

Natural Orbital Functional for Correlation in Polymers

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ABSTRACT: We extend a natural orbital functional to calculate correlation energies for periodic polymers. We generalize the proposed correlation matrix in a two-particle reduced density matrix to achieve a size-consistent functional. Because of the linearity in two-electron integrals, our functional does not behave properly for weakly interacting systems. We separate the Coulomb operator into two parts and consider only the short-range operator for the two-electron integrals in the correlation term of the energy functional. The long-range interactions will be included in the future development of the functional to consider dispersion interactions. Application is made to alternating *trans*-polyacetylene. The experimentally observed reduction of the Hartree–Fock lattice spacing by the inclusion of electron correlation is correctly predicted. © 2004 Wiley Periodicals, Inc. *Int J Quantum Chem* 102: 90–97, 2005

Key words: reduced density matrix; natural orbital functional; electron correlation; polyacetylene; bond length alternation

I. Introduction

The development of contemporary quantum chemical methods provides a powerful predictive tool to study the chemical and physical properties of quasi-infinite systems like polymers. For periodic polymers, the computational approach takes into account the translational symmetry of the system, which leads, in the Hartree–Fock (HF) approximation, to the crystal orbital (CO) equations [1–3]. Corrections of the HF CO results to account for electron correlation at the ab initio level have

been achieved by coupled-cluster (CC) [4–7] and many-body perturbation theories (MBPT) [8–11]. Recently, a series of CC/MBPT methods were formulated and implemented for periodic polymers [12]. Nevertheless, we observe that even for medium-size elementary cells the application of these wavefunction-based methods is still very time consuming. Density functional theory (DFT) provides an alternative way of estimating the correlation effects at relatively modest costs [13, 14]. At present several methods for DF calculations of polymers have been reported [9, 15–18].

Recently, we proposed a one-particle reduced density matrix (1-RDM) functional, in terms of the natural orbitals, to account for electronic correlation

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in molecular systems [19]. A major advantage of a density matrix formulation is that the kinetic energy and the exchange energy are explicitly defined using the 1-RDM and do not require the construction of a functional. The unknown functional in a 1-RDM theory only needs to incorporate electron correlation. The purpose of this article is to formulate and implement our natural orbital functional (NOF) for quasi-1-D periodic polymers.

The obtained NOF satisfies general properties of reduced density matrices (proper normalization, nonnegativity of the diagonal elements, particle permutational symmetry, fermionic antisymmetry, hermiticity). However, other conditions have to be satisfied by the 1-RDM functional [20]. One of these is size consistency.

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 $N \rightarrow \infty$. Accordingly, 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. Unfortunately, in the current form our functional did not have this property. To achieve this property we generalize here our proposed correlation matrix in the two-particle reduced density matrix (2-RDM), which yields a size-consistent functional.

The known asymptotic behavior of the total energy of two weakly interacting systems imposes other conditions on the exchange-correlation energy as a functional of the 1-RDM [21]. The first-order conditions that involve two-electron integrals are satisfied by our NOF. However, because of its linearity in two-electron integrals, our functional is unable to fulfill the second-order expressions. We propose to ignore the dispersion component of the interaction energy in the correlation term of the functional by partitioning the Coulomb operator into a rapidly decaying short-range function, $S(r)$, and a smooth long-range function, $L(r)$, and subsequently disregarding the integrals over the last operator. This type of partition of the Coulomb problem into two subproblems is a well-known procedure [22] and constitutes the first step in the development of linear solutions to the Coulomb problem in the KWIK approach [23]. The splitting of the Coulomb operator has also been used in other contexts [24–26]. The dispersion interactions will be included, at least in terms quadratic in two-electron integrals, in the future development of our functional.

As a suitable test case we choose *trans*-polyacetylene (PA), which is a chain with alternating carbon–carbon single and double bonds. At the HF level the bond length alternating structure is more stable than the equidistant one. However, experiment [27] as well as numerous calculations [6, 9, 28, 29] have shown that the correlation effects significantly reduce the bond length alternation in the PA.

