

PNOF5 calculations based on the “thermodynamic fragment energy method”: C_nH_{2n+2} ($n = 1, 10$) and $(FH)_n$ ($n = 1, 8$) as test cases

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Abstract The performance of the “thermodynamic fragment energy method” (FEM) in the context of natural orbital functional theory (NOFT) in its PNOF5 implementation is assessed. Two test cases are considered: the linear chains C_nH_{2n+2} ($n = 1, 10$) and the hydrogen-bonded $(FH)_n$ ($n = 1, 8$) clusters. Calculations show a fast convergence of the PNOF5-FEM method, which allows the treatment of extended system at a fractional cost of the whole calculation. We show that this type of methodologies could expand the range of systems achievable by NOFT due to the significant reduction in the computational cost.

Keywords Natural orbital functional theory · Fragment energy method · APSG wavefunction

1 Introduction

In the last decade, a series of functionals has been developed [1, 2] using a reconstruction proposed by Piris [3] of the two-particle reduced density matrix (2-RDM) in terms of the one-particle RDM (1-RDM). In particular, the Piris natural orbital functional 5 (PNOF5) [4, 5] has proved to

be comparable to accurate quantum chemistry methods in many cases [4–18]. So far this is the only natural orbital functional (NOF) that has been obtained by top-down and bottom-up methods [19]. In the bottom-up method, the functional was generated by progressive inclusion of known necessary N -representability conditions on the 2-RDM, whereas the top-down method was used through reducing the energy expression generated from an N -particle wavefunction to a functional of the occupation numbers and natural orbitals [5]. In the case of PNOF5, this wavefunction is an antisymmetrized product of strongly orthogonal geminals (APSGs), with the expansion coefficients explicitly expressed by the occupation numbers [20, 21].

The idea of a function of this type dates back to the early fifties [22, 23] and is inspired by the valence bond theory [24, 25]; in fact, PNOF5 can also be considered as a type of GVB-PP method with fixed signs for the expansion coefficients of the corresponding determinants. Many scientists have worked actively in the field of strongly orthogonal geminals, and one of them is Professor Péter R. Surján to whom is dedicated this Festschrift. Indeed, an excellent review summarizing the evolution of the geminal theory up to 1999 can be found at his work [26]. An overview of geminal-based perturbative techniques for describing electron correlation was given recently [27].

Consequently, PNOF5 is an orbital-pairing approach that takes into account most of the non-dynamical effects, but also an important part of the dynamical electron correlation corresponding to the intrapair (intrageminal) interactions. The existence of a generating wavefunction confirms that PNOF5 is strictly N -representable, i.e., the 2-RDM is derived from a function that is antisymmetric in N -particles [28]. Moreover, it demonstrates the size extensivity and size consistency of PNOF5, which is an inherent property to the generating singlet-type APSG wavefunction [29, 30].

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In NOF theory [31], the solution is established optimizing the energy functional with respect to the occupation numbers and to the natural orbitals, separately. If PNOF5 is employed, the occupancies can be expressed through auxiliary variables in order to enforce automatically the N -representability bounds on the 1-RDM, so the variation can be performed without constraints. A self-consistent procedure proposed in Ref. [32] yields the natural orbitals. This scheme requires computational times that scale as n^4 , n being the number of basis functions, like in the Hartree–Fock (HF) approximation. However, our implementation in the molecular basis set requires also four-index transformation of the electron repulsion integrals, which is the time-consuming step though a parallel implementation of this part of the code has substantially improved the performance of our program. Besides the matrix scaling carried out in [32], the direct inversion in the iterative subspace (DIIS) method has recently been implemented in our code, but new techniques should be considered to reduce the number of iterations required to achieve the convergence.

In spite of its promising performance, the computational cost of PNOF5 calculations prevents them for a wider use. In this sense, any strategy to reduce calculation times is highly interesting, as it would expand the range of applicability of NOF theory. The fragmentation technique has allowed to span the range of systems attainable by wavefunction-based and density-functional theories, by means of a dividing approach that allows the calculation of the whole system fragmented in subsystems. In the present paper, we use such an approach, the so-called thermodynamic fragment energy method (FEM) [33], to assess the performance of PNOF5 in the context of fragment energy calculations.

