The dynamic electron-correlation energy in the NOF-MP2 method from the orbital-invariant perturbation theory

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The original formulation (Phys. Rev. Lett. 119, 063002, 2017) of the natural orbital functional - second-order Möller–Plesset (NOF-MP2) method is based on the MP2 that uses the canonical Hartree-Fock molecular orbitals. The current work presents a reformulation of the dynamic energy correction based on the orbital-invariant MP2, which allows to attain both dynamic and static correlations even for those systems with strong orbital localizability and significant multiconfigurational character. To improve the reference Slater determinant formed with natural orbitals, the natural orbital functional that generates them is also modified to take into account only the inter-pair static correction. This more general NOF-MP2 is able to dissociate properly noble gas dimers, which remain as non-bound species within the canonical formulation. Test calculations in a selected set of 30 polyatomic molecules demonstrate a substantial improvement not only of the relative energies but also of the total energies calculated with the NOF-MP2 method.

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A reliable electronic structure method must be able to describe in a balanced way both static (non-dynamic) and dynamic electron correlation [1, 2]. Recently [3], a single-reference global method for electron correlation was introduced taking as reference the Slater determinant of natural orbitals (NOs) obtained from an approximate natural orbital functional (NOF) [4]. In this approach, the total energy is formed as \( \tilde{E}_{HF} + E^{\text{dyn}} + E^{\text{sta}} \), where \( \tilde{E}_{HF} \) is the Hartree-Fock (HF) energy obtained with NOs, the dynamic energy \( E^{\text{dyn}} \) is derived from a modified second-order Möller–Plesset perturbation theory (MP2), and the non-dynamic energy \( E^{\text{sta}} \) is obtained from the static component of the NOF.

The success of the method, called NOF-MP2, is determined by the NOs used to generate the reference. In [3], orbitals were obtained from the Piris natural orbital functional 7 (PNOF7) there proposed, an interacting-pair model that recovers the intra-pair but only static inter-pair correlation. As a consequence, PNOF7 NOs can be localized in certain regions of space, depending on the degree of interaction between the electron pairs. When the inter-pair non-dynamic correlation is negligible, these orbitals turn out to be close to the known NOs of the independent-pair model (PNOF5) [3]. In general, NOs will be located in those regions where their atomic orbitals responsible for the intra-pair and static correlation are found. It is worth noting that localized NOs provide an orbital picture with a clear chemical meaning [6] that is not easy to obtain using canonical orbitals.

On the other hand, \( E^{\text{dyn}} \) was formulated [3] from traditional MP2 energy that involves the use of canonical HF molecular orbitals, therefore, a reformulation of dynamic energy correction is necessary so that any type of orbital can be used. Perturbation theory with non-canonical orbitals (in most cases localized orbitals) has been used formerly [7, 8] in order to speed up processing times. As Pulay pointed out [9], the increase in computational cost associated with the increase in the number of electrons is not justified and is mainly due to the use of canonical orbitals. In the last three decades, the orbital localizability has been exploited by several approaches known as linear-scaling methods [10]. The latter have extended the applicability of wavefunction-based correlation methods to larger electronic systems. Consequently, an additional motivation for a reformulation of \( E^{\text{dyn}} \) is the possibility of computer savings.

The present work pursues two objectives. On the one hand, improve NOs with which the reference determinant is built and, on the other hand, propose a correction \( E^{\text{dyn}} \) based on the orbital-invariant (oi) MP2 energy. As a result, a new variant of the method we will call NOF-oiMP2 emerges, whereas from now on we will refer to the original version as NOF-cMP2.

In NOF theory [11, 12], the ground-state electronic energy \( E \) is given in terms of the NOs \( \{ \phi_i \} \) and their occupation numbers (ONs) \( \{ n_i \} \). Unfortunately, the exact reconstruction \( E[\{ n_i, \phi_i \}] \) has been an unattainable goal so far, therefore we are talking about orbitals that diagonalize the one-particle reduced density matrix (1-RDM) corresponding to an approximate ground-state energy, and it is more appropriate to talk about NOF instead of a 1-RDM functional due to the existing dependence on the reconstructed two-particle RDM (2-RDM).