Our article is organized as follows. In Section II, we generalize our previous 2-RDM and introduce the splitting of the Coulomb operator. In Section III, we give the basic formulas of our method for infinite periodic systems. Our results are presented and discussed in Section IV, and our conclusions in Section V.

II. Size-Consistent Functional

We will not give here the detailed formulation of our NOF, which is presented in a previous article [19].

The electronic energy functional is

$$E[\{|q\rangle\}, \{n_q\}] = 2 \sum_q h_q n_q + \sum_{q,q'} [2J_{q,q'} - K_{q,q'}] n_q n_{q'} - \sum_{q,q'} [J_{q,q'} + K_{q,q'}] \gamma_{q,q'} \quad (1)$$

in which

$$\gamma_{q,q'} = f_q f_{q'} - g_q g_{q'} + \frac{1}{2} \delta_{q,q'} [n_q(1 - n_q) + g_q^2 - f_q^2 - S \cdot f_q], \quad (2)$$

$$S = \sum_q f_q, \quad (3)$$

where h_q is the matrix element of the kinetic energy and nuclear attraction terms and $J_{q,q'}$ ($K_{q,q'}$) are the Coulomb (exchange) integrals. The states $\{|q\rangle\}$ constitute a complete orthonormal set of single-particle wave functions, where q denotes the orbital and $\{n_q\}$ are their occupations. f_q and g_q are correlation functions that depend on the product of the level occupation n_q and the level vacancy $1 - n_q$ to annihilate the correlation corrections for the HF case. The functional forms of them will be given in the next section.

Consider a system that consists of two subsystems A and B separated by a large distance R_{AB} .

Under such assumption, the two-electron integrals involving an orbital q on one subsystem and an orbital q' on the other subsystem will be zero because of the large distance between the basis functions. The correlation matrix $\gamma_{q,q'}$ is not prevented by this because the last term in Eq. (2) contains a common sum S , instead of two sums S_A and S_B according to the nonvanishing interactions. The sum S (3) takes into account all functions $f_{q'}$, and consequently the minimization of the energy functional (1) leads to a vanishing correlation energy. Therefore, the correlation matrix $\gamma_{q,q'}$ should depend on the distance between orbitals q and q' , and sums S_q depend on the corresponding orbital q . To fix this problem, we propose the following generalization of the correlation matrix:

$$\begin{aligned}\gamma_{q,q'} &= \kappa_{q,q'}(f_q f_{q'} - q_q q_{q'}) + \frac{1}{2} \delta_{q,q'}[n_q(1 - n_q) \\ &\quad + \kappa_{qq}(g_q^2 - f_q^2) - S_q f_q],\end{aligned}\quad (4)$$

$$S_q = \sum_{q'} \kappa_{q,q'} f_{q'}, \quad (5)$$

where $\kappa_{q,q'}$ depends on the distance between the orbitals q and q' . In the limit, when the orbitals are separated by an infinite distance, $\kappa_{q,q'}$ tends to zero, otherwise we consider its value equal to one. If the members of the orbital set $\{|q\rangle\}$ are completely localized within the subsystem A (B), all sums $S_q = S_A$ ($S_q = S_B$) and the obtained 2-RDM yields a size-consistent functional. Note that the proposed matrix $\gamma_{q,q'}$ still satisfies Eq. (11) of Ref. [19], which is a consequence of the 1-RDM nonidempotent condition:

$$\gamma_{qq} + \sum_{q'} \gamma_{q,q'} = n_q(1 - n_q). \quad (6)$$

There is certainly an intermediate region for the distance between orbitals where the $\kappa_{q,q'}$ cannot be described with this simple proposed dependence. These distances are important to obtain a functional with a proper behavior for weakly interacting systems. As Cioslowski and Pernal [21] demonstrated, a NOF with linear exchange-correlation energy does not satisfy the second-order conditions that ensure an asymptotic expression for dispersion energy scaling like R_{AB}^{-6} . Hereafter, because of 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,

$$\frac{1}{r} = S(r) + L(r) = \frac{f(r)}{r} + \frac{1 - f(r)}{r}, \quad (7)$$

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 Eq. (1).

