

The one-electron picture in the Piris natural orbital functional 5 (PNOF5)

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Abstract The natural orbital functional theory provides two complementary representations of the one-electron picture in molecules, namely, the natural orbital (NO) representation and the canonical orbital (CO) representation. 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. In general, the one-particle reduced-density matrix (1-RDM) and the Lagrangian cannot be simultaneously brought to the diagonal form, except for the special Hartree-Fock case. The 1-RDM is diagonal in the NO representation, but not the Lagrangian, which is only a Hermitian matrix. Conversely, in the CO representation, the Lagrangian is diagonal, but not the 1-RDM. Combining both representations we have the whole picture concerning the occupation numbers and the orbital energies. The Piris

natural orbital functional 5 leads generally to the localization of the molecular orbitals in the NO representation. Accordingly, it provides an orbital picture that agrees closely with the empirical valence shell electron pair repulsion theory and the Bent's rule, along with the theoretical valence bond method. On the other hand, the equivalent CO representation can afford delocalized molecular orbitals adapted to the symmetry of the molecule. We show by means of the extended Koopmans' theorem that the one-particle energies associated with the COs can yield reasonable principal ionization potentials when the 1-RDM remains close to the diagonal form. The relationship between NOs and COs is illustrated by several examples, showing that both orbital representations complement each other.

Keywords Molecular orbitals · Orbital energies · One-particle reduced-density matrix · Natural orbital functional · PNOF5

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1 Introduction

One-electron pictures have long helped to our understanding of chemical bonding. The simplest one-electron model is based on the independent-particle Hartree-Fock (HF) approximation [8, 12]. However, it shows limitations due to the lack of the electron correlation. Many-electron effects can be taken into account with an adequate approximation of the 2-RDM since the molecular energy is determined exactly by the two-particle reduced-density matrix (2-RDM). Correlated wavefunction theory (WFT) approximations provide accurate 2-RDMs, hence Brueckner [2] and Dyson orbitals [23, 35] are reliable methods for determining a set of one-particle functions [36].

Unfortunately, such theories demand significant computational resources as the size of the systems of interest increase.

On the other hand, the density functional theory (DFT) [37] has become very popular in the computational community because electron correlation is treated in an effective one-particle framework. DFT replaces the two-particle problem with a one-particle exchange-correlation potential. In doing so, a calculation comparable to a HF one is possible with a relatively low computational cost, even though practical DFT methods suffer from several errors like those arising from electron self-interaction, the wrong long-range behavior of the Kohn-Sham (KS) [17] potentials, etc. Current implementations of DFT are mainly based on the KS formulation, in which the kinetic energy is not constructed as a functional of the density, but rather from an auxiliary Slater determinant. Since the non-interacting kinetic energy differs from the many-body kinetic energy, there is a contribution from a part of the kinetic energy contained in the correlation potential. The incorrect handling of the correlation kinetic energy is one main source of problems of present-day KS functionals.

The density matrix functional theory (DMFT) has emerged in recent years as an alternative method to conventional WFT and DFT. The idea of a one-particle reduced-density matrix (1-RDM) functional appeared few decades ago [9, 21, 22, 56]. The major advantage of a density matrix formulation is that the kinetic energy is explicitly defined, and it does not require the construction of a functional. The unknown functional only needs to incorporate electron correlation. The 1-RDM functional is called natural orbital functional (NOF) when it is based upon the spectral expansion of the 1-RDM. The natural orbitals (NOs) [25] are orthonormal with fractional occupancies, allowing to unveil the genuine electron correlation effects in terms of one-electron functions. Valuable literature related to the NOF theory (NOFT) can be found in Refs. [42] and [43].

It is important to note that functionals currently in use are only known in the basis where the 1-RDM is diagonal. This implies that they are not functionals explicitly dependent on the 1-RDM and retain some dependence on the 2-RDM. So far, all known NOFs suffer from this problem including the exact NOF for two-electron closed-shell systems [11]. The only exception is the special case of the HF energy that may be viewed as a 1-RDM functional. Accordingly, the NOs obtained from an approximate functional are not the exact NOs corresponding to the exact expression of the energy. In this vein, they are NOs as the orbitals that diagonalize the 1-RDM corresponding to an approximate expression of the energy, like those obtained from an approximate WFT.

One route [51, 52] to the construction of approximate NOF involves the employment of a reconstruction functional based on the cumulant expansion [19, 29] of the 2-RDM. We shall use the reconstruction functional proposed in [41], in which the two-particle cumulant is explicitly reconstructed in terms of two matrices, $\Delta(\mathbf{n})$ and $\Pi(\mathbf{n})$, \mathbf{n} being the set of the occupation numbers. The $\Delta(\mathbf{n})$ and $\Pi(\mathbf{n})$ matrices satisfy known necessary N -representability conditions [30, 32] and sum rules of the 2-RDM, or equivalently, of the functional. Moreover, precise constraints that the two-particle cumulant matrix must fulfill in order to conserve the expectation values of the total spin and its projection have been formulated and implemented for the matrices $\Delta(\mathbf{n})$ and $\Pi(\mathbf{n})$ [46]. Appropriate forms of the matrices $\Delta(\mathbf{n})$ and $\Pi(\mathbf{n})$ led to different implementations of NOF, known in the literature as PNOFi ($i = 1-5$) [41, 44, 45, 47, 48]. A detailed account of these functionals can be found elsewhere [43]. Because PNOF theory is based on both the 1- and the 2-RDMs, it has connections to the parametric 2-RDM methods of Refs. [31, 54]

It has recently been pointed out [28] that PNOF5 [24, 27, 44] can provide a NO picture that agrees closely with the empirical valence shell electron pair repulsion theory (VSEPR) [10] and the Bent's rule [1], along with the popular theoretical valence bond (VB) method [13, 58]. Although PNOF5 can predict additionally three- and four-center two-electron bonds, in general, the solutions of the PNOF5 equations lead to orbital hybridization and to localization of the NOs in two centers, providing a natural language for the chemical bonding theory.