Restrictions on the ONs to the range \( 0 \leq n_i \leq 1 \) represent the necessary and sufficient conditions for ensemble N-representability of 1-RDM [13] under the normalization condition \( \sum_i n_i = N \). Note that we focus on the N-representability problem for statistical one-matrix ensembles, since to guarantee the pure-state N-representability conditions [14, 15] only 1-RDM ensem-
ble constraints are necessary if $E\{\{n_i, \phi_i\}\}$ is a pure N-representable functional \[16, 17\].

In approximate one-particle theories, the 2-RDM plays a dominant role that determines the functional N-representability \[18\]. The use of 2-RDM ensemble N-representability conditions \[19\] for generating a reconstruction functional was proposed in Ref. \[19\], where auxiliary matrices $\triangle$ and $\Pi$ were introduced to reconstruct the two-particle cumulant \[20\]. In this communication, we address only singlet states and adopt a restricted spin theory, so that energy reads

$$E = 2 \sum n_p \mathcal{H}_{pp} + \sum \Pi_{pq} \mathcal{L}_{pq} + \sum (n_q n_p - \Delta_{qp}) (2J_{pq} - K_{pq})$$

where $\mathcal{H}_{pp}$ denotes the diagonal elements of the core-Hamiltonian, while $J_{pq}$, $K_{pq}$, and $\mathcal{L}_{pq}$ are the direct, exchange, and exchange-time-inversion integrals \[21\]. Appropriate forms of matrices $\triangle$ and $\Pi$ lead to different implementations known in the literature as PNOFi ($i=1-7$) \[3, 22, 23\]. Remarkable is the case of PNOF5 \[24, 25\] which turned out to be pure N-representable \[26, 27\].

The conservation of the total spin allows to derive the diagonal elements $\Delta_{qp} = n_q^2$ and $\Pi_{pp} = n_p^2$. The 2-RDM N-representability $\triangle$ and $Q$ conditions lead to inequalities $\Delta_{qp} \leq n_q n_p$ and $\Delta_{qp} \leq h_q h_p$ \[19\], where $h_p = 1 - n_p$. To fulfill the $G$ condition, the off-diagonal elements of the $\Pi$-matrix must satisfy the constraint \[20\]

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

For a given approximation of $\Delta_{qp}$, it is evident that the modulus of $\Pi_{qp}$ is determined from Eq. \[2\] assuming the equality, however, there is no hint to determine the sign of $\Pi_{qp}$. The requirement that for any two-electron singlet the NOF \[1\] yields the accurate energy expression obtained from the exact wavefunction \[28\], implies \[20\] that $\Delta_{qp} = n_q n_p$ and $|\Pi_{qp}| = \sqrt{n_q n_p}$, respectively. Furthermore, the phase factor of $\Pi_{qp}$ can be $+1$ if $q, p \in (1, \infty)$, and $-1$ otherwise.

To achieve a model of independent pairs with $N>2$, the orbital space $\Omega$ is divided into $N/2$ mutually disjoint subspaces $\Omega_g$, so each subspace contains one orbital $g$ below the level $N/2$, and $N_g$ orbitals above it, which is reflected in additional sum rules for the ONs ($\sum n_g = 1, p \in \Omega_g$). In what follows, let’s consider $N_g$ equal to a fixed number that corresponds to the maximum value allowed by the basis set used. Keeping $\Delta_{qp} = n_q n_p$, and generalizing the two-electron expression for off-diagonal elements of $\Pi$-matrix, namely, $\Pi_{qp}^2 = \sqrt{n_q n_p}$ if $q, p > N/2$, and $\Pi_{qp}^2 = -n_q n_p$ if $q=g$ or $p=g$, we obtain the extended PNOF5 \[25\].

In Ref. \[3\], non-zero $\Pi_{qp}$ elements were considered among orbitals belonging to different subspaces \[3\], whereas $\Delta_{qp} = 0$. From Eq. \[2\] follows that provided the $\Delta_{qp}$ vanishes, $|\Pi_{qp}| \leq \Phi_q \Phi_p$ with $\Phi_q = \sqrt{n_q h_q}$. Assuming equality, and generalization of the sign convention adopted for extended PNOF5, i.e., $\Pi_{qp}^2 = \Phi_q \Phi_p$, if $q, p > N/2$, and $\Pi_{qp}^2 = -\Phi_q \Phi_p$ otherwise, led to PNOF7 \[3\].