For simplicity, our choice of the separator function is a Gaussian one:

$$f(r) = e^{-\omega r^2}, \quad (8)$$

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

$$Z[f] = \int \left[f^2(r) + \left| \nabla \left[\frac{1 - f(r)}{r} \right] \right|^2 \right] d\mathbf{r}, \quad (9)$$

which leads to an optimal partition of the Coulomb operator for the considered separator function [30].

III. The NOF Theory of Quasi-1-D Periodic Polymers

A. TRANSLATION SYMMETRY

We consider a 1-D periodic polymer containing m orbitals in the elementary cell of n_A^{cell} atoms. The number of elementary cells in the direction of the polymer axis is taken equal to N . 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 also depends only on the orbital number of the cell, given that it is a function of the occupations. Then, our NOF electronic energy for a system with $(2N + 1)$ cells is given by the expression

$$\begin{aligned}E_{\text{elec}} &= 2 \sum_{\xi=1}^m n_{\xi} \sum_{p=-N}^N h_{p,\xi} + \sum_{\xi,\xi'=1}^m n_{\xi} n_{\xi'} \sum_{p,p'=-N}^N (2J_{p,\xi,p',\xi'} \\ &\quad - K_{p,\xi,p',\xi'}) - \sum_{\xi,\xi'=1}^m \gamma_{\xi,\xi'} \sum_{p,p'=-N}^N (\bar{J}_{p,\xi,p',\xi'} + \bar{K}_{p,\xi,p',\xi'}). \quad (10)\end{aligned}$$

In Eq. (10), $h_{p,\xi}$ is the matrix element of the one-electron operator; $J_{p,\xi;p',\xi'}$ and $K_{p,\xi;p',\xi'}$ are the Coulomb and exchange electron repulsion integrals, respectively; and $\bar{J}_{p,\xi;p',\xi'}$ and $\bar{K}_{p,\xi;p',\xi'}$ are the direct and exchange two-electron integrals of the short-range operator $S(r)$. In this equation, the first term is the sum of the kinetic energy and the electron-nuclei potential energy. The second term is the well-known sum of the HF Coulomb and exchange energies. The last two terms are energies that adjust the correlation of particles with antiparallel spins for neighboring charge distributions.

$\gamma_{\xi,\xi'}$ is the correlation matrix

$$\gamma_{\xi,\xi'} = \alpha_{\xi,\xi'}(f_{\xi}f_{\xi'} - g_{\xi}g_{\xi'}) + \frac{1}{2}\delta_{\xi,\xi'} \times [n_{\xi}(1 - n_{\xi}) + \alpha_{\xi,\xi}(g_{\xi}^2 - f_{\xi}^2) - S_{\xi}f_{\xi}], \quad (11)$$

in which

$$S_{\xi} = \sum_{\xi'=1}^m \alpha_{\xi,\xi'} f_{\xi'}, \quad (12)$$

and the functions g_{ξ} are compelled to obey the constraint

$$\sum_{\xi'=1}^m \alpha_{\xi,\xi'} g_{\xi'} = 0. \quad (13)$$

The 2-RDM used in the NOF (10) guarantees general 2-RDM properties: proper normalization, particle permutational symmetry, fermionic antisymmetry, hermiticity, and size consistency. Equation (13) is a consequence of the 1-RDM nonidempotent condition (6).

We must also keep in mind that the occupation numbers $\{n_{\xi}\}$ have to satisfy the first-order density matrix trace condition

$$\text{Tr}({}^1\Gamma) = n_e. \quad (14)$$

In polymers, this constraint condition is

$$2 \sum_{\xi=1}^m n_{\xi} = n_e^{\text{cell}}. \quad (15)$$

The correlation functions f_{ξ} and g_{ξ} depend on the product of the level occupation n_{ξ} and the level vacancy $1 - n_{\xi}$ to annihilate the correlation correc-

tions for the HF case. Their exact functional forms require a distinction between occupied and virtual HF orbitals. Moreover, we consider a different functional form for the lower occupied levels. We proposed [19] the following potential dependences for the occupied HF levels:

$$f_{\xi} = -n_{\xi}^{120000+10^{-13}\varepsilon_{\xi}^{12}}(1 - n_{\xi})^{0.22}, \\ g_{\xi} = [n_{\xi}(1 - n_{\xi})]^{0.9}, \quad \varepsilon_{\xi} < \varepsilon_{cf} \quad (16)$$

$$f_{\xi} = n_{\xi}^{-20\varepsilon_{\xi}}(1 - n_{\xi})^{0.22}, \quad g_{\xi} = [n_{\xi}(1 - n_{\xi})]^{0.9}, \\ \varepsilon_{\xi} > \varepsilon_{cf}, \quad (17)$$

where ε_{cf} is the value of the energy where the functions f_{ξ} change their signs, and ε_{ξ} is the one-particle energy of the level ξ obtained by summing over all cells, i.e.,

$$\varepsilon_{\xi} = n_{\xi} \sum_{p=-N}^N h_{p,\xi} + n_{\xi} \sum_{\xi'=1}^m n_{\xi'} \sum_{p,p'=-N}^N (2J_{p,\xi;p',\xi'} \\ - K_{p,\xi;p',\xi'}) - \sum_{\xi'=1}^m \gamma_{\xi,\xi'} \sum_{p,p'=-N}^N (\bar{J}_{p,\xi;p',\xi'} + \bar{K}_{p,\xi;p',\xi'}). \quad (18)$$

Considering these energies, the expectation energy value (10) can be rewritten as

$$E_{\text{elec}} = \sum_{\xi=1}^m \left(n_{\xi} \sum_{p=-N}^N h_{p,\xi} + \varepsilon_{\xi} \right). \quad (19)$$

For the case of virtual HF orbitals the exponent values of function f_{ξ} must be set equal to unity,

$$f_{\xi} = n_{\xi}(1 - n_{\xi}), \quad g_{\xi} = -[n_{\xi}(1 - n_{\xi})]^{0.9}. \quad (20)$$

The exponential values are critical to fulfill the 2-RDM nonnegativity condition (D -condition). We 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 correlation energy. The huge values for the exponents in Eq. (16) are necessary to guarantee that occupations for the lower occupied levels approach to unity.

The functions f_{ξ} and g_{ξ} obtained with these exponents are appropriate ones. They fulfill all prop-

erties of the RDMs mentioned 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.

B. DELOCALIZED ORBITALS

Because 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,

$$|p, \xi\rangle = \sum_{q=-N}^N \sum_{\nu=1}^m C_{q,\nu;p,\xi} |q, \nu\rangle. \quad (21)$$

Integers p and ξ run over $-N, \dots, 0, \dots, N$ and $1, \dots, m$, respectively. Further, $|q, \nu\rangle$ is the ν th atomic orbital (AO) in the cell characterized by the vector $R_q = qa$,

$$E_{\text{elec}} = \sum_{q,r=-N}^N \sum_{\nu,\eta=1}^m \left\{ \left[h_{r,\eta;q,\nu} + J_{r,\eta;q,\nu} - \frac{1}{2} K_{r,\eta;q,\nu} \right] D_{q,\nu;r,\eta} - \frac{1}{2} \sum_{\xi,\xi'=1}^m \gamma_{\xi,\xi'} [\bar{J}_{r,\eta;q,\nu}^{\xi'} + \bar{K}_{r,\eta;q,\nu}^{\xi'}] D_{q,\nu;r,\eta}^{\xi} \right\}, \quad (22)$$

where we have introduced the following matrices

$$D_{q,\nu;r,\eta} = \sum_{\xi=1}^m n_{\xi} D_{q,\nu;r,\eta}^{\xi} \quad (23)$$

$$D_{q,\nu;r,\eta}^{\xi} = 2 \sum_{p=-N}^N C_{q,\nu;p,\xi} C_{p,\xi;r,\eta}^{+} \quad (24)$$