Nevertheless, in some systems the electronic structure is better understood through orbital delocalization. Typical cases are the aromatic systems like benzene molecule. This point of view was introduced by Hund [14] and Mulliken [34] within the framework of the linear combination of atomic orbitals-molecular orbital (LCAO-MO) theory, in which orbitals can extend over the entire molecule. Later, Koopmans [18] demonstrated, using the HF approximation in the framework of the LCAO-MO theory, one of the most important connections between orbitals and the experiment: the HF orbital energies are directly associated with ionization energies. Accordingly, it raises the question of how to achieve a delocalized one-particle orbital representation that complements the NO representation in PNOF5.

In this paper, we introduce an equivalent orbital representation to the NO one, in which the molecular orbitals are delocalized. These orbitals are not obtained arbitrarily, but arise from the diagonalization of the matrix of Lagrange multipliers, or the Lagrangian, obtained in the NO representation, so we will call them canonical orbitals (COs) by analogy to the HF COs. It is important to recall that only for functionals explicitly dependent on the 1-RDM, the

1-RDM and the Lagrangian may be simultaneously brought to the diagonal form by the same unitary transformation [6]. On the contrary, in our case, the functional still depends on the 2-RDM, hence both matrices do not commute. Moreover, we cannot expect that it should be possible to bring the 1-RDM and the Lagrangian simultaneously to diagonal form in the case of finite order of the one-particle set [25]. In summary, only in the HF case, it is possible to find one representation in which both matrices are diagonal. For all the other known NOFs, there are two unique representations that diagonalize separately each matrix.

In the NO representation, the 1-RDM is diagonal, but not the Lagrangian, so the eigenvalues of the former afford the occupation numbers of the NOs corresponding to the proposed approximate functional. On the other hand, in the CO representation, the matrix of Lagrange multipliers is diagonal, but not anymore the 1-RDM. Taking into account the terminology developed by Coulson and Longuet-Higgins [3], we have in the CO representation the charge order of the orbital in the diagonal elements of the 1-RDM and the bond order of two orbitals in the off-diagonal elements. But even here, the charge order may be interpreted as the average number of particles in the orbital under consideration [25].

In contrast to the NO representation, the diagonal elements of the Lagrangian in the CO representation can be physically meaningful. We demonstrate below, using the extended Koopmans' theorem (EKT) [4, 5, 33, 55], that the new one-particle energies can describe satisfactorily the principal ionization potentials (IPs), when the 1-RDM is close to the diagonal form in the CO representation. These one-particle energies account for the electron correlation effects, but evidently they neglect relaxation of the orbitals in the $(N - 1)$ -state and consequently tend to produce too positive IPs. In the next section, the theory related to PNOF5 COs is presented. The relationship between NOs and COs is examined then by several examples.

2 Theory

The Piris natural orbital functional (PNOF) for singlet states reads as [41]

$$E = 2 \sum_p n_p H_{pp} + \sum_{pq} \Pi_{qp} L_{pq} + \sum_{pq} (n_q n_p - \Delta_{qp}) (2J_{pq} - K_{pq}) \quad (1)$$

where p denotes the spatial NO and n_p its occupation number (ON). H_{pp} is the p th matrix element of the kinetic energy and nuclear attraction terms, whereas $J_{pq} = \langle pq|pq \rangle$ and $K_{pq} = \langle pq|qp \rangle$ are the usual Coulomb

and exchange integrals, respectively. $L_{pq} = \langle pplqq \rangle$ is the exchange and time-inversion integral [40, 50]. Note that if Δ and Π vanish, then our reconstruction yields the HF energy, as expected. Moreover, for real orbitals exchange integrals and exchange and time-inversion integrals coincide, $L_{pq} = K_{pq}$. In PNOF5, we have adopted the following expressions [44]

$$\Delta_{pq} = n_p^2 \delta_{pq} + n_p n_{\tilde{p}} \delta_{\tilde{p}q} \quad (2)$$

$$\Pi_{pq} = n_p \delta_{pq} - \sqrt{n_p n_{\tilde{p}}} \delta_{\tilde{p}q} \quad (3)$$

The \tilde{p} -state defines the coupled NO to the orbital p , namely, $\tilde{p} = N - p + 1$, N being the number of particles in the system. Bounds that stem from imposing N -representability-necessary conditions on the 2-RDM imply that the ON of the \tilde{p} level must coincide with that of the hole of its coupled state p , namely,

$$n_{\tilde{p}} = h_p, \quad n_{\tilde{p}} + n_p = 1, \quad (4)$$

where h_p denotes the hole $1 - n_p$ in the spatial orbital p . In accordance to the Eq. (4), all occupancies vanish for $p > N$. Assuming a real set of NOs, the PNOF5 energy for a singlet state of an N -electron system is cast as [44]:

$$E = \sum_{p=1}^N [n_p (2H_{pp} + J_{pp}) - \sqrt{n_{\tilde{p}} n_p} K_{p\tilde{p}}] + \sum_{p,q=1}^N {}'' n_q n_p (2J_{pq} - K_{pq}), \quad (5)$$

The double prime in Eq. (5) indicates that both the $q = p$ term and the coupled one-particle state terms $p = \tilde{p}$ are omitted from the last summation. One must look for the pairs of coupled orbitals (p, \tilde{p}) that yield the minimum energy for the functional of Eq. (5). The actual p and \tilde{p} orbitals paired are not constrained to remain fixed along the orbital optimization process. As a consequence, an orbital localization occurs generally, which corresponds to the most favorable orbital interactions [28]. This situation contrasts with our previous approximations PNOFi ($i = 1-4$) [41, 45, 47, 48], in which, the off-diagonal elements Δ_{pq} and Π_{pq} were formulated for all possible (p, q) pairs, leading to delocalized NOs.

