensuring the *N*-representability of the fundamental variable will guarantee the *N*-representability also of the functional. However, this exact reconstruction has been an unattainable goal until now, and we have to settle for making approximations. One possibility may be to employ the exact energy expression $E[D]$ but using solely a reconstruction functional $D[\Gamma]$ or $D[\rho]$ as required. This implies that the exact ground-state energy will not, in general, be entirely rebuilt.

Approximating the energy functional has important consequences. First, the theorems obtained for the exact functionals $E[\Gamma]$ and $E[\rho]$ are no longer valid. The point is that an approximate functional still depends on the 2RDM [31]. This situation is completely analogous to that arising when approximate wavefunctions are used instead of the exact wavefunction. An undesired implication of the 2RDM dependence is that the functional *N*-representability problem arises, that is, we have to comply the requirement that D reconstructed in terms of Γ or ρ must satisfy the same *N*-representability conditions as those imposed on unreconstructed 2RDMs to ensure a physical value of the approximate ground-state energy. Otherwise, the functional approximation will not be correct since there will not be an *N*-electron system with an energy value $E[D]$. In summary, we are no longer really dealing with the 1RDMFT or DFT, but with approximate one-particle theories, where the 2RDM continues to play the dominant role.

Unfortunately, most of the approximate functionals currently in use are not *N*-representable, and that is why energy is often obtained far below true energy. It has been generally assumed that there is no *N*-representability problem of the functional, as it is believed that only *N*-representable conditions on the 1RDM or density are sufficient. The ensemble *N*-representability constraints for acceptable Γ or ρ are easy to implement, but are insufficient to guarantee that the reconstructed 2RDM is *N*-representable, and thereby the approximate functional either. To date, only a few papers have drawn attention to this problem. Among these exceptions are the work of Ayers and Liu [32] on *N*-representability in DFT, and the more recent work by Ludeña, Torres, and Costa [33] who also deals with *N*-representability in 1RDMFT.

In case of the density, the construction of approximate functionals through the reconstruction of the 2RDM has not been the norm. At the moment we only know some attempts like the one of Colle and Salvetti [34], complemented with the recon-

struction of Lee, Yang and Parr [35], but it is not N-representable [36]. A similar situation is found in case of the 1RDM, where the approximate functionals have been proposed using heuristic or reasonable physical arguments [37]. Only the PNOFi ($i = 1 - 7$) [38, 39, 40, 41] family of functionals relies on the reconstruction of the 2RDM subject to necessary N-representability conditions. Remarkable is the case of PNOF5 [6, 7] which turned out to be strictly pure N-representable [8, 9].

Apart from the special case of the Hartree-Fock (HF) approximation that may be viewed as the simplest approximate $\Gamma-$functional, none of the known approximate functionals are explicitly given in terms of the 1RDM, including the familiar functional that accurately describes two-electron closed-shell systems [42, 43]. There are energy expressions, including those proposed by Muller [44], Csanyi and Arias [45], Sharma, Dewhurst, Lathiotakis, and Gros [46], that avoid the well-known phase dilemma [47] of the 1RDMFT, so they seem to depend properly on the 1RDM. However, these functionals violate the antisymmetric requirement for the 2RDM, consequently none of these functionals affords an N-representable 2RDM [48], nor can they reproduce the simplest two-electron case. Extensive N-representability violations have been recently reported [49] for these functionals. One can obtain quite reasonable results for some systems using them, but this does not guarantee that the calculations made are accurate since there is no N-particle density matrix that support their existence.

The functionals currently in use are constructed in the basis where the 1RDM is diagonal, which is the definition of a natural orbital functional (NOF). Accordingly, it is more appropriate to speak of a NOF rather than a functional of the 1RDM due to the existing dependence on the 2RDM. In this vein, in the NOF theory (NOFT) [50, 51], the natural orbitals (NOs) are the orbitals that diagonalize the 1RDM corresponding to an approximate energy expression, such as those obtained from an approximate wavefunction. This energy is not invariant with respect to a unitary transformation of the orbitals, and the resulting functional is only implicitly dependent on Γ or ρ through the contraction relations that determine them from D.

