Natural orbital functional theory: Molecules and polymers

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Abstract

A natural orbital functional (NOF) satisfying the properties of the reduced density matrices is critically reviewed. Test calculations of the total and ionization energies, dipole moments, equilibrium geometries and harmonic vibrational frequencies of several molecules in the ground state demonstrate the reliability of the formalism. The extension of NOF theory to calculate correlation energies for periodic polymers is analyzed. The experimentally observed reduction of the Hartree-Fock lattice spacing by the inclusion of electron correlation is correctly predicted for trans-polyacetylene.

I. Introduction

In 1940, it was realized by Husimi [1] that the energy of a quantum mechanical N-electron state is an exact functional of one- and two-particle reduced density matrices Γ and D, respectively, or even just of D, because D determines Γ. This was emphasized

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later by Löwdin in 1955 [2]. Although this functional is known, the two-matrix has not replaced the wave function as the fundamental quantity of electronic structure because a simple set of necessary and sufficient conditions for ensuring that **D** corresponds to an N-particle wave function is not known (the N-representability problem) [3]. The minimization of the energy with respect to a two-matrix constrained by the well-known D-, Q- and G-necessary conditions [3,4] has been presented [5] with accurate results. The contracted Schrödinger equation (CSE), also known as the density equation, offers a non-variational approach to constrain the two-matrix to be approximately N-representable [6]. The difficulty with this method lies in the need for the 3- and 4-reduced density matrices which have to be reconstructed from the two-matrix. The number of elements in the two-matrix in general is still very large.

Hohenberg and Kohn [7] demonstrated that the ground state energy is even a functional of the one-electron density ρ only. It appeared that there is not N-representability problem for density functional theory (DFT) since the conditions that ensure that a one-particle density comes from an N-particle wave function are well-known [8]. However, here the obstacle is the construction of the functional $E[\rho]$ capable of describing a quantum-mechanical N-electron system. Unfortunately, attempts to construct it have not been very successful due to the strong nonlocality of the kinetic energy term. Implementations of the DFT [9] that followed the recipe of Kohn-Sham (KS) [10], i.e., in which the kinetic energy is not constructed as a functional of ρ but rather from an auxiliary Slater determinant, are currently of common use. Although present-day density functionals are remarkably accurate, there are many problems for which they are not good enough.

Somewhere intermediate between a **D**-based theory and one based on ρ are attempts to formulate the energy as a functional of the one-particle density matrix Γ. The existence [11] and properties [12,13] of the total energy functional of the one-matrix are well-known. A major advantage of a density matrix formulation is that the kinetic energy and the exchange energy are explicitly defined using the one-matrix and do not require the construction of a functional. The unknown functional in a Γ-based theory only needs to incorporate electron correlation. It does not rely on the concept of a fictitious non-interacting system. Consequently, density matrix schemes are not expected to suffer from the numerous problems of KS methods.

The idea of a one-matrix functional appeared some decades ago [14]. More recently, Goedecker and Umrigar (GU) [15] proposed a simple functional without adjustable parameters. The basic form of this functional can be traced to Müller [16] and has also been studied by Buijse and Baerends [17]. Holas [18], Cioslowski and Pernal [19] have proposed different generalizations of this functional. The GU functional satisfies the Hermiticity and particle permutation conditions but violates the non-negativity condition for the diagonal elements of the two-matrix. Moreover, the GU functional gives a wrong description of the occupation numbers for the lower occupied levels [19]. Csanyi and Arias (CA) [20] proposed another functional from the condition that the two-matrix is a tensor product of one-particle operators and that it satisfies the Hermiticity and particle-permutation constraints. Unfortunately, the CA functional gives almost vanishing correlation energies in contrast to the GU functional. All these functionals can be

classified in two types: corrected Hartree (CH) and corrected Hartree-Fock (CHF), using the terminology of Csanyi and Arias [20]. A Γ-based functional combining the properties of the CH and CHF approximations was also proposed [21]. An improved CHF-type functional leading to better results for the free-electron gas has been suggested [22] too. The N-representability and the variational stability of these proposals have been recently investigated [23] in detail.

K. Yasuda [24] has obtained a correlation energy functional E_c of the one-matrix from the first- and second-order density equations together with the decoupling approximations for the 3- and 4-reduced density matrices. The Yasuda functional is capable of properly describing a high-density homogeneous electron gas [25] and encouraging results have been reported for atoms and molecules [24]. Some shortcomings of this functional are also pointed out [26]. D. A. Mazziotti [27] has proposed a geminal functional theory (GFT) where an antisymmetric two-particle function (geminal) serves as the fundamental parameter. The one-matrix-geminal relationship allowed him to define a Γ-based theory from GFT [28]. An implicit one-matrix functional based on the Hartree-Fock-Bogolyubov theory has also been reported [29]. However, this interesting approach relates the functional to a non-size consistent wave function.

The straightforward route to the construction of approximate one-matrix functional involves employment of expressions for E and Γ afforded by some size-consistent formalism of electronic structure theory. Cioslowski *et al.* [13] have provided a prescription for deriving one-matrix functionals from the ground-state energy expression of any approximate electronic structure method. In the case of four-electron systems, an approximate expression for the electron-electron repulsion energy has been proposed [30] using a permanent-based parametrization of coefficients in a pair-excitation configuration interaction (CI) expansion. Moreover, a particular parametrization of coefficients in a CI expansion leaded to an explicit functional in terms of the Coulomb and exchange integrals over natural orbitals, and an idempotent matrix, diagonal elements of which equal the occupation numbers [31]. However, the obtained functional cannot be employed in practical calculations due to the necessity of carry out minimization over a large number of possible combinations of CI coefficient signs (phase dilemma).

Recently, we have proposed [32] a new one-matrix functional satisfying the most general properties of the reduced density matrices. This functional yields correlation energies as good as those obtained from the density functionals, and the obtained dipole moments approach to the experimental values. Calculations of polarizabilities show that the proposed natural orbital functional has predictive capabilities for the electric response properties [33]. Its extension to calculate correlation energies for periodic polymers has also been presented [34].

We start with a presentation of the basic concepts and notations relevant to density matrix functional theory (Section II). We then review the fundaments of the Γ-based theory (Section III) and present our natural orbital functional (Section IV). The cumulant of the two-matrix and the size-consistent property of the functional are discussed in detail here. The following section is devoted to the extension of the functional to quasi-one-dimensional periodic polymers (Section V). We end with a short presentation of the variational procedure (Section VI) and some results for selected molecules and polyacetylene (Section VII).

II. Basic concepts and notations

We consider an N-electron Coulombic system described by the Hamiltonian

$$\widehat{H} = \sum_{ij} h_{ij}\widehat{\Gamma}_{ji} + \sum_{ijkl} < ij|kl > \widehat{D}_{kl,ij}$$

(1)

where h_{ij} denote the one-electron matrix elements of the core-Hamiltonian $\hat{h}$,

$$h_{ij} = < \chi_i| -\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{r}_I|} |\chi_j> = \int\int d\mathbf{x}\chi_i^*(\mathbf{x})\left[-\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{r}_I|}\right]\chi_j(\mathbf{x})$$

(2)

and $< ij|kl >$ denote the two-electron matrix elements of the Coulomb interaction

$$< ij|kl > = < \chi_i\chi_j| r_{12}^{-1} |\chi_k\chi_l> = \int\int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2) r_{12}^{-1}\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2)$$

(3)

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 spin-orbitals $\{\chi_i(\mathbf{x})\} = \{\psi_i(\mathbf{r})\sigma(\mathbf{s})\}$ constitute a complete orthonormal set of single-particle functions,

$$< \chi_i|\chi_j> = \int d\mathbf{x}\chi_i^*(\mathbf{x})\chi_j(\mathbf{x}) = \delta_{ij}$$

(4)

with an obvious meaning of the Kronecker delta δ_{ij}. The one- and two-particle density matrix operators,

$$\widehat{\Gamma}_{ji} = \widehat{a}_j^+\widehat{a}_i$$

(5)

and

$$\widehat{D}_{kl,ij} = \left(\frac{1}{2}\right)\widehat{a}_k^+\widehat{a}_l^+\widehat{a}_j\widehat{a}_i$$

(6)

are constructed from the familiar creation and annihilation operators, $\{\hat{a}_i^+\}$ and $\{\hat{a}_i\}$ [35], respectively, associated with the set of spin-orbitals $\{\chi_i(\mathbf{x})\}$.