The solution is established by optimizing the energy functional (5) with respect to the ONs and to the NOs, separately. PNOF5 allows constraint-free minimization with respect to the ONs, which yields substantial savings of computational time [44]. Therefore, one has to minimize the energy (5) with respect to the real orbitals $\{\varphi_p(\mathbf{r})\}$ under the orthonormality constraints. Introducing the matrix of symmetric Lagrange multipliers $\Lambda = \{\lambda_{qp}\}$, the functional whose extremum we seek is given by

$$\Omega = E - 2 \sum_{pq} \lambda_{qp} [\langle \varphi_p | \varphi_q \rangle - \delta_{pq}] \quad (6)$$

The Euler equations for the functions $\{\varphi_p(\mathbf{r})\}$ are,

$$n_p \hat{V}_p |\varphi_p\rangle = \sum_q \lambda_{qp} |\varphi_q\rangle \quad (7)$$

Multiplying Eq. (7) by $\langle \varphi_q |$, the matrix representation of this equation is

$$n_p \langle \varphi_q | \hat{V}_p | \varphi_p \rangle = \lambda_{qp} \quad (8)$$

The one-particle operator \hat{V}_p is given by

$$\begin{aligned} \hat{V}_p(1) = & \hat{H}(1) + \hat{J}_p(1) - \sqrt{\frac{h_p}{n_p}} \hat{K}_{\bar{p}}(1) \\ & + \sum_{q=1}^N n_q [2\hat{J}_q(1) - \hat{K}_q(1)] \end{aligned} \quad (9)$$

with

$$\hat{J}_q(1) = \langle \varphi_q | r_{12}^{-1} | \varphi_q \rangle, \hat{K}_q(1) = \langle \varphi_q | r_{12}^{-1} \hat{P}_{12} | \varphi_q \rangle$$

The \hat{P}_{12} operator permutes electrons 1 and 2, and the integration is carried out only over the coordinates of 2. Notice that the \hat{V}_p operator is p th orbital dependent, it is not a mean field operator like, for instance, the Fock operator. One consequence of this is that the Lagrangian matrix $\mathbf{\Lambda}$ and the 1-RDM $\mathbf{\Gamma}$ do not commute; $[\mathbf{\Lambda}, \mathbf{\Gamma}] \neq 0$, therefore, they cannot be simultaneously brought to diagonal form by the same unitary transformation \mathbf{U} . Thus, Eq. (7)–(8) cannot be reduced to a pseudo-eigenvalue problem by diagonalizing the matrix $\mathbf{\Lambda}$. Actually, apart from the special HF case, where the 1-RDM is idempotent and the energy may be viewed as a 1-RDM functional, none of the currently known NOFs have effective potentials that allow to diagonalize simultaneously both matrices $\mathbf{\Gamma}$ and $\mathbf{\Lambda}$.

In this paper, the efficient self-consistent eigenvalue procedure proposed in [53] is employed to solve Eq. (7). It yields the NOs by iterative diagonalization of a Hermitian matrix \mathbf{F} . The off-diagonal elements of the latter are determined from the hermiticity of the matrix of the Lagrange multipliers $\mathbf{\Lambda}$. An expression for diagonal elements is absent, so a generalized Fockian is undefined in the conventional sense; nevertheless, they may be determined from an aufbau principle [53].

Using the expressions for diagonal elements of $\mathbf{\Lambda}$, let us rewrite the energy functional (5) as follows:

$$E = \sum_{p=1}^N [n_p H_{pp} + \lambda_{pp}] \quad (10)$$

Let us recall that the trace of an $N \times N$ square matrix is the

sum of its diagonal elements, then the Eq. (10) can be rewritten as

$$E = \text{Tr}(\mathbf{H}\mathbf{\Gamma} + \mathbf{\Lambda}) \quad (11)$$

Taking into account that the trace of a matrix is invariant under a unitary transformation \mathbf{U} , the energy (11) keeps constant under such transformation of the orbitals, that is,

$$\begin{aligned} \text{Tr}(\mathbf{H}\mathbf{\Gamma} + \mathbf{\Lambda}) &= \text{Tr}(\mathbf{U}^\dagger \mathbf{H} \mathbf{U} \mathbf{U}^\dagger \mathbf{\Gamma} \mathbf{U} + \mathbf{U}^\dagger \mathbf{\Lambda} \mathbf{U}) \\ &= \text{Tr}(\mathbf{H}'\mathbf{\Gamma}' + \mathbf{\Lambda}') \end{aligned} \quad (12)$$

Accordingly, it is always possible to find a matrix \mathbf{U} such that the transformation $\mathbf{\Lambda}' = \mathbf{U}^\dagger \mathbf{\Lambda} \mathbf{U}$ diagonalizes $\mathbf{\Lambda}$. It is worth to note that the transformed 1-RDM $\mathbf{\Gamma}' = \mathbf{U}^\dagger \mathbf{\Gamma} \mathbf{U}$ is not anymore a diagonal matrix. Such unitary transformation exists and is unique. Orbitals $\{\chi_p(\mathbf{r})\}$, for which the matrix of Lagrange multipliers is diagonal, will be called COs by analogy to the HF COs. One should note that the Lagrangian $\mathbf{\Lambda}$ is a symmetric matrix only at the extremum; ergo, this procedure for obtaining the COs can be solely used after the NOs have been obtained. In contrast to PNOF5 NOs, which are localized, more in line with our intuitive feeling for chemical bonds, the PNOF5 COs will generally be delocalized.