So far only the NOFT has proven to be able to take into account the functional N-representability in one-particle theories, thereby from now on we focus on it. This chapter continues with a presentation of the basic concepts and notations relevant to NOFT (section 22.2). The following section 22.3 is devoted to present our theory. Here, I discuss in details the reconstruction of the 2RDM that leads to PNOF approximations. The independent pair model PNOF5, as well as two results obtained with Professor March using PNOF5, namely, the behavior of the von Weizsäcker kinetic energy with the increase of N, and the calculation of chemical potential in neutral atoms, are analyzed in sections 22.4, 22.5 and 22.6, respectively. The chapter is ended with a discussion on the pure-state N-representability , which so far has been only accomplished for PNOF5 (Section 22.7).

22.2 Natural Orbital Functional Theory (NOFT)

The density matrix is the suitable mathematical object for describing an *N*-particle quantum mechanical system, since it is equally applicable to pure states and statistical ensembles [52]. Thus, consider an *N*-electron system described by the density matrix

$$\mathfrak{D} = \sum_i \omega_i \Psi_i \left(\mathbf{x}_1', \dots, \mathbf{x}_N' \right) \Psi_i^* \left(\mathbf{x}_1, \dots, \mathbf{x}_N \right) \tag{22.1}$$

In Eq. (22.1), ω_i are positive real numbers with sum one, so that $\mathfrak{D}$ corresponds to a sum of pure states with weight ω_i. Here and in the following $\mathbf{x} \equiv (\mathbf{r}, \mathbf{s})$ stands for the combined spatial and spin coordinates, $\mathbf{r}$ and $\mathbf{s}$, respectively.

The electronic energy E, in atomic units, for such *N*-electron system subject to an external potential $v(\mathbf{r})$ is an exactly and explicitly known functional of Γ and D, namely,

$$E = -\frac{1}{2} \int \nabla_1^2 \Gamma \left(\mathbf{r}_1', \mathbf{r}_1 \right) |_{\mathbf{r}_1' = \mathbf{r}_1} d\mathbf{r}_1$$

$$+ \int \Gamma(\mathbf{r}_1, \mathbf{r}_1) v(\mathbf{r}_1) d\mathbf{r}_1 + \int \frac{D(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \tag{22.2}$$

where Γ and D are obtained by contraction of $\mathfrak{D}$,

$$\Gamma \left(\mathbf{r}_1', \mathbf{r}_1 \right) = N \sum_{\sigma_1} \int \mathfrak{D} \left(\mathbf{r}_1' \sigma_1 \dots, \mathbf{r}_1 \sigma_1 \dots \right) d\mathbf{x}_2 \dots d\mathbf{x}_N \tag{22.3a}$$

$$D(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \sum_{\sigma_1, \sigma_2} \int \mathfrak{D} \left(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N \right) d\mathbf{x}_3 \dots d\mathbf{x}_N. \tag{22.3b}$$

In Eqs. (22.3), we employ Löwdin's normalization convention in which the trace of the 1RDM equals the number of electrons, and the trace of the 2RDM gives the number of electron pairs in the system.

The *N*-electron Hamiltonian does not contain any spin coordinates, hence both operators $\widehat{S}_z$ and $\widehat{S}^2$ commute with it. Consequently, the eigenfunctions of the Hamiltonian are also eigenfunctions of these two spin operators. For $\widehat{S}_z$ eigenstates, only density matrix blocks that conserve the number of each spin type are non-vanishing. Specifically, the 1RDM has two nonzero blocks $\Gamma^{\alpha\alpha}$ and $\Gamma^{\beta\beta}$, whereas the 2RDM has three independent nonzero blocks, $D^{\alpha\alpha}$, $D^{\alpha\beta}$, and $D^{\beta\beta}$. The parallel-spin components of the two-matrix must be antisymmetric, but $D^{\alpha\beta}$ possess no special symmetry [50].

In NOFT, the spectral decomposition of the 1RDM

$$\Gamma \left(\mathbf{x}', \mathbf{x} \right) = \sum_i n_i \phi_i \left(\mathbf{x}' \right) \phi_i^* \left(\mathbf{x} \right) \tag{22.4}$$

is used to approximate the electronic energy in terms of the NOs and their occupation numbers (ONs), namely,

$$E = \sum_i n_i \mathscr{H}_{ii} + \sum_{ijkl} D[n_i, n_j, n_k, n_l] \langle kl|ij \rangle \tag{22.5}$$

Here, $\mathscr{H}_{ii}$ denotes the diagonal elements of the core-Hamiltonian, $\langle kl|ij \rangle$ are the matrix elements of the two-particle interaction, and $D[n_i, n_j, n_k, n_l]$ represents the reconstructed 2RDM from the ONs.

