Global Method for Electron Correlation

Mario Piris

Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), P.K. 1072, 20080 Donostia, Spain
Donostia International Physics Center (DIPC), 20018 Donostia, Spain
IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain

The current work presents a new single-reference method for capturing at the same time the static and dynamic electron correlation. The starting point is a determinant wave function formed with natural orbitals obtained from a new interacting-pair model. The latter leads to a natural orbital functional (NOF) capable of recovering the complete intrapair, but only the static interpair correlation. Using the solution of the NOF, two new energy functionals are defined for both dynamic (E^{dyn}) and static (E^{sta}) correlation. E^{dyn} is derived from a modified second-order Møller-Plesset perturbation theory (MP2), while E^{sta} is obtained from the static component of the new NOF. Double counting is avoided by introducing the amount of static and dynamic correlation in each orbital as a function of its occupation. As a result, the total energy is represented by the sum $\tilde{E}_{\mathrm{HF}} + E^{\mathrm{dyn}} + E^{\mathrm{sta}}$, where $\tilde{E}_{\mathrm{HF}}$ is the Hartree-Fock energy obtained with natural orbitals. The new procedure called NOF-MP2 scales formally as $O(M^5)$ (where M is the number of basis functions), and is applied successfully to the homolytic dissociation of a selected set of diatomic molecules, paradigmatic cases of near-degeneracy effects. The size consistency has been numerically demonstrated for singlets. The values obtained are in good agreement with the experimental data.

In electronic structure theory, accurate solutions require a balanced treatment of both static (nondynamic) and dynamic correlation. Static correlation generally implies a limited number of nearby delocalized orbitals with significant fractional occupations. Conversely, dynamic correlation involves a large number of orbitals and configurations, each with a small weight.

Nowadays, it is necessary to resort to multireference methods for correctly handling both types of correlation; however, these techniques are often expensive and demand prior knowledge of the system. On the other hand, single-reference correlation methods are well-established for dynamic correlation, but are unsatisfactory for systems with static correlation. The aim of this work is to propose a single-reference method capable of achieving both dynamic and static correlation even for those systems with significant multiconfigurational character.

In our approach, a natural orbital functional (NOF) [1] is firstly used for capturing all static correlation effects. Then, the total energy is approximated as $\tilde{E}_{\mathrm{HF}} + E^{\mathrm{dyn}} + E^{\mathrm{sta}}$, where $\tilde{E}_{\mathrm{HF}}$ is the Hartree-Fock energy obtained with corresponding natural orbitals (NOs). The dynamic energy correction (E^{dyn}) is derived from a properly modified second-order Møller-Plesset perturbation theory (MP2) [2], while the nondynamic correction (E^{sta}) is obtained from the pure static component of the new NOF. Let us start with the NOF.

In NOF theory, the spectral decomposition of the one-particle reduced density matrix ($\Gamma = \sum_i n_i |\phi_i\rangle\langle\phi_i|$) is used to approximate the electronic energy in terms of the NOs and their occupation numbers (ONs), namely,

$$E = \sum_i n_i \mathcal{H}_{ii} + \sum_{ijkl} D[n_i, n_j, n_k, n_l]\langle kl|ij\rangle. \quad (1)$$

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

It is noteworthy that the resulting approximate functional $E[\{n_i, \phi_i\}]$ can solely be implicitly dependent on Γ [3] since the Gilbert's theorem [4] on the existence of the explicit functional $E[\Gamma]$ is valid only for the exact ground-state energy. In this vein, NOs are the orbitals that diagonalize the one matrix corresponding to an approximate energy that still depends on the 2-RDM [3]. Consequently, the energy is not invariant with respect to a unitary transformation of the orbitals, and it is more appropriate to speak of a NOF rather than a functional $E[\Gamma]$. A detailed account of the state of the art of the NOF theory can be found elsewhere [5,6].

