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Natural Orbital Functional Theory and Reactivity Studies of Diradical Rearrangements: Ethylene Torsion as a Case Study

Xabier Lopez,^{*,[a]} Mario Piris,^[a, b] Jon M. Matxain,^[a] Fernando Ruipérez,^[a] and Jesus M. Ugalde^[a]

Natural orbital functional theory (NOFT) in its PNOF3 and PNOF4 implementations is used to investigate the potential energy surface (PES) of ethylene torsion. This rearrangement is taken as a case study to illustrate the satisfactory performance of the Piris Natural Orbital Functional (PNOF) toward rearrangements sensible to non-dynamical electron correlation or near-degeneracy effects. We show that the fulfillment of the G-posi-

tivity condition, as implemented in PNOF4, is key to yield a correct description of structures with significant diradical character. We have found that PNOF4 yields an accurate description of these delicate PES and predicts the correct trends of the occupation numbers as compared with multiconfigurational wavefunction methods.

Diradicals are species with two electrons occupying two energy (near) degenerate orbitals.^[1–3] The spin coupling of these two electrons might yield either triplet or singlet states. The former poses no additional difficulties to single-reference-based electronic-structure methods, but the latter is far more difficult for its proper description relies on the handling of non-dynamical electron correlation. Two or more orbitals become degenerate in many fundamental chemical processes and its understanding is key to describe the homolytic dissociation of chemical bonds, torsions around double bonds, and the existence and the (meta)stability of diradicals. From the theoretical point of view, it was early recognized that the description of such electronic structure was challenging for most theoretical methods. Regarding wave-function methods, the use of single-reference methods such as Hartree–Fock (HF) leads to incorrect results and, therefore the need to include several determinants in the corresponding wavefunction. Other alternative methods, such as DFT, also suffer from important methodological problems to treat this type of situations.

Natural orbital functional theory (NOFT)^[4] is being configured as an alternative formalism to both DFT and wavefunction methods, by describing the electronic structure in terms of the natural orbitals and their occupation numbers. A detailed account of the state of the art of NOFT till 2006 can be found elsewhere.^[5] Since then, further developments have been reported in the literature.^[6–13] Within the Piris reconstruction functionals, PNOF3 has shown an outstanding performance for the energetics of atoms and molecules.^[10,11] Additionally, it has also been shown that it can describe the correct topology of

potential energy surfaces of highly correlated systems.^[12] This suggests that this functional renders a balanced description of electron correlation in both equilibrium and transition-state structures. However, analysis of the dissociation curves for various diatomics^[13] has shown that PNOF3 might occasionally overestimate electron correlation effects at structures with significant elongation of covalent bonds, namely, when near-degeneracy effects between molecular orbitals occupied by less than two electrons become important. We have also shown^[13] that this behavior is related to the role of the *N*-representability conditions, in particular, to the violation of the *G*-positivity condition by PNOF3. In fact, the use of a more restricted functional, PNOF4,^[13] satisfying rigorously all known necessary *N*-representability conditions (*D*, *Q* and *G*), led to the proper description of dissociation curves. Moreover, satisfactory description of diradical and diradicaloids have been obtained recently with PNOF4.^[14]

Herein, we assess the performance of PNOF3 and PNOF4 to treat rearrangements with structures showing a significant diradical character. We have chosen ethylene torsion as a case study, since it is the quintessential example of processes governed by non-dynamical electron correlation. Thus, at the equilibrium geometry, the ethylene molecule shows negligible diradical character, so that a single-reference wavefunction yields a qualitative correct description of the electronic structure. However, at the transition state, the bonding (π) and antibonding (π^*) orbitals become degenerate and wavefunction methods have to include at least two configurations to properly take into account the minimal physical features of this degeneracy effect. A proper method to describe the rearrangement profile should therefore be flexible enough as to treat, in a balanced way, diradical character, non-diradical character, and situations in-between. Therefore, this system has been often taken as a case study to assess the performance of methods aimed at treating diradicals, and diradical rearrangements.^[15]

Assuming a real set of natural orbitals, the Piris NOF (PNOF) energy for *N*-electron singlet-state systems can be cast as [Eq. (1)]:^[16]