Restriction of the ONs to the range $0 \leq n_i \leq 1$ represents a necessary and sufficient condition for ensemble N-representability of the 1RDM [10] under the normalization condition $\sum_i n_i = N$. The NOs $\{\phi_i(\mathbf{x})\}$ constitute a complete orthonormal set of single-particle functions,

$$\langle \phi_k | \phi_i \rangle = \int d\mathbf{x} \phi_k^*(\mathbf{x}) \phi_i(\mathbf{x}) = \delta_{ki} \tag{22.6}$$

with an obvious meaning of the Kronecker delta δ_{ki}.

For simplicity, we will address only singlet states in this chapter. The spin-orbital set $\{\phi_i(\mathbf{x})\}$ may be split into two subsets: $\{\varphi_p^\alpha(\mathbf{r})\alpha(\mathbf{s})\}$ and $\{\varphi_p^\beta(\mathbf{r})\beta(\mathbf{s})\}$. In order to avoid spin contamination effects, the spin restricted theory will be employed, in which a single set of orbitals is used for α and β spins: $\varphi_p^\alpha(\mathbf{r}) = \varphi_p^\beta(\mathbf{r}) = \varphi_p(\mathbf{r})$, and the parallel spin blocks of the RDMs are equal as well.

It should be noted that the first term of Eq. (22.5) has an explicit dependence on Γ, in contrast to ρ, so we do not need to reconstruct the non-interacting part of the electronic energy. In addition, we neglect any explicit dependence of D on the NOs themselves because the energy functional has already a strong dependence on the NOs via the one- and two-electron integrals. Consequently, the resulting approximate functional $E[N, \{n_i, \phi_i\}]$ can solely be implicitly dependent on Γ since the theorems on the existence of the functional $E[\Gamma]$ are valid only for the exact ground-state energy. In this vein, NOs are the orbitals that diagonalize the 1RDM corresponding to an approximate energy that still depends on the 2RDM *ergo* the energy is not invariant with respect to a unitary transformation of the orbitals. If we remember that D determines Γ, then it becomes clear that the construction of an N-representable functional given by Eq. (22.5) is related to the N-representability problem of $D[n_i, n_j, n_k, n_l]$.

22.3 PNOF Theory

A systematic application of the ensemble N-representability conditions in the reconstruction of $D[n_i, n_j, n_k, n_l]$ by means of an explicit approximation [38] of the two-particle cumulant has led to the series of Piris NOFs. Consider the cumulant expansion [53] of the 2RDM in the NO representation,

$$D_{kl,ij} = \frac{n_i n_j}{2} \left(\delta_{ki}\delta_{lj} - \delta_{li}\delta_{kj} \right) + \lambda_{kl,ij}. \tag{22.7}$$

Here, the 2RDM has been partitioned into an antisymmetric product of the 1RDMs, which is simply the HF approximation, and a correction λ to it. The latter is called the cumulant or correlation matrix. It is worth noting that matrix elements of $\boldsymbol{\lambda}$ are non-vanishing only if all its labels refer to partially occupied NOs with ONs different from 0 or 1.

The cumulant matrix must fulfill as many necessary *N*-representability conditions as possible to ensure the *N*-representability of *D* since requiring all conditions is not practicable due to their dependence on higher-order RDMs. The use of the (2,2)-positivity *N*-representability conditions [15] for reconstructing λ was proposed in reference [38]. This particular reconstruction is based on the introduction of two auxiliary matrices $\boldsymbol{\Delta}$ and Π expressed in terms of the ONs. In a spin restricted formulation, the structure of the two-particle cumulant is

$$\lambda_{pq,rt}^{\sigma\sigma} = -\frac{1}{2}\Delta_{pq} \left(\delta_{pr}\delta_{qt} - \delta_{pt}\delta_{qr} \right) \tag{22.8a}$$

$$\lambda_{pq,rt}^{\alpha\beta} = -\frac{1}{2}\Delta_{pq}\delta_{pr}\delta_{qt} + \frac{1}{2}\Pi_{pr}\delta_{pq}\delta_{rt}. \tag{22.8b}$$