The aim of this work is to determine how PNOF5-FEM energies converge to the exact PNOF5 values for selected oligomers, namely the polyalkene chains C_nH_{2n+2} and planar zigzag $(FH)_n$ clusters. The size-consistency property, and the fact that the functional tends to localize spatially the natural orbitals, makes this functional an exceptional candidate for fragment calculations. We demonstrate that the convergence of fragment energy calculations is very fast, especially in those cases where the interaction between fragments is small.

2 Methods

2.1 The functional

At the beginning [4], PNOF5 was formulated as an orbital-pairing approach that involves coupling each orbital g , below the Fermi level ($g \leq F = N/2$), with only one orbital above F ($N_g = 1$). This model was further improved by

a better description of the electron pair in the so-called extended PNOF5 [5], in which each orbital g was coupled with $N_g > 1$ orbitals above F . This pairing condition is reflected in the following sum rule for the occupation numbers:

$$\sum_{p \in \Omega_g} n_p = 1; \quad g = \overline{1, F} \quad (1)$$

where p is the running index referring to the spatial part of natural spin orbitals and n_p their occupation numbers. Notice that for spin-compensated systems the spatial part of α and β natural spin orbitals are the same, so that the total occupation number for a given natural spatial orbital is $n_p^{occ} = n_p^\alpha + n_p^\beta = 2 \times n_p$ and therefore can take values between [0, 2].

In Eq. (1), Ω_g is the subspace containing the orbital g and its N_g coupled orbitals. It is worth to note that these subspaces are mutually disjoint ($\Omega_{g_1} \cap \Omega_{g_2} = \emptyset$), i.e., each orbital belongs only to one subspace Ω_g . The PNOF5 energy for a singlet state of an N -electron system can be cast as

$$E = \sum_{g=1}^F E_g + \sum_{g_1 \neq g_2}^F \sum_{p \in \Omega_{g_1}} \sum_{q \in \Omega_{g_2}} E_{pq}^{int} \quad (2)$$

The first term of the energy (2) draws the system as independent F electron pairs described by

$$E_g = \sum_{p \in \Omega_g} n_p (2\mathcal{H}_{pp} + \mathcal{J}_{pp}) + \sum_{p, q \in \Omega_g, p \neq q} \Pi(n_p, n_q) \mathcal{L}_{qp} \quad (3)$$

$$\Pi(n_p, n_q) = \begin{cases} -\sqrt{n_p n_q}, & p = g \text{ or } q = g \\ \sqrt{n_p n_q}, & p, q > F \end{cases} \quad (4)$$

where \mathcal{H}_{pp} denotes for the one-particle matrix elements of the core Hamiltonian. $\mathcal{J}_{pq} = \langle pq|pq \rangle$ and $\mathcal{K}_{pq} = \langle pq|qp \rangle$ are the usual direct and exchange integrals, respectively. $\mathcal{L}_{pq} = \langle pp|qq \rangle$ is the exchange and time-inversion integral [34], which only differs in phases of the natural orbitals with respect to the exchange integrals, so $\mathcal{L}_{pq} = \mathcal{K}_{pq}$ for real orbitals. The interaction energy E_{pq}^{int} is given by

$$E_{pq}^{int} = n_q n_p (2\mathcal{J}_{pq} - \mathcal{K}_{pq}) \quad (5)$$

Accordingly, the last term of Eq. (2) contains the contribution to the HF mean field of the electrons belonging to different pairs. It is clear that the weaknesses of this Ansatz is the absence of the interpair electron correlation. Recently [35], a new functional PNOF6, which includes interpair correlations, has been developed. The latter is able to treat orbital delocalization in aromatic systems such as in benzene, a key aspect in radical stabilization. In this work, we study systems in which such effects are not present, so it seems proper to use the PNOF5 approach. Moreover, we

will limit ourselves to the simplest formulation of the functional, i.e., we consider $N_g = 1$. Besides, in the present paper we will fix the n associated with core orbitals to 1.