The construction of a N-representable functional given by (1), i.e., derived from an antisymmetric N-particle wave function [7], is obviously related to the N representability problem of the 2-RDM. The use of the (2,2)-positivity N-representability conditions [8] for generating a reconstruction functional was proposed in Ref. [9]. This particular reconstruction is based on the introduction of two auxiliary matrices Δ and Π expressed in terms of the ONs to reconstruct the cumulant part of the 2-RDM [10]. In a spin-restricted formulation, the energy functional for singlet states reads as

$$E = 2\sum_p n_p \mathcal{H}_{pp} + \sum_{qp} \Pi_{qp} \mathcal{L}_{pq}$$
$$+ \sum_{qp} (n_q n_p - \Delta_{qp})(2\mathcal{J}_{pq} - \mathcal{K}_{pq}), \qquad (2)$$

where $\mathcal{J}_{pq}$, $\mathcal{K}_{pq}$, and $\mathcal{L}_{pq}$ are the direct, exchange, and exchange-time-inversion integrals [11]. Appropriate forms of matrices Δ and Π lead to different implementations known in the literature as the ith Piris natural orbital functional (PNOFi, $i = 1$–6) [5].

The conservation of the total spin allows us to derive the diagonal elements $\Delta_{pp} = n_p^2$ and $\Pi_{pp} = n_p$ [12]. The N-representability D and Q matrix conditions of the 2-RDM impose the following inequalities on the off diagonal elements of Δ [9]:

$$\Delta_{qp} \leq n_q n_p, \qquad \Delta_{qp} \leq h_q h_p, \qquad (3)$$

while to fulfill the G matrix condition, the elements of the Π matrix must satisfy the constraint [13]

$$\Pi_{qp}^2 \leq (n_q h_p + \Delta_{qp})(h_q n_p + \Delta_{qp}), \qquad (4)$$

where h_p denotes the hole $1 - n_p$. Notice that for singlets the total hole for a given spatial orbital p is $2h_p$.

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

$$\sum_{p \in \Omega_g} n_p = 1, \qquad g = 1, 2, \ldots, N/2. \qquad (5)$$

Taking into account the spin, each subspace contains solely an electron pair, and the normalization condition for Γ ($2\sum_p n_p = N$) is automatically fulfilled. It is important to note that orbitals satisfying the pairing conditions (5) are not required to remain fixed throughout the orbital optimization process [14].

The simplest way to comply with all constraints leads to an independent pair model (PNOF5) [15,16],

$$\Delta_{qp} = n_p^2 \delta_{qp} + n_q n_p (1 - \delta_{qp}) \delta_{q\Omega_g} \delta_{p\Omega_g},$$
$$\Pi_{qp} = n_p \delta_{qp} + \Pi_{qp}^g (1 - \delta_{qp}) \delta_{q\Omega_g} \delta_{p\Omega_g},$$
$$\Pi_{qp}^g = \begin{cases} -\sqrt{n_q n_p}, & p = g \quad \text{or} \quad q = g \\ +\sqrt{n_q n_p}, & p, q > N/2 \end{cases},$$
$$\delta_{q\Omega_g} = \begin{cases} 1, & q \in \Omega_g \\ 0, & q \notin \Omega_g \end{cases}. \qquad (6)$$

Interestingly, an antisymmetrized product of strongly orthogonal geminals (APSG) with the expansion coefficients

explicitly expressed by the ONs also leads to PNOF5 [16,17]. This demonstrates that the functional is strictly N representable. In addition, PNOF5 is size extensive and size consistent, inherent properties to singlet-type APSG wave functions.

