A natural orbital functional for multiconfigurational states

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An explicit formulation of the Piris cumulant $\lambda(\Delta, \Pi)$ matrix is described herein, and used to reconstruct the two-particle reduced density matrix (2-RDM). Then, we have derived a natural orbital functional, the Piris Natural Orbital Functional 5, PNOF5, constrained to fulfill the D, Q, and G positivity necessary conditions of the N-representable 2-RDM. This functional yields a remarkable accurate description of systems bearing substantial (near)degeneracy of one-particle states. The theory is applied to the homolitic dissociation of selected diatomic molecules and to the rotation barrier of ethylene, both paradigmatic cases of near-degeneracy effects. It is found that the method describes correctly the dissociation limit yielding an integer number of electrons on the dissociated atoms. PNOF5 predicts a barrier of 65.6 kcal/mol for the ethylene torsion in an outstanding agreement with Complete Active Space Second-order Perturbation Theory (CASPT2). The obtained occupation numbers and pseudo one-particle energies at the ethylene transition state account for fully degenerate π orbitals. The calculated equilibrium distances, dipole moments, and binding energies of the considered molecules are presented. The values obtained are accurate comparing those obtained by the complete active space self-consistent field method and the experimental data. © *2011 American Institute of Physics*. [doi:10.1063/1.3582792]

The energy of a system of N fermions, which involves at most two-particle interactions, can be expressed exactly in terms of the one- and two-particle reduced density matrices (1- and 2-RDMs), denoted hereafter as Γ and $\mathbf{D}$, respectively,

$$E[\Gamma, \mathbf{D}] = \sum_{ik} H_{ik} \Gamma_{ki} + \sum_{ijkl} < ij|kl > D_{kl,ij}. \quad (1)$$

In Eq. (1), H_{ik} denotes the one-particle matrix elements of the core-Hamiltonian, and $\langle ij|kl \rangle$ are the matrix elements of the two-particle interaction. The 2-RDM can be approximated in terms of the 1-RDM by means of a reconstruction functional $\mathbf{D}[\Gamma]$, which once used in Eq. (1) yields a 1-RDM functional, $E[\Gamma]$, for the energy. The idea of a density-matrix functional appeared some decades ago.[1] A major advantage of the method is that both the kinetic energy and the exchange energy are explicitly defined in terms of the 1-RDM and hence, do not require the construction of an approximate functional. The unknown functional only needs to incorporate correlation effects.

This unknown functional of the 1-RDM can be expressed in terms of the natural orbitals, $\{\phi_i(\mathbf{x})\}$, and their occupation numbers, $\{n_i\}$, by means of the spectral expansion of the 1-RDM,

$$\Gamma(\mathbf{x}_1'|\mathbf{x}_1) = \sum_i n_i \phi_i(\mathbf{x}_1') \phi_i^*(\mathbf{x}_1), \quad (2)$$

$\mathbf{x} \equiv (\mathbf{r}, \mathbf{s})$ being the composite space-spin coordinate for a single particle. This transforms the density-matrix functional, $E[\Gamma]$, into the natural orbital functional $E[\{n_i, \phi_i\}]$. A detailed account of the state of the art of the natural orbital functional (NOF) theory can be found elsewhere.[2] Recently, additional promising developments of NOF theory have been achieved.[3–12]

In essence, given the reconstruction functional, one has to minimize the resulting energy expression with respect to both, the natural orbitals and their occupation numbers, under the appropriate constrains. Other advantage of NOF theory is that restricting the occupation numbers $\{n_i\}$ into the range $0 \leq n_i \leq 1$ fulfills the necessary and sufficient easily implementable condition for the N-representability of the 1-RDM.[13] Nevertheless, it is worth emphasizing that this does not fully overcome the N-representability problem of the energy functional, for the latter is related to the N-representability problem of the 2-RDM,[14] via the reconstruction functional $\mathbf{D}[\Gamma]$.