2.2 The “fragment energy method” (FEM)

We follow the “fragment energy method” (FEM) proposed by Suárez et al. [33], in which the total energy of a molecule \mathbf{P} composed by a linear chain of M interconnected fragments A_i ($A_1 - A_2 - \dots - A_M$) is estimated as the sum of the energy of the fragments. Thus,

$$E(\mathbf{P}) = E_R^F(\mathbf{P}) + \delta E \quad (6)$$

where δE is the error committed by the approximation.

The fragment energy $E_R^F(\mathbf{P})$ is defined according to

$$E_R^F(\mathbf{P}) = E(A_1 - B_1^R) - \sum_{i=1}^{M-1} E(Y_i - B_i^R) + \sum_{i=2}^{M-1} E(Y_{i-1} - A_i - B_i^R) + E(Y_{M-1} - A_M) \quad (7)$$

where B_i^R are buffer regions that include a number of atoms around the fragments according to a well-defined R -dependent criterium (i.e., a distance and a number of monomer units), and Y_i are atoms or functional groups introduced to cap the boundaries upon fragmentation of covalent bonds. For details, we refer to the work of Suarez et al. [33]. The evaluation of fragment energies is less demanding computationally than the evaluation of the energy of the whole molecule. As the size of the buffer region increases, more accurate calculations are performed and smaller δE errors are obtained, but at higher computational cost. We have to take into account that PNOF5 scales as $f(m) \times N^4$ (where $f(m)$ is a prefactor related to the m number of iterations), due to the required four-index transformation of the J and K integrals in the molecular orbital basis (N^4 scaling). At present, the code is time-consuming since the required consistency on the minimization over occupations and coefficients of the natural orbital lead to the need of performing several cycles (large m). Moreover, this scaling prefactor increases with the size of the system. Therefore, there is a big advantage of using fragment energies. The aim of this work is to analyze the convergence of these errors with the fragment sizes for PNOF5 method.

3 Results and discussion

Geometries were optimized at the B3LYP/6-31+G(d) [36] level of theory using the GAUSSIAN09 program package [37]. For the $(\text{FH})_n$ clusters, we first optimized the $(\text{FH})_8$ cluster,

and the rest of geometries were taken by deleting FH units, to prevent the collapse of the cluster of lower size to geometries other than zigzag ones. All PNOF5 calculations have been carried out using our computational code DoNOF with the 6-31G and 6-31G(d,p) basis set [38] and the correlation-consistent valence double- ζ (cc-pVDZ) developed by Dunning et al. [39]. The matrix element of the kinetic energy and nuclear attraction terms, as well as the electron repulsion integrals, are inputs to our computational code. In the current implementation, we have used the GAMESS program [40, 41] for this task. The convergence criteria applied for PNOF solutions is 10^{-8} a.u. in the energy and 10^{-5} for the tolerance of the hermiticity of the matrix of Lagrange multipliers λ (see reference [32] for details on the iterative diagonalization procedure).

3.1 Polyalkene chain $\text{C}_n\text{H}_{2n+2}$

PNOF5/6-31G energies for oligomers of size $n = 1, 10$ and PNOF5/cc-pVDZ energies for $n = 1, 8$ can be found in Table 1. In order to calculate fragment energies, we will particularize Eq. (7) for the $\text{C}_n\text{H}_{2n+2}$ oligomers. In this case, the fragments are constituted by $A_i = -(\text{CH}_2)_i-$ units and the terminal $-\text{CH}_3$. H atoms are used to cap the boundaries upon fragmentation ($Y_i = \text{H}$). Finally, the buffer region is constituted by a number of $-\text{CH}_2-$ units, namely $B_i^R = -(\text{CH}_2)_R - \text{H}$. For this particular case, Eq. (7) can be cast as