A quantum mechanical pure state of our N-particle system can be characterized by a normalized wave function Ψ or a system density matrix Γ_N

$$\Gamma_N(\mathbf{x}_1', \mathbf{x}_2', ..., \mathbf{x}_N'; \mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \Psi^*(\mathbf{x}_1', \mathbf{x}_2', ..., \mathbf{x}_N')\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$$

(7)

The expectation value of the Hamiltonian (1) for the state Ψ is then

$$E = <\Psi|\,\widehat{H}\,|\Psi>= \sum_{ij} h_{ij}\Gamma_{ji} + \sum_{ijkl} <ij|kl> D_{kl,ij} \tag{8}$$

where the one- and two-particle reduced density matrices, or briefly the one- and two matrices, are defined as

$$\Gamma_{ji} = <\Psi|\,\widehat{a}_j^+\widehat{a}_i\,|\Psi> \tag{9}$$

$$D_{kl,ij} = \frac{1}{2} <\Psi|\,\widehat{a}_k^+\widehat{a}_l^+\widehat{a}_j\widehat{a}_i\,|\Psi> \tag{10}$$

According to expression (8) the energy E of a state Ψ is an exactly and explicitly known functional of $\boldsymbol{\Gamma}$ and $\mathbf{D}$.

The reduced density matrices satisfy important sum rules [36]. The trace of the one-matrix equals the number of electrons

$$\mathrm{Tr}\,\boldsymbol{\Gamma} = \sum_i \Gamma_{ii} = N \tag{11}$$

and the trace of the two-matrix gives the number of electron pairs in the system

$$\mathrm{Tr}\,\mathbf{D} = \sum_{ij} D_{ij,ij} = \frac{N(N-1)}{2} = \binom{N}{2} \tag{12}$$

Their diagonal elements are always non-negative, since Γ_{ii} is related to the probability of finding one electron at i, and $D_{ij,ij}$ is related to the probability of finding one electron at i and another at j.

$\mathbf{D}$ satisfies several relations which follow directly from the anticommutation rules and the Hermiticity of the operators $\{\hat{a}_i^+\}$ and $\{\hat{a}_i\}$, namely, the Hermiticity,

$$D_{kl,ij} = D_{ij,kl}^* \tag{13}$$

the particle permutational symmetry,

$$D_{kl,ij} = D_{lk,ji} \tag{14}$$

and the antisymmetry,

$$D_{kl,ij} = -D_{lk,ij} = -D_{kl,ji} \tag{15}$$

There is an important contraction relation between one- and two-matrices that is in agreement with the previous normalization (11)-(12),

$$\Gamma_{ji} = \frac{2}{N-1} \sum_k D_{jk,ik} \tag{16}$$

This implies that the energy functional (8) is just of the two-matrix, because **D** determines Γ. However, attempts to determine the energy by minimizing $E[\mathbf{D}]$ are complicated due to the lack of a simple set of necessary and sufficient conditions for ensuring that the two-matrix corresponds to an N-particle wave function (the N-representability problem) [3]. However, some necessary conditions have been derived [37]. The so called D-condition is equivalent to the requirement that the two-matrix be positive. The G- and Q-conditions state that the electron-hole density matrix **G** and the two-hole density matrix **Q**:

$$G_{kl,ij} = < \Psi | \hat{a}_k^+ \hat{a}_l \hat{a}_j^+ \hat{a}_i | \Psi > \tag{17}$$

$$Q_{kl,ij} = < \Psi | \hat{a}_k \hat{a}_l \hat{a}_j^+ \hat{a}_i^+ | \Psi > \tag{18}$$

must be positive semidefinite. There are also other two necessary conditions for the N-representability of a fermion two-matrix which were named B- and C-conditions. A discussion of relations among these *positivity* conditions is given in Ref. [38].

Using the anticommutation relations for creation and annihilation operators and definitions of the one- and two-matrices given in Eqs. (9)-(10), the matrices **G** and **Q** can be derived from the matrices **D** and Γ as follows:

$$G_{kl,ij} = \delta_{lj}\Gamma_{ki} - 2D_{kj,il} \tag{19}$$

$$Q_{kl,ij} = (\delta_{ki}\delta_{lj} - \delta_{kj}\delta_{li}) - (\delta_{ki}\Gamma_{jl} + \delta_{lj}\Gamma_{ik}) + (\delta_{kj}\Gamma_{il} + \delta_{li}\Gamma_{jk}) + 2D_{ij,kl} \tag{20}$$

III. The Γ-based theory

Let us replace the last term in Eq. (8), which is an explicit functional of the two-matrix, by an unknown functional of the one-matrix,

$$E[\mathbf{\Gamma}] = \sum_{ij} h_{ij}\Gamma_{ji} + V_{ee}[\mathbf{\Gamma}] \tag{21}$$

The Levy constrained-search formalism provides a proof [11] by construction of the existence of this universal functional, in other words, it is given by the expression

$$V_{ee}[\mathbf{\Gamma}] = \min_{\Psi \to \Gamma} < \Psi | \hat{V}_{ee} | \Psi > \tag{22}$$

where the minimization is over all wave functions that yield the one-matrix Γ. $\hat{V}_{ee}$ is the electron-electron repulsion potential energy operator

$$\widehat{V}_{ee} = \sum_{ijkl} <ij|kl> \widehat{D}_{kl,ij} \tag{23}$$

The functional (22) is universal in the sense that it is independent of the external field. Its properties are well-known [12]. Moreover, the exact one-matrix functional for the two-electron closed-shell systems like H_2 or He is known too [39,40]. However, it is highly difficult to approximate because what we have done is to change the variational unknown from the complicated many-variable function Ψ to a single one-matrix Γ.

The one-matrix Γ can be diagonalized by a unitary transformation of the spin-orbitals $\{\chi_i(\mathbf{x})\}$ with the eigenvectors being the natural spin-orbitals and the eigenvalues $\{n_i\}$ representing the occupation numbers of the latter,

$$\Gamma_{ji} = n_i \delta_{ji} \tag{24}$$

Restriction of the occupation numbers $\{n_i\}$ to the range $0 \le n_i \le 1$ represents a necessary and sufficient condition for N-representability of the one-matrix [3]. In the following, all representations used are assumed to refer to the basis of natural spin-orbitals.

We must note that the functional and the one-matrix N-representability problems are entirely different. The former refers to the conditions that guarantee the one-to-one correspondence between $E[\Psi]$ and $E[\Gamma]$, which is a related problem to the N-representability of the two-matrix. Consequently, any approximation for $V_{ee}[\Gamma]$ or equivalently $V_{ee}[\{n_i, \chi_i\}]$, where $\{n_i, \chi_i\}$ denotes the complete set of natural occupations numbers and natural spin-orbitals, must comply at least with the known necessary conditions for the N-representability of the two-matrix.