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

where p denotes the spatial orbital, and n_p its occupation. H_{pp} is the 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. The primes indicate that the $q=p$ term is omitted from the summations. We should notice that a single set of spatial orbitals, $\{\varphi_p(\mathbf{r})\}$, is used for α and β spins, so $\{n_p\}$ must fulfill the following constrain [Eq. (2)]:

$$2 \sum_p n_p = N \quad (2)$$

The Piris reconstruction functional is based on the cumulant expansion^[17] of the two-particle-reduced density matrix.^[18] The two-particle cumulant is defined through the two-index matrices Δ and Π .^[16] Imposing the conservation of the total spin yielded the diagonal elements $\Delta_{pp}^{\alpha\beta} = n_p^2$ and $\Pi_{pp} = n_p$.^[9] In PNOF3,^[10] we do not consider the parallel spin components of the cumulant ($\Delta^{\alpha\alpha} = 0$), whereas in PNOF4,^[13] $\Delta_{qp}^{\alpha\alpha} = \Delta_{qp}^{\alpha\beta} = \Delta_{qp}$. The detailed expression for Δ can be found in ref. [7]. The expression for the Π matrix in PNOF4 is derived taking into account the \mathbf{G} -positivity condition that implies the following inequality [Eq. (3)]:

$$\Pi_{qp}^2 \leq n_q h_q n_p h_p + \Delta_{qp} (n_q h_p + h_q n_q) + \Delta_{qp}^2 \quad (3)$$

A detailed description of the Π matrix for PNOF3 and PNOF4 can be found in refs. [10 and 13], respectively.

In NOFT, the solution is usually established optimizing the corresponding energy functional with respect to the occupancies and to the natural orbitals, separately. A novel procedure was recently introduced,^[8] which yields the orthogonal natural orbitals by an iterative diagonalization method. Bounds on the occupation numbers are easily enforced by setting $n_p = \cos^2 \gamma_p$. Then, the SQP technique^[19] is used for performing the optimization of the energy with respect to the auxiliary variables γ_p constraining the occupancies only to the sum rules of Equation (2).

Geometries were optimized at the CASSCF(4,4) level of theory with the correlation-consistent valence double- ζ basis set (cc-pVDZ) developed by Dunning et al.^[20] At these geometries, single-point energies were evaluated using HF, CASSCF(12,12), CASPT2(12,12) and PNOF3/PNOF4 levels of theory with cc-pVDZ basis set for the scanned calculations and with both cc-pVDZ and aug-cc-pVDZ for the stationary points defining the minimum and TS geometries. In addition, for the stationary points, we calculated the barriers using broken-symmetry solutions at various DFT functionals, namely, B3LYP,^[21] PBE0,^[22] and M06-2X.^[23] The PNOF3 and PNOF4 calculations were performed with the PNOFID code,^[24] the CASSCF geometry optimizations and DFT calculations were carried out using the GAUSSIAN09

program package,^[25] and the CASSCF and CASPT2 single-point energies using the MOLCAS program.^[26] For the partially optimized structures used to depict the torsion potential, additional geometrical restrictions were added to ensure the planarity of the two carbon molecules, and therefore induce the largest possible diradical character into the system. The full optimizations carried out at the minimum and transition state stationary points were subjected to no restrictions and frequency calculations confirmed the nature of both stationary points.

In Figure 1, we show the potential energy surface (PES) as a function of the torsional angle from 90° (transition state, TS) to 180° (ethylene minimum). Relative energies, in kcal mol⁻¹, with respect to the 180° structure are depicted. In addition, the change in the corresponding HF HOMO/LUMO (Hartree-Fock highest occupied molecular orbital/lowest unoccupied molecular orbital) occupancy is also shown, along with the degree of violation of the \mathbf{G} -positivity condition for the PNOF3 functional. Absolute and relative energies for the relevant fully optimized stationary points (minima and transition state) can be found in Table 1.