$$E_R^F(\mathbf{P}_n) = E(\mathbf{P}_{R+1}) + (n - R - 1)[E(\mathbf{P}_R) - E(\mathbf{P}_{R-1})] \quad (8)$$

where n is the order of the oligomer. Equation (8) implies that the evaluation of fragment energy of a n -size oligomer with a R -buffer region requires the calculation of three oligomers of size $R + 1$, R and $R - 1$. Therefore, the size of the buffer region determines the size of the largest oligomer in the fragment energy calculation. Obviously, the larger the R -size, the more accurate the results, but also the higher computational cost. The formula above can be further simplified by taking into account that $E(\mathbf{P}_R) - E(\mathbf{P}_{R-1})$ is a measure of the bond energy between fragments, and this bond energy can also be estimated more accurately by $E(\mathbf{P}_{R+1}) - E(\mathbf{P}_R)$. Hence,

$$E_R^F(\mathbf{P}_n) = (n - R)E(\mathbf{P}_{R+1}) - (n - R - 1)E(\mathbf{P}_R) \quad (9)$$

For convenience, we will use the index l for the largest oligomer size in fragment calculations, namely

$$E_l^F(\mathbf{P}_n) = (n - l + 1)E(\mathbf{P}_l) - (n - l)E(\mathbf{P}_{l-1}) \quad (10)$$

In summary, the evaluation of a fragment energy requires the evaluation of the energy for two oligomers of size l and $l - 1$. The size of the largest oligomer in the fragment calculations is determined by the size of the buffer region according to $l = R + 1$.

Table 1 PNOF5/6-31G energies $E(P_n)$ and fragment energies $E_l^F(P_n)$ (Eq. 10), in a.u., for the C_nH_{2n+2} oligomers, and the corresponding error, δE , in kcal/mol

6-31G				cc-pVDZ				6-31G(d,p)			
n	$E(P_n)$ (a.u.)	1	$\delta E/n$ (kcal/mol)	n	$E(P_n)$ (a.u.)	1	$\delta E/n$ (kcal/mol)	n	$E(P_n)$ (a.u.)	1	$\delta E/n$ (kcal/mol)
1	-40.24169045			1	-40.25889725			1	-40.262046		
2	-79.30382845			2	-79.34030290			2	-79.344005		
3	-118.367272	2	-0.273	3	-118.422678	2	-0.203	3	-118.426983	2	-0.213
4	-157.430646	2	-0.399	4	-157.505028	2	-0.300	4	157.509836	2	-0.300
		3	0.011	4		3	0.004			3	0.020
5	-196.493955	2	-0.466	5	-196.587301	2	-0.349	5	-196.592634	2	-0.345
		3	0.026			3	0.016			3	0.038
		4	0.008			4	0.010			4	0.007
6	-235.557275	2	-0.512	6	-235.669573	2	-0.382	6	-235.675439	2	-0.376
		3	0.034			3	0.024			3	0.050
		4	0.012			4	0.016			4	0.011
		5	-0.001			5	0.000			5	0.000
7	-274.620592	2	-0.545	7	-274.751846	2	-0.405				
		3	0.041			3	0.030				
		4	0.016			4	0.021				
		5	-0.002			5	0.000				
		6	0.000			6	0.000				
8	-313.683917	2	-0.570	8	-313.834122	2	-0.422				
		3	0.045			3	0.034				
		4	0.018			4	0.024				
		5	-0.003			5	0.000				
		6	0.000			6	0.000				
		7	-0.001			7	0.000				
9	-352.747238	2	-0.589								
		3	0.048								
		4	0.019								
		5	-0.003								
		6	0.000								
		7	-0.001								
		8	0.000								
10	-391.810562	2	-0.604								
		3	0.051								
		4	0.021								
		5	-0.004								
		6	0.000								
		7	-0.001								
		8	0.000								
		9	0.000								