One route to the reconstruction[15] is based on the cumulant expansion[16] of $\mathbf{D}$, namely,

$$D_{kl,ij} = \frac{1}{2}(\Gamma_{ki}\Gamma_{lj} - \Gamma_{li}\Gamma_{kj}) + \lambda_{kl,ij}. \quad (3)$$

The spin-orbital set $\{\phi_i(\mathbf{x})\}$ may be split into two subsets: $\{\varphi_p^\alpha(\mathbf{r})\alpha(\mathbf{s})\}$ and $\{\varphi_p^\beta(\mathbf{r})\beta(\mathbf{s})\}$. In order to avoid spin contamination effects, the spin restricted theory is employed, in which a single set of orbitals is used for α and β spins: $\varphi_p^\alpha(\mathbf{r}) = \varphi_p^\beta(\mathbf{r}) = \varphi_p(\mathbf{r})$. We consider a spin-independent Hamiltonian, so only density-matrix blocks that conserve the number of each spin type are nonvanishing. Specifically, the 1-RDM has two nonzero blocks, Γ^α and Γ^β, whereas the 2-RDM has three nonzero blocks, $\mathbf{D}^{\alpha\alpha}$, $\mathbf{D}^{\alpha\beta}$, and $\mathbf{D}^{\beta\beta}$. In this work we deal only with singlet states, so the occupancies for particles with α and β spin, and the parallel spin blocks of the 2-RDM are equal: $n_p^\alpha = n_p^\beta = n_p$, $\mathbf{D}^{\beta\beta} = \mathbf{D}^{\alpha\alpha}$.

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We shall use hereafter the Piris reconstruction functional,[17] PNOF, which has the following structure for the two-particle cumulant of singlet states,

$$\lambda_{pq,rt}^{\sigma\sigma} = -\frac{\Delta_{pq}}{2}(\delta_{pr}\delta_{qt} - \delta_{pt}\delta_{qr}); \quad \sigma = \alpha, \beta,$$

$$\lambda_{pq,rt}^{\alpha\beta} = -\frac{\Delta_{pq}}{2}\delta_{pr}\delta_{qt} + \frac{\Pi_{pr}}{2}\delta_{pq}\delta_{rt}, \quad (4)$$

where $\mathbf{\Delta}$ is a real symmetric matrix and $\mathbf{\Pi}$ is a spin-independent Hermitian matrix. The conservation of the total spin allowed us[18] to derive the diagonal elements $\Delta_{pp} = n_p^2$ and $\Pi_{pp} = n_p$. The sum rules that must fulfill the blocks of the cumulant yield the following constraint:[17]

$$\sideset{}{'}\sum_q \Delta_{qp} = n_p h_p, \quad (5)$$

where h_p denotes the hole $1-n_p$ in the spatial orbital p. The prime indicates here that the $q = p$ term is omitted from the summation. The PNOF energy for singlet states reads as

$$E = \sum_p n_p(2H_{pp} + J_{pp}) + \sideset{}{'}\sum_{pq}(n_q n_p - \Delta_{qp})$$
$$(2J_{pq} - K_{pq}) + \sideset{}{'}\sum_{pq}\Pi_{qp}L_{pq}, \quad (6)$$

where $J_{pq} = \langle pq|pq \rangle$ and $K_{pq} = \langle pq|qp \rangle$ are the usual direct and exchange integrals, respectively. $L_{pq} = \langle pp|qq \rangle$ is the exchange and time-inversion integral.[19] Notice that $L_{pq} = K_{pq}$ for real orbitals.

Appropriate forms of matrices $\mathbf{\Delta}(\{n_p\})$ and $\mathbf{\Pi}(\{n_p\})$ have led to different implementations of the PNOF.[10–12, 17, 20] These approximations have satisfactorily predicted several properties, the most accurate results being those obtained with the recent formulation PNOF4.[12] Unfortunately, $\mathbf{\Delta}$ and $\mathbf{\Pi}$ matrices are defined through a variable S_F (see Eqs. (7)–(11) of Ref. 12), which represents the sum of holes (h_p) up to the $F = N/2$ level or the sum of occupations (n_p) above it. This S_F varies with the geometry of the system and leads to inconsistencies for singlet-state systems with more than four degenerate natural orbitals. In these cases, $S_F > 1$, and the off-diagonal elements of $\mathbf{\Delta}$ can violate the bounds imposed by the two-positivity N-representability conditions, leading to an overestimation of the correlation energy. It is worth emphasizing that the term "degeneracy" is used here for orbitals which have degenerate occupation numbers and degenerate pseudo one-particle energies,[21] $(\lambda_p + n_p H_{pp})$, where the λ_p's are the diagonal elements of the Lagrange multipliers matrix associated with the orbitals' Euler equations (*vide infra*).