To go beyond the independent-pair approximation, let us maintain $\Delta_{qp} = 0$ and consider nonzero the Π elements between orbitals belonging to different subspaces. From Eq. (4), note that provided the Δ_{qp} vanishes, $|\Pi_{qp}| \leq \Phi_q \Phi_p$ with $\Phi_q = \sqrt{n_q h_q}$. Assuming the equality, one can generalize the sign convention (6), namely, $\Pi_{qp}^\Phi = \Phi_q \Phi_p$ if $q, p > N/2$, and $\Pi_{qp}^\Phi = -\Phi_q \Phi_p$, otherwise. Thus, the energy (2) becomes

$$E = \sum_{g=1}^{N/2} E_g + \sum_{f \neq g}^{N/2} E_{fg},$$
$$E_g = \sum_{p \in \Omega_g} n_p (2\mathcal{H}_{pp} + \mathcal{J}_{pp}) + \sum_{q, p \in \Omega_g, q \neq p} \Pi_{qp}^g \mathcal{L}_{pq},$$
$$E_{fg} = \sum_{p \in \Omega_f} \sum_{q \in \Omega_g} [n_q n_p (2\mathcal{J}_{pq} - \mathcal{K}_{pq}) + \Pi_{qp}^\Phi \mathcal{L}_{pq}]. \qquad (7)$$

This new approach will henceforth refer to as PNOF7. The first term of the Eq. (7) is the sum of the pair energies described accurately by the two-electron functional E^g. In the second term, E^{fg} correlates the motion of the electrons in different pairs with parallel and opposite spins. It is clear that the main weakness of the approach (7) is the absence of the interpair dynamic electron correlation since Π_{qp}^Φ has significant values only when the ONs differ substantially from 1 and 0. Consequently, PNOF7 is expected to be able to recover the complete intrapair, but only the static interpair correlation.

The solution in NOF theory is established by optimizing the energy functional with respect to the ONs and to the NOs separately, for which the iterative diagonalization procedure proposed by Piris and Ugalde [14] has been employed. The performance of the PNOF7 has been tested by the dissociation of a dozen diatomic molecules. The selected systems comprise different types of bonding, which span a wide range of values for binding energies and bond lengths. However, in all cases, the correct dissociation limit implies a high degree of degeneracy effects. For simplicity, we consider N_g equal to a fixed number that corresponds to the maximum value allowed by the basis set used.

Representative potential energy curves (PECs) of these molecules are depicted in Fig. 1 (see Supplemental Material [18] for absolute energies). PNOF7 produces qualitatively correct PECs with right dissociation limits for all cases, even in the case of the highest degeneracy (N_2). In Table I, selected electronic properties, including equilibrium bond lengths (R_e), dissociation energies (D_e), and harmonic vibrational frequencies (ω_e) can be found. In this work, the experimental R_e and ω_e are taken from the National Institute of Standards and Technology (NIST) database [19], whereas the experimental D_e result from a combination of
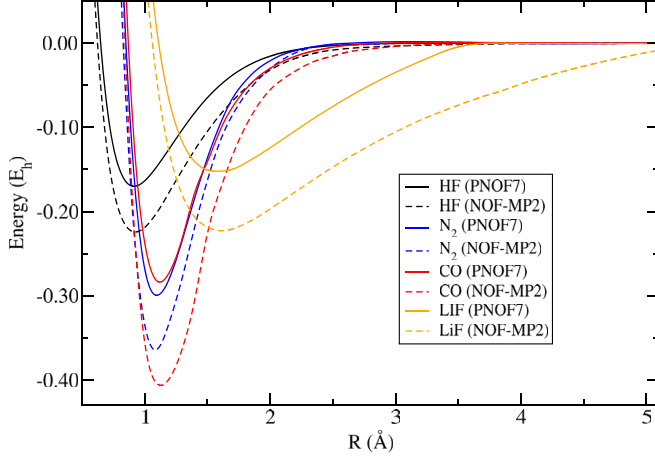
FIG. 1.   Potential energy curves (cc-pVTZ).

Refs. [19] and [20]. The correlation-consistent valence triple-ζ basis set (cc-pVTZ) [21] was used throughout, except for the anionic species (OH$^-$ and CN$^-$) where the augmented basis set (aug-cc-pVTZ) was used.