Another possible option, that favors decreasing of the energy \[1\], is to consider all the inter-pair factors negative, ergo, $\Pi_{qp}^2 = -\Phi_q \Phi_p$. Recently \[31\], we have analyzed several examples with strong static correlation, specifically, the one-dimensional Hubbard model with up to 14 sites and rings with up to 16 hydrogens. Comparing with accurate diagonalization calculations, our results indicate that all negative inter-pair factors is a better option.

In addition, it would be convenient to take into account the inter-pair static correlation in the NOF from the outset, thus preventing the ONs and NOs from suffering an inter-pair non-dynamic influence, however small, in the dynamic correlation domains. Taking into account the $f$-$g$-th inter-pair static correlation energy \[3\],

$$E_{fg}^\text{sta} = \sum_{p \in \Omega_f} \sum_{q \in \Omega_g} 4\Phi_p \Phi_q \Pi_{qp}^2 \mathcal{L}_{pq} = \sum_{p \in \Omega_f} \sum_{q \in \Omega_g} \Pi_{qp}^2 \mathcal{L}_{pq},$$

we attain the new NOF:

$$E = \sum_{g=1}^{N/2} [n_p (2\mathcal{H}_{pp} + J_{pp}) + \sum \Pi_{qp}^2 \mathcal{L}_{pq}]$$

$$+ \sum_{f \neq g} \sum_{p \in \Omega_f} \sum_{q \in \Omega_g} [n_q n_p (2J_{pq} - K_{pq}) + \Pi_{qp}^2 \mathcal{L}_{pq}]$$

where $\Pi_{qp}^2 = -4n_q h_q n_p h_p$. This new approach will henceforth refer to as PNOF7s and will provide the reference NOs to form $E_{hf}$ in the NOF-oiMP2 method. The "s" emphasizes that this interacting-pair model takes into account only the static correlation between pairs, and therefore avoids double counting in the regions where the dynamic correlation predominates, already in the NOF optimization.

Like PNOF7, PNOF7s produces qualitatively correct potential energy curves (PECs) for the dozen diatomic molecules studied in reference \[3\]. These systems cover a wide range of values for binding energies ($D_e$) and bond lengths ($R_e$), however, in all cases the correct dissociation limit implies an homolytic cleavage of the bond with high degree of degeneracy effects. In Table \[3\] a comparison between both functionals is shown. The experimental bond lengths are taken from the National Institute of Standards and Technology (NIST) Database \[32\], whereas the experimental dissociation energies result from a combination of Refs. \[32\] and \[33\]. The correlation-consistent valence triple-$\zeta$ basis set (cc-pVTZ) developed by Dunning \[34\] was used throughout, except for the anionic species where the augmented basis set (aug-cc-pVTZ) was used.

Table \[3\] shows a slight shortening of the equilibrium distances obtained with PNOF7s compared to those obtained with PNOF7, whereas the dissociation energies experience a slight increase, except in the cases of $N_2$ and CN$^-$. These minor effects are related to the prevention of considering non-dynamic correlation between
pairs in the equilibrium regions where the dynamic correlation prevails, and should lead to an improvement in the $R_e$ and $D_e$ calculated with the NOF-MP2 method. As was pointed out in Ref. [3], the results are in good agreement with the experiment for the smaller diatomics, for which the electron correlation effect is almost entirely intrapair. When the number of pairs increases, the theoretical value deteriorates especially for the dissociation energies. This is related to a better description of the asymptotic region with respect to the equilibrium, therefore it is necessary to add the dynamic electron correlation between pairs.

Now we focus on the reformulation of $E^{\text{dyn}}$. In the mid eighties, Pulay and Saebø introduced an orbital invariant formulation of MP2, the details of which can be found elsewhere [7, 35]. The first-order wavefunction is a linear combination of all doubly excited configurations, and their amplitudes $T_{pq}^{(f)}$ are obtained by solving the equations for the MP2 residuals. The MP2 energy correction takes the form

$$E^{(2)} = \sum_{g,f=1}^{N/2} \sum_{p,q>N/2} \langle gf | pq \rangle \left[ 2T_{pq}^{(f)} - T_{pq}^{(g)} \right]$$

where $M$ is the number of basis functions, and $\langle gf | pq \rangle$ are the matrix elements of the two-particle interaction. In NOF-cMP2, $E^{\text{dyn}}$ is obtained as the canonical $E^{(2)}$ modified to avoid double counting of the electron correlation [3]. The latter is divided into intra- and inter-pair contributions, and the amount of dynamic correlation in each orbital $p$ is defined by functions $C_p$, of its occupancy, namely,