The aim of the present research is to propose a more inclusive general ansatz for $\mathbf{\Delta}$ and $\mathbf{\Pi}$ matrices. This new approach defines a new energy functional which we will henceforth refer to as PNOF5. We will show that PNOF5 results are in good agreement with those obtained by methods to deal with (near)degenerated states, such as multiconfigurational wave-function methods.

Let us now focus on Eq. (5) for $p \leq F$. The simplest way to fulfill this sum rule is to neglect all terms Δ_{qp} except one, $\Delta_{\tilde{p}p}$, which will play the leading role in the correlation vector $\mathbf{\Delta}_p$, therefore the $\tilde{p}$-state must be located above the F level, namely, $\tilde{p} = 2F - p + 1$. We will hereafter refer to the pair

of levels $(p, \tilde{p})$ as to coupled natural orbitals. It is worth noting at this point that within this ansatz, we will be looking for the pairs of coupled orbitals $(p, \tilde{p})$ which yield the minimum energy for the functional of Eq. (6). However, the actual p and $\tilde{p}$ orbitals which are paired is not constrained to remain fixed along the orbital optimization process. Consequently, the pairing scheme of the orbitals is allowed to vary along the optimization process till the most favorable orbital interactions are found. Furthermore, in accordance to this assumption, all occupancies vanish for $p > 2F$. Let us notice that $2F = N$ for singlet states, N being the number of particles in the system, hence $\tilde{p} = N - p + 1$. It is straightforward to verify from Eq. (5) that

$$\Delta_{\tilde{p}p} = n_p h_p. \quad (7)$$

Recall that the N-representability D and Q necessary conditions of the 2-RDM impose the following bounds on the off-diagonal elements of $\mathbf{\Delta}$:[17]

$$\Delta_{qp} \leq n_q n_p, \qquad \Delta_{qp} \leq h_q h_p. \quad (8)$$

We assume henceforth the maximum possible value for $\Delta_{\tilde{p}p}$ according to the first inequality, namely,

$$\Delta_{\tilde{p}p} = n_{\tilde{p}} n_p. \quad (9)$$

Taking into account Eq. (7), we must impose the occupation of the $\tilde{p}$ level to coincide with the hole of its coupled state p, namely,

$$n_{\tilde{p}} = h_p, \qquad n_{\tilde{p}} + n_p = 1. \quad (10)$$

It is not difficult to verify that the right-hand side inequality of Eq. (8) reduces to $n_{\tilde{p}} + n_p \leq 1$, hence $\Delta_{\tilde{p}p}$, Eq. (9) also satisfies this constraint. Moreover, from the symmetry of $\mathbf{\Delta}$ it follows that $\Delta_{p\tilde{p}} = n_p n_{\tilde{p}} = h_{\tilde{p}} n_{\tilde{p}}$ ensuring the sum rule and the corresponding bounds for $p > F$.

To fulfill the N-representability G-condition of the 2-RDM, elements of the $\mathbf{\Pi}$-matrix must satisfy the following inequality[12]:

$$\Pi_{qp}^2 \leq n_q h_q n_p h_p + \Delta_{qp}(n_q h_p + h_q n_p) + \Delta_{qp}^2. \quad (11)$$