Table I shows that the results are in good agreement with the experiment for the smaller diatomics, for which the electron correlation effect is almost entirely intrapair. When the number of pairs increases, the theoretical values deteriorate especially for the dissociation energies. This is related to a better description of the asymptotic region with respect to the equilibrium where the dynamic correlation prevails. It is therefore mandatory to add the interpair dynamic electron correlation to improve these results.

The second-order Møller-Plesset [2] perturbation theory (MP2) is the simplest and cheapest way of properly incorporating dynamic electron correlation effects. The Hartree-Fock (HF) wave function is taken as the starting point in MP2, so let us consider a Slater determinant formed by the NOs as the zeroth-order wave function, and define the zeroth-order Hamiltonian $\hat{H}^{(0)}$ by the expansion

TABLE I.   Comparison of R_e (Å), D_e (kcal/mol), and ω_e (cm^{-1}) calculated at the PNOF7/cc-pVTZ level of theory with the experimental values.

Molecule	R_e	R_e^{expt}	D_e	D_e^{expt}	ω_e	ω_e^{expt}
H$_2$	0.743	0.743	108.6	109.5	4404	4401
LiH	1.604	1.595	56.1	58.0	1404	1406
Li$_2$	2.667	2.673	23.3	24.4	330	351
BH	1.232	1.232	75.7	81.5	2370	2367
OH$^{-\text{a}}$	0.966	0.964	87.0	$\cdots$	3010	3770
HF	0.915	0.917	106.7	141.1	4139	4138
LiF	1.576	1.564	95.4	139.0	668	911
N$_2$	1.097	1.098	188.9	228.3	2290	2359
CN$^{-\text{a}}$	1.186	1.177	212.0	240.7	1999	2035
CO	1.120	1.128	178.1	259.3	2316	2170
NO$^+$	1.056	1.063	179.9	$\cdots$	2412	2377
F$_2$	1.579	1.412	2.6	39.2	422	917

$^{\text{a}}$aug-cc-pVTZ was used.

$\sum_i \varepsilon_i |\phi_i\rangle\langle\phi_i|$. Here, ε_i is the ith diagonal element of the Fock matrix ($\mathcal{F}$) in the NO representation. The first-order energy correction leads to an energy ($\tilde{E}_{hf}$) that differs from the true HF energy since NOs are used instead of the canonical HF orbitals. Besides, the Fock matrix is no longer diagonal; therefore, single excitations in addition to doubles contribute to the MP2 energy correction, namely,

$$
\begin{aligned}
E^{(2)} = &2 \sum_{g=1}^{N/2} \sum_{p>N/2}^{M} \frac{|\mathcal{F}_{pg}|^2}{\varepsilon_g - \varepsilon_p} \\
&+ \sum_{g,f=1}^{N/2} \sum_{p,q>N/2}^{M} \frac{\langle gf|pq\rangle[2\langle pq|gf\rangle - \langle pq|fg\rangle]}{\varepsilon_g + \varepsilon_f - \varepsilon_p - \varepsilon_q},
\end{aligned} \quad (8)
$$

where M is the number of basis functions.

In general, MP2 lacks nondynamic correlation, which is well recovered by PNOF7, but we cannot simply add these contributions since double counting occurs. With this in mind, new dynamic (E^{dyn}) and static (E^{sta}) energy functionals have to be defined from the MP2 and PNOF7, respectively, so that the total energy of the system will be given by

$$
E = \tilde{E}_{hf} + E^{\text{corr}} = \tilde{E}_{hf} + E^{\text{sta}} + E^{\text{dyn}}. \quad (9)
$$

