H$_4$ : A Challenging System For Natural Orbital Functional Approximations

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The correct description of nondynamic correlation by electronic structure methods not belonging to the multireference family is a challenging issue. The transition of $D_{2h}$ to $D_{4h}$ symmetry in H$_4$ molecule is among the most simple archetypal examples to illustrate the consequences of missing nondynamic correlation effects. The resurgence of interest in density matrix functional methods has brought several new methods including the family of Piris Natural Orbital Functionals (PNOF). In this work we compare PNOF5 and PNOF6, which include nondynamic electron correlation effects to some extent, with other standard ab initio methods in the H$_4$ $D_{4h}/D_{2h}$ potential energy surface. Thus far, the wrongful behavior of single-reference methods at the $D_{2h} - D_{4h}$ transition of H$_4$ has been attributed to wrong account of nondynamic correlation effects, whereas in geminal-based approaches it has been assigned to a wrong coupling of spins and the localized nature of the orbitals. We will show that actually interpair nondynamic correlation is the key to a cusp-free qualitatively correct description of H$_4$ PES. By introducing interpair nondynamic correlation, PNOF6 is shown to avoid cusps and provide the correct smooth PES features at distances close to the equilibrium, total and local spin properties along with the correct electron delocalization, as reflected by natural orbitals and multicenter delocalization indices.

I. INTRODUCTION

The correct description of nondynamic correlation effects is a challenging task for electronic structure methods. In wave function approaches, a multireference ansatz is needed to properly account for these effects. The computational scaling cost of such methods limits their use to systems of moderate size. Within density functional theory (DFT) the proper inclusion of nondynamic correlation effects is an open problem. In practice, a broken-symmetry calculation is usually performed producing wrong spin densities.

An alternative to both wave function and DFT methods is natural orbital functional theory (NOFT). In recent years, several functionals have been proposed by reconstruction of the two-particle reduced density matrix (2-RDM) in terms of the one-particle reduced density matrix (1-RDM). In particular, within the family of Piris Natural Orbital Functionals (PNOF),\textsuperscript{2,12–21} PNOF5 and PNOF6\textsuperscript{10,11} are among the best candidates to treat nondynamic correlated systems. They describe properly the dissociation limit of several molecules, recovering the correct integer number of electrons on each fragment upon dissociation.\textsuperscript{10,11} Both PNOF5 and PNOF6 belong to the family of orbital-pairing approaches, but the former only includes intrapair electron correlation while in the latter electrons on different pairs are also correlated. The inclusion of interpair electron correlation in PNOF6 allows a better description of correlation effects and it also removes the symmetry-breaking artifacts that are present in independent-pairs approaches such as PNOF5 when treating delocalized systems.\textsuperscript{10}

The purpose of this manuscript is to analyze the effect of interpair electron correlation on the treatment of nondynamic correlation by investigating the performance of PNOF5 and PNOF6 and several standard ab initio computational methods. To this end we will examine the $D_{4h}/D_{2h}$ potential energy surface of the planar H$_4$ model (hereafter, simply PES).

H$_4$ has been extensively used to test single-reference post-Hartree-Fock methods\textsuperscript{2,12–21} and geminal-based theories\textsuperscript{22,23} Hartree-Fock, MP2 and MP3 show a spurious cusp on the PES of H$_4$ as the system evolves from $D_{2h}$ to $D_{4h}$ symmetry. The cusp is the maximum energy value along the symmetry transition. Conversely, traditional coupled cluster (CC) methods predict a cusp but this cusp is a local minimum in the $D_{2h} - D_{4h}$ transition. Recently, Bulik \textit{et al.} have shown that an improvement of the description of correlated systems can be also achieved by removing terms in traditional CC theory.\textsuperscript{24} Variational CC approaches also improve this wrong behavior of the traditional CC implementations,\textsuperscript{12,13,19} however, most of these approaches revert the local minimum to a local maximum but most of them do not avoid the presence of a spurious cusp. Geminal-based theories predict a (maximum) cusp at the square geometry. Jeszenszki \textit{et al.}\textsuperscript{22} have attributed this failure to an insufficient account of spin couplings and the localized character of the orbitals. By including triplet components in the geminals, the orbitals become delocalized and the characteristic cusp vanishes, but the resultant PES is not completely smooth and wave function becomes spin contaminated. The authors also examined the local spin\textsuperscript{22} of the system using different geminal-based approaches. Jeszenszki \textit{et al.}\textsuperscript{22} have found that singlet-coupled geminals fail to describe correctly local spins at the D$_{4h}$ geometry. The inclusion of triplet components improve the results but the local spin values are not smooth along the PES.