$$C_{\text{intra}}^p = \begin{cases} 1 - 4h_p^2 & p \leq N/2 \\ 1 - 4n_p^2 & p > N/2 \end{cases}$$

$$C_{\text{inter}}^p = \begin{cases} 1 & p \leq N/2 \\ 1 - 4h_p n_p & p > N/2 \end{cases}$$

where $h_p$ and $n_p$ are the number of occupied and virtual MOs of the orbital $p$, respectively, in the active space. According to Eq. (6), fully occupied and empty orbitals yield a maximal contribution to dynamic correlation, whereas orbitals with half occupancies contribute nothing. It is worth noting that $C_{\text{inter}}^p$ is not considered if the orbital is below $N/2$. Using these functions as the case may be (intra-pair or inter-pair), we define modified off-diagonal elements of the Fock matrix (\(\tilde{\mathcal{F}}\)) as

$$\tilde{\mathcal{F}}_{pq} = \begin{cases} C_{pq}^{\text{intra}} C_p^{\text{intra}} \mathcal{F}_{pq}, & p, q \in \Omega \\ C_{pq}^{\text{inter}} C_p^{\text{inter}} \mathcal{F}_{pq}, & \text{otherwise} \end{cases}$$

(7)

as well as modified two-electron integrals:

$$\langle pq | rt \rangle = \begin{cases} C_{pq}^{\text{intra}} C_{pq}^{\text{intra}} C_r^{\text{intra}} \langle pq | rt \rangle, & p, q, r, t \in \Omega \\ C_{pq}^{\text{inter}} C_{pq}^{\text{inter}} C_r^{\text{inter}} \langle pq | rt \rangle, & \text{otherwise} \end{cases}$$

(8)

where the subspace index $q = 1, \ldots, N/2$. This leads to the following linear equation for the modified MP2 residuals

$$\tilde{R}_{ij}^{(f)} = \langle ab | ij \rangle + (\mathcal{F}_{aa} + \mathcal{F}_{bb} - \mathcal{F}_{ii} - \mathcal{F}_{jj}) T_{ij}^{(f)} + \sum_{c \neq a} \tilde{T}_{ac}^{(f)} T_{cj}^{(f)} + \sum_{c \neq b} \tilde{T}_{bc}^{(f)} T_{cj}^{(f)} - \sum_{k \neq i} \tilde{T}_{ik}^{(f)} T_{kj}^{(f)} - \sum_{k \neq j} \tilde{T}_{ik}^{(f)} T_{kj}^{(f)} = 0$$

(9)

where $i, j, k$ refer to the strong occupied NOs, and $a, b, c$ to weak occupied ones. It should be noted that diagonal elements of the Fock matrix ($\tilde{\mathcal{F}}$) are not modified.

By solving the linear system of equations (9) the amplitudes $T_{pq}^{(f)}$ are obtained, which are inserted into the Eq. (3) to achieve $E^{\text{dyn}} = E^{(2)}$. Following Ref. [3], the total energy of the system will be given by

$$E = \tilde{E}_{hf} + E^{\text{corr}} = E_{hf} + E^{\text{sta}} + E^{\text{dyn}}$$

(10)

where $\tilde{E}_{hf}$ is the HF energy obtained with the NOs of PNOF7s, Eq. (4), and $E^{\text{sta}}$ is the sum of energies (5),

$$E_{\text{stat}}^{\text{inter}} = \sum_{f \neq g} E_f^{\text{stat}} = \sum_{f \neq g} \sum_{p \in \Omega_f, q \in \Omega_g} \Pi_{qp}^{*} \mathcal{L}_{pq} \, \sum_{f \neq g}$$

(11)
plus the static intra-pair electron correlation energy 3,

\[ E_{\text{intra}} = \frac{N}{2} \sum_{g=1}^{N/2} \sum_{p=1}^{\Omega_g} \sqrt{\Lambda_g \Lambda_p \Pi_{qp} \Lambda_{pq}} \]  

(12)

In Eq. (12), note that \( q, p \in \Omega_g \), and \( \Lambda_p = 1 - |1 - 2n_p| \) is the amount of intra-pair static electron correlation in each orbital \( p \) as a function of its occupancy.