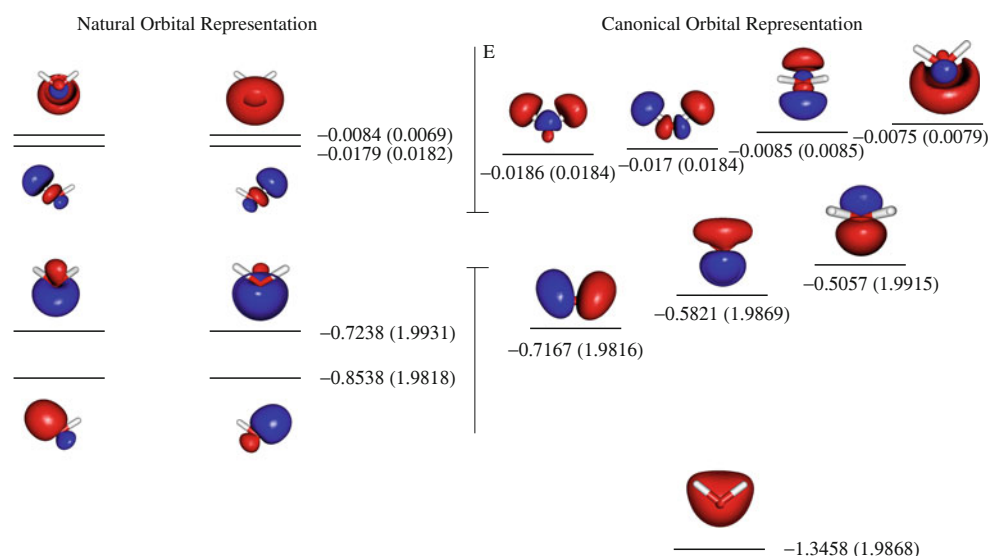
Analogously to HF COs, PNOF5 COs may also form a basis for an irreducible representation of the point group of the molecule. Similar to the Fock matrix, the Lagrangian $\mathbf{\Lambda}$ depends itself on the orbitals that have to be determined. It is well known that if there is any symmetry present in the initial guess of the HF COs, then this symmetry will be preserved at the SCF solution [15]. In this vein, if the initial guess for the NOs was adapted to the point group symmetry of the molecule, although optimal NOs are mostly not adapted to the symmetry, the Lagrangian contains all symmetry information, so the latter can be transferred to the COs after diagonalization of $\mathbf{\Lambda}$. It is worth to notice that the matrix of the Lagrange multipliers plays the role of the generalized Fock matrix in the NOFT.

Both $\{\varphi_p(\mathbf{r})\}$ and $\{\chi_p(\mathbf{r})\}$ sets of orbitals are pictures of the same solution; therefore, they complement each other. In the Sect. 3, the obtained results are discussed.

2.1 Orbital energies and ionization potentials

The Eq. (10), which now includes correlation effects, looks exactly the same as the total energy of an independent-particle system, hence λ_{pp} can be considered as a one-particle energy of the spatial orbital p . However, in contrast to the HF one-particle energies, $-\lambda_{pp}$ are not IPs of the molecule via the Koopmans' theorem [18]. The IPs in the NOFT [20, 38, 49] must be obtained from the extended Koopmans' theorem [4, 5, 33, 55]. The equation for the EKT may be derived by expressing the wavefunction of the

Fig. 1 PNOF5 valence natural and canonical orbitals for H₂O, along with their corresponding diagonal Lagrange multipliers in Hartrees, and diagonal elements of the 1-RDM, in parenthesis



$(N - 1)$ -electron system as the following linear combination

$$|\Psi^{N-1}\rangle = \sum_i C_i \hat{a}_i |\Psi^N\rangle \quad (13)$$

In Eq. (13), \hat{a}_i is the annihilation operator for an electron in the spin-orbital $|\phi_i\rangle = |\varphi_p\rangle \otimes |\sigma\rangle (\sigma = \alpha, \beta)$, $|\Psi^N\rangle$ is the wavefunction of the N -electron system, $|\Psi^{N-1}\rangle$ is the wavefunction of the $(N - 1)$ -electron system and $\{C_i\}$ are the set of coefficients to be determined. Optimizing the energy of the state Ψ^{N-1} with respect to the parameters $\{C_i\}$ and subtracting the energy of Ψ^N gives the EKT equations as a generalized eigenvalue problem,

$$\mathbf{FC} = \mathbf{\Gamma C v} \quad (14)$$

where \mathbf{v} are the EKT IPs, and the transition matrix elements are given by

$$F_{ji} = \langle \Psi^N | \hat{a}_j^\dagger [\hat{\mathcal{H}}, \hat{a}_i] | \Psi^N \rangle \quad (15)$$

Eq. (14) can be transformed by a symmetric orthonormalization using the inverse square root of the 1-RDM. Hence, the diagonalization of the matrix $\mathbf{\Gamma}^{1/2} \mathbf{F} \mathbf{\Gamma}^{-1/2}$ yields the IPs as eigenvalues. In a spin-restricted NOFT, it is not difficult to demonstrate that transition matrix elements are given by $-\lambda_{qp}$ [49]. Accordingly, the diagonalization of the matrix \mathbf{v} with elements

$$v_{qp} = -\frac{\lambda_{qp}}{\sqrt{n_q n_p}} \quad (16)$$

affords the IPs in the NO representation. If the off-diagonal elements of the Lagrangian may be neglected, then from Eq. (16) follows that $-\lambda_{pp}/n_p$ will be good approximations for the ionization energies. Our calculations have shown that this rarely occurs. On the other hand, $-\Lambda'$ corresponds

to the transition matrix \mathbf{F}' in the CO representation, hence the diagonalization of the matrix \mathbf{v}' with elements

$$v'_{qp} = -\sum_r \left(\Gamma'_{qr} \right)^{-1/2} \lambda'_{rr} \left(\Gamma'_{rp} \right)^{-1/2} \quad (17)$$

provides alternatively the IPs too. In many cases, we have found that the 1-RDM remains close to the diagonal form in the CO representation, so the values $-\lambda'_{pp}/\Gamma'_{pp}$ may be taken as ionization energies. We show below, in Sect. 4, that the one-particle energies associated with the COs may be considered as good estimations of the principal ionization potentials, for several molecules, via this formula.