Thus far, the wrongful behavior of single-reference methods at the $D_{2h} - D_{4h}$ transition of H$_4$ has been ascribed to

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II. Theory

A. PNOF5/PNOF6

In this section we will briefly review the formulation of PNOF5\textsuperscript{2} and PNOF6\textsuperscript{24} Both PNOF5 and PNOF6 belong to the family of orbital-pairing methods, which divide the spatial orbital space into subspaces (a set of orbitals) that contain two electrons each. These methods couple each orbital \( g \) below the Fermi level (\( F = N/2 \), where \( N \) is the number of electrons of the system) with \( N_n \) orbitals above it, being \( \Omega_g \) the subspace containing orbital \( g \) and its coupled counterparts. The original formulations of both functionals were introduced for \( N_n = 1 \) but subsequently extended versions (\( N_n > 1 \)) were reported\textsuperscript{27,28}. The sum rule for the occupation numbers (\( n \)) is fulfilled for each of the \( N/2 \) subspaces \( \Omega_g \),

\[
\sum_{p \in \Omega_g} n_p = 1 \tag{1}
\]

where \( p \) denotes a spatial natural orbital (NO) and \( n_p \) its occupation number.

The PNOF5 and PNOF6 energy expressions for a singlet state system can be written as

\[
E = \sum_{g=1}^{F} E_g + \sum_{f \neq g \in \Omega_f} \sum_{q \in \Omega_g} E_{pq}^{\text{int}}. \tag{2}
\]

The first term of Eq. (2) corresponds to the sum of energies of \( F \) independent pairs with energy \( E_g \), namely,

\[
E_g = \sum_{p \in \Omega_g} n_p (2\mathcal{H}_{pp} + J_{pp}) + \sum_{p, q \in \Omega_g, p \neq q} E_{pq}^{\text{int}}, \tag{3}
\]

where \( \mathcal{H}_{pp} \) is the matrix element of the kinetic energy plus nuclear-electron attraction terms and \( J_{pp} = \langle pp|pp \rangle \) is the Coulomb interaction between two electrons with opposite spins at the spatial orbital \( p \). The term \( E_{pq}^{\text{int}} \) contains the interaction energy between electrons in different spatial orbitals \( p \) and \( q \),

\[
E_{pq}^{\text{int}} = (n_q n_p - \Delta_{pq}) (2J_{pq} - K_{pq}) + \Pi_{pq} \mathcal{L}_{pq} \tag{4}
\]

where \( J_{pq} = \langle pq|pq \rangle \) and \( K_{pq} = \langle pq|qp \rangle \) are the direct and exchange integrals, respectively and \( \mathcal{L}_{pq} = \langle pp|qq \rangle \) is the exchange and time-inversion integral. Matrices \( \Delta \) and \( \Pi \) are auxiliary matrices proposed\textsuperscript{26} to reconstruct the 2-RDM in terms of the NO occupancies. The diagonal elements of these matrices are \( \Delta_{pp} = n_p^2 \) and \( \Pi_{pp} = n_p \). The off-diagonal elements of \( \Delta \) and \( \Pi \) determine the different implementation of the PNOF\( i \) (\( i = 1 \ldots 6 \)) series. In particular, PNOF5 and PNOF6 differ on the treatment of the interaction between electrons on different pairs.

In PNOF5, when orbitals \( p \) and \( q \) belong to the same subspace \( \Omega_g \), the off-diagonal elements of \( \Delta \) and \( \Pi \) are \( \Delta_{pq} = n_q n_p \) and

\[
\Pi_{pq} = \begin{cases} -\sqrt{n_q n_p}, & p = g \text{ or } q = g \\frac{1}{n_q n_p}, & p, q > F, \end{cases} \tag{5}
\]

respectively, and they vanish when \( p \) and \( q \) belong to different subspaces. Consequently, the second term of Eq. (2) becomes

\[
\sum_{f \neq g \in \Omega_f} \sum_{q \in \Omega_g} E_{pq}^{\text{int}} \text{(PNOF5)} = n_q n_p (2J_{pq} - K_{pq}) \tag{6}
\]