Geometries were optimized at the B3LYP/6-31+G(d) level of theory

As mentioned above, the aim of this work is to determine how fragment energies converge to the exact PNOF5 energy for a given size of the oligomer as function of l . Fragment energies, $E_l^F(\mathbf{P}_n)$, for the oligomers of size ($n = 3, 10$) calculated with the 6-31G basis set can be found in Table 1,

along with the difference between the two energies per oligomer unit, $\delta E/n$, in kcal/mol. In Fig. 1, we represent $\delta E/n$ as a function of the largest oligomer size (l) used in the fragment calculation. Calculations were repeated with the cc-pVDZ basis set for $n = (3, 8)$ and 6-31G(d,p) basis set

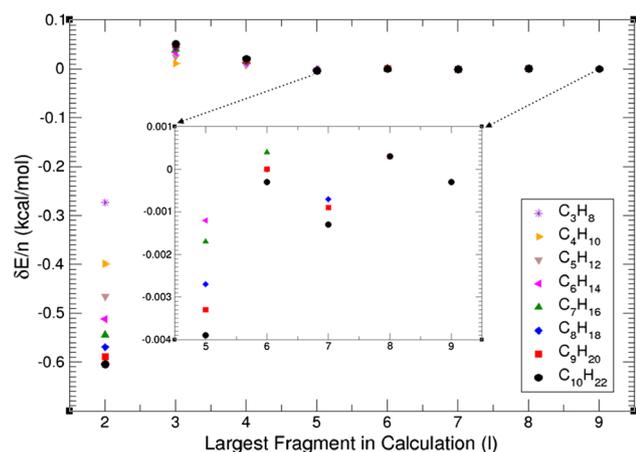


Fig. 1 Difference in energy between oligomer energy ($E(\mathbf{P}_n)$) and fragment energies ($E_l^F(\mathbf{P}_n)$) per oligomer size, namely $\delta E/n = [E(\mathbf{P}_n) - E_l^F(\mathbf{P}_n)]/n$, in kcal/mol. Calculations done at the PNOF5/6-31G level of theory for oligomers of size $n = 1, 10$

for ($n = 3, 6$), obtaining similar results. Therefore, we will analyze the PNOF5/6-31G results for which a larger dataset of oligomers was calculated.

There is a very good convergence of the fragment calculations for any of the oligomer size. It is remarkable, that in all cases, we are within chemical accuracy (as defined by an error of <1 kcal/mol per oligomer unit) for any oligomer and fragment size calculation. For instance, if we consider the largest oligomer, namely $C_{10}H_{22}$, the $\delta E/n$ error of the fragment energies for $l = 2, 9$ is $-0.604, 0.051, 0.021, -0.004, 0.000, -0.001, 0.000, 0.000$ kcal/mol, respectively. Thus, the errors in the energy converge very fast and gradually between $l = 2$ to $l = 6$. For higher fragment sizes, we can say that the results are converged within the accuracy of the method.

As expected for a given l , the errors get bigger as the size of the oligomer increases, but it is very relevant that these increases are very low. For instance, if we consider the smallest fragment calculation ($l = 2$), the error obtained for the different oligomer sizes is all within the same order of magnitude. Thus, for $l = 2$, we obtain a $\delta E/n$ of only -0.273 kcal/mol (C_3H_8), -0.399 (C_4H_{10}), -0.466 (C_5H_{12}), -0.512 (C_6H_{14}), -0.545 (C_7H_{16}), -0.570 (C_9H_{20}), -0.589 , -0.604 ($C_{10}H_{22}$).

As one can see from Table 1, the improvement on the basis set implies no dramatic changes, even a slight amelioration of the convergence is observed in fragment energies. There is a very fast and good convergence of PNOF5 fragment energies with fragment size. In all cases when considering $l \approx n/2$, results are very accurate with errors within the chemical accuracy.

It is clear that linear C_nH_{2n+2} oligomers are a very favorable case for fragment energy calculations. This is not

surprising due to the nonpolar nature of the bonds between fragments, and the small interaction expected among the monomers of the chain. Therefore, we decided to investigate a less favorable case: a chain of hydrogen bonds among units with polar bonds: $(FH)_n$.