Taking into account expressions (9) and (10) for the off-diagonal elements $\Delta_{\tilde{p}p}$, one finds that $|\Pi_{\tilde{p}p}| \leq \sqrt{n_{\tilde{p}} n_p}$. The signs of the off-diagonal elements of $\mathbf{\Pi}$ depend on the kind of the interaction between fermions in the system under study. For repulsive interactions, the convenient choice is the negative sign. Hence,

$$\Pi_{\tilde{p}p} = -\sqrt{n_{\tilde{p}} n_p}. \quad (12)$$

From Eq. (11), note that provided the Δ_{qp} vanishes, $|\Pi_{qp}| \leq \Phi_q \Phi_p$ with $\Phi_q = \sqrt{n_q h_q}$. For simplicity, we assume further that $\Pi_{qp} = 0$ if $\Delta_{qp} = 0$. Taking into account Eqs. (6), (9), and (12), the energy for the ground singlet state of any Coulombic system can be cast as

$$E^{\text{PNOF5}} = \sum_{p=1}^N [n_p(2H_{pp} + J_{pp}) - \sqrt{n_{\tilde{p}} n_p} K_{p\tilde{p}}]$$
$$+ \sideset{}{''}\sum_{p,q=1}^N n_q n_p (2J_{pq} - K_{pq}) \quad (13)$$

Here the double prime indicates that both, the $q = p$ term, and the coupled one-particle state terms are omitted from the summation. Recall that $\tilde{p} = N - p + 1$, and the number of particles N corresponds in Eq. (13) to the maximum possible value of the running index p for the spatial orbital φ_p with $n_p \neq 0$.

The solution in NOF theory is established optimizing the energy functional with respect to the occupation numbers and to the natural orbitals, separately. It is well known that the orbital optimization is the bottleneck of this algorithm since direct minimization of the orbitals has been proven to be a costly method.[22]

In the present study, the recent successful implementation of an iterative diagonalization procedure[21] has been employed. This novel self-consistent procedure yields the natural orbitals by the iterative diagonalization of a Hermitian matrix **F**. The off-diagonal elements of **F** are determined explicitly by the hermiticity of the Lagrange multipliers. On the other hand, the expression for the diagonal elements is absent, hence our **F** cannot be considered as a generalized Fock matrix. Fortunately, the first-order perturbation theory applying to each cycle of the diagonalization process provides an aufbau principle for determining the diagonal elements F_{ii}^0. In each step of the iterative scheme, we use the diagonal values of the previous diagonalization, so the method is dependent upon the initial guess. We have found that a suitable starting approximation is that obtained from a single diagonalization of the matrix of the Lagrange multipliers calculated with the HF orbitals after the occupation optimization. To assist the convergence, we use a variable scaling factor, which avoids large values of the off-diagonal elements of **F**, and keep them within the same order of magnitude. The comparison of elapsed CPU times with those required by a direct optimization highlighted the efficiency of the method.[21]

Relevant for the current investigation is that the number of particles is always conserved ($N = 2\sum_p n_p$) due to relation (10) for the occupation numbers of the coupled one-particle states. Equation (10) and the N-representability bounds ($0 \leq n_p \leq 1$) of Γ are easily enforced by setting $n_p = \cos^2\gamma_p$ and $n_{\tilde{p}} = \sin^2\gamma_p$. Then, PNOF5 is the first NOF that allows constraint-free minimization with respect to the auxiliary variables $\{\gamma_p\}$, which yields substantial savings of computational time.

The performance of the PNOF5 has been tested by the homolitic dissociation of selected diatomic molecules, and the rotation barrier of ethylene. All calculations were carried out with the PNOFID code.[23] For the calculations of diatomic molecules, we have used the correlation-consistent valence triple-ζ basis set (cc-pVTZ) developed by Dunning.[24] In the case of ethylene, the used basis set was the double-ζ cc-pVDZ. For comparison, we have also calculated complete active space self-consistent field (CASSCF) (N, N) data, i.e., N electrons in N orbitals, N being the total number of electrons of the system, using MOLCAS 7.4 suite of programs.[25] In the case of ethylene, we considered a window formed by 12 electrons in 12 orbitals, which corresponds to include all valence electrons. The experimental data reported here were taken from the NIST Database,[26] except for the
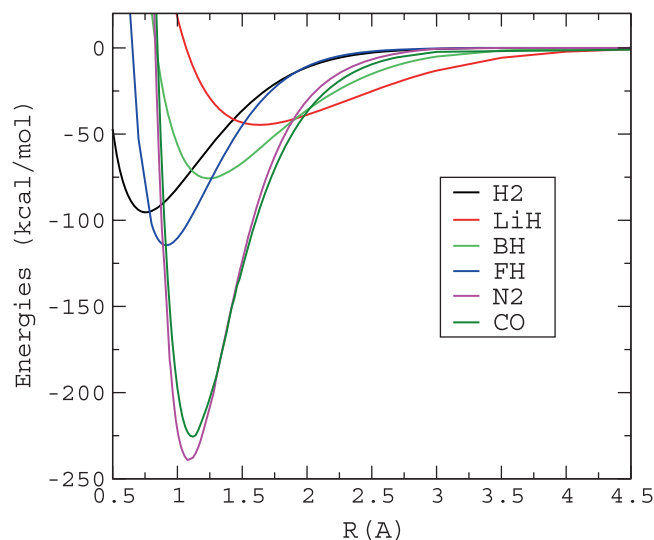