The expression above indicates that the interaction between electrons in different pairs is treated at the mean-field level. Therefore, PNOF5 lacks correlation between electrons in different pairs. In contrast, the PNOF6 \( \Delta_{pq} \) and \( \Pi_{pq} \) matrices (when \( p \) and \( q \) belong to different subspaces these matrices do not vanish) include terms that account for interpair electron correlation. The off-diagonal elements \( \Delta_{pq} \) and \( \Pi_{pq} \) in PNOF6 read as

\[
\Delta_{pq} = e^{-2S} h_q h_p, \quad \Pi_{pq} = e^{-S} (h_q h_p)^{1/2}, \tag{7}
\]

where \( h_p \) is the hole (1 \( \rightarrow \) \( n_p \)) in the spatial orbital \( p \) and \( S, \gamma_p, S_{\gamma}, \) and \( \Pi_{\gamma} \) are defined as

\[
S = \sum_{q=1}^{F} h_q, \quad \alpha_p = \begin{cases} e^{-S} h_p, & p \leq F \\ e^{-S} n_p, & p > F \end{cases}, \tag{8}
\]

\[
S_{\alpha} = \sum_{q=1}^{F} \alpha_q, \quad \gamma_p = n_p h_p + \alpha_p^2 - \alpha_p S_{\alpha}, \tag{9}
\]

\[
S_{\gamma} = \sum_{q=1}^{F} \gamma_q, \quad \Pi_{\gamma} = \left( n_q h_p + \frac{\gamma_q}{S_{\gamma}} \right)^{1/2} \left( h_q n_p + \frac{\gamma_p}{S_{\gamma}} \right)^{1/2}. \tag{10}
\]

Recently, PNOF5 has been proved equivalent to an antisymmetrized product of strongly orthogonal geminals (APSG)\textsuperscript{31,32}. Conversely, PNOF6 is not related to geminal theories but it keeps the orbital-pairing scheme, Eq. (1). In this
work we have used the $N_c = 1$ version of the functionals. That is, each orbital subspace contains two spatial orbitals and then only $N$ spatial orbitals are correlated. In this sense, both functionals take into account most of the nondynamic correlation effects, but while PNOF5 includes only intrapair correlation, PNOF6 incorporates also the interpair correlation, through $\Delta$ and $\Pi$ matrices defined in Eq. (7) (see Eq. (4)).

### B. Local Spin And Electron Delocalization

Local spins can be obtained by decomposing the expectation value of the total spin square operator $\langle \hat{S}^2 \rangle$ into atomic or fragment contributions as

$$\langle \hat{S}^2 \rangle = \sum_A \langle \hat{S}^2 \rangle_A + \sum_{A \neq B} \langle \hat{S}^2 \rangle_{AB},$$

(9)

where $\langle \hat{S}^2 \rangle_A$ is the local spin on fragment $A$ and $\langle \hat{S}^2 \rangle_{AB}$ accounts for the coupling between spins on fragments $A$ and $B$. Recently some of us have presented a general formulation of the local spin that fulfills a set of physical constrains$^{24,25}$

For singlet systems, the formulation reads as

$$\langle \hat{S}^2 \rangle_A = \frac{3}{4} \left( 2 \text{Tr} \left( \hat{D} S^A \right) - \text{Tr} \left( \hat{D} S^{A1} \hat{D} \right) \right)$$

(10)

$$+ \frac{1}{2} \sum_{ijkl} \Gamma_{ijkl} S^A_{kl} S^A_{ij} - \frac{1}{2} \sum_{ijkl} \Gamma_{ijkl} S^A_{li} S^A_{kj}$$

and

$$\langle \hat{S}^2 \rangle_{AB} = \frac{1}{2} \sum_{ijkl} \Gamma_{ijkl} S^A_{kl} S^B_{ij} - \frac{1}{2} \sum_{ijkl} \Gamma_{ijkl} S^A_{li} S^B_{kj}$$

(11)

where $\hat{D}$, $\Gamma$, and $S^A$ are the spinless 1-RDM, the spinless cumulant of the 2-RDM, and the fragment orbital overlap matrix$^{22}$

The correct description of local spins has been recently put forward as a stringent condition to test natural-orbital based cumulant matrix (or 2-RDM) approximations$^{26}$

and has been used to characterize and quantify the diradical and triradical character of molecules$^{23,44}$ In this work, we will use the local spin analysis to study the effect of the interpair electron correlation in PNOF5 and PNOF6 on the spin coupling of electrons located at different atoms.