$$h_{r,\eta;q,\nu} = \langle r, \eta | \hat{h} | q, \nu \rangle \quad (25)$$

$$J_{r,\eta;q,\nu} = \frac{1}{2} \sum_{s,t=-N}^N \sum_{\lambda,\mu=1}^m \left\langle r, \eta; t, \mu \left| \frac{1}{r_{12}} \right| q, \nu; s, \lambda \right\rangle \times D_{s,\lambda;t,\mu} \quad (26)$$

$$K_{r,\eta;q,\nu} = \frac{1}{2} \sum_{s,t=-N}^N \sum_{\lambda,\mu=1}^m \left\langle r, \eta; t, \mu \left| \frac{1}{r_{12}} \right| s, \lambda; q, \nu \right\rangle \times D_{s,\lambda;t,\mu} \quad (27)$$

$$\bar{J}_{r,\eta;q,\nu}^{\xi'} = \frac{1}{2} \sum_{s,t=-N}^N \sum_{\lambda,\mu=1}^m \langle r, \eta; t, \mu | S(r_{12}) | q, \nu; s, \lambda \rangle \times D_{s,\lambda;t,\mu}^{\xi'} \quad (28)$$

$$\bar{K}_{r,\eta;q,\nu}^{\xi'} = \frac{1}{2} \sum_{s,t=-N}^N \sum_{\lambda,\mu=1}^m \langle r, \eta; t, \mu | S(r_{12}) | s, \lambda; q, \nu \rangle \times D_{s,\lambda;t,\mu}^{\xi'}. \quad (29)$$

The previous defined matrices of dimensions $m(2N + 1)$ 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 [31]. Hence we can write the identity

$$A_{q,\nu;r,\eta} \equiv A_{\nu,\eta}(q - r). \quad (30)$$

Here, A denotes the matrices determined by Eqs. (23)–(29). In 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

$$E_{\text{elec}}^{\text{cell}} = \frac{E_{\text{elec}}}{2N + 1} = \sum_{q=-N}^N \sum_{\nu,\eta=1}^m \times \left\{ \left[h_{\eta,\nu}(q) + J_{\eta,\nu}(q) - \frac{1}{2} K_{\eta,\nu}(q) \right] D_{\nu,\eta}(q) - \frac{1}{2} \sum_{\xi,\xi'=1}^m \gamma_{\xi,\xi'} [\bar{J}_{\eta,\nu}^{\xi'}(q) + \bar{K}_{\eta,\nu}^{\xi'}(q)] D_{\nu,\eta}^{\xi}(q) \right\}, \quad (31)$$

where

$$D_{\nu,\eta}(q) = \sum_{\xi=1}^m n_{\xi} D_{\nu,\eta}^{\xi}(q) \quad (32)$$

$$D_{\nu,\eta}^{\xi}(q) = 2 \sum_{p=-N}^N C_{q,\nu;p,\xi} C_{p,\xi;0,\eta}^{+} \quad (33)$$

$$h_{\eta,\nu}(q) = \langle 0, \eta | \hat{h} | q, \nu \rangle \quad (34)$$

$$J_{\eta,\nu}(q) = \frac{1}{2} \sum_{s,t=-N}^N \sum_{\lambda,\mu=1}^m \left\langle 0, \eta; t, \mu \left| \frac{1}{r_{12}} \right| q, \nu; s, \lambda \right\rangle \times D_{\lambda,\mu}(s-t) \quad (35)$$

$$K_{\eta,\nu}(q) = \frac{1}{2} \sum_{s,t=-N}^N \sum_{\lambda,\mu=1}^m \left\langle 0, \eta; t, \mu \left| \frac{1}{r_{12}} \right| s, \lambda; q, \nu \right\rangle \times D_{\lambda,\mu}(s-t) \quad (36)$$

$$\bar{J}_{\eta,\nu}^{\xi'}(q) = \frac{1}{2} \sum_{s,t=-N}^N \sum_{\lambda,\mu=1}^m \langle 0, \eta; t, \mu | S(r_{12}) | q, \nu; s, \lambda \rangle \times D_{\lambda,\mu}^{\xi'}(s-t) \quad (37)$$

$$\bar{K}_{\eta,\nu}^{\xi'}(q) = \frac{1}{2} \sum_{s,t=-N}^N \sum_{\lambda,\mu=1}^m \langle 0, \eta; t, \mu | S(r_{12}) | s, \lambda; q, \nu \rangle \times D_{\lambda,\mu}^{\xi'}(s-t). \quad (38)$$