IV. The natural orbital functional (NOF)

In order to turn into a practical method, it remains to find approximations for the two-matrix in terms of the one-matrix. The two-matrix can be partitioned into an antisymmetrized product of the one-matrices, which is simply the Hartree-Fock (HF) approximation, and a correction λ to it,

$$D_{kl,ij} = \frac{1}{2}\left(\Gamma_{ki}\Gamma_{lj} - \Gamma_{kj}\Gamma_{li} + \lambda_{kl,ij}\right) \tag{25}$$

This decomposition of the two-matrix is well-known from the cumulant theory. λ is the cumulant matrix [41] or the connected part [24,42] of the two-matrix. It should be noted that λ cannot be decomposed into terms that depend only on one-matrix elements because it arises from interactions in the Hamiltonian, and might therefore also be called the pair correlation matrix. This definition of correlation differs from the traditional one since Γ is the one-matrix of the correlated system and not that corresponding to independent particles.

The first two terms on the rhs of Eq. (25) together satisfy properties (13)-(15) of the two-matrix. Therefore, the cumulant matrix λ should satisfy these relations too. We further see that matrix elements of λ are nonvanishing only if all its labels refer to partially occupied natural spin-orbitals with occupation number different from 0 or 1. For a single Slater determinant the cumulant matrix vanish,

$$\lambda_{kl,ij} = 0, \ \forall n_m = 0 \text{ or } 1, \ m = i, j, k, l \tag{26}$$

It can be easily shown from Eq. (16), taking into account the normalization condition for the one-matrix (11), that the corrected Γ satisfies the following *non-idempotent* condition:

$$\sum_k \left(\Gamma_{jk}\Gamma_{ki} - \lambda_{jk,ik} \right) = \Gamma_{ji} \tag{27}$$

It is important to note that the two-matrix $\mathbf{D}$ is not additively separable (extensive), but its cumulant matrix λ satisfies this essential property [43]. Finally, we must note that the trace of λ is of $O(N)$, i.e., it scales linearly with the size of the system, while the trace of the corresponding two-matrix is of $O(N^2)$,

$$\text{Tr } \lambda = \sum_i \left(\Gamma_{ji}^2 - \Gamma_{ii} \right) = \sum_i \left(n_i^2 - n_i \right) = O(N) \tag{28}$$

Let us assume that our N-electron system is spin compensated (non-spin-polarized). The one-matrix of $\hat{S}_z$ eigenstates has then spin diagonal blocks $\Gamma^\alpha \equiv \Gamma^{\alpha\alpha} = \Gamma^{\beta\beta} \equiv \Gamma^\beta$, i.e.,

$$n_i^\alpha = n_i^\beta = n_i \tag{29}$$

and the natural orbitals are the same for opposite spin directions,

$$\psi_i^\alpha(\mathbf{r}) = \psi_i^\beta(\mathbf{r}) = \psi_i(\mathbf{r}) \tag{30}$$

The trace of the one-matrix (11) becomes

$$2 \sum_i n_i = N \tag{31}$$

In general, the two-matrix has 16 spin blocks. As a result of the requirement $m_s(1) + m_s(2) = m_s(1') + m_s(2')$ for $\hat{S}_z$ eigenstates, only six spin components are non-zero. In fact only three of these are independent and we may take the independent components to be $\mathbf{D}^{\alpha\alpha} \equiv \mathbf{D}^{\alpha\alpha,\alpha\alpha}$, $\mathbf{D}^{\beta\beta} \equiv \mathbf{D}^{\beta\beta,\beta\beta}$, and $\mathbf{D}^{\alpha\beta} \equiv \mathbf{D}^{\alpha\beta,\alpha\beta}$. This follows readily from the properties (14)-(15) of $\mathbf{D}$ [44], we have

$$D_{kl,ij}^{\alpha\beta,\alpha\beta} = -D_{lk,ij}^{\beta\alpha,\alpha\beta} = -D_{kl,ji}^{\alpha\beta,\beta\alpha} = D_{lk,ji}^{\beta\alpha,\beta\alpha} \tag{32}$$

For singlet states $\mathbf{D}^{\alpha\alpha} = \mathbf{D}^{\beta\beta}$, so in this work we deal only with $\mathbf{D}^{\alpha\alpha}$ and $\mathbf{D}^{\alpha\beta}$.

It is well-known that the HF approximation accounts for most of the correlation effects between electrons with parallel spins. The unknown functional in a $\mathbf{\Gamma}$-based theory only needs in principle to incorporate correlation effects between electrons with opposite spins. Therefore, we can obtain a suitable approximation for λ if we assume the spin block $\lambda^{\alpha\alpha} = 0$. This implies a parallel-spin component

$$D_{kl,ij}^{\alpha\alpha} = \frac{1}{2}\left(\Gamma_{ki}^{\alpha}\Gamma_{lj}^{\alpha} - \Gamma_{kj}^{\alpha}\Gamma_{li}^{\alpha}\right) \tag{33}$$

For the opposite-spin component, the two-matrix of interest has the form

$$D_{kl,ij}^{\alpha\beta} = \frac{1}{2}\left(\Gamma_{ki}^{\alpha}\Gamma_{lj}^{\alpha} + \lambda_{kl,ij}^{\alpha\beta}\right) \tag{34}$$

In the following, we remove the spin indices and all indices will denote spatial orbitals. A large number of choices for the cumulant λ is possible. It has a dependence of four indices and direct computation with such magnitudes is too expensive to be applied to large systems. We want to maximize the physical content of λ to a few number of terms. We express λ by means of a two-index hermitian matrix γ,

$$\lambda_{kl,ij} = -\gamma_{ij}\left(\delta_{ki}\delta_{lj} + \delta_{kj}\delta_{li}\right) \tag{35}$$

According to the non-idempotent condition (27) matrix γ must satisfy the relation

$$\gamma_{ii} + \sum_{j}\gamma_{ij} = n_i\left(1 - n_i\right) \tag{36}$$

Using Eqs. (24), (29), (33), (34), and (25), the Energy Eq. (8) reads as

$$E = 2\sum_{i}n_i h_{ii} + \sum_{ij}\left(2J_{ij} - K_{ij}\right)n_i n_j - \sum_{ij}\left(J_{ij} + K_{ij}\right)\gamma_{ij} \tag{37}$$

with $J_{ij} = <ij|ij>$ and $K_{ij} = <ij|ji>$. In this equation, the first term is the sum of the kinetic and electron-nuclei potential energies. It can be seen that the electron correlation modifies this term directly, since the value of n_i may now be fractional. The second term is the well-known sum of the Coulomb and exchange energies. The last term is an energy that adjust the correlation of particles with opposite spins.

The dependence of γ_{ij} on the indices i and j is perhaps a difficult one. We proposed [32] a rather simple dependence, satisfying always the above non-idempotent set of conditions (36),

$$\gamma_{ij} = \varkappa_{ij} f_i f_j - g_i g_j + \frac{1}{2} \delta_{ij} \left[n_i \left(1 - n_i \right) + g_i^2 - \varkappa_{ii} f_i^2 - S_i f_i \right] \tag{38}$$

in which

$$S_i = \sum_j \varkappa_{ij} f_j \tag{39}$$

and the functions g_i are compelled to obey the constraint

$$\sum_i g_i = 0 \tag{40}$$

$\varkappa_{ij}$ is a matrix depending on the distance between the orbitals i and j to guarantee the size-consistency of the functional [34].

A. Size-consistency

The size-consistency implies that the energy of a many-particle system, even in the presence of interactions, becomes proportional to the number of particles (N) in the limit $N \to \infty$. For example, the energy of a polymer has to be proportional to the number of constituent monomers although the total energy is not simply N times the energy of an isolated molecule.