Henceforth, the energy obtained with the Eq. (9) is called the NOF-MP2 energy. From Eq. (7), it is evident that we must differentiate between intra- and interpair contributions for both functionals. In accordance, one has

$$
E^{\text{corr}}_{\text{intra}} = \sum_{g=1}^{N/2} (E^{\text{sta}}_g + E^{\text{dyn}}_g)
$$

$$
E^{\text{corr}}_{\text{inter}} = \sum_{f \neq g}^{N/2} (E^{\text{sta}}_{fg} + E^{\text{dyn}}_{fg}); \quad (10)
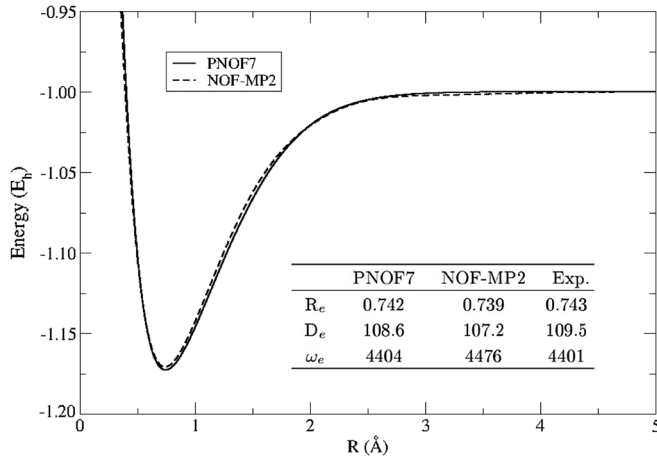$$

hence, $E^{\text{corr}} = E^{\text{corr}}_{\text{intra}} + E^{\text{corr}}_{\text{inter}}$ as well. To avoid double counting, we are going to consider the amount of static electron correlation in each orbital as a function of its occupancy,

$$
\Lambda_p = 1 - |1 - 2n_p|. \quad (11)
$$

Note that Λ_p goes from zero for empty or fully occupied orbitals to one if the orbital is half occupied. Using this function, let us define the static and dynamic gth intrapair electron correlation energies as

$$
E^{\text{sta}}_g = \sum_{q \neq p} \sqrt{\Lambda_q \Lambda_p} \, \Pi^g_{qp} \mathcal{L}_{pq}
$$

$$
\begin{aligned}
E^{\text{dyn}}_g = &2C_g \sum_{p>N/2}^{M} C_p \frac{|\mathcal{F}_{pg}|^2}{\epsilon_g - \epsilon_p} \\
&+ C_g^2 \sum_{p,q>N/2}^{M} C_p C_q \frac{\langle gg|pq\rangle\langle pq|gg\rangle}{2\epsilon_g - \epsilon_p - \epsilon_q},
\end{aligned} \quad (12)
$$

FIG. 2.   Potential energy curves for H_2.

TABLE II.   Comparison of R_e (Å), D_e (kcal/mol), and ω_e (cm^{-1}) calculated at the NOF-MP2/cc-pVTZ level of theory with the experimental values.

Molecule	R_e	R_e^{expt}	D_e	D_e^{expt}	ω_e	ω_e^{expt}
Be_2[a]	2.303	2.460	2.6	2.7	543	⋯
OH^-[a]	0.967	0.964	121.6	⋯	3820	3770
HF	0.924	0.917	139.4	141.1	4151	4138
LiF	1.614	1.564	140.7	139.0	955	911
N_2	1.084	1.098	224.2	228.3	2764	2359
CN^-[a]	1.180	1.177	238.6	240.7	1961	2035
CO	1.129	1.128	255.1	259.3	2092	2170
NO^+	1.060	1.063	261.1	⋯	2403	2377
F_2	1.397	1.412	34.5	39.2	949	917

[a]aug-cc-pVTZ was used.

where $q, p \in \Omega_g$, and $C_p = 1 - \Lambda_p^2$. The PECs for the archetypal two-electron singlet, H_2, are depicted in Fig. 2. It is remarkable the excellent agreement between the results obtained with the new intrapair energy functionals given by Eq. (12) and those of PNOF7, which in this case is practically exact [22].