3 PNOF5 orbitals

In general, PNOF5 yields localized orbitals in the NO representation, whereas it affords delocalized orbitals in the CO representation. The former ones arise directly from the energy minimization process. The COs are obtained from the diagonalization of the matrix of Lagrange multipliers after the NOs have been obtained. Here, both NO and CO representations of PNOF5 valence orbitals are given for a selected set of molecules, namely, H₂O, CH₄, (BH₃)₂, BrF₅ and C₆H₆. These molecules have been chosen to show the equivalency between both pictures of the orbitals and how these two pictures are connected. In all figures, the corresponding diagonal elements of the matrix of Lagrange multipliers and 1-RDM have been included. For the latter, twice of its values are reported, for example, the double of the occupancies in the case of the NO representation, and the double of the average number of particles in the orbital under consideration, for the CO representation.

Fig. 2 PNOF5 valence natural and canonical orbitals for CH_4 , along with their corresponding diagonal Lagrange multipliers in Hartrees, and diagonal elements of the 1-RDM, in parenthesis

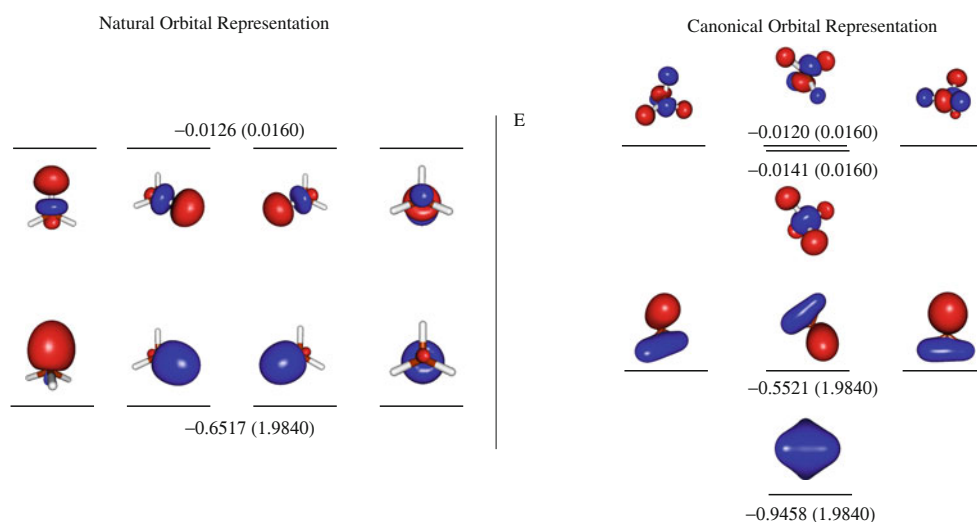
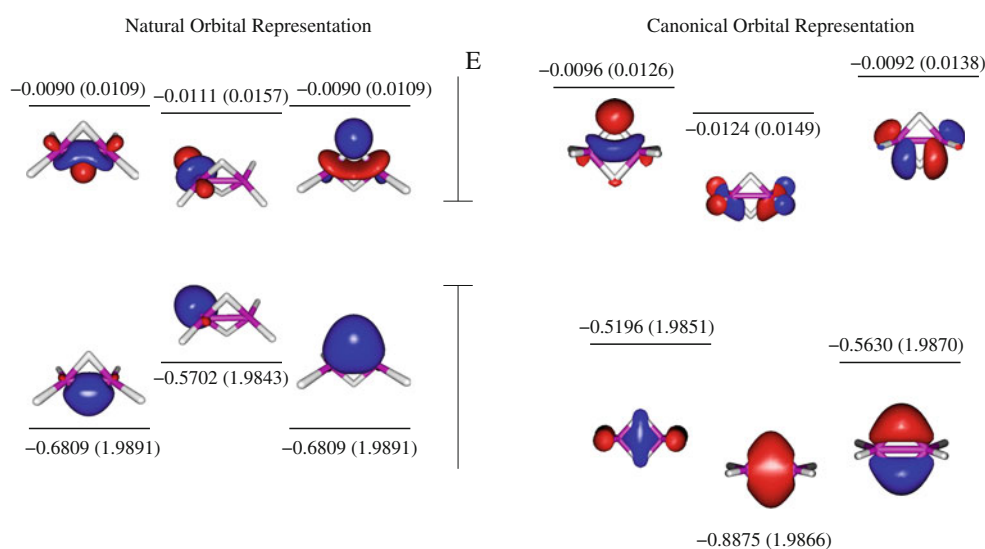


Fig. 3 PNOF5 valence natural and canonical orbitals for $(\text{BH}_3)_2$, along with their corresponding diagonal Lagrange multipliers in Hartrees, and diagonal elements of the 1-RDM, in parenthesis



All calculations have been carried out at the experimental geometries [16], using the PNOFID code [39]. The correlation-consistent cc-pVDZ-contracted Gaussian basis sets [7, 57] have been employed. No important differences were observed for orbitals obtained with larger basis sets.