$\boldsymbol{\Delta}$ is a real symmetric matrix, whereas Π is a spin-independent Hermitian matrix. The *N*-representability *D* and *Q* conditions of the 2RDM impose the following inequalities on the off-diagonal elements of $\boldsymbol{\Delta}$ [38],

$$\Delta_{qp} \leq n_q n_p, \qquad \Delta_{qp} \leq h_q h_p, \tag{22.9}$$

while to fulfill the *G* condition, the elements of the Π-matrix must satisfy the constraint [54]

$$\Pi_{qp}^2 \leq (n_q h_p + \Delta_{qp})(h_q n_p + \Delta_{qp}), \tag{22.10}$$

where h_p denotes the hole $1 - n_p$ in the spatial orbital p. Furthermore, the sum rules that must fulfill the blocks of the cumulant yield a sum rule for $\boldsymbol{\Delta}$,

$$\sum_{p,q;p\neq q} \Delta_{qp} = n_p h_p. \tag{22.11}$$

Within this reconstruction, the energy for singlet states reads as

$$E = \sum_p n_p \left(2\mathscr{H}_{pp} + \mathscr{J}_{pp} \right) + \sum_{p,q;p\neq q} \Pi_{qp}\mathscr{L}_{pq} + \sum_{p,q;p\neq q} \left(n_q n_p - \Delta_{qp} \right) \left(2\mathscr{J}_{pq} - \mathscr{K}_{pq} \right), \tag{22.12}$$

where $\mathscr{J}_{pq} = \langle pq|pq\rangle$ and $\mathscr{K}_{pq} = \langle pq|qp\rangle$ are the usual direct and exchange integrals, respectively. $\mathscr{J}_{pp}$ is the Coulomb interaction between two electrons with opposite spins at the spatial orbital p, whereas $\mathscr{L}_{pq} = \langle pp|qq\rangle$ is the exchange and time-inversion integral [55], so the functional (22.12) belongs to the $\mathscr{J}\mathscr{K}\mathscr{L}$-only family of NOFs.

The conservation of $\widehat{S}^2$ allows to derive the diagonal elements $\Delta_{pp} = n_p^2$ and $\Pi_{pp} = n_p$ [56]. Appropriate forms of matrices Δ and Π lead to different implementations of the NOF known in the literature as PNOFi ($i = 1 - 7$) [38, 39, 40, 41]. The performance of these functionals is comparable to those of best quantum chemistry methods in many cases, being particularly interesting the case of PNOF3 [57] in relation with the functional N-representability.

PNOF3 showed [57] exceptional performance for atoms and molecules, both for spin-compensated and spin-non-compensated. This NOF can describe the correct topology of potential energy surfaces highly sensitive to electron correlation, giving reaction barriers and isomerization energies with an accuracy of less than 1 kcal/mol [58]. However, a closer analysis of the dissociation curves for various diatomics [54], as well as the description of diradicals and diradicaloids [59], revealed that PNOF3 overestimates the amount of electron correlation, when orbital near-degeneracy effects become important.

This is a paradigmatic case of how highly accurate results achieved with a functional can be misleading. The PNOF3 satisfies the D and Q N-representability conditions given by Eq. (22.9), but violates the G condition (22.10). It was demonstrated [54] that the ill behavior of PNOF3 is related to the violation of the latter conditions. Only the progressive inclusion of N-representability conditions can lead to reconstructions with physical meaning since it is the only way to ensure that the energy corresponds to a density matrix of N electrons. This approach has been called the bottom-up method [33].

22.4 Independent pair approximation

Let's divide the orbital space Ω into $N/2$ mutually disjoint subspaces Ω_g, so each orbital belongs only to one subspace. Consider each subspace contains one orbital g below the Fermi level ($N/2$), and N_g orbitals above it, which is reflected in additional sum rules for the ONs:

$$\sum_{p \in \Omega_g} n_p = 1; \quad g = 1, 2, \dots, N/2. \tag{22.13}$$

Taking into account the spin, each subspace contains solely an electron pair, and the normalization condition for Γ ($2\sum_p n_p = N$) is automatically fulfilled. Coupling each orbital g below the Fermi level with only one orbital above it ($N_g = 1$) also leads to an orbital perfect pairing. It is important to note that orbitals satisfying the pairing conditions (22.13) are not required to remain fixed throughout the orbital optimization process [60].