FIG. 1. PNOF5/cc-pVTZ dissociation curves for the diatomic molecules H$_2$, LiH, BH, FH, N$_2$, and CO. For each of the curves the zero energy point has been set at their corresponding energy at 10 Å.

experimental dissociation energies (D_e) which are taken from a combination of Refs. 27 and 28.

The selected molecules comprise different types of bonding characters: from the prototypical covalent bond of H$_2$ to the highly electrostatic bond of LiH, passing through molecules with different degree of polarity in their covalent bonds, such as BH and FH. We also consider two cases with multiple bond character, namely, CO and N$_2$. These cases span a wide range of values for binding energies and bond lengths. Observe, nonetheless, that in all cases the correct dissociation limit implies an homolitic cleavage of the bond with high degree of near-degeneracy effects. In the case of H$_2$, LiH, BH, and FH the dissociation limit corresponds to a two-fold degeneracy with the generation of two doublet atomic states. In the case of CO and N$_2$, the degeneracy augments to four and six, respectively, generating an atomic dissociation limit with the formation of two triplet states C (^{3}P) + O (^{3}P), and two quartet states N (^{4}S) + N(^{4}S).
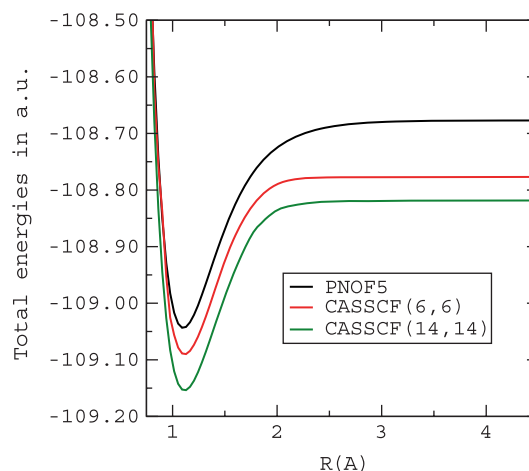

FIG. 2. PNOF5, CASSCF(6, 6), and CASSCF(14, 14) dissociation curves for N$_2$ using cc-pVDZ.

TABLE I. Comparison of selected molecular properties calculated at the PNOF5 and CASSCF(N, N), being N the total number of electrons of the system, levels of theory with the experimental data. Notice that for the active space of the CASSCF is (4, 8). The equilibrium bond length (R_e, in Å), dipole moment (μ, in D), dissociation energy (D_e, in kcal/mol) and total energy at the experimental distance ($E_e(R_{exp})$ in Hartrees) were calculated using cc-pVTZ basis set.