3.2 Hydrogen-bonded chain $(FH)_n$

This case is a prototypical system bound by a chain of hydrogen bonds. We have constructed a planar zigzag $(FH)_8$ cluster and employed only the cc-pVDZ basis set. The incremental energies per cluster unit are depicted in Fig. 2. As the size of the cluster increases, the energy per FH unit decreases indicating some cooperativity among the whole hydrogen-bonded chain in the hydrogen bond interaction between two neighbor FH units. Notice that as the size of the clusters increases, one should reach a limiting value, still not attained by the size of the clusters of the present work.

Contrary to the alkane series, in this case, the higher the cluster size, the lower the energy per cluster unit. This is expected for a system bound by hydrogen bonds, due to the cooperative nature of the hydrogen bonding network. As the cluster size increases, the increments in energy per cluster unit tend to increase linearly. For instance, at $n = 2$, we obtain a value of 1.9 kcal/mol, and at $n = 8$, a value of 4.9 kcal/mol, at the PNOF5/cc-pVDZ level of theory. Remind that these structures are frozen.

Note that in this case there is no need to introduce cap atoms, since the fragments are constituted by each FH unit. The buffer region will be formed of R -number of FHs. It is straightforward to demonstrate that the fragment energies can be calculated according to a formula analogous to the one used in the previous section, namely

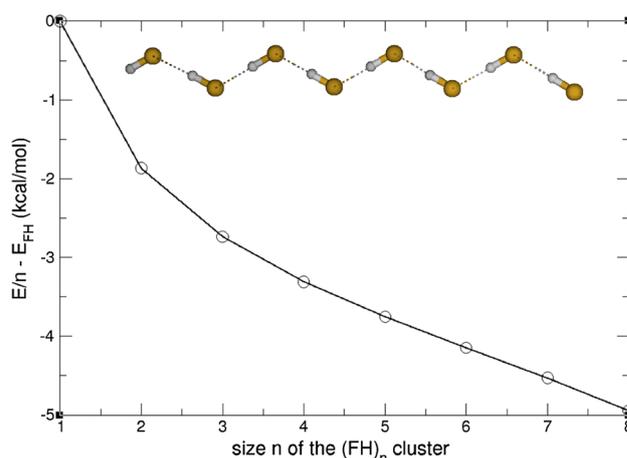


Fig. 2 Energy per oligomer unit (E/n) of the $(FH)_n$ clusters with respect to the energy of the hydrogen fluoride (E_{FH}). Calculations done at the PNOF5/cc-pVDZ level of theory

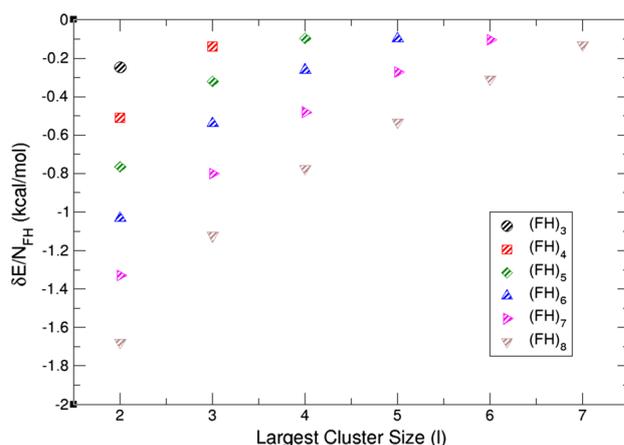
Table 2 PNOF5/cc-pVDZ energies, $E(P_n)$ and fragment energies $E_l^F(P_n)$ (Eq. 11), in a.u., for the $(\text{FH})_n$ clusters, and the corresponding error divided by the number of FH units, $\delta E/N_{\text{FH}}$, in kcal/mol

n	$E(P_n)$ (a.u.)		$\delta E/N_{\text{FH}}$ (kcal/mol)
1	-100.076915	1	
2	-200.159778		
3	-300.243820	2	-0.247
4	-400.328752	2	-0.510
		3	-0.140
5	-500.414457	2	-0.764
		3	-0.320
		4	-0.097
6	-600.501109	2	-1.033
		3	-0.540
		4	-0.261
		5	-0.099
7	-700.588907	2	-1.328
		3	-0.799
		4	-0.480
		5	-0.273
		6	-0.103
8	-800.678348	2	-1.678
		3	-1.123
		4	-0.774
		5	-0.532
		6	-0.309
		7	-0.129