We can see in Figure 1 and Table 1 that restricted Hartree-Fock (RHF), as expected, shows serious failures in describing the torsion of ethylene. As it has been shown before,^[15] RHF reproduces a curve with an unphysical cusp and a barrier that is significantly higher, 108.4 kcal mol⁻¹ with the aug-cc-pVDZ basis set, than the one of CASPT2(12,12)/aug-cc-pVDZ, that is, 65.2 kcal mol⁻¹. It is well known that a single-reference method cannot yield a good description for this system; for instance, even at the CCSD/DZP level of theory, a barrier of 89.9 kcal mol⁻¹ has been reported^[27] with the presence of a cusp in the rearrangement profile. PNOF3 and PNOF4 are successful in decreasing these barriers to numbers that are within the range of the CASSCF method with PNOF3 showing a lower barrier 57.2 kcal mol⁻¹ and PNOF4 higher, 73.2 kcal mol⁻¹, with the aug-cc-pVDZ basis set. Shao et al.^[15] reported a value of around 75 kcal mol⁻¹ at a high level of theory, TCSCF-CISD, with a basis set, DZP, of similar quality to the ones used herein. With the same basis set, other authors have reported values between 67.3–78.9 kcal mol⁻¹ using various approaches based on spin-flip methods.^[27,28] However, a closer look at the rearrangement profile shows an unphysical jump in the PES of PNOF3, when passing from 105° to 100°. An analysis of the corresponding RHF HOMO and LUMO occupancies as a function of the torsional angle is very revealing. Going from the ethylene minimum up to structures with a torsional angle of 120°, there is a continuous and steady decrease in the occupation of the HOMO orbital with a concomitant steady increase in the occupation of the LUMO orbital in the CASSCF(12,12) wavefunction. In this zone (from 180° to 120°), occupancies for the HOMO orbital are kept greater than 1.8, and occupancies of the LUMO are lower than 0.2. However, from 120° to the transition state (90°), the decrease/increase of HOMO/LUMO occupancies is accelerated, until we reach the torsional transition state, for which there is a 1/1 occupancy for HOMO/LUMO, and therefore, a full diradical character. In summary, the torsion around the double C=C bond in ethylene shows an in-

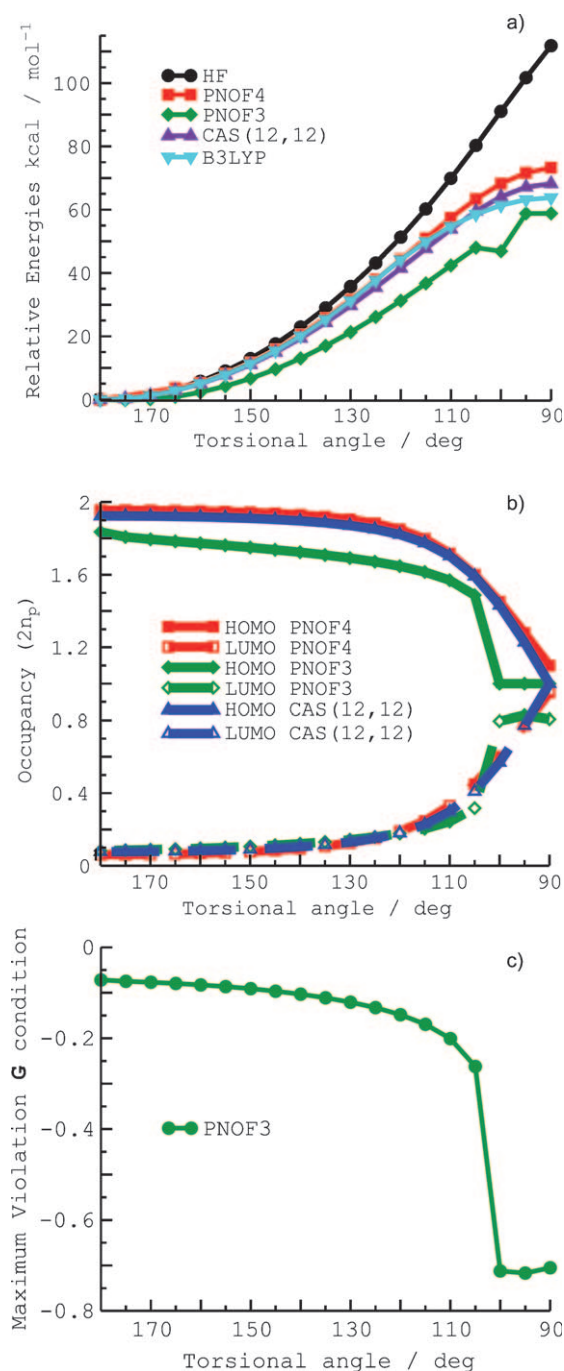


Figure 1. a) Ethylene torsion potential, results obtained from single-point energies at CAS(4,4)/cc-pVDZ partially optimized geometries with the torsional angle frozen at values that range from 90° to 180° with 5° variation. All calculations were done with the cc-pVDZ basis set. The relative energies, in kcal mol⁻¹, are calculated with respect to the energy of the 180° structure. b) Change in CASSCF(12,12) natural occupation numbers, and PNOF3/PNOF4 total occupancies ($2n_p$) for the formal HOMO and LUMO orbitals. c) Maximum violation of the G-positivity condition for PNOF3.

creasing degree of diradical character, but it does not evolve linearly.