The calculation of electron delocalization among different fragments can be performed through the NO-weighted overlap multiplications involving the different fragments. This is commonly known as Giambiagi’s multicenter index$^{35}$ and its expression reads$^{36}$

$$I_{ABCD} = \sum_{ijkl} n_i n_j n_k n_l S^A_{ij} S^B_{kl} S^C_{li} S^D_{kj}$$

(12)

The quantity has been successfully used to account for several multicenter delocalization phenomena including multicenter bonding$^{27}$, conjugation effects$^{28}$ and aromaticity$^{29-31}$.

### III. COMPUTATIONAL DETAILS

In this work we have computed the $D_{4h}/D_{2h}$ PES of $H_4$ employing the following methods: Hartree-Fock (HF), CC singles and doubles (CCSD), CCSD with perturbative estimation of triple excitations (CCSD(T)), complete active space self-consistent field CASSCF (with a 4 electrons in 4 orbitals active space), PNOF5, PNOF6 and full configuration interaction (FCI). This benchmark data set includes methods that mostly include dynamic correlation effects (CCSD and CCSD(T)) or nondynamic correlation effects (CASSCF) and will be used as benchmark references to measure the amount of dynamic and nondynamic correlation effects included in PNOF5 and PNOF6.

All calculations based on wave function methods have been performed with the Gaussian03$^{41}$ set of programs except those at the FCI level that were performed with a modified version of the program of Knowles and Handy$^{42,43}$ NOF calculations have been carried out using DoNOF program. The matrix elements of the kinetic energy, the nuclear-electron attraction energies, and the one- and two-electron integrals needed to perform the PNOF calculations have been obtained from GAMESS$^{44,45}$ The correlation-consistent aug-cc-pVDZ$^{36}$ basis set has been employed for all the calculations. The local spin analysis has been performed using DMN$^{46}$ to compute the 2-RDM and APOST-3D$^{47}$ to calculate the local spins using the topological fuzzy Voronoi cells to define the atomic regions$^{39}$.

### IV. RESULTS

The PES of $H_4$ is characterized using two parameters, $\theta$ and $\phi$ (see Fig. 1). The former, controls the distance between each H atom and the center of mass while the latter measures the angle formed by two neighbor H atoms and the center of mass (see Fig. 1). At $\theta = 90^\circ$, the system possesses $D_{4h}$ symmetry and two configurations with symmetries $a_1^g$ and $a_2^u$ become degenerate. By modifying $\theta$ one can control the degree of symmetry distortion with respect to the $D_{4h}$ ($\theta = 90^\circ$) structure, thus modulating the multireference character (and hence the nondynamic correlation) of the system.

In this sense, the $H_4$ PES represents a challenging system for most electronic structure methods as it combines nondynamic correlation and dynamic correlation effects.

The relative energies with respect to the minimum energy at $\theta = 70^\circ$ for each method of the $H_4$ model keeping $R$ constant for different distances and modifying $\theta$ are shown in Fig. 2. The system is symmetric at $\theta = 90^\circ$ and it is described by two degenerate configurations, which correspond to the minimum HF solutions at $\theta < 90^\circ$ and $\theta > 90^\circ$, respectively. The FCI curve has an energy maximum at $\theta = 90^\circ$ and the energy curve is smooth along the entire range of angles. The energy needed to change from $\theta = 70^\circ$ to the $D_{4h}$ geometry decreases gradually as the radius $R$ increases until the PES...
becomes considerably flat. The CASSCF curves show the right qualitatively features, i.e., a maximum at $\theta = 90^\circ$ and a smooth transition from $\theta = 70^\circ$ to $\theta = 110^\circ$. However, due to missing dynamic correlation energy that becomes important at the $\theta \gg 90^\circ$ and $\theta \ll 90^\circ$ regions, CASSCF relative values are downshifted to lower energies.

At $\theta = 90^\circ$ two configurations become degenerate and the HF solution presents symmetry-breaking artifacts that in a HF calculation. Importantly, both solutions showed in Fig. 3 for $R = 1.70 \text{\AA}$ and $\theta = 90^\circ$. PNOF6 energies are in all cases closer to FCI than PNOF6. This is due to the repulsive electron-electron interpair correlation energy term that is included in the PNOF6 functional. PNOF6 improves qualitatively the shape of the PES, provides good relative energies at the price of higher absolute energies.