Molecule	PNOF5				CASSCF				Experimental		
	R_e	μ	D_e	$E_e(R_{exp})$	R_e	μ	D_e	$E_e(R_{exp})$	R_{exp}	μ	D_e
H$_2$	0.76	0.00	95.3	-1.151420	0.76	0.00	95.3	-1.151420	0.74	0.00	109.5
LiH	1.63	5.75	44.6	-8.016570	1.61	5.83	51.5	-8.030716	1.60	5.88	58.0
BH	1.24	1.50	75.7	-25.171903	1.25	1.28	75.2	-25.181986	1.23	1.27	81.5
HF	0.91	1.87	114.5	-100.125167	0.93	1.91	125.4	-100.197095	0.92	1.82	141.1
N$_2$	1.09	0.00	238.9	-109.085394	1.10	0.00	221.7	-109.187559	1.10	0.00	228.3
CO	1.12	0.22	225.6	-112.862342	1.14	-0.05	254.1	-112.976390	1.13	0.11	259.3

The corresponding dissociation curves for these molecules are depicted in Fig. 1. It is remarkable that PNOF5 is able to reproduce the correct dissociation curves for all cases, with the right dissociation limit, even in the case of the highest degeneracy (N$_2$). For the latter, we show in Fig. 2 the dissociation curves obtained at the PNOF5, CASSCF(6, 6), and CASSCF (14, 14) levels of theory using the double-ζ cc-pVDZ basis set. One may observe that all PNOF5 total energies lie above the energies of both CASSCF calculations along the curve. Similar results have been obtained for the rest of the molecules. Moreover, integer number of electrons have been found on the dissociated atoms, in contrast to the fractional charges observed recently in calculations using the variational 2-RDM method under the P, Q, and G conditions.[29] Our preliminary calculations at an internuclear distance of 20 Å for the 14-electron isoelectronic series, including N$_2$, CO, CN, NO$^+$, and O$_2^{+2}$, lead always to the dissociation limit with integer number of electrons on the dissociated atoms.

In Table I, a number of selected electronic properties, including equilibrium bond lengths, dissociation energies, dipole moments, and total energies at the experimental bond lengths can be found. PNOF5 and CASSCF energies are similar when the CASSCF window is of small size, such as in H$_2$, BH, and LiH. However, as the size of the window is augmented, there is a larger difference between PNOF5 and CASSCF energies, with the largest differences obtained for CO and N$_2$. Fulfillment of the known N-representability conditions of the 2-RDM yields total energies for our PNOF5 functional a bit above the accurate CASSF(N, N), with N being the number

of electrons, energies, as expected, and point to the fact that the variations of our PNOF5 functional could have been carried out in the allowed domain of N-representable 2-RDMs. Recall that we have imposed only the necessary conditions for the N-representability of the 2-RDM, the sufficient conditions are not known yet. Notice that lower energies than the "exact" ones are obtained with earlier functionals, such as PNOF3 (Ref. 11) and AC3,[5] which violate one, or more, of the above mentioned N-representability conditions. Furthermore, almost all current implementations of approximate electron-density functionals yield total energies well below the *exact* ones. Dissociation energies are in general lower than the experimental ones showing a better agreement with CASSCF results. The trends in dissociation energies predicted by PNOF5 is LiH < BH < H$_2$ < HF < CO < N$_2$, in agreement with both CASSCF and experimental trends, except for N$_2$.

The quality of the PNOF5 for the description of the electronic structure can also be tested by the analysis of the corresponding dipole moments. The different type of bonding in

TABLE III. Occupations of the natural orbitals and the corresponding pseudo one-particle energies, in Hartrees, for the ground and transition states of the ethylene.

Ground state		Transition state	
$2n_p$	$\lambda_p + n_p H_{pp}$	$2n_p$	$\lambda_p + n_p H_{pp}$
2.0000	-32.9627	2.0000	-32.7429
2.0000	-32.9608	2.0000	-32.7412
1.9932	-9.3509	1.9891	-8.8429
1.9838	-7.0708	1.9847	-6.9809
1.9838	-7.0708	1.9847	-6.9809
1.9838	-7.0708	1.9847	-6.9809
1.9838	-7.0708	1.9847	-6.9809
1.9089	-6.8577	1.0000	-3.4080
0.0911	-0.3457	1.0000	-3.4080
0.0162	-0.0604	0.0153	-0.0565
0.0162	-0.0604	0.0153	-0.0565
0.0162	-0.0604	0.0153	-0.0565
0.0162	-0.0604	0.0153	-0.0565
0.0068	-0.0348	0.0109	-0.0531
0.0000	0.0000	0.0000	0.0000
0.0000	0.0000	0.0000	0.0000

TABLE II. Total energies, in Hartrees, and energy barriers (ΔE) (in kcal/mol) for the ethylene torsion at HF, PNOF5, CASSCF, and CASPT2 levels of theory using cc-pVDZ basis set.