Let us consider a system which consists of two subsystems A and B separated by a large distance R_{AB}. Under such assumption, the two-electron integrals involving an orbital i on one subsystem and an orbital j on the other subsystem will be zero because of the large distance between the basis functions. The sum S_i (39) takes into account all functions $\{f_j\}$ and has to be prevented from this fact, i.e., we must obtain two sums S_A and S_B according to the nonvanishing interactions. On the contrary, the energy functional (37) leads to a vanishing correlation energy. Matrix $\varkappa_{ij}$ fixes this problem since it depends on the distance between the orbitals i and j. In the limit, when the orbitals are separated by an infinite distance, $\varkappa_{ij}$ tends to zero, otherwise we consider its value equal one. If the members of the orbital set $\{ \psi_i (\mathbf{r}) \}$ are completely localized within the subsystem A (B), all sums $S_i = S_A$ ($S_i = S_B$) and the obtained 2-matrix yields a size-consistent functional.

There is certainly an intermediate region for the distance between orbitals where the $\varkappa_{ij}$ can not be described with this simple proposed dependence. These distances are important to obtain a functional with a proper behavior for weakly interacting systems. As it was demonstrated by Cioslowski *et al.* [45] a NOF with linear exchange-correlation energy does not satisfy the second-order conditions which ensure an asymptotic expression for dispersion energy scaling like R_{AB}^{-6}. Hereafter, due to the linearity of our correlation functional, we will attenuate the Coulomb interactions in the correlation term of our functional.

Using a separator function $f(r)$, the Coulomb operator can be split into a rapidly decaying short-range part and a slowly decaying long-range part,

$$\frac{1}{r} = S(r) + L(r) = \frac{f(r)}{r} + \frac{1 - f(r)}{r} \tag{41}$$

where the separator $f(r)$ decays rapidly and $f(0) = 1$. Function $S(r)$, because it is negligible for large r, needs to be applied only to neighboring distributions. The long-range function $L(r)$ will be ignored completely in the two-electron integrals of the last term of equation (37).

For the sake of simplicity, our choice of the separator function is a gaussian one

$$f(r) = e^{-\omega r^2} \tag{42}$$

where the parameter $\omega = 0.866$. This value can be easily obtained from the minimization of the functional

$$Z[f] = \int \left[f^2(r) + \left| \nabla \left[\frac{1 - f(r)}{r} \right] \right|^2 \right] d\mathbf{r} \tag{43}$$

which leads to an optimal partition of the Coulomb operator for the considered separator function [46]. Then, our NOF electronic energy is given by the expression

$$E = 2 \sum_i n_i h_{ii} + \sum_{ij} \left(2 J_{ij} - K_{ij} \right) n_i n_j - \sum_{ij} \left(\overline{J}_{ij} + \overline{K}_{ij} \right) \gamma_{ij} \tag{44}$$

where

$$\overline{J}_{ij} = < \psi_i \psi_j | \frac{e^{-\omega r_{12}^2}}{r_{12}} | \psi_i \psi_j > \tag{45}$$

$$\overline{K}_{ij} = < \psi_i \psi_j | \frac{e^{-\omega r_{12}^2}}{r_{12}} | \psi_j \psi_i > \tag{46}$$

B. Correlation functions f_i and g_i

Concerning the choice of the type of the correlation functions f_i and g_i, we think that they should depend on the product of the level occupation n_i and the level vacancy $1 - n_i$ to annihilate the correlation corrections for the HF case. The exact functional forms of them are probably rather complicated, requiring a distinction between occupied and virtual HF orbitals. Moreover, we consider a different functional form for the lower

occupied levels. To be specific we propose the following potential dependences for the occupied HF levels,

$$f_i = -\ n_i^{120000+10^{-13}\varepsilon_i^{12}}(1-n_i)^{0.22} \quad , \qquad g_i = [n_i(1-n_i)]^{0.9} \quad , \qquad \varepsilon_i < \varepsilon_{cf} \qquad (47)$$

$$f_i = \ n_i^{-20\varepsilon_i}(1-n_i)^{0.22} \qquad\qquad , \qquad g_i = [n_i(1-n_i)]^{0.9} \quad , \qquad \varepsilon_i > \varepsilon_{cf} \qquad (48)$$

where ε_{cf} is the value of the energy where the functions f_i change their signs, and ε_i is the one-particle orbital energy of the level i,

$$\varepsilon_i = n_i h_{ii} + n_i \sum_j \left(2J_{ij} - K_{ij}\right) n_j - \sum_{ij} \left(\overline{J}_{ij} + \overline{K}_{ij}\right) \gamma_{ij} \qquad (49)$$

Considering these energies the expectation energy value (44) can be rewritten as

$$E = \sum_i \left(n_i h_{ii} + \varepsilon_i\right) \qquad (50)$$

For the case of virtual HF orbitals the exponent values of function f_i must be set equal to unity,

$$f_i = n_i(1-n_i) \quad , \qquad g_i = -\ [n_i(1-n_i)]^{0.9} \qquad (51)$$

The exponential values are critical to fulfill the D-condition. We have fixed their values to obtain the CI total energy with inclusion of single, double, triple and quadruple excitations (CI-SDTQ) for the water molecule. It is well-known that this kind of calculation on this molecule yields more than 99% of the basis-set correlation energy [47]. The huge values for the exponents in Eq. (47) are necessary to guarantee that occupations for the lower occupied levels approach to unity.

The functions f_i and g_i obtained with these exponents are appropriate ones. They fulfill all properties of the reduced density matrices imposed before, and give a good description of the occupation numbers. We recall that all occupation numbers must be fractional to guarantee that all orbitals have the same chemical potential.

C. MO-LCAO

Let us apply the well-known procedure of taking molecular orbitals as linear combination of atomic orbitals (MO-LCAO),

$$\psi_i\left(\mathbf{r}\right) = \sum_\nu C_{\nu i}\varphi_\nu\left(\mathbf{r}\right) \qquad (52)$$

The electronic energy (44) will then be a functional

$$E\left[\{\mathbf{C}_i\}, \{n_i\}\right] = \sum_{\nu\eta}\left\{\left[h_{\eta\nu} + J_{\eta\nu} - \frac{1}{2}K_{\eta\nu}\right]\Gamma_{\nu\eta} - \frac{1}{2}\sum_{ij}\gamma_{ij}\left[\overline{J}_{\eta\nu}^j + \overline{K}_{\eta\nu}^j\right]\Gamma_{\nu\eta}^i\right\} \qquad (53)$$

where it has been introduced the following matrices

$$\Gamma_{\nu\eta} = \sum_i n_i \Gamma_{\nu\eta}^i \;, \quad \Gamma_{\nu\eta}^i = 2C_{\nu i} C_{i\eta}^+ \tag{54}$$

$$J_{\eta\nu} = \frac{1}{2} \sum_{\lambda\mu} < \varphi_\eta \varphi_\mu | r_{12}^{-1} | \varphi_\nu \varphi_\lambda > \Gamma_{\lambda\mu} \tag{55}$$

$$K_{\eta\nu} = \frac{1}{2} \sum_{\lambda\mu} < \varphi_\eta \varphi_\mu | r_{12}^{-1} | \varphi_\lambda \varphi_\nu > \Gamma_{\lambda\mu} \tag{56}$$

$$\overline{J}_{\eta\nu}^j = \frac{1}{2} \sum_{\lambda\mu} < \varphi_\eta \varphi_\mu | \frac{e^{-\omega r_{12}^2}}{r_{12}} | \varphi_\nu \varphi_\lambda > \Gamma_{\lambda\mu}^j \tag{57}$$

$$\overline{K}_{\eta\nu}^j = \frac{1}{2} \sum_{\lambda\mu} < \varphi_\eta \varphi_\mu | \frac{e^{-\omega r_{12}^2}}{r_{12}} | \varphi_\lambda \varphi_\nu > \Gamma_{\lambda\mu}^j \tag{58}$$

The orthonormality condition (4) reads as follows:

$$\sum_{\nu\mu} C_{j\mu}^+ S_{\mu\nu} C_{\nu i} = \delta_{ji} \qquad \left(\mathbf{C}^+ \mathbf{S} \mathbf{C} = \mathbf{I} \right) \tag{59}$$

where $S_{\mu\nu} = < \varphi_\mu | \varphi_\nu >$ is the overlap matrix.