APSG, which is the antisymmetric wavefunction behind PNOF5, has been shown to also exhibit this spurious maximum cusp at $\theta = 90^\circ$. The failure of APSG has been attributed to the localized nature of its orbitals and the wrong account of spin coupling. Szabados and coworkers have demonstrated that APSG using delocalized orbitals, which correspond to a solution of the APSG equations, eliminates the cusp. In Fig. 3 we plot the orbitals that arise from PNOF6 and PNOF5 at $R = 1.0 \text{\AA}$ and $\theta = 90^\circ$. PNOF6 NO are localized on $H - H$ bonds and each bonding orbital is coupled with its antibonding counterpart. At this value of $\theta$, the same picture with the orbitals horizontally localized is equivalent. On the other hand, the PNOF6 NO present the expected delocalized character and mimic the canonical orbitals obtained in a HF calculation. Importantly, both solutions showed in Fig. 3 for $R = 1.70 \text{\AA}$ and $\theta = 90^\circ$ present delocalized orbitals. Unlike PNOF5, PNOF6 equations do not lead to a stationary solution that corresponds to a set of localized orbitals.

The inclusion of interpair correlation also affects the occupation numbers of the corresponding NO (see Table III). For small values of $R$ at the CASSCF level, the $b_g$ orbital remains almost doubly occupied along the PES. The $b_{2u}$ is doubly occupied for $\theta \ll 90^\circ$ and there is a smooth transition from these structures to the $\theta \gg 90^\circ$ ones in which the doubly occupied orbital is the $b_{3u}$. At $\theta = 90^\circ$ both orbitals become almost indistinguishable.

Table II gathers the relative energies at $\theta = 90^\circ$ with respect to the energy at $\theta = 90^\circ$. For $R = 0.8 \text{\AA}$, $R = 1.00 \text{\AA}$, and $R = 1.20 \text{\AA}$ PNOF6 improves PNOF5 (as to compared to FCI) by 13.44, 9.69 and 4.14 kcal/mol, respectively. At larger values of $R$, PNOF5 improves over PNOF6 but the difference between them does not exceed 3 kcal/mol. CASSCF results are closer to FCI than PNOF6 for all the distances. The difference attains its maximum at $R = 1.20 \text{\AA}$, in which CASSCF is 12.29 kcal/mol closer to FCI than PNOF6. These deviations put forward the current limits of PNOF6 to fully account for correlation effects.

In Table III we collect FCI, PNOF5, and PNOF6 absolute energies for $R = 0.80 \text{\AA}$, $1.20 \text{\AA}$, and $1.70 \text{\AA}$. PNOF5 energies and the lately introduced CCD0 and OQVCCD(T), breaks down for $\theta = 90^\circ$. Like VCC, PNOF5 —unlike PNOF5, which —at variance with PNOF5, is miss-

\begin{table}[h]
\centering
\caption{Relative energies (kcal/mol) as the difference between the absolute energies at $\theta = 90^\circ$ and $\theta = 70^\circ$ for different values of $R(\text{\AA})$.}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Method & $R=0.80$ & $R=1.00$ & $R=1.20$ & $R=1.40$ & $R=1.60$ & $R=1.80$ \\
\hline
FCI & 68.75 & 61.54 & 48.92 & 35.58 & 23.79 & 14.72 \\
HF & 99.15 & 99.43 & 93.38 & 85.20 & 76.59 & 68.33 \\
CASSCF & 66.61 & 58.19 & 45.44 & 32.68 & 21.66 & 13.27 \\
PNOF5 & 87.63 & 78.87 & 71.88 & 43.67 & 27.94 & 16.47 \\
PNOF6 & 74.19 & 68.98 & 57.74 & 44.48 & 30.68 & 18.17 \\
\hline
\end{tabular}
\end{table}
degenerate in terms of occupancies. The PNOF5 bonding orbitals are almost doubly occupied along the PES while the antibonding ones remain almost unoccupied. No degeneracy is observed in this case. By including interpair electron correlation, PNOF6 NO and occupancies qualitatively mimic the CASSCF ones. It is worth noting that at $\theta = 90^\circ$ the $b_{3u}$ and $b_{2u}$ do not have exactly the same occupancy for most of the values of $R$ shown in Fig. 3. This might indicate that the interpair description is not fully recovered by PNOF6. The second solution shown in Fig. 3 as PNOF6(sol. 2), that
FIG. 3. Absolute PNOF6 energies in a.u. for \( R = 1.70 \text{Å} \) (top) and \( R = 1.90 \text{Å} \) (bottom). PNOF6(Sol. 1) and PNOF6(Sol. 2) stand for the two solutions that show a crossing and PNOF6 (min.) stand for the minim energy solution of each value of \( \theta \).