Geometries were optimized at the B3LYP/6-31+G(d) level of theory

$$E_l^F(P_n) = (n - l + 1)E(l) - (n - l)E(l - 1) \quad (11)$$

with $l = R + 1$. Results can be found in Table 2 and Fig. 3. The first aspect to remark is that the errors in fragment energies are bigger than for the alkane series. For instance, the error $\delta E/n$ for the $(\text{FH})_8$ cluster with $l = 4$ is -0.7739 kcal/mol, whereas for C_8H_{16} is one order of magnitude less, 0.0239 kcal/mol. The convergence of fragment energies with l is significantly slower than in the case of $\text{C}_n\text{H}_{2n+2}$. The decay in $\delta E/n$ for $(\text{FH})_8$ with $l = \overline{2, 7}$ is -1.678 , -1.229 , -0.774 , -0.532 , -0.309 , -0.129 kcal/mol, respectively. This is a significant reduction in error but at a much lower rate than for $\text{C}_n\text{H}_{2n+2}$ system. On the other hand, notice that these errors show a systematic behavior, approaching the total energy of the cluster from above, due to the gradual recovery of the cooperative effects in the hydrogen bonding network as the size of the fragments increases and approaches the total size of the cluster. For a given size l , the errors also increase when the cluster grows at a higher rate than in the alkane series; for instance, for $l = 2$ the error in evaluating the energy for $(\text{FH})_n$ increases

**Fig. 3** Error in PNOF5/cc-pVDZ fragment energies, $E_l^F(P_n)$, with respect to the energy of the cluster $E(P_n)$ for the $(\text{FH})_n$ clusters, divided by the number of FH units in the cluster, $\delta E/N_{\text{FH}}$, in kcal/mol

with the value of $n = \overline{3, 8}$ as -0.247 , -0.510 , -0.764 , -1.033 , -1.328 , -1.678 kcal/mol, respectively.

The origin of the worst performance of fragment energies for $(\text{FH})_n$ cluster is the interaction between fragments. The interaction between hydrogen-bonded species is of long range type. Accordingly, the interaction is extended over large number of clusters and gives rise to cooperative effects among the hydrogen bonding network. The use of fragment energies will therefore have a sizable effect. However, in the case of alkane, even though we fragment the molecule through covalent bonds, the apolar nature of the fragments makes them more amenable for fragment calculations. However, one has to highlight that the convergence is still quite good, and considering fragment calculations of size $l \approx n/2$, chemical accuracy is obtained for all the clusters.

4 Conclusions

We can conclude that the size-consistent and localized orbital nature of PNOF5 allows for a good performance of fragment calculations. For fragment calculations of size $l \approx n/2$, the chemical accuracy is obtained for all the clusters, even in the case of hydrogen bond interactions between the units. This leads to very significant computational gains, at least of one order of magnitude. Therefore, the PNOF5-FEM method could be a promising tool to extend the size of systems amenable for PNOF-type calculations.