V. The NOF theory of quasi-one-dimensional periodic polymers

Let us now consider a one-dimensional periodic polymer containing m orbitals in the elementary cell of n_{cell} atoms. The number of elementary cells in the direction of the polymer axis is taken equal to *M*. Because of the polymer translational symmetry, we will assume that the occupation depends only on the orbital number of the cell (energy band number). Consequently, the correlation matrix depends only on the orbital number of the cell too, since it is a function of the occupations. Then, our NOF electronic energy (44) for a system with $(2M + 1)$ cells is given by the expression

$$E = 2 \sum_{i=1}^{m} n_i \sum_{p=-M}^{M} h_{pi,pi} + \sum_{i,j=1}^{m} n_i n_j \sum_{p,q=-M}^{M} \left(2 J_{pi,qj} - K_{pi,qj} \right)$$

$$- \sum_{i,j=1}^{m} \gamma_{ij} \sum_{p,q=-M}^{M} \left(\overline{J}_{pi,qj} + \overline{K}_{pi,qj} \right) \tag{60}$$

and the trace condition (31) can be written as

$$2\sum_{i=1}^{m} n_i = N_{cell} \tag{61}$$

The correlation matrix γ_{ij} and correlation functions $\{f_i\}$ and $\{g_i\}$ are given by the Eqs. (38), (47), (48), and (51), but now ε_i is the one-particle energy of the level i obtained by summing over all cells, i.e.,

$$\varepsilon_i = n_i \sum_{p=-M}^{M} h_{pi,pi} + n_i \sum_{j=1}^{m} n_j \sum_{p,q=-M}^{M} (2J_{pi,qj} - K_{pi,qj})$$

$$-\sum_{j=1}^{m} \gamma_{ij} \sum_{p,q=-M}^{M} \left(\overline{J}_{pi,qj} + \overline{K}_{pi,qj}\right) \tag{62}$$

Considering these energies the expectation energy value (60) can be rewritten as

$$E = \sum_{i=1}^{m} \left(n_i \sum_{p=-M}^{M} h_{pi,pi} + \varepsilon_i \right) \tag{63}$$

Since there is an interaction between orbitals belonging to different elementary cells, we assume the polymer orbitals as a linear combination of atomic orbitals (LCAO), that is,

$$\psi_{pi}(\mathbf{r}) = \sum_{q=-M}^{M} \sum_{\nu=1}^{m} C_{q\nu,pi} \varphi_{q\nu}(\mathbf{r}) \tag{64}$$

Integers p and i run over $-M$, ..., 0, ..., M and 1, ..., m respectively. Further, $\varphi_{q\nu}(\mathbf{r})$ is the νth atomic orbital (AO) in the cell characterized by the vector $R_q = qa$,

$$E = \sum_{q,r=-M}^{M} \sum_{\nu,\eta=1}^{m} \left\{ \left[h_{r\eta,q\nu} + J_{r\eta,q\nu} - \frac{1}{2} K_{r\eta,q\nu} \right] \Gamma_{q\nu,r\eta} \right.$$

$$\left. -\frac{1}{2} \sum_{i,j=1}^{m} \gamma_{ij} \left[\overline{J}_{r\eta,q\nu}^{j} + \overline{K}_{r\eta,q\nu}^{j} \right] \Gamma_{q\nu,r\eta}^{i} \right\} \tag{65}$$

where we have introduced the following matrices

$$\Gamma_{q\nu,r\eta} = \sum_{i=1}^{m} n_i \Gamma_{q\nu,r\eta}^{i} \quad , \quad \Gamma_{q\nu,r\eta}^{i} = 2 \sum_{p=-M}^{M} C_{q\nu,pi} C_{pi,r\eta}^{+} \tag{66}$$

$$h_{r\eta,q\nu} = <\varphi_{r\eta}| -\frac{1}{2}\nabla^2 - \sum_{s=-M}^{M} \sum_{I=1}^{n_{cell}} \frac{Z_I}{|\mathbf{r} - \mathbf{r}_I^s|} |\varphi_{q\nu}> \tag{67}$$

$$J_{r\eta,q\nu} = \frac{1}{2} \sum_{s,t=-M}^{M} \sum_{\lambda,\mu=1}^{m} <\varphi_{r\eta}\varphi_{t\mu}|r_{12}^{-1}|\varphi_{q\nu}\varphi_{s\lambda}> \Gamma_{s\lambda,t\mu} \tag{68}$$

$$K_{r\eta,q\nu} = \frac{1}{2} \sum_{s,t=-M}^{M} \sum_{\lambda,\mu=1}^{m} <\varphi_{r\eta}\varphi_{t\mu}|r_{12}^{-1}|\varphi_{s\lambda}\varphi_{q\nu}> \Gamma_{s\lambda,t\mu} \tag{69}$$

$$\overline{J}_{r\eta,q\nu}^{j} = \frac{1}{2} \sum_{s,t=-M}^{M} \sum_{\lambda,\mu=1}^{m} <\varphi_{r\eta}\varphi_{t\mu}|\frac{e^{-\omega r_{12}^2}}{r_{12}}|\varphi_{q\nu}\varphi_{s\lambda}> \Gamma_{s\lambda,t\mu}^{j} \tag{70}$$

$$\overline{K}_{r\eta,q\nu}^{j} = \frac{1}{2} \sum_{s,t=-M}^{M} \sum_{\lambda,\mu=1}^{m} <\varphi_{r\eta}\varphi_{t\mu}|\frac{e^{-\omega r_{12}^2}}{r_{12}}|\varphi_{s\lambda}\varphi_{q\nu}> \Gamma_{s\lambda,t\mu}^{j} \tag{71}$$

where $\mathbf{r}_I^S$ stands for the position vector of the Ith nucleus in the cell characterized by R_s. The previous defined matrices of dimensions $m(2M + 1)$ have submatrices of dimension m consisting of interactions between orbitals belonging to different elementary cells. As a consequence of the translational symmetry of the polymer and of the Born-von Karman periodic boundary conditions, all these matrices are cyclic hypermatrices [48]. Hence, we can write the identity

$$A_{q\nu,r\eta} \equiv A_{\nu\eta}\left(q - r\right) \tag{72}$$

Here, A denotes the matrices determined by equations (66)-(71). As a matter of fact, submatrices $q - r = 0$ represent the interactions within the elementary cells, submatrices $q - r = 1$ and $q - r = -1$ correspond to the first-neighbor interactions, and so on. Accordingly, the corresponding ground state energy per cell can be written as

$$E_{cell} = \frac{E}{2M+1} = \sum_{q=-M}^{M} \sum_{\nu,\eta=1}^{m} \left\{ \left[h_{\eta\nu}(q) + J_{\eta\nu}(q) - \frac{1}{2}K_{\eta\nu}(q) \right] \Gamma_{\nu\eta}(q) \right.$$

$$\left. -\frac{1}{2} \sum_{i,j=1}^{m} \gamma_{ij} \left[\overline{J}_{\eta\nu}^{j}(q) + \overline{K}_{\eta\nu}^{j}(q) \right] \Gamma_{\nu\eta}^{i}(q) \right\} \tag{73}$$