It is well known that there exists a unitary hypermatrix

$$U_{p,\xi;q,\nu} = \frac{1}{\sqrt{2N+1}} \exp\left(\frac{2\pi i}{2N+1} pq\right) \delta_{\xi,\nu} \quad (39)$$

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

$$\mathbf{A} = \mathbf{U} \tilde{\mathbf{A}} \mathbf{U}^+, \quad \tilde{\mathbf{A}} = \mathbf{U}^+ \mathbf{A} \mathbf{U}, \quad \tilde{A}_{q,\nu;r,\eta} = \tilde{A}_{\nu,\eta}(q) \delta_{q,r}. \quad (40)$$

With the help of transformation (39), we express the density matrix (32) as follows:

$$D_{\nu,\eta}(q-r) = \frac{1}{2N+1} \sum_{p=-N}^N \times \exp\left[\frac{2\pi i}{2N+1} p(q-r)\right] \tilde{D}_{\nu,\eta}(p), \quad (41)$$

where the block-diagonalized density matrix $\tilde{\mathbf{D}}$ can be written with the new coefficient matrix $\tilde{\mathbf{C}}$ as

$$\tilde{D}_{\nu,\eta}(p) = 2 \sum_{t=-N}^N \sum_{\xi=1}^m \tilde{C}_{p,\nu;t,\xi} \tilde{C}_{t,\xi;p,\eta}^+ n_{\xi}, \quad \tilde{\mathbf{C}} = \mathbf{U}^+ \mathbf{C}. \quad (42)$$

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

$$\tilde{C}_{p,\nu;t,\xi} = c_{p,\nu;p,\xi} \delta_{t,p} = c_{\nu,\xi}(p) \delta_{t,p}. \quad (43)$$

Consequently, Eq. (41) becomes

$$D_{\nu,\eta}(q-r) = \frac{2}{2N+1} \sum_{p=-N}^N \sum_{\xi=1}^m c_{\nu,\xi}(p) c_{\xi,\eta}^+(p) n_{\xi} \times \exp\left[\frac{2\pi i}{2N+1} p(q-r)\right]. \quad (44)$$

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

$$k = \frac{2\pi p}{a(2N+1)}. \quad (45)$$

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

$$D_{\nu,\eta}(q-r) = \frac{a}{\pi} \int_{-\pi/a}^{\pi/a} \sum_{\xi=1}^m c_{\nu,\xi}(k) c_{\xi,\eta}^+(k) n_{\xi} \times \exp[ik(R_q - R_r)] dk = \sum_{\xi=1}^m n_{\xi} D_{\nu,\eta}^{\xi}(q-r). \quad (46)$$

The NOF energy (31) becomes

$$E_{\text{elec}}^{\text{cell}} = \sum_{q=-\infty}^{\infty} \sum_{\nu,\eta=1}^m \left\{ \left[h_{\eta,\nu}(q) + J_{\eta,\nu}(q) - \frac{1}{2} K_{\eta,\nu}(q) \right] D_{\nu,\eta}(q) - \frac{1}{2} \sum_{\xi,\xi'=1}^m \gamma_{\xi,\xi'} [\bar{J}_{\eta,\nu}^{\xi'}(q) + \bar{K}_{\eta,\nu}^{\xi'}(q)] D_{\nu,\eta}^{\xi}(q) \right\}. \quad (47)$$

Matrices $\mathbf{J}(q)$, $\mathbf{K}(q)$, $\bar{\mathbf{J}}^{\xi'}(q)$, and $\bar{\mathbf{K}}^{\xi'}(q)$ are obtained from Eqs. (35)–(38), substituting N by ∞ in all summations, and using the density matrix given by Eq. (46).