The simplest way to comply with all required constraints leads to an independent pair model (PNOF5) [6, 7]:

$$\Delta_{qp} = n_p^2 \delta_{qp} + n_q n_p (1 - \delta_{qp}) \delta_{q\Omega_g} \delta_{p\Omega_g} \tag{22.14a}$$

$$\Pi_{qp} = n_p \delta_{qp} + \Pi_{qp}^g (1 - \delta_{qp}) \delta_{q\Omega_g} \delta_{p\Omega_g} \tag{22.14b}$$

$$\Pi_{qp}^g = \begin{cases} -\sqrt{n_q n_p} & p = g \text{ or } q = g \\ +\sqrt{n_q n_p} & p, q > N/2 \end{cases} \tag{22.14c}$$

$$\delta_{q\Omega_g} = \begin{cases} 1, & q \in \Omega_g \\ 0, & q \notin \Omega_g \end{cases} \quad g = 1, 2, \dots, N/2. \tag{22.14d}$$

Given this functional form of the auxiliary matrices Δ and Π, the energy (22.12) of the PNOF5 can be conveniently written as

$$E = \sum_{g=1}^{N/2} E_g + \sum_{f \neq g}^{N/2} E_{fg} \tag{22.15a}$$

$$E_g = \sum_{p \in \Omega_g} n_p (2\mathcal{H}_{pp} + \mathcal{J}_{pp}) + \sum_{p,q \in \Omega_g, p \neq q} \Pi_{qp}^g \mathcal{L}_{pq} \tag{22.15b}$$

$$E_{fg} = \sum_{q \in \Omega_f} \sum_{p \in \Omega_g} n_q n_p (2\mathcal{J}_{pq} - \mathcal{K}_{pq}). \tag{22.15c}$$

The first term of the energy draws the system as $N/2$ independent electron pairs, whereas the second term contains the contribution to the HF mean-field of the electrons belonging to different pairs.

Several performance tests have shown that PNOF5 yields remarkably accurate descriptions of systems with near-degenerate one-particle states and dissociation processes [61, 62, 63, 4]. In this sense, the results obtained with PNOF5 for the electronic structure of transition metal complexes are probably the most relevant [64]. This functional correctly takes into account the multiconfigurational nature of the ground state of the chromium dimer, known as a benchmark molecule for quantum chemical methods due to the extremely challenging electronic structure of the ground state and potential energy curve.

PNOF5 has also been successfully used to predict vertical ionization potentials and electron affinities of a selected set of organic and inorganic spin-compensated molecules, by means of the extended Koopmans' theorem [65]. The improvement due to the inclusion of more orbitals in the description of each pair was also observed by visualizing the electron densities by means of the Bader's theory of atoms in molecules in the case of a set of light atomic clusters: Li_2, Li_3^+, Li_4^{2+} and H_3^+ [7]. The size-consistency property, and the fact that the functional tends to localize spatially the NOs, make PNOF5 an exceptional candidate for fragment calculations. The latter showed a fast convergence, which allowed the treatment of extended system at a fractional cost of the whole calculation [66].

As mentioned above, NOFs still depend explicitly on the 2RDM, so the energy is not invariant with respect to a unitary transformation of the orbitals. Because of this, the NOFT provides two complementary representations of the one-electron picture, namely, the NO representation and the canonical orbital representation [67].

The former arises directly from the optimization process solving the corresponding Euler equations, whereas the latter is attained from the diagonalization of the matrix of Lagrange multipliers obtained in the NO representation. Both set of orbitals represent unique correlated one-electron pictures of the same energy minimization problem, *ergo,* they complement each other in the analysis of the molecular electronic structure. The orbitals obtained in both representations, using the electron pairing approaches in NOFT, have shown [68, 69, 63, 70] that the electron pairs with opposite spins continue to be a suitable language for the chemical bond theory.

In this tribute to Professor March, two results obtained with PNOF5 deserve special attention: the behavior of the von Weizsäcker kinetic energy with the increase of N [1], and the calculation of chemical potential in neutral atoms [2].

22.5 von Weizsäcker kinetic energy term for diatomic molecules

In 1983, Mucci and March reported [71] on the importance of density gradients for molecular binding in diatomics. The simplest density gradient kinetic energy term was introduced by von Weizsäcker [72] as follows

$$T_w = \frac{\hbar^2}{8m} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} \qquad (22.16)$$

Recently [1], Eq. (22.16) was used to calculate the von Weizsäcker energy for some 30 homonuclear diatomic molecules at their experimental equilibrium geometry employing densities obtained from PNOF5. We considered only spin singlets for these molecules, although in some cases their ground state are triplets. In addition, all calculations were made at the non-relativistic level of theory.