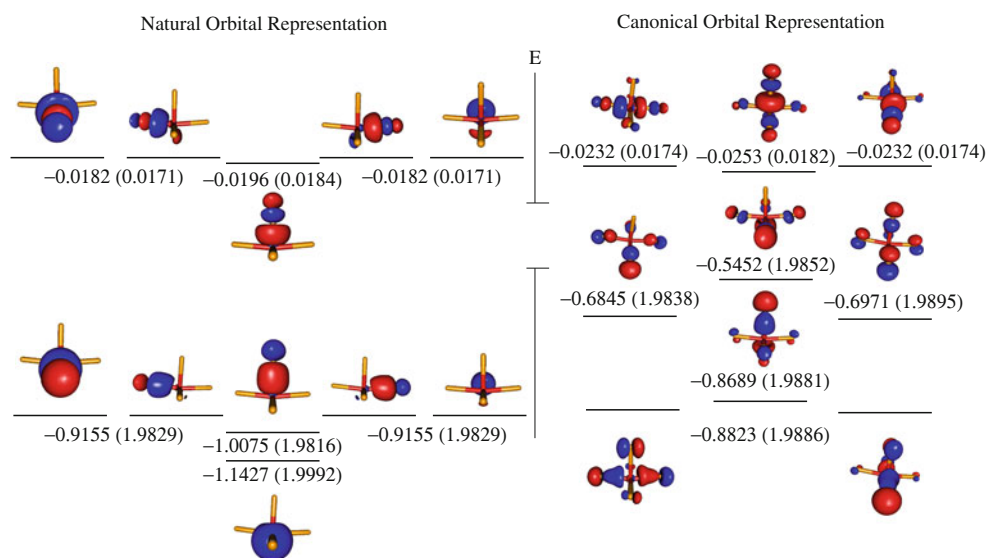
In Fig. 1, the PNOF5 valence natural and canonical orbitals calculated for the water molecule are shown. It is observed that NOs agree closely to the picture emerging from chemical bonding arguments: the O atom has sp^3 hybridization, two of these orbitals are used to bound to H atoms, leading to two degenerate oxygen-hydrogen σ bonds, and the remaining two are degenerated lone pairs. NO representation provides a theoretical basis to the VSEPR model. On the other hand, in the CO representation, the obtained orbitals are symmetry adapted and resemble those obtained by usual molecular orbital theories, for example, HF or DFT.

The valence natural and canonical orbitals of methane are depicted in Fig. 2. The NO representation describes the bonding picture in methane as four equivalent C–H bonds, resembling those that can be obtained with the VB method. Carbon is hybridized to form four sp^3 -type orbitals. Each of such orbitals form a covalent bond with the $1s$ of one of the H atoms. The calculated orbital energies and occupation numbers are the same for these four orbitals.

On the contrary, the COs are symmetry adapted, and one can observe that the fourfold degeneracy is broken into one orbital of a_1 symmetry and threefold degenerate t_2 orbitals.

Focussing on the diagonal elements of the 1-RDM in both representations, we note that these values are close to 1 or 0. Moreover, the off-diagonal elements are exactly zero in the NO representation, and they can be neglected in the CO representation; ergo, the 1-RDM is practically idempotent in both representations. Because the

Fig. 4 PNOF5 valence natural and canonical orbitals for BrF_5 , along with their corresponding diagonal Lagrange multipliers in Hartrees, and diagonal elements of the 1-RDM, in parenthesis



off-diagonal elements of the Lagrangian are not negligible in the NO representation, $-\lambda_{pp}$ cannot approximate the IP, and it is completely wrong to expect one valence ionization energy fourfold degenerate in methane. On the contrary, the obtained $-\lambda'_{pp}$ may be considered as good estimation for the IP. In [26], it was shown that PNOF5 is able to describe the two peaks of the vertical ionization spectra of methane via the EKT. The obtained here IPs for methane, by means of the negative value of the CO energies, are 15.02 and 25.74 eV, which are very close to the PNOF5-EKT values of 15.14 and 25.82 eV, and to the experimental IPs of 14.40 and 23.00 eV, respectively [26]. This is an example of how both one-electron pictures complement each other. It is evident that the NO representation agrees perfectly with the chemical bonding arguments, whereas the CO representation solves the problem raised for the ionization potentials.

Diborane (BH_3)₂ is an electron deficient molecule. The PNOF5 valence NO scheme predicts three-center two-electron (3c–2e) bonds, linking together both B atoms through intermediate H atoms, as can be seen on the left side of Fig. 3. Four degenerated B–H σ bonding orbitals are predicted to be coupled with their corresponding antibonding orbitals, while two degenerated B–H–B bonding orbitals are coupled with their corresponding antibonding orbitals. The CO scheme, depicted on the right side of Fig. 3, shows a similar delocalized picture as the standard molecular orbital calculations. According to this picture, the 3c–2e bonds are correctly described.

In Fig. 4, the PNOF5 orbitals calculated for BrF_5 are given. The NO representation depicts the bonding in this molecule as four degenerated Br–F σ bonds on the equatorial plane, and one Br–F σ bond on the axial axis. Each F atom has sp^3 hybridization, having the three lone pairs (not

Fig. 5 PNOF5 valence natural and canonical orbitals for C_6H_6 , along with their corresponding diagonal Lagrange multipliers in Hartrees, and diagonal elements of the 1-RDM, in parenthesis