Taking into account the square root that already appears in the definition of the Φ magnitudes, we can similarly introduce the following functionals for the fgth interpair static and dynamic correlation energies:

$$E_{fg}^{\text{sta}} = \sum_{p \in \Omega_f} \sum_{q \in \Omega_g} 4\Phi_p \Phi_q \Pi_{qp}^{\Phi} \mathcal{L}_{pq}$$

$$E_{fg}^{\text{dyn}} = 2 \sum_{p>N/2}^{M} \delta_{p\Omega_f} C_p^{\Phi} \frac{|\mathcal{F}_{pg}|^2}{\epsilon_g - \epsilon_p} + \sum_{p,q>N/2}^{M} \delta_{p\Omega_f} C_p^{\Phi} \delta_{q\Omega_g} C_q^{\Phi}$$

$$\times \frac{\langle gf|pq\rangle[2\langle pq|gf\rangle - \langle pq|fg\rangle]}{\epsilon_g + \epsilon_f - \epsilon_p - \epsilon_q}. \qquad (13)$$

In Eq. (13), $2\Phi_p$ plays the same role of $\sqrt{\Lambda_p}$ in Eq. (12); hence, $C_p^{\Phi} = 1 - 4\Phi_p^2 = 1 - 4n_p h_p$. Again, fully occupied and empty orbitals contribute nothing to static correlation; this time interpair, whereas orbitals with half occupancies yield a maximal contribution. The opposite occurs for dynamic correlation. It is worth noting that C^{Φ} is not considered if the orbital is below $N/2$.

Table II collects the electronic properties previously analyzed for the systems in which the interpair correlation becomes important. The data reveal an outstanding improvement in the dissociation energies, as well as a nice agreement of R_e and w_e with the experimental marks. It is worth mentioning the case of F_2 and the recovered correct order in the dissociation energies of the N_2 and CO (see also Fig. 1).

The included Beryllium dimer requires special attention. PNOF7 predicts a metastable minimum with a negative D_e, whereas the NOF-MP2 method recovers sufficient dynamic correlation to be able of predicting a stable Be_2 molecule.

The obtained equilibrium distance is still underestimated, but the dissociation energy approaches the experimental value. For weaker bonds, e.g., He_2, the NOF-MP2 method does not predict bound due to a better description of the dissociated atoms with respect to the equilibrium region. In these cases, neglecting static correlation and using HF MP2 leads to a binding PEC. The alternative is to include higher-order perturbative corrections.

The size consistency of the NOF-MP2 method, i.e., the ability of the method to reproduce the additivity of the energy for a system composed of independent subsystems, has been numerically addressed too. It has been checked that total energies of spin-compensated dimers (He_2, Be_2, and HeNe) at an internuclear separation of 100 Å differ from the double value of the total energies of the corresponding atoms lesser than 10^{-5} hartrees (< 0.01 kcal/mol).

Preliminary calculations on systems with more than two atoms confirm that the results are promising. The absolute energies obtained with the NOF-MP2 method improve over the PNOF7 values by recovering an important part of the dynamic correlation and getting closer to the values obtained by accurate wave-function-based methods (see Supplemental Material [18]).

In summary, a new size-consistent method for singlet states has been proposed that scales formally as $O(M^5)$. The resulting working formulas allow for static and dynamic correlation to be achieved in one shot, as is the case in the standard single-reference perturbation theory. Note that the NOF-MP2 method is not limited to PNOF7 NOs, it can also be used with NOs obtained from an approximation able of recovering nondynamic electron correlation. In addition, the number of orbitals involved in the optimization can be easily reduced by establishing a cutoff in the value of the ONs, since the dynamic correlation for which the orbitals with small ONs are responsible will be properly recovered by E^{dyn}. With efficient approaches, based on recent developments of NOF and MP2 theories, the NOF-MP2 method

could become a valuable tool for treating large systems with hundreds of atoms.