Our results, from H_2 to Ge_2, reveal [1] a slowly varying character of T_w/N^2, where N is the total number of electrons in the molecule under consideration. For example, from N_2 to Ge_2, the variation was from 0.44 to 0.49 atomic units. This led us to conclude that the Schrödinger's non-relativistic equation predicts, at the equilibrium, the following relationship

$$T_w \to \frac{1}{2}N^2 \qquad (22.17)$$

as N becomes large, say at Cr_2 and higher N cases.

22.6 The chemical potential

The solution in PNOF5 theory is established by optimizing the energy functional (22.15) with respect to the ONs and NOs separately, for which the iterative diagonalization procedure proposed by Piris and Ugalde [60] is employed. The orbitals must

satisfy the orthonormality requirement, Eq. (22.6), whereas the occupancies have to conform to the electron pairing constraints (22.13) and ensemble *N*-representability conditions for the 1RDM ($0 \leq n_p \leq 1$). The latter bounds can be easily enforced by setting $n_p = \cos^2 \gamma_p$, and varying $\{\gamma_p\}$ without these constraints. The other conditions may be easily taken into account by the method of Lagrange multipliers.

Let us focus on the minimization of $\{\gamma_p\}$ for a fixed set of NOs. We associate the Lagrange multipliers $\{\mu_g\}$ with conditions (22.13), and define the auxiliary functional Ω by the formula

$$\Omega\left[N, \{\gamma_p\}\right] = E - 2 \sum_{g=1}^{N/2} \mu_g \left(\sum_{p \in \Omega_g} \cos^2 \gamma_p - 1 \right) \tag{22.18}$$

The functional (22.18) has to be stationary with respect to variations in $\{\gamma_p\}$,

$$\delta\Omega = \sum_{g=1}^{N/2} \sum_{p \in \Omega_g} \sin\left(2\gamma_p\right) \left[2\mu_g - \frac{\partial E}{\partial n_p} \right] d\gamma_p = 0 \tag{22.19}$$

The partial derivative $(\partial E / \partial n_p)$ is taken holding the orbitals fixed. It satisfies the relation

$$\frac{\partial E}{\partial n_p} = 2\mathscr{H}_{pp} + \frac{\partial V_{ee}}{\partial n_p} = 2\mu_g, \quad \forall p \in \Omega_g, \tag{22.20}$$

where the partial derivative of electron-electron repulsion energy V_{ee} is given by the expression

$$\frac{\partial V_{ee}}{\partial n_p} = \mathscr{J}_{pp} + 2 \sum_{q \in \Omega_g, q \neq p} \frac{\partial \Pi_{qp}^g}{\partial n_p} \mathscr{L}_{qp} + 2 \sum_{f \neq g}^{N/2} \sum_{q \in \Omega_f} n_q \left(2\mathscr{J}_{qp} - \mathscr{K}_{qp} \right), \forall p \in \Omega_g. \tag{22.21}$$

Accordingly, the Lagrange multipliers $\{\mu_g\}$ can be written as

$$\mu_g = \mathscr{H}_{pp} + \frac{1}{2} \frac{\partial V_{ee}}{\partial n_p}, \quad \forall p \in \Omega_g \tag{22.22}$$

It follows from Eq. (22.22) that we have $N/2$ Lagrange multipliers which can be identified as chemical potentials in virtue of the result obtained in [73]. An infinitesimal change in the number of electrons is energetically more advantageous when added to an orbital associated with the smallest μ_g. Therefore, we identify [2] the latter with the chemical potential μ of an *N*-electron open system in a singlet ground state.

In Ref. [2], calculations of the chemical potential in 36 neutral atoms of the first three rows of periodic table (H-Kr) were presented and compared and contrasted with available experimental values. The chemical potential of a single atom in its multiplet ground state was obtained from the calculation made in the corresponding dimer in a singlet state considering the homonuclear diatomics at infinite separation (50 Å) between atoms. This is possible because the functional PNOF5 is

size-extensive and size-consistent [7]. In general, our results showed that the chemical potentials overestimate the experimental values of the ionization (I) although the expected oscillatory behavior was maintained. There were exceptions where the value of μ lies quite close to the experimental marks, namely, H, Li, B, C, N, Na, Al, Si, P, K, Ga, Ge, and As.