TABLE III. CASSCF(4,4), PNOF5, and PNOF6 NO occupation numbers at \( \theta = 90^\circ \) for different values of \( R \).

\[
\begin{array}{cccccc}
R(\text{Å}) & n_1 & n_2 & n_3 & n_4 \\
\hline
\text{CASSCF} & & & & & \\
0.80 & 1.939 & 1.000 & 1.000 & 0.061 \\
1.00 & 1.882 & 1.000 & 1.000 & 0.118 \\
1.20 & 1.795 & 1.000 & 1.000 & 0.205 \\
1.50 & 1.604 & 1.000 & 1.000 & 0.396 \\
1.70 & 1.458 & 1.000 & 1.000 & 0.542 \\
1.90 & 1.327 & 1.000 & 1.000 & 0.673 \\
20.00 & 1.000 & 1.000 & 1.000 & 1.000 \\
\text{PNOF5} & & & & & \\
0.80 & 1.923 & 1.921 & 0.079 & 0.077 \\
1.00 & 1.835 & 1.835 & 0.165 & 0.165 \\
1.20 & 1.704 & 1.704 & 0.296 & 0.296 \\
1.50 & 1.472 & 1.471 & 0.529 & 0.528 \\
1.70 & 1.335 & 1.335 & 0.665 & 0.666 \\
1.90 & 1.229 & 1.229 & 0.771 & 0.771 \\
20.00 & 1.000 & 1.000 & 1.000 & 1.000 \\
\text{PNOF6} & & & & & \\
0.80 & 1.971 & 1.185 & 0.815 & 0.029 \\
1.00 & 1.942 & 1.197 & 0.803 & 0.058 \\
1.20 & 1.894 & 1.191 & 0.809 & 0.106 \\
1.50 & 1.771 & 1.150 & 0.850 & 0.230 \\
1.70 & 1.645 & 1.110 & 0.891 & 0.355 \\
1.90 & 1.495 & 1.068 & 0.932 & 0.505 \\
20.00 & 1.000 & 1.000 & 1.000 & 1.000 \\
\end{array}
\]

becomes the minimum energy solution for certain values of \( \theta \) when \( R = 1.70 \text{Å} \) and \( R = 1.90 \text{Å} \) and is the minimum solution found for larger values of \( R \), presents perfect degeneracy in terms of occupation numbers of the \( b_{3u} \) and \( b_{2u} \) orbitals for all values of \( \theta \) and \( R \).

The wrong coupling between spins located in different centers of the molecule is one of the causes for the failure of singlet-couplet geminal approaches to describe the \( \text{H}_4 \) system. Jeszenszki et al. have used the local spin analysis to show that the inclusion of triplet components in geminals improves the APSG results but spin contamination appears when the triplet component in the geminal becomes important. The local spin value of one \( \text{H} \) atom of the \( \text{H}_4 \) system is shown in Fig. 5. As the system approaches the \( D_{4h} \) symmetry, there is an increase of the diradical character of the system and
V. CONCLUSIONS

The PES of the planar $D_{4h}/D_{2h}$ H$_4$ model has been computed at several levels of theory. Single-reference methods show a spurious cusp at the $D_{4h}$ structure that thus far was attributed to nondynamic correlation. PNOF5 (which affords a correct description of molecular dissociation and other intrapair nondynamic correlation effects) also shows a spurious cusp at $D_{4h}$, whereas PNOF6 provides a qualitatively correct description of this phenomenon.

Since PNOF5 and PNOF6 mainly differ from each other by the inclusion of interpair correlation, the factors responsible for the spurious description of the $D_{4h}/D_{2h}$ H$_4$ PES can be narrowed down to missing interpair nondynamic correlation effects. Indeed, the inclusion of interpair correlation in the pairing-orbital NOFT ansatz is key to recover the delocalized orbitals picture, remove the spurious cusp in the PES and properly account for the coupling between the spins located at different centers. On the other hand, inclusion of more terms to fully account for electron correlation seems to be needed to recover the smoothness of the curves at $R = 1.70\,\text{Å}$ and $1.90\,\text{Å}$, to obtain quantitative results, and to recover the important correlation effects that separate PNOF6 results from FCI. We hope that this study will shed light on the effect of interpair electron correlation and pave the way to the development of new electronic structure methods within NOFT or methods based on geminal expansion of the wave function. Research in this direction is underway in our laboratory.

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