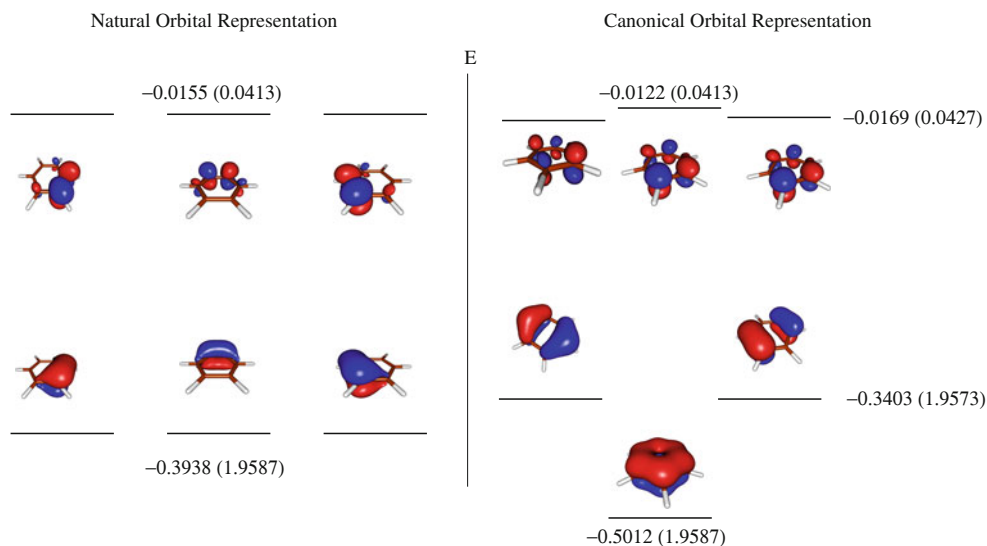


Table 1 First vertical ionization potentials, in eV, obtained at the HF and PNOF5 levels of theory by means of the KT and EKT, respectively, along with the negative values of the corresponding orbital energies in the canonical orbital representation ($-\lambda'_{pp}$)

		HF-KT	PNOF5-EKT	$-\lambda'_{pp}$	EXP
N ₂	σ_g	17.05 (1.45)	16.45 (0.85)	16.98 (1.38)	15.60
F ₂	π_g	18.03 (2.16)	17.23 (1.36)	18.12 (2.25)	15.87
LiH	σ	8.17 (0.47)	7.53 (−0.17)	8.60 (0.90)	7.70
HF	π	17.12 (0.93)	16.76 (0.77)	17.55 (1.36)	16.19
HCl	π	12.82 (0.09)	12.63 (−0.06)	12.99 (0.22)	12.77
CO	σ	14.93 (0.92)	14.16 (0.15)	14.81 (0.80)	14.01
SiO	σ	11.78 (0.17)	11.82 (0.21)	11.98 (0.37)	11.61
H ₂ O	b_1	13.42 (0.64)	13.06 (0.28)	13.76 (0.98)	12.78
NH ₃	a_1	11.41 (0.61)	11.05 (0.25)	11.67 (0.87)	10.80
H ₂ CO	b_2	11.84 (0.94)	11.74 (0.84)	12.24 (1.34)	10.90
C ₆ H ₆	e_{1g}	9.05 (−0.20)	9.20 (−0.05)	9.26 (0.01)	9.25
CO ₂	π_g	14.59 (0.81)	13.96 (0.18)	14.89 (1.11)	13.78
SO ₂	a_1	13.24 (0.74)	13.00 (0.50)	13.47 (0.97)	12.50
BrF ₅	a_1	14.46 (1.29)	13.62 (0.45)	14.84 (1.67)	13.17
ClF ₃	b_1	14.52 (1.47)	13.53 (0.48)	14.66 (1.61)	13.05
CH ₃ CClO	a'	10.73 (−0.30)	11.13 (0.10)	12.65 (1.62)	11.03
HCOOH	a'	12.43 (0.93)	12.29 (0.79)	12.98 (1.48)	11.50
CH ₃ OCH ₃	b_1	11.36 (1.26)	11.24 (1.14)	11.62 (1.52)	10.10
HOC-CHO	a_g	11.75 (1.15)	11.58 (0.98)	12.02 (1.42)	10.60
HCONH ₂	a''	11.20 (1.04)	10.34 (0.18)	11.49 (1.33)	10.16
CH ₃ SH	a	9.56 (0.12)	9.33 (−0.11)	9.73 (0.29)	9.44

Differences between theoretical values and the experiment, in parenthesis. The cc-pVDZ basis sets have been employed

shown in the figure) as far apart as possible, in accordance to the VSEPR model. In principle, this NO representation of the PNOF5 orbitals provides a picture that could resemble that predicted by the molecular orbital theories. In the axial Br–F bonds, the quasilinear F–Br–F two bonds are constructed mainly by the same bromine p orbital. Consequently, these two bonds are “connected” by the same p orbital in the center.

A better agreement with the molecular orbital pictures is indeed obtained in the complementary CO representation. It may be observed that COs describe perfectly the three-center four-electron (3c–4e) bonds, where four electrons are delocalized along the quasilinear F–Br–F bonds. Furthermore, the obtained COs are symmetry-adapted.

Benzene can be considered as a model molecule for aromatic systems. It is well known that aromaticity can be described by both localized and delocalized orbitals. VB theory describes the π delocalization by combinations of structures containing localized π bonds between adjacent carbon atoms. On the other hand, HF approximation can predict the delocalization effects with only one Slater determinant, in accordance to the Huckel model. The six p orbitals of carbon atoms involved in the π system form six molecular orbitals, one with 0 nodes, 2 degenerate orbitals

with 2 nodes, 2 degenerate orbitals with 4 nodes and finally a totally antibonding orbital with six nodes.

In Fig. 5, the PNOF5 NOs and COs for benzene are shown. For the sake of clarity, only the orbitals involved in the π system are depicted. Focusing on the NO representation, three degenerate π orbitals are obtained, coupled with their corresponding antibonding orbitals. According to this picture, one could infer that the delocalization effects are not fully taken into account for benzene; however, there are significant values for the off-diagonal elements of the matrix of Lagrange multipliers that contain this information. The CO representation corroborates this hypothesis showing the typical orbital picture. It should be mentioned that, in the NO representation, the remaining σ -type orbitals are localized C–C and C–H bonds, while in the CO representation, these σ -type orbitals are delocalized along the molecule. The obtained COs are symmetry adapted as in above described cases. Accordingly, PNOF5 can also handle aromatic systems.