In case of noble gas atoms, the chemical potential doubled approximately the value of $-I$. It is known [73] that μ presents a discontinuity at integer particle number equals to the fundamental gap, *i.e.,* the difference between the electron affinity and the ionization potential for a given number of electrons. In closed-shell systems, like noble gas atoms, no energy is given off when a neutral atom of these elements picks up an electron, hence, there is no electron affinity, or these atoms have electron affinities with opposite sign. Our estimation of the chemical potentials reflected this situation by increasing the expected value referred to the ionization potential.

22.7 Pure *N*-representability

So far in this work, we have focused on the *N*-representability problem for statistical ensembles. The fact that Coleman obtained [10] the restrictions on the ONs ($0 \leq n_i \leq 1$, $\sum_i n_i = N$), also known as Pauli constraints, so that the 1RDM is representable by at least one *N*-electron density matrix, prompted the search for similar conditions on the pure-state *N*-representability. In 1972, Borland and Dennis showed [74] computationally that additional constraints on Γ are necessary for it to be representable by at least one pure *N*-electron density matrix. It was not until very recently that these conditions named generalized Pauli constraints (GPCs) have been obtained [75, 76], taking the form

$$\kappa_{0j} + \sum_{i=1}^{r} \kappa_{ij} n_i \geq 0, \qquad j = 1, 2, \ldots < \infty, \tag{22.23}$$

where $\{\kappa_{ij}\}$ are integer constants, r is the rank of the orbital space Ω, and the ONs are decreasingly ordered. The Pauli conditions define the set $E(N,r)$ of ensemble *N*-representable 1RDMs, whereas the inequalities (22.23) in combination with the formers define the set $P(N,r)$ of pure *N*-representable 1RDMs. Spectra $\{n_i\}$ lying outside of the pure set can only correspond to a mixed state.

A relevant result on the necessity of using the pure-state *N*-representability conditions in the minimization of the exact functional $E[\Gamma]$, was obtained by Nguyen-Dang, Ludeña and Tal [77]. They demonstrated that if we define an universal energy functional in the domain $E(N,r)$ then it will be exactly equal to the universal energy functional defined in the domain $P(N,r)$ over this last set, that is, over the set of pure-state *N*-representable 1RDMs. This equality justified the use of the ensemble *N*-representability necessary and sufficient conditions on Γ, but it required an adequate construction of the functional which would guarantee that $\Gamma \in P(N,r)$, as they showed. In fact, they corroborated Valone's thesis [28] that in order to guarantee the

pure-state *N*-representability conditions in the minimization of the energy only the ensemble constraints are necessary if the functional is an appropriate one. But what will happen if the functional is approximate?

If the approximate NOF is strictly pure-state *N*-representable, *i.e.,* it is obtained from the reconstruction of a strictly pure-state *N*-representable 2RDM, then the 1RDM that *D* determines by contraction will also be automatically pure-state *N*-representable. Therefore, for approximate functionals it is also valid to take into account solely the ensemble constraints in the minimization with respect to Γ if the functional is an appropriate one. A palpable example is PNOF5.

Two years after PNOF5 was proposed using the bottom-up method (vide supra Sec. 22.4), the natural geminals of PNOF5 were analyzed [78] and it was realized by Pernal [8] that this NOF corresponds to the energy obtained from a wavefunction of an antisymmetrized product of strongly orthogonal geminals if the expansion of the $N/2$ geminals is limited to two-dimensional subspaces with fixed signs for the expansion coefficients of the corresponding geminals. Shortly after this ansatz was extended to include more orbitals in the description of the electron pairs [7]. This finding demonstrated that PNOF5 is strictly a pure-state *N*-representable functional.

Looking more closely at the Eq. (22.13), we realize that the pairing conditions meet the requirements to be GPCs (22.23). Indeed, the equality conditions obtained [79] for 3 electrons in a space of 6 natural spin-orbitals are exactly the perfect-pairing conditions proposed in Ref. [6] to satisfy the sum rules (22.11) for Δ-matrix, *i.e.,* for the two-electron cumulant in PNOF5. It is important to note that the success of PNOF5 relies on the use of GPCs in the formulation of the reconstruction $D[n_i, n_j, n_k, n_l]$, and not in its later use to limit the domain of the trial one-matrices.