The performance of NOF-oiMP2 has been tested in several examples. Let’s start with noble-gas dimers, which are held together by dispersion, a manifestation of long-range dynamic correlation. These species are not bound at the PNOF7 level of theory, and they remain so even after adding \( E_{\text{dyn}} \) using the canonical formulation. With the new formulation of \( E_{\text{dyn}} \) based on the orbital-invariant MP2, the orbital localizability in noble-gas atoms can now be taking into account, so that NOF-oiMP2 predicts bound species.

Figure 1: Potential energy curves of noble-gas dimers calculated at the NOF-oiMP2/aug-cc-pVTZ level of theory. The zero-energy point has been set at 10 Å for each system.

| Dimer  | MP2   | NOF-oiMP2       | Experiment |
|--------|-------|-----------------|------------|
|        | \( R_e \) | \( D_e \)       | \( R_e \) | \( D_e \) | \( R_e \) | \( D_e \) |
| He\(_2\) | 3.09   | 0.013           | 3.12      | 0.013     | 2.97      | 0.022     |
| HeNe   | 3.12   | 0.038           | 3.17      | 0.035     | 3.03      | 0.041     |
| Ne\(_2\) | 3.18   | 0.076           | 3.21      | 0.074     | 3.09      | 0.084     |

The potential energy curves (PECs) of He\(_2\), HeNe and Ne\(_2\) are depicted in Fig. 1. For each of the curves, the zero-energy point has been set at their corresponding energy at 10 Å. It can be seen that NOF-oiMP2 produces qualitatively correct PECs. In Table II the equilibrium bond lengths (\( R_e \)) and dissociation energies (\( D_e \)) at the MP2 and NOF-oiMP2 levels of theory can be found. The experimental values were taken from Ref. [36]. The augmented correlation-consistent valence triple-\( \zeta \) basis set (aug-cc-pVTZ) [37, 38] was used in theoretical calculations. It is worth noting that larger basis set is needed to adequately compare them with the experiment. In addition, only valence electrons have been included in the correlation treatment. It can be observed that both methods underestimate the binding energies and overestimate the equilibrium distances, being these effects more perceptible for the NOF-oiMP2. He\(_2\) is the worst case since only a 60\% of the binding energy is recovered, while for the other two systems it is between 85-92\%.

Figure 2: Potential energy curves with homolytic cleavage of the bond calculated at the NOF-oiMP2/cc-pVTZ level of theory. The zero-energy point has been set at 10 Å for each system.

There are no significant differences between the results obtained with NOF-cMP2 and NOF-oiMP2 methods for diatomic systems analyzed in Table I. Representative PECs of these molecules are depicted in Fig. 2. Table III collects the electronic properties previously analyzed for systems showed in Fig. 1. The data reveals an outstanding improvement in the dissociation energies with respect to PNOF7 and PNOF7s, respectively. A slight improvement of the theoretical equilibrium distances calculated with NOF-oiMP2 is also observed over those obtained with NOF-cMP2.

The situation is quite different in polyatomic systems where the orbital localizability changes drastically the results obtained with NOF-cMP2 and NOF-oiMP2. Both methods have been tested on a set of 30 selected molecules with a dominant dynamic electron correlation to compare with reliable MP2 energies. We must be aware that the applicability of standard MP2 is restricted to cases without static correlation, otherwise, we obtain an excess of correlation energy. An example is the case of ozone which has an important multiconfigurational character. In this case, NOF-oiMP2 predicts a total energy that is about 57 kcal/mol higher than the MP2 value for the cc-pVTZ basis set [34]. Consequently, an upper bound to the total MP2 energy can be expected in most
Table III: Comparison between NOF-cMP2 and NOF-oiMP2 using the cc-pVTZ basis set. \( ^{(a)} \) aug-cc-pVTZ was used.

| Molecule   | \( R_e \) (Å) | \( D_e \) (kcal/mol) |
|------------|--------------|---------------------|
|            | NOF-cMP2     | NOF-oiMP2 | Exp. | NOF-cMP2 | NOF-oiMP2 | Exp. |
| F\(_2\)    | 1.397        | 1.382     | 1.412 | 34.5     | 46.0     | 39.2 |
| HF         | 0.924        | 0.916     | 0.917 | 139.4    | 140.9    | 141.1 |
| LiF        | 1.614        | 1.579     | 1.564 | 140.7    | 141.1    | 139.0 |
| N\(_2\)    | 1.084        | 1.098     | 1.098 | 224.2    | 230.7    | 228.3 |
| CN\(^{(a)}\) | 1.180       | 1.180     | 1.177 | 238.6    | 239.0    | 240.7 |