[1] M. Piris, Natural orbital functional theory, Adv. Chem. Phys. **134**, 385 (2007).

[2] C. Moller and M. S. Plesset, Note on an approximate treatment for many-electron systems, Phys. Rev. **46**, 618 (1934).

[3] R. A. Donnelly, On fundamental difference between energy functionals based on first- and second-order density matrices, J. Chem. Phys. **71**, 2874 (1979).

[4] T. L. Gilbert, Hohenberg-Kohn theorem for nonlocal external potentials, Phys. Rev. B **12**, 2111 (1975).

[5] M. Piris and J. M. Ugalde, Perspective on natural orbital functional theory, Int. J. Quantum Chem. **114**, 1169 (2014), and references therein.

[6] K. Pernal and K. J. H. Giesbertz, Reduced density matrix functional theory (RDMFT) and linear response time-dependent RDMFT (TD-RDMFT), Top. Curr. Chem. **368**, 125 (2016).

[7] A. J. Coleman, Structure of fermion density matrices, Rev. Mod. Phys. **35**, 668 (1963).

[8] D. A. Mazziotti, Structure of Fermionic Density Matrices: Complete N-Representability Conditions, Phys. Rev. Lett. **108**, 263002 (2012).

[9] M. Piris, A new approach for the two-electron cumulant in natural orbital, Int. J. Quantum Chem. **106**, 1093 (2006).

[10] D. A. Mazziotti, Approximate solution for electron correlation through the use of Schwinger probes, Chem. Phys. Lett. **289**, 419 (1998).

[11] M. Piris, A generalized self-consistent-field procedure in the improved BCS theory, J. Math. Chem. **25**, 47 (1999).

[12] M. Piris, J. M. Matxain, X. Lopez, and J. M. Ugalde, Spin conserving natural orbital functional theory, J. Chem. Phys. **131**, 021102 (2009).

[13] M. Piris, J. M. Matxain, X. Lopez, and J. M. Ugalde, The role of the positivity N-representability conditions in natural orbital functional theory, J. Chem. Phys. **133**, 111101 (2010).

[14] M. Piris and J. M. Ugalde, Iterative diagonalization for orbital optimization in natural orbital functional theory, J. Comput. Chem. **30**, 2078 (2009).

[15] M. Piris, X. Lopez, F. Ruipérez, J. M. Matxain, and J. M. Ugalde, A natural orbital functional for multiconfigurational states, J. Chem. Phys. **134**, 164102 (2011).

[16] M. Piris, J. M. Matxain, and X. Lopez, The intrapair electron correlation in natural orbital functional theory, J. Chem. Phys. **139**, 234109 (2013).

[17] K. Pernal, The equivalence of the Piris Natural Orbital Functional 5 (PNOF5) and the antisymmetrized product of strongly orthogonal geminal theory, Comput. Theor. Chem. **1003**, 127 (2013).

[18] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.119.063002 for a comparison of the total energies, in Hartrees, calculated at the experimental equilibrium geometries using the cc-pVTZ basis set. Moreover, the potential energy curves for HF, LiF, N2 and CO molecules obtained with the cc-pVTZ basis set are also shown.

[19] NIST Standard Reference Database Number 101, edited by R. D. Johnson III http://cccbdb.nist.gov/, Release 18 (2016).

[20] M. W. Chase, Jr., NIST-JANAF thermochemical tables, J. Phys. Chem. Ref. Data Monogr. **9**, 1 (1998).

[21] T. H. Dunning Jr., Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, J. Chem. Phys. **90**, 1007 (1989).

[22] J. O. Hirschfelder and P. O. Löwdin, Long-range interaction of two ls-hydrogen atoms expressed in terms of natural spin-orbitals, Mol. Phys. **2**, 229 (1959).