GPCs have recently [80] received increased attention in NOFT following the discovery of a systematic way to derive them for any number of electrons and any finite dimensionality of the Hilbert space. Unfortunately, it has been found that the number of conditions increases dramatically with the number of NOs, so it can be quite difficult to handle them in practical implementations. On the other hand, the verification of the fulfillment of these conditions for some current non-*N*-representable approximations in 3-electron systems showed [80] that, in all cases, some of the pure-state conditions were violated. The enforcement of additional GPCs in the minimization led to an improvement of the total energy and of the optimal 1RDM with respect to those obtained by imposing only the Pauli constraints.

There is no doubt that the application of GPCs restricts the 1RDM variational space leading to improvements in energy and Γ, but it does not improve the reconstruction of the approximate functional per se. A 1RDM that represents a pure state does not guarantee that the reconstructed electron-electron potential energy will be pure-state *N*-representable, except that the reconstruction is the exact one, something that until now has not been possible to reach. The functional *N*-representability problem continues to exist for pure states when we make approximations for the functional, and it is still related to the *N*-representability, in this case for pure states, of the 2RDM.

22.8 Closing remarks

In this chapter, the N-representability problem in one-particle functional theories has been analyzed. It turns out that here this problem is twofold. First, we have the N-representability problem of the fundamental variable, Γ or ρ, as the case may be. Fortunately, the necessary and sufficient conditions that guarantee the ensemble N-representability of Γ and ρ are well established and are very easy to implement, which makes one-particle theories extremely attractive. The other side however is trickier.

On the one hand we have that for the exact functional of the density or 1RDM, it suffices to require the N-representability of the fundamental variable to guarantee that the ground-state energy corresponds to an N-electron density matrix. However, exact formulations of DFT and 1RDMFT do not have an appropriate form for computation and we have to settle for making approximations, which imply that the theorems obtained for the exact functionals $E[\Gamma]$ and $E[\rho]$ are no longer valid.

The main approach route is to use the well-known exact energy expression $E[D]$ with a reconstruction $D[\Gamma]$ or $D[\rho]$ as required. Such an approximate functional still depends on the 2RDM. An eventual outcome of this D-dependence is the functional N-representability problem, that is, for a 2RDM reconstructed in terms of Γ or ρ we have to impose the same N-representability conditions that we enforce on unreconstructed 2RDMs to ensure a physical value of the approximate ground-state energy. This is the only way of assurance that there is an N-electron system with an energy value $E[D]$. We are no longer really dealing with the 1RDMFT or DFT, but with approximate one-particle theories, where the 2RDM continues to play the dominant role.

Most of the approximate functionals currently in use are not N-representable hence this second side of the N-representability in one-particle functional theories has not received sufficient attention. Breaking the particle number symmetry can sometimes give qualitative descriptions of the phenomena at cost of the good quantum number N. These types of methods are well known in physics but a projection is always imposed to the correct N-conserving quantum state.

So far only the NOF theory, where functionals are constructed in the basis where the 1RDM is diagonal, has proven to be able to take into account the functional N-representability in one-particle theories. In particular, the PNOF family of functionals relies on the reconstruction of the 2RDM subject to necessary N-representability conditions. Remarkable is the case of PNOF5 which turned out to be strictly pure N-representable since it maintains a one-to-one correspondence with the energy obtained from an N-particle wavefunction.

The most direct method to generate a pure-state N-representable NOF is by reducing the energy expression obtained from an approximate N-particle wavefunction to a functional of the occupation numbers and natural orbitals. By doing this, we automatically avoid the N-representability problem of the 2RDM, or what is the same, of the functional. However, this is a formidable task that is far from being something attainable in most cases. Only PNOF5 has achieved this goal including the electron correlation.

The success of PNOF5 relies on the use of additional pairing conditions in the reconstruction of the 2RDM, which can be seen as generalized Pauli constraints. The use of these conditions when reconstructing the 2RDM will give rise to *N*-representable functionals that will go beyond the independent pair model.

Finally, if the approximate NOF is strictly pure-state *N*-representable, *i.e.,* it is obtained from the reconstruction of a strictly pure-state *N*-representable 2RDM, then the 1RDM will also be automatically pure-state *N*-representable. Therefore, for approximate functionals it is valid to take into account solely the ensemble constraints in the minimization with respect to the 1RDM if a pure-state *N*-representable functional is employed.

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