where

$$\Gamma_{\nu\eta}(q) = \sum_{i=1}^{m} n_i \Gamma_{\nu\eta}^i(q) \quad , \qquad \Gamma_{\nu\eta}^i(q) = 2 \sum_{p=-M}^{M} C_{q\nu,pi} C_{pi,0\eta}^+ \tag{74}$$

$$h_{\eta\nu}(q) = <\varphi_{0\eta}| \; -\frac{1}{2}\nabla^2 - \sum_{s=-M}^{M} \sum_{I=1}^{n_{cell}} \frac{Z_A}{|\mathbf{r} - \mathbf{r}_I^s|} \; |\varphi_{q\nu}> \tag{75}$$

$$J_{\eta\nu}(q) = \frac{1}{2} \sum_{s,t=-M}^{M} \sum_{\lambda,\mu=1}^{m} <\varphi_{0\eta}\varphi_{t\mu}|r_{12}^{-1}|\varphi_{q\nu}\varphi_{s\lambda}> \Gamma_{\lambda\mu}(s-t) \tag{76}$$

$$K_{\eta\nu}(q) = \frac{1}{2} \sum_{s,t=-M}^{M} \sum_{\lambda,\mu=1}^{m} <\varphi_{0\eta}\varphi_{t\mu}|r_{12}^{-1}|\varphi_{s\lambda}\varphi_{q\nu}> \Gamma_{\lambda\mu}(s-t) \tag{77}$$

$$\overline{J}_{\eta\nu}^j(q) = \frac{1}{2} \sum_{s,t=-M}^{M} \sum_{\lambda,\mu=1}^{m} <\varphi_{0\eta}\varphi_{t\mu}|\frac{e^{-\omega r_{12}^2}}{r_{12}}|\varphi_{q\nu}\varphi_{s\lambda}> \Gamma_{\lambda\mu}^j(s-t) \tag{78}$$

$$\overline{K}_{\eta\nu}^j(q) = \frac{1}{2} \sum_{s,t=-M}^{M} \sum_{\lambda,\mu=1}^{m} <\varphi_{0\eta}\varphi_{t\mu}|\frac{e^{-\omega r_{12}^2}}{r_{12}}|\varphi_{s\lambda}\varphi_{q\nu}> \Gamma_{\lambda\mu}^j(s-t) \tag{79}$$

It is well known that there exists a unitary hypermatrix

$$U_{pi,q\nu} = \frac{1}{\sqrt{2M+1}} \exp\left(\frac{2\pi i}{2M+1}pq\right) \delta_{i\nu} \tag{80}$$

which block-diagonalizes these cyclic hypermatrices independently of the values of the elements in the submatrices, i.e.,

$$\mathbf{A} = \mathbf{U}\widetilde{\mathbf{A}}\mathbf{U}^+ \qquad , \qquad \widetilde{\mathbf{A}} = \mathbf{U}^+\mathbf{A}\mathbf{U} \qquad , \qquad \widetilde{A}_{q\nu,r\eta} = \widetilde{A}_{\nu\eta}(q)\delta_{qr} \tag{81}$$

With the help of the transformation (80), we express the density matrix (74) as follow

$$\Gamma_{\nu\eta}(q-r) = \frac{1}{2M+1} \sum_{p=-M}^{M} \text{éxp}\left[\frac{2\pi i}{2M+1}p(q-r)\right] \widetilde{\Gamma}_{\nu\eta}(p) \tag{82}$$

where the block-diagonalized density matrix $\widetilde{\Gamma}$ can be written with the new coefficient matrix $\widetilde{C}$ as

$$\widetilde{\Gamma}_{\nu\eta}(p) = 2 \sum_{t=-M}^{M} \sum_{i=1}^{m} \widetilde{C}_{p\nu,ti} n_i \widetilde{C}_{ti,p\eta}^+ \qquad , \qquad \widetilde{\mathbf{C}} = \mathbf{U}^+\mathbf{C} \tag{83}$$

Remembering that in the hypervector $\tilde{\boldsymbol{C}}_{p\nu}$ the pth segment corresponds to the reference cell, we can introduce the equality

$$\widetilde{C}_{p\nu,ti} = c_{p\nu,pi}\delta_{tp} = c_{\nu i}(p)\delta_{tp} \tag{84}$$

Consequently, equation (82) becomes

$$\Gamma_{\nu\eta}(q-r) = \frac{2}{2M+1} \sum_{p=-M}^{M} \sum_{i=1}^{m} c_{\nu i}(p) n_i c_{i\eta}^{+}(p) \exp\left[\frac{2\pi i}{2M+1} p(q-r)\right] \tag{85}$$

The next step is to increase M up to infinite ($M \rightarrow \infty$) and to introduce the continuous variable

$$k = \frac{2\pi p}{a(2M+1)} \tag{86}$$

Since the quantity p takes the values $-M$, …, 0, …M, k will take values between $-\pi/a$ and π/a. Integration over k instead of summation over p yields

$$\Gamma_{\nu\eta}(q-r) = \frac{a}{\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \sum_{i=1}^{m} c_{\nu i}(k) n_i c_{i\eta}^{+}(k) \exp\left[ik(R_q - R_r)\right] dk = \sum_{i=1}^{m} n_i \Gamma_{\nu\eta}^{i}(q-r) \tag{87}$$

The NOF energy (73) becomes

$$E_{cell} = \sum_{q=-\infty}^{\infty} \sum_{\nu,\eta=1}^{m} \left\{ \left[h_{\eta\nu}(q) + J_{\eta\nu}(q) - \frac{1}{2}K_{\eta\nu}(q)\right] \Gamma_{\nu\eta}(q) \right.$$

$$\left. -\frac{1}{2} \sum_{i,j=1}^{m} \gamma_{ij} \left[\overline{J}_{\eta\nu}^{j}(q) + \overline{K}_{\eta\nu}^{j}(q)\right] \Gamma_{\nu\eta}^{i}(q) \right\} \tag{88}$$

Matrices $\mathbf{J}(q)$, $\mathbf{K}(q)$, $\overline{\mathbf{J}}^{j}(q)$ and $\overline{\mathbf{K}}^{j}(q)$ are obtained from equations (76) - (79) substituting M by ∞ in all summations, and using the density matrix given by equation (87).

VI. Variational procedure

Fully variational calculations with NOFs require minimization of the energy functional with respect to all its variables. In contrast to Hartree-Fock theory, minimization of a more general functional with fractional occupation numbers cannot be cast as a self-consistent eigenvalue problem. This corresponds to the nonidempotency of the one-matrix. Instead, direct minimization of $E[\{\mathbf{C}_i\}, \{n_i\}]$ is required, subject to the constraints:

1. The N-representability condition of the one-matrix ($0 \leq n_i \leq 1$).
2. The constant number of particles ($2\sum_i n_i = N$).
3. The consequence of the non-idempotent condition $\sum_i g_i = 0$.
4. The orthonormality condition $\mathbf{C}^\dagger \mathbf{S} \, \mathbf{C} = \mathbf{I}$.

One has to calculate the gradient of the functional both with respect to natural orbitals coefficients $\{\mathbf{C}_i\}$ and the occupation numbers $\{n_i\}$. Since the minimization with respect to occupations is much cheaper than with respect to the orbitals, one can decouple the variation of the occupation numbers from that of the natural orbitals, a procedure used by us in the IBCS method [29]. In the inner loop we find the optimal occupation numbers for a given set of orbitals under constraints 2 and 3. Bounds on the occupation numbers are enforced by setting $n_i = (\sin \gamma_i)^2$ and varying the γ_i without constraints. In the outer loop we minimize with respect to the orbital coefficients under the constraints of mutual orthonormality. Both the inner- and outer-loop optimizations has been implemented using a sequential quadratic programming (SQP) method [49].