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References

1. Piris M (2013) *Int J Quantum Chem* 113:620–630
2. Piris M, Ugalde JM (2014) *Int J Quantum Chem* 114:1169–1175
3. Piris M (2006) *Int J Quantum Chem* 106:1093–1104
4. Piris M, Lopez X, Ruipérez F, Matxain JM, Ugalde JM (2011) *J Chem Phys* 134:164102
5. Piris M, Matxain JM, Lopez X (2013) *J Chem Phys* 139(23):234109
6. Matxain JM, Piris M, Ruipérez F, Lopez X, Ugalde JM (2011) *Phys Chem Chem Phys* 13:20129–20135
7. Matxain JM, Piris M, Mercero JM, Lopez X, Ugalde JM (2012) *Chem Phys Lett* 531:272–274
8. Matxain JM, Piris M, Uranga J, Lopez X, Merino G, Ugalde JM (2012) *ChemPhysChem* 13:2297–2303
9. Piris M, Matxain JM, Lopez X, Ugalde JM (2012) *J Chem Phys* 136:174116
10. Lopez X, Ruipérez F, Piris M, Matxain JM, Matito E, Ugalde JM (2012) *J Chem Theory Comput* 8:2646–2652
11. Piris M, Matxain JM, Lopez X, Ugalde JM (2013) *Theor Chem Acc* 132:1298
12. Ruipérez F, Piris M, Ugalde JM, Matxain JM (2013) *Phys Chem Chem Phys* 15:2055–2062
13. Matxain JM, Ruipérez F, Infante I, Lopez X, Ugalde JM, Merino G, Piris M (2013) *J Chem Phys* 138:151102
14. Piris M (1003) *Comput Theor Chem* 2013:123–126
15. Lopez X, Piris M, Nakano M, Champagne B (2014) *J Phys B Atomic Mol Opt Phys* 47:015101
16. Piris M, March NH (2014) *Phys Chem Liq* 52:804–814
17. Ramos-Cordoba E, Salvador P, Piris M, Matito E (2014) *J Chem Phys* 141:234101
18. Piris M, March NH (2015) *Phys Chem Liq*. doi:10.1080/00319104.2015.1029478
19. Ludeña EV, Torres FJ, Costa C (2013) *J Mod Phys* 04:391–400
20. Pernal K (1003) *Comput Theor Chem* 2013:127–129
21. Piris M (2013) *J Chem Phys* 139:064111
22. Fock FA (1950) *Dokl Akad Nauk USSR* 73:735
23. Hurley AC, Lennard-Jones J, Pople JA (1953) *Proc R Soc Lond A* 220:446–455
24. Heitler W, London F (1927) *Z Phys* 44:455
25. Shaik S, Hiberty PC (2008) *A chemist's guide to valence bond theory*. Wiley, London
26. Surjan PR (1999) *Topics in current chemistry*, vol 203. Springer, Berlin
27. Jeszenszki P, Nagy PR, Zoboki T, Szabados A, Surjan PR (2014) *Int J Quantum Chem* 114:1048–1052
28. Coleman AJ (1963) *Rev Mod Phys* 35:668–687
29. Rassolov VA (2002) *J Chem Phys* 117:5978
30. Rassolov VA, Xu F (2007) *J Chem Phys* 127:044104
31. Piris M (2007) In: Mazziotti DA (ed) *Reduced-density-matrix mechanics: with applications to many-electron atoms and molecules*. Wiley, Hoboken, pp 387–427 chapter 14
32. Piris M, Ugalde JM (2009) *J Comput Chem* 30:2078–2086
33. Suárez E, Díaz N, Suárez D (2009) *J Chem Theory Comput* 9:1667–1679
34. Piris M (1999) *J Math Chem* 25:47–54
35. Piris M (2014) *J Chem Phys* 141:044107
36. Zhao Y, Truhlar DG (2008) *Theor Chem Acc* 120:215–241
37. Gaussian 09, Revision D.01, Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ, Gaussian, Inc., Wallingford CT, 2009
38. Hehre WJ, Ditchfield R, Pople JA (1972) *J Chem Phys* 56:2257–2261
39. Dunning TH, Dunning TH Jr (1989) *J Chem Phys* 90:1007–1023
40. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Shyjun SU, Dupuis M, Montgomery JA (1993) *J Comput Chem* 14:1347–1363
41. Gordon MS, Schmidt MW (2005) *Theory and applications of computational chemistry*. Elsevier, Philadelphia