IV. Results

At present, the procedure for minimization with respect to the orbital coefficients is too expensive. Calculations have shown that the optimal occupation numbers for the set of HF orbitals give a significant amount of the correlation energy in molecules. Moreover, the proposed NOF has predictive capabilities for dipole moments and polarizabilities [32]. Consequently, we expected that minimization of the energy with respect to the occupation numbers $\{n_q\}$ will give reliable values for polymers.

The constraints that have to be satisfied simultaneously in the minimization process are

1. The N -representability condition of the 1-RDM [33]: $0 \leq n_q \leq 1$.
2. The 1-RDM trace condition (15).
3. The nonidempotent condition (13).

PA still remains the prime model to test the reliability of electron correlation theories in quasi-one-dimensional polymers. Because of serious material problems, experiments still do not provide sufficiently accurate structural information for PA [34]. 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.

The following discussion will focus only on the most stable parameters relevant for the bond alter-

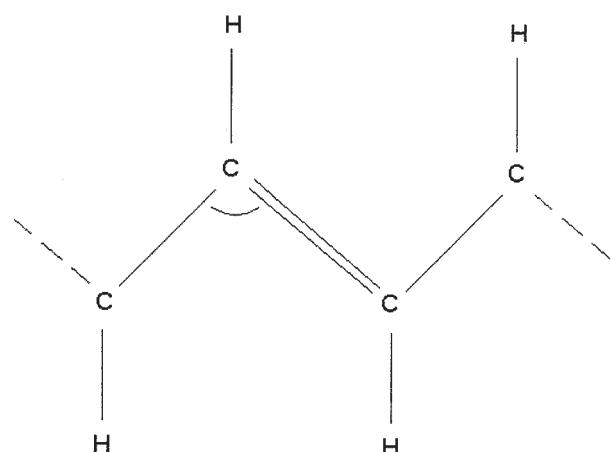


FIGURE 1. The geometrical structure of the quasi-one-dimensional polyacetylene (PA) chain.

TABLE I
Optimized geometries of PA at the HF and NOF levels.

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

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, and C—C—C bond angle is in °.

* Experimental values (Ref. [27]).

nation: 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 [27]. Figure 1 shows the geometrical structure of the quasi-1-D PA chain used in our calculations. The polymer was always kept planar.

In Table I 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 [35] 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 [6]. 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.

V. Conclusions

The original natural orbital functional developed for molecules has been extended to calculate corre-

lation energies for periodic polymers. It was considered a generalized correlation matrix in the two-particle reduced density matrix (2-RDM), which yields to a size-consistent functional. The 2-RDM becomes zero in the limit where all of elements of the Coulomb interaction between two complementary sets tend to zero.

The obtained NOF satisfies the first-order conditions imposed by a proper asymptotic behavior for weakly interacting systems but, lacking terms quadratic in two-electron integrals, is unable to satisfy the second-order expressions. On the other hand, the dynamic electron correlation in nonmetallic systems is a short-range effect with a distance dependence $\propto R^{-6}$. Using a separator function, the Coulomb operator was splitted into a rapidly decaying short-range part and a slowly decaying long-range part. The second term was ignored completely in the correlation term of the energy and will be included to account for dispersion effects. A promising perspective of this splitting is the more efficient evaluation of the two-electron integrals, which would imply a development of linear scaling NOF.

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 $\Delta r = 0.132 \text{ \AA}$ at the HF level to $\Delta r = 0.105 \text{ \AA}$ at the NOF level, a value that is closer to the experimentally observed one for PA, which is about 0.09 \AA [27].