VII. Results and discussion

In this section, calculations of total and ionization energies, dipole moments, equilibrium geometries and harmonic vibrational frequencies for selected molecules using contracted Gaussian basis sets 6-31G** [50] are presented. It has to be emphasized that at present we did not aim to reproduce experimental values for the properties therefore, we have chosen a medium-size basis set for the calculations and we have compared the results with the results using other methods at the same level. We are aware of the fact that very large basis sets are required to estimate experimental values.

Among the approaches compared are the coupled cluster technique including all double excitations (CCD), as well as the Becke-3-Lee-Yang-Parr (B3LYP) density functional [47]. The CCD and B3LYP values were calculated with the GAUSSIAN 94 system of programs [51].

A. Total energies

In Table I we report the values obtained for the total energies of several molecules, employing the experimental geometry [52,53]. For comparison, we have included into this Table the total energies calculated at the CCD and B3LYP levels.

According to Table I, the values we have obtained are in general lower than those obtained with the CCD method. Our NOF calculations on 10-electron molecules (FH, H_2O, NH_3, CH_4) give total energies close to the CCD ones which are very accurate results for the basis set correlation energies. We note that the percentage of the correlation energy obtained by CCD decreases as the size of the molecule increases, whereas our functional keeps giving a substantial portion of the correlation energy closer then to B3LYP values.

Table I. Total energies (E_{total}) in Hartrees.

Molecule	HF^1	CCD^2	NOF^3	$B3LYP^4$
FH	-100.0098	-100.1959	-100.2090	-100.4258
H_2O	-76.0226	-76.2256	-76.2146	-76.4179
NH_3	-56.1950	-56.3960	-56.3716	-56.5563
CH_4	-40.2014	-40.3851	-40.3598	-40.5240
BeO	-89.4066	-89.6330	-89.7258	-89.8984
C_2H_2	-76.8206	-77.0937	-77.1968	-77.3277
BF	-124.1006	-124.3431	-124.5411	-124.6561
CO	-112.7360	-113.0188	-113.1476	-113.3067
N_2	-108.9408	-109.2520	-109.3749	-109.5240
HCN	-92.8752	-93.1661	-93.2896	-93.4218
C_2H_4	-78.0377	-78.3461	-78.5176	-78.6048
F_2	-198.6696	-199.0316	-199.5440	-199.4955

[1]Hartree-Fock total energies.

[2]Coupled Cluster Doubles total energies.

[3]Natural Orbital Functional total energies computed in this work.

[4]B3LYP total energies.

B. Ionization energies

The ionization of a molecule by photoionization or by electron impact is governed by the Franck-Condon principle, which states that the most probable ionizing transition will be that in which the positions and moments of the nuclei are unchanged. Accordingly we calculated the vertical ionization energy, that is, the energy change corresponding to formation of the ion in a configuration, which is effectively the same as that which is dominant the ground state of the neutral molecule at the equilibrium geometry.

The simplest treatment is based on Koopman's theorem, which states that the ionization potential is given by the HF orbital energy with opposite sign ($-\varepsilon_i$), calculated in the neutral system. This approach ignores the relaxation of the molecular orbitals after the ionization. In order to take the orbital relaxation into account the ionization potential is approximated by the energy difference: $E_{SCF}^+ - E_{SCF}^0$ (ΔSCF potential). Nevertheless, both approaches disregard the change in correlation energy associated with the ionization. This missing correlation effect is considered here by calculating the NOF total energies for ions and neutral molecules. Then, the ionization potential is obtained by the energy difference: $E_{NOF}^+ - E_{NOF}^0$ (ΔNOF).

The energy of the $N-1$ electron system can be reasonably well approximated by an orbital ionization. We will assume that the annihilation of one electron occurs at the highest occupied molecular orbital (HOMO) of the Hartree-Fock approximation. According to this hypothesis the other electrons are populating all available states with $2n_i$, except the HOMO which is populated with $n_{HOMO} = 1$. With this assumption, the ground state of the ion is a $\hat{S}_z$ eigenstate. The value of the energy can be obtained straightforward from the Eq. (44)

$$E = 2\sum_i^{cl} n_i h_{ii} + \sum_{ij}^{cl} \left(2J_{ij} - K_{ij}\right) n_i n_j - \sum_{ij}^{cl} \left(\overline{J}_{ij} + \overline{K}_{ij}\right) \gamma_{ij}$$

$$+ \left(h_{kk} + \sum_i^{cl} \left(2J_{ik} - K_{ik}\right) n_i\right)_{k=HOMO} \tag{89}$$

where cl denotes the number of closed shells.

Table II. Vertical Ionization Potential (VIP) in eV.

Molecule	$Koopmans'$[1]	ΔSCF[2]	ΔNOF[3]	EXP[4]
FH	17.06	15.35	15.80	16.12
H_2O	13.53	14.28	12.31	12.62
NH_3	11.44	9.64	11.00	10.85
CH_4	14.75	13.73	14.99	14.40[a]
BeO	10.34	8.28	10.06	10.10[b]
C_2H_2	10.86	9.79	11.81	11.49
BF	10.63	10.07	12.51	11.12[b]
CO	14.90	13.70	14.88	14.01
N_2	16.63	16.01	17.60	15.58
HCN	13.32	12.14	14.48	13.61
C_2H_4	10.05	8.91	11.12	10.68
F_2	17.88	15.29	20.14	15.70

[1] Negative values of the HF highest occupied molecular orbital energy $(-\varepsilon_{HOMO})$.

[2] $\Delta SCF = E_{SCF}^+ - E_{SCF}^0$.

[3] $\Delta NOF = E_{NOF}^+ - E_{NOF}^0$.

[4] Experimental vertical ionization potential from ref. [54].

[a] Experimental vertical ionization potential for CH_4 from ref. [55].

[b] Experimental adiabatic ionization potential from ref. [54].

The vertical ionization potentials (VIP) are reported in table II. The results are in good agreement with the corresponding experimental VIPs [54] considering the small basis sets used for these calculations. One can hope to obtain a better agreement by improving further the basis sets. For example, in the case of water molecule, the addition of diffuse functions (6-31++G**) gives a $\Delta SCF = 11.47$ eV (Note that ΔSCF is greater than Koopmans' VIP for the 6-31G** basis sets) and $\Delta NOF = 12.66$ eV closer to the experimental value of 12.62 eV.

A survey of Table II reveals that the prevailing trend is that our calculated values are systematically greater than the experimental VIPs. This behavior might be due to the expected underestimation of the correlation energy for ions. In fact, according to our working hypothesis for the ion ground state, the HOMO does not contribute to the electron correlation ($\forall_i$, $\gamma_{i,HOMO} = 0$).

C. Dipole moments

For molecules with dipole moments (μ) different from zero, we have also evaluated this property (Table III). For comparison, we have included into this Table the reported experimental values [56] of μ and those calculated with the GAUSSIAN 94 system of programs at the CCD and B3LYP levels.

The results clearly underline the importance of the correlation effects. For the reported molecules, the correlated dipole moments are lower compared to HF μ. In the

Table III. Dipole Moments (μ) in Debyes.

Molecule	HF^1	CCD^2	NOF^3	$B3LYP^4$	EXP^5
FH	1.97	1.88	1.85	1.81	1.82
H_2O	2.19	2.11	2.08	2.03	1.85
NH_3	1.88	1.83	1.79	1.78	1.47
BeO	6.86	5.92	6.47	5.52	-
BF	0.90	0.85	1.02	1.13	-
CO	0.32*	0.01	0.05	0.13	0.11
HCN	3.23	2.93	3.13	2.83	2.98

[1]Hartree-Fock dipole moments.