Table IV: Comparison of total electronic energies, in Hartrees, calculated using the cc-pVTZ basis set at the experimental geometry.

| No. | Molecule   | NOF-cMP2 | NOF-oiMP2 | MP2 |
|-----|------------|----------|-----------|-----|
| 1   | H\(_2\)O   | -76.316438 | -76.317906 | -76.320480 |
| 2   | NH\(_3\)   | -56.447022 | -56.452165 | -56.454549 |
| 3   | CH\(_4\)   | -40.404095 | -40.411188 | -40.412721 |
| 4   | HCN        | -93.212795 | -93.216612 | -93.223664 |
| 5   | C\(_2\)H\(_2\) | -77.148255 | -77.154876 | -77.160778 |
| 6   | PH\(_3\)   | -342.643167 | -342.657773 | -342.661029 |
| 7   | Si\(_2\)H\(_6\) | -581.624090 | -581.641714 | -581.643376 |
| 8   | H\(_2\)Si  | -115.494590 | -115.514704 | -115.519139 |
| 9   | H\(_2\)S   | -398.885411 | -398.903604 | -398.907289 |
| 10  | C\(_2\)H\(_4\) | -78.378826 | -78.397165 | -78.401267 |
| 11  | CH\(_3\)OH | -115.494590 | -115.514704 | -115.519139 |
| 12  | H\(_2\)O\(_2\) | -151.308915 | -151.325929 | -151.334177 |
| 13  | BF\(_3\)   | -324.146891 | -324.165476 | -324.172517 |
| 14  | C\(_2\)H\(_6\) | -79.603872 | -79.628190 | -79.631938 |
| 15  | CH\(_3\)NH\(_2\) | -95.631675 | -95.655525 | -95.659988 |
| 16  | N\(_2\)H\(_4\) | -111.629997 | -111.656518 | -111.661187 |
| 17  | H\(_2\)Cl   | -535.339074 | -535.356795 | -535.363297 |
| 18  | C\(_2\)H\(_4\) | -116.358023 | -116.383694 | -116.392120 |
| 19  | CH\(_3\)Cl  | -499.486888 | -499.518970 | -499.522907 |
| 20  | CH\(_2\)SH  | -438.083227 | -438.117335 | -438.123037 |
| 21  | C\(_2\)FH\(_3\) | -177.487929 | -177.523874 | -177.532492 |
| 22  | CH\(_3\)OCH\(_3\) | -154.670334 | -154.703999 | -154.727219 |
| 23  | C\(_2\)H\(_6\) | -117.566157 | -117.614170 | -117.629057 |
| 24  | C\(_2\)H\(_4\)O | -154.450942 | -153.496429 | -153.504674 |
| 25  | H\(_2\)C\(_2\)F\(_3\) | -337.770010 | -337.814755 | -337.824683 |
| 26  | C\(_2\)H\(_4\)N | -133.585955 | -133.635764 | -133.643763 |
| 27  | COF\(_2\)  | -312.560599 | -312.607818 | -312.620274 |
| 28  | CO\(_2\)   | -188.240066 | -188.301643 | -188.311990 |
| 29  | OCS        | -510.822787 | -510.879404 | -510.891218 |
| 30  | BCl\(_3\)  | -1403.962819 | -1404.036515 | -1404.045130 |

cases, since a fraction, however small, of non-dynamic correlation is present.

The collection of total energies for the selected set of molecules, calculated at their experimental geometries using the cc-pVTZ basis set [34], can be found in Table IV. For the whole set, the average differences in the NOF-cMP2 and NOF-oiMP2 energies from MP2 are 34.5, and 6.3 mHartree, respectively. The data reveals an outstanding improvement in the total energies of the NOF-oiMP2 over the NOF-cMP2.

To summarize, it has been shown that a reformulation of the dynamic electron-correlation energy based on the orbital-invariant MP2 allows to extend the NOF-MP2 method to any type of orbitals, including the typical localized orbitals of electron-pair-based NOFs. The global character of the method was demonstrated in terms of relative and total energies, since the dynamic and static correlation can be recovered in one shot for any type of system, including weakly bound van der Waals species.

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