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References

1. Löwdin, P. O. *Advan Phys* 1956, 5, 1.
2. Del Re, G.; Ladić, J.; Biczo, G. *Phys Rev* 1967, 155, 997.
3. Andre, J.-M.; Leroy, G.; Gouvernour, A. *Int J Quantum Chem* 1967, 1, 427.
4. Förner, W.; Knab, R.; Cizek, J.; Ladić, J. *J Chem Phys* 1997, 106, 10248.
5. Reinhardt, P. *Theor Chem Acc* 2000, 104, 426.
6. Yu, M.; Kalvoda, S.; Dolg, M. *Chem Phys* 1997, 224, 121.
7. Abdurahman, A.; Shukla, A.; Dolg, M. *Chem Phys* 2000, 257, 301; *J Chem Phys* 2000, 112, 4801.
8. Liegener, C.-M. *J Chem Phys* 1988, 88, 6999.
9. Suhai, S. *J Chem Phys* 1994, 101, 9766; *Phys Rev B* 1994, 50, 14791; *Phys Rev B* 1995, 51, 16553.
10. Hirata, S.; Iwata, S. *J Chem Phys* 1998, 109, 4147.
11. Sun, J.-Q.; Bartlett, R. J. *J Chem Phys* 1998, 108, 301; *Phys Rev Lett* 1998, 80, 349.
12. Hirata, S.; Grabowski, I.; Tobita, M.; Bartlett, R. *J Chem Phys Lett* 2001, 345, 475.
13. Mintmire, J. W.; White, C. T. *Phys Rev Lett* 1983, 50, 101; *Phys Rev B* 1983, 28, 3283.
14. Modern Density Functional Theory, A Tool for Chemistry; Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995.
15. von Boehm, J.; Kuivalainen, P.; Calais, J.-L. *Phys Rev B* 1987, 35, 8177.
16. Springborn, M.; Andersen, O. K. *J Chem Phys* 1987, 87, 7125.
17. te Velde, G.; Baerends, E. J. *Phys Rev B* 1991, 44, 7888.
18. Hirata, S.; Iwata, S. *J Chem Phys* 1997, 107, 10075.
19. Piris, M.; Otto, P. *Int J Quantum Chem* 2003, 94, 317.
20. Cioslowski, J.; Pernal, K.; Ziesche, P. *J Chem Phys* 2002, 117, 9560.
21. Cioslowski, J.; Pernal, K. *J Chem Phys* 2002, 116, 4802.
22. Ewald, P. P. *Ann Phys* 1921, 64, 253.
23. Dombroski, J. P.; Taylor, S. W.; Gill, P. M. W. *J Phys Chem* 1996, 100, 6272. Adamson, R. D.; Dombroski, J. P.; Gill, P. M. W. *Chem Phys Lett* 1996, 254, 329. Gill, P. M. W.; Adamson, R. D. *Chem Phys Lett* 1996, 261, 105.
24. Panas, I. *Chem Phys Lett* 1995, 245, 171.
25. Stoll, H.; Savin, A. In *Density Functional Methods in Physics*; Dreizler, R. M., Ed.; Plenum: New York, 1985.
26. Leininger, T.; Stoll, H.; Werner, H.-J.; Savin, A. *Chem Phys Lett* 1997, 275, 151.
27. Kahlert, H.; Leitner, O.; Leising, G. *Syn Met* 1987, 17, 467.
28. Suhai, S. *Phys Rev B* 1983, 27, 3506; *Chem Phys Lett* 1983, 96, 619; *Phys Rev B* 1984, 29, 4570.
29. Baeriswyl, D.; Campbell, D. K.; Mazumdar, S. In *Conjugated Conducting Polymers*; Kiess, H. G., Ed.; Springer Series in Solid-State Sciences 102; Springer: Berlin, 1992.
30. Lee, A. M.; Taylor, S. W.; Dombroski, J. P.; Gill, P. M. W. *Phys Rev A* 1997, 55, 3233.
31. Ladik, J. *Quantum Theory of Polymers as Solids*; Plenum Press: New York-London, 1988.
32. Piris, M.; Martinez, A.; Otto, P. *Int J Quantum Chem* 2004, 97, 827.
33. Coleman, A. *J Rev Mod Phys* 1963, 35, 668.
34. Zhu, Q.; Fisher, J. E. *Solid State Commun* 1992, 83, 179.
35. Gianolio, I.; Clementi, E. *Gazz Chim Ital* 1980, 110, 179.