Method	Planar	TS	ΔE
HF	-78.038732	-77.860622	111.8
PNOF5	-78.136524	-78.032063	65.6
CASSCF(12, 12)	-78.184173	-78.075470	68.2
CASPT2(12, 12)	-78.342567	-78.238122	65.5

TABLE IV. Total (E_{tot}) and correlation energies (E_{cor}) of the He, Be, and Ne dimers, the absolute difference $\Delta E = |E_{tot}(dimer) - 2 \times E_{tot}(atom)|$ $|E_{tot}(dimer) - 2 \times E_{tot}(atom)|$, in Hartrees, and the percentage deviation $\Delta = 100 \times [E_{cor}(dimer) - 2 \times E(Atom)]/E_{cor}(dimer)$ of the correlation energy, at large interatomic separation (20Å) using the cc-pVTZ basis set.

	$E_{tot}(dimer)$	$2 \times E_{tot}(atom)$	ΔE	$E_{cor}(dimer)$	$2 \times E_{cor}(atom)$	$\Delta(\%)$
He	-5.754180	-5.754180	0.000000	-0.031872	-0.031872	0.000
Be	-29.203258	-29.203266	0.000008	-0.057508	-0.057516	0.014
Ne	-257.167375	-257.167390	0.000015	-0.103355	-0.103374	0.018

these molecules is reflected in their dipole moments. For instance, the most apolar heteronuclear diatomic molecule in our study is the paradigmatic CO molecule. Although oxygen is more electronegative, and one could expect the O atom as being partially negatively charged, but it occurs the opposite. PNOF5 predicts a dipole of 0.22 D, with the correct sign, contrary to the CASSCF result of -0.05 D, although slightly larger than the experimental one, 0.11 D. On the other hand, LiH shows a large dipole moment of 5.75 D, in very good agreement with the experimental value of 5.88 D. The dipole moment of polar molecules, such as BH and FH is also well reproduced.

We have also investigated the performance of PNOF5 to treat near-degeneracy effects in reactions in which diradicals are formed. We take as a case study the barrier for ethylene torsion, a paradigmatic case of near-degeneracy effects along a reaction coordinate. In Table II, we can find the total energies obtained for planar ethylene and the transition state (TS) corresponding to the ethylene torsion with the two carbons forced to adopt an sp^2 hybridization. It is well known, that at this TS, there is a full degeneracy of the π orbital system, as reveal by inspection of the data shown in Table III. This fact makes mandatory to treat the system with multideterminantal wavefunctions. In terms of relative energies, Hartree–Fock (HF) yields a very high barrier, 111.8 kcal/mol, as expected, which decreases when near-degeneracy effects are considered by CASSCF and CASPT2 methods, obtaining barriers of 68.2 and 65.5 kcal/mol, respectively. PNOF5 predicts a barrier of 65.6 kcal/mol, in outstanding agreement with CASPT2 result. Moreover, the PNOF5 occupation numbers at the TS of the corresponding HF HOMO and LUMO orbitals are 1.00, as it corresponds to the correct fully degenerate description of these valence π orbitals.

Finally, we want to address numerically the size consistency of PNOF5. Recently, it has been studied that the size consistency of various approximations within the NOF theory, concretely, their ability to reproduce the additivity of the total energy of a system composed of identical independent subsystems.[30] In Table IV, the total and correlation energies of the He, Be, and Ne dimers at an internuclear separation of 20 Å, as well as, the double value of the total and correlation energies of the corresponding atoms, are reported. For these calculations, we have used the correlation-consistent valence triple-ζ basis set developed by Dunning[24] We can observe that a very small size inconsistency is present for our functional. It is remarkable that the calculated occupation numbers of the dimers are twice the occupation numbers calculated in the atoms, which is in agreement with the near size consistency of the method, at least

for the singlet states of the spin-compensated systems studied here.

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