[2]Coupled Cluster Doubles dipole moments.

[3]Natural Orbital Functional dipole moments computed in this work.

[4]B3LYP dipole moments.

[5]Experimental dipole moments from ref. [56].

*This value has an opposite sign relative to the experimental value

case of BF, we have to mention that with CCD method the dipole moment is decreased with respect to the HF result, whereas the NOF and B3LYP yield a higher value. An important case is the CO molecule for which the HF approximation gives a dipole moment in the wrong direction, whereas correlation methods approach it to the experimental value.

D. Equilibrium geometries and harmonic vibrational frequencies

Since presently the analytical derivatives of the energy with respect to the coordinates of the atoms (the forces acting on atoms) are not available for our NOF, we have employed the non-gradient geometry optimization to determine the equilibrium bond distances (r_e) of the studied diatomic molecules. For each molecule, we have calculated the total energy $U(r)$ at a dense grid of bond distances r, separated from each other by 10^{-3} Å.

The harmonic vibrational frequencies (ω_e) are determined from the second derivatives of the energy with respect to the nuclear positions. In the present study, the equilibrium force constants $k_e = U''(r_e)$ were obtained from least squares fits of the energy to a second-order polynomial in the distances,

$$U(r) = U(r_e) + \frac{1}{2}k_e \left(r - r_e\right)^2 \tag{90}$$

The optimized bond lengths of the six diatomic molecules are given in Table IV. The bond distances predicted by Hartree-Fock calculations are too short, whereas the

Table IV. Bond length (r_e) of the selected diatomic molecules in Å.

Molecule	HF^1	CCD^2	NOF^3	$B3LYP^4$	EXP^5
FH	0.901	0.920	0.910	0.925	0.917
BeO	1.296	1.330	1.318	1.328	1.331
BF	1.260	1.281	1.285	1.273	1.263
CO	1.114	1.139	1.124	1.138	1.128
N$_2$	1.078	1.112	1.082	1.106	1.098
F$_2$	1.345	1.416	1.407	1.403	1.412

[1] Hartree-Fock equilibrium geometries.

[2] Coupled Cluster Doubles equilibrium geometries.

[3] Natural Orbital Functional equilibrium geometries computed in this work.

[4] B3LYP equilibrium geometries.

[5] Experimental equilibrium geometries from ref. [52].

Table V. Vibrational frequencies (ω_e) of the selected diatomic molecules in cm^{-1}.

Molecule	HF^1	CCD^2	NOF^3	$B3LYP^4$	EXP^5
FH	4493	4211	4223	4082	4138
BeO	1741	1578	1657	1548	1487
BF	1473	1402	1332	1402	1402[a]
CO	2439	2251	2283	2209	2170
N_2	2758	2434	2669	2457	2359[b]
F_2	1245	1005	1119	1062	917

[1]Hartree-Fock vibrational frequencies.

[2]Coupled Cluster Doubles vibrational frequencies.

[3]Natural Orbital Functional vibrational frequencies computed in this work.

[4]B3LYP vibrational frequencies.

[5]Experimental vibrational frequencies from ref. [52].

[a]Experimental vibrational frequency from ref. [57].

[b]Experimental vibrational frequency from ref. [58].

inclusion of electron correlation increases them, leading to bond distances closer to experimental ones. For the six studied molecules the equilibrium geometries are in good agreement with the tendency showed by CCD and B3LYP methods. According to the Table, the values that we have obtained for the equilibrium geometries are in good agreement with the experimental ones [52].

In Table V we report the values of the harmonic vibrational frequencies for the selected molecules. The Hartree-Fock vibrational frequencies are well known to be too large, whereas correlated methods provide close agreement with experiment [?,57,58] for ω_e. By all correlated methods, the harmonic experimental value is overestimated, except in the case of BF molecule and the B3LYP vibrational frequency for FH.

If we compare the results obtained from different correlated methods for both investigated properties, we see that the errors are of the same order of magnitude for a given molecule.

E. Bond alternation in trans-polyacetylene (PA)

The PA still remains the prime model to test the reliability of electron correlation theories in quasi-one-dimensional polymers. At the HF level the bond length alternating structure of PA is more stable than the equidistant one, but the computed difference between carbon-carbon single and double bonds (Δr) is larger than the experimental value. The inclusion of electron correlation effects reduces significantly Δr in PA.

Table VI. Optimized geometries of PA at the HF and NOF levels. The C-C single and double bond lengths, r_1 and r_2, the bond alternation Δr and the lattice constant a are given in Å, the C-C-C bond angle is in $^\circ$.

Method	C-C-C	a	r_1	r_2	Δr
HF	122.8	2.554	1.520	1.388	0.132
NOF	122.2	2.563	1.516	1.411	0.105
Exp.*	122	2.458	1.45	1.36	0.09

* Experimental values from ref. [59]

The following discussion will focus only on the most stable parameters relevant for the bond alternation: C-C single (r_1) and C=C double (r_2) bond distances as well as the lattice constant a of the PA chain. The C-H bond length (1.09 Å) and the C-C-H bond angle (120.02°) of the unit cell were fixed at their experimental values [59]. The polymer was always kept planar.

In Table VI the results obtained with our NOF are summarized. For comparison, we also show the corresponding calculations at the HF level. We have performed the *ab-initio* HF ground state energy calculations using nine neighbors' interaction approximation in the strict sense and 101 k points in the numerical integration over k in the first half of the Brillouin zone. Our purpose is to demonstrate that the treatment presented here does give correct results rather than to obtain definitive values for the bond distances and lattice constant. Thus, Clementi's minimum basis set [60] was employed in all calculations.

Our results for the C-C bond lengths of 1.516 and 1.411 Å are in modest agreement with the experimental values, i.e., 1.45 and 1.36 Å. However, the inclusion of electron correlation by means of our NOF decreases the C-C single (r_1) and increases the C=C double (r_2) bond distances with respect to the HF obtained values of 1.520 and 1.388 Å respectively. This general trend has been reported using other correlation methods [61]. Consequently, electron correlation effects reduce the bond length alternation in PA from $\Delta r = 0.132$ Å at the HF level to $\Delta r = 0.105$ Å at the NOF level.

VIII. Concluding remarks

A Natural Orbital Functional (NOF) to calculate correlation energies for molecules and periodic polymers has been reviewed. The approach presented here is a well-comprehensible density matrix theory which does not require the introduction of a non-interacting kinetic energy functional. The resultant two-matrices satisfy the *D*-condition, while the one-matrices are exactly *N* representable.

The results are encouraging, a simple functional yields correlation energies as good as those obtained from the density functionals. The calculated NOF values wit the

6-31G** basis set for the ionization energies, dipole moments, equilibrium geometries and vibrational frequencies are in good agreement with the tendency showed by CCD and B3LYP methods. Comparison with experimental results shows the NOF values to be comparable to those predicted by the reported methods with this particular basis set.

The trans-polyacetylene (PA) was chosen as a system to study the effects of the electron correlation on the bond length alternation in conjugated polymers. The correlation contribution on the structural parameters of PA reduces the bond alternation from $\Delta r = 0.132$ Å at the HF level to $\Delta r = 0.105$ Å at the NOF level, a value that is closer to the experimentally observed one for PA which is about 0.09 Å.

There is clearly still much work to do for improvement. The functional presented here does not reduce to the exact expression for $V_{ee}[\Gamma]$ in two-electron systems. Moreover, it is not capable of accounting for dispersion interactions. Derivation of such functionals is in progress.

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