PNOF4 gives an outstanding description of these different diradical character situations. It reproduces both HOMO and LUMO total occupancy ($2n_p$) curves remarkably well, giving a

Table 1. Energies [a.u.] and relative energies (ΔE) [kcal mol⁻¹] for the ethylene minimum and torsional transition-state structure.

| Structure | Energies | | ΔE |
|-----------------------|--------------------------------|--------------------------------|------------|
| Ethylene | | | |
| | MIN(D_{2h}) ^[a] | TS (D_{2d}) ^[a] | |
| cc-pVDZ | | | |
| HF | −78.038732 | −77.860622 | 111.8 |
| CAS(12,12) | −78.184173 | −78.075470 | 68.2 |
| CASPT2(12,12) | −78.342567 | −78.238122 | 65.5 |
| PNOF3 | −78.377707 | −78.284024 | 58.8 |
| PNOF4 | −78.095090 | −77.978391 | 73.2 |
| B3LYP ^[b] | −78.591976 | −78.490308 | 63.8 |
| PBE0 ^[b] | −78.485589 | −78.388529 | 60.9 |
| M06-2X ^[b] | −78.543689 | −78.437072 | 66.9 |
| aug-cc-pVDZ | | | |
| HF | −78.042471 | −77.869698 | 108.4 |
| CAS(12,12) | −78.187289 | −78.078703 | 68.1 |
| CASPT2(12,12) | 78.359290 | −78.255448 | 65.2 |
| PNOF3 | −78.388529 | −78.304011 | 57.2 |
| PNOF4 | −78.098780 | −77.982058 | 73.2 |
| B3LYP ^[b] | −78.599006 | −78.498263 | 63.2 |
| PBE0 ^[b] | −78.490686 | −78.394419 | 60.4 |
| M06-2X ^[b] | −78.549260 | −78.444128 | 66.0 |

[a] Optimized at the CASSCF(4,4)/cc-pVDZ level of theory. [b] Energies obtained for the broken symmetry solution. The value of $\langle S^2 \rangle$ for the TS structures was 1.01 for the B3LYP, PBE0, and M06-2X levels of theory and with both cc-pVDZ and aug-cc-pVDZ basis sets.

very good description of the diradical character not only at the TS (occupancy of 1.10/0.95 for HOMO/LUMO), but also for intermediate structures with a similar behavior in terms of the zones described above. However, the PNOF3 occupancies for the HOMO and LUMO orbitals show a different behavior. Specially important is the sudden drop/rise in the occupancy of the HOMO/LUMO orbital as we approach the TS at 100°. Obviously, this is related to the jump observed in the PES at this torsional angle. As seen in Figure 1 c, this drop/rise in the occupancy of the HOMO/LUMO orbital can be traced back to an increase of the maximum violation of the G-condition for those structures, which goes from -0.26 to -0.71—almost three times larger. This underlines the importance of fulfilling the N -representability conditions in NOF theories to give a proper description of the system with a significant degree of near-degeneracy or non-dynamical electron correlation.

We emphasize that the solutions obtained at the CASSCF and PNOF levels of theory satisfy the spin symmetry of the system, and therefore, the spin state is conserved, being $\langle S^2 \rangle = 0$ along the whole rearrangement profile. We remark that one can also calculate good energy values for the torsional barrier of ethylene within DFT if broken-symmetry solutions are allowed. For instance, the values for the energy barriers at broken-symmetry B3LYP, PBE0 and M06-2X can be found in Table 1. The three functionals give reasonable values for the barrier, between 60–67 kcal mol⁻¹, when broken-symmetry solutions are considered, in which an α electron is located at one of the carbons and a β electron in the other. However, the resultant determinant constructed from these Khon–Sham orbitals is not spin-adapted, and consequently, highly spin-contaminated, with $\langle S^2 \rangle \approx 1.01$.

In summary, we have shown that NOFT in its PNOF4 implementation can describe in a balanced way chemical rearrangements with significant degree of non-dynamical electron correlation, one of the most eagerly sought goals of theoretical chemistry. In this sense, the present calculations support the idea that PNOF4, in which both natural orbitals and their occupation numbers are optimized, can give an accurate description of both diradical and non-diradical character. To do so, it is important to introduce the required restrictions in the functional as to ensure the fulfillment of the known necessary *N*-representability conditions of the corresponding reduced density matrices. This work highlights the significant advances towards chemical accuracy made within the NOFT formalism in the last years, and the potentiality of these methods to yield a balanced description of electron correlation both at equilibrium and non-equilibrium structures, even when the difficult near-degeneracy effects are present.

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Keywords: ab initio calculations • computer chemistry • correlation energy • electronic structure • radicals

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