4 Vertical ionization potentials

We have shown above, in Subsect. 2.1, that if the 1-RDM keeps close to the diagonal form in the CO representation, then the values $-\lambda'_{pp}/\Gamma'_{pp}$ may be considered as good estimations of the principal ionization potentials. Even more, if the 1-RDM is almost idempotent, the negative values of the CO energies may be taken as well. In this section, the calculated vertical ionization energies of an enlarged set of molecules are shown.

Table 1 lists the obtained vertical IPs calculated as $-\lambda'_{pp}$ for a selected set of molecules. For these systems, the 1-RDM is close to the corresponding idempotent matrix, with diagonal elements near to 1 or 0. For comparison, the ionization energies obtained at the HF level of theory, by means of KT, as well as the PNOF5 IPs via the EKT have been included.

We observe that the negative values of the corresponding orbital energies in the CO representation agree well with the experimental data. The better agreement between the HF IPs and the experiment is due to the partial cancellation of the electron correlation and orbital relaxation effects, an issue that has been long recognized in the literature. In our case, $-\lambda'_{pp}$ takes into account the electron correlation, but neglect the orbital relaxation in the $(N-1)$ -state, hence, the corresponding orbital energies in the canonical orbital representation tend to produce too positive IPs.

Table 2 collects a selected set of molecules with vertical IPs, calculated as $-\lambda'_{pp}$, that are smaller than the IPs obtained via EKT. In the CO representation, these molecules have 1-RDMs which could be considered rather

Table 2 First vertical ionization potentials, in eV, obtained at the HF and PNOF5 levels of theory by means of the KT and EKT, respectively, along with the negative values of the corresponding orbital energies in the canonical orbital representation ($-\lambda'_{pp}$ and $-\lambda'_{pp}/\Gamma'_{pp}$)

		HF-KT	PNOF5-EKT	$-\lambda'_{pp}/\Gamma'_{pp}$	$-\lambda'_{pp}$	EXP
Li ₂	σ	4.91 (−0.23)	5.20 (0.06)	5.21 (0.07)	4.89 (0.25)	5.14
P ₂	π_u	10.03 (−0.62)	10.57 (−0.08)	10.56 (−0.09)	10.05 (−0.60)	10.65
CH ₄	t_2	14.78 (0.38)	15.14 (0.74)	15.14 (0.74)	15.02 (0.62)	14.40
C ₂ H ₂	π_u	11.06 (−0.43)	11.61 (0.12)	11.60 (0.11)	11.26 (−0.23)	11.49
C ₂ H ₄	$1b_{3u}$	10.14 (−0.37)	10.87 (0.36)	10.87 (0.36)	10.39 (−0.12)	10.51
HCN	π	13.37 (−0.24)	13.96 (0.35)	14.09 (0.48)	13.64 (0.03)	13.61
CH ₃ CN	a'	12.43 (−0.03)	12.97 (0.51)	13.13 (0.67)	12.77 (0.31)	12.46

Differences between theoretical values and the experiment, in parenthesis. The cc-pVDZ basis sets have been employed

diagonal instead of idempotent. Certainly, the off-diagonal elements of the CO 1-RDM can be neglected, and in most cases diagonal values Γ'_{pp} differ significantly from 1 and 0. In these particular systems, where both Γ' and Λ' can be considered diagonal matrices, the estimated IPs via EKT reduces to $-\lambda'_{pp}/\Gamma'_{pp}$ according to Eq. (17). We observe an outstanding agreement between the fourth and fifth columns of Table 2.

Exceptions are HCN and CH₃CN. These molecules have values different from 1 and 0 in the diagonal of the new 1-RDM Γ , and in addition, the off-diagonal elements cannot be neglected as in previous cases. Accordingly, the orbital energy in the CO representation yields an smaller estimation for the IP than EKT, but the corrected value obtained dividing $-\lambda'_{pp}$ by the corresponding diagonal element of Γ' is larger than it.

5 Conclusions

It has been shown that PNOF5 provides two complementary pictures of the electronic structure of molecules, namely, the NO and the CO representations. In the NO representation, the matrix of Lagrange multipliers is a symmetric non-diagonal matrix, whereas the 1-RDM is diagonal. Conversely, the matrix of Lagrange multipliers is transformed to yield a diagonal matrix in the CO representation, but the 1-RDM becomes a symmetric non-diagonal matrix. This transformation can be done only after solving the problem in the NO representation because Λ is symmetric only at the extremum. Hence, we are forced to obtain firstly the NOs which minimize the energy, and afterward, Λ is transformed from the NO representation, in which it is not diagonal, to the CO representation in which it is diagonal. Unfortunately, both matrices cannot be diagonalized simultaneously; however, NO and CO representations are unique one-particle pictures of the same solution, ergo, complement each other in the description of the electronic structure.

PNOF5 NOs are localized orbitals that nicely agree with the chemical intuition of chemical bonding, VB and VSEPR bonding pictures. On the contrary, PNOF5 COs are symmetry-adapted delocalized orbitals similar to those obtained by molecular orbital theories. The shape of COs obtained for diborane (BH₃)₂, bromine pentafluoride (BrF₅) and benzene (C₆H₆) supports the idea that PNOF5 is able to describe correctly the electronic structure of molecules containing three-center two-electron (3c–2e) bonds, three-center four-electron (3c–4e) bonds and the delocalization effects related to the aromaticity.

The new COs arises directly from the unitary transformation that diagonalizes the matrix of Lagrange multipliers of the NO representation. The values of this diagonal Lagrangian in the CO representation can be interpreted in the same vein as HF case, but including electron correlation effects, that is, the ionization energies are the negative of the corresponding orbital energies. We have shown theoretically and numerically that this approximation is valid when the obtained CO 1-RDM is close to the idempotent one. In some particular cases, where both the Lagrangian and 1-RDM can be considered diagonal matrices, the corrected value obtained dividing by the corresponding diagonal element of the 1-RDM yields practically same estimations as the EKT.

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