Global Method for Electron Correlation

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The current work presents a new single-reference method for capturing at the same time the static and dynamic electron correlation. The starting-point is a determinant wavefunction formed with natural orbitals obtained from a new interacting-pair model. The latter leads to a natural orbital functional (NOF) capable of recovering the complete intra-pair, but only the static inter-pair correlation. Using the solution of the NOF, two new energy functionals are defined for both dynamic ($E^{\text{dyn}}$) and static ($E^{\text{sta}}$) correlation. $E^{\text{dyn}}$ is derived from a modified second-order Møller–Plesset perturbation theory (MP2), while $E^{\text{sta}}$ is obtained from the static component of the new NOF. Double counting is avoided by introducing the amount of static and dynamic correlation in each orbital as a function of its occupation. As a result, the total energy is represented by $E_{\text{hf}} + E^{\text{dyn}} + E^{\text{sta}}$, where $E_{\text{hf}}$ is the Hartree-Fock energy obtained with natural orbitals. The new procedure called NOF-MP2 scales formally as $O(M^5)$ ($M$: number of basis functions), and is applied successfully to the homolytic dissociation of a selected set of diatomic molecules, paradigmatic cases of near-degeneracy effects. Its size-consistency has been numerically demonstrated for singlets. The values obtained are in good agreement with the experimental data.

In electronic structure theory, accurate solutions require a balanced treatment of both static (non-dynamic) and dynamic correlation. Static correlation generally implies a limited number of nearby delocalized orbitals with significant fractional occupations. Conversely, dynamic correlation involves a large number of orbitals and configurations, each with a small weight.

Nowadays, it is necessary to resort to multi-reference methods for correctly handling both types of correlation, however, these techniques are often expensive and demand prior knowledge of the system. On the other hand, single-reference correlation methods are well-established for dynamic correlation, but are unsatisfactory for systems with static correlation. The aim of this work is to propose a single-reference method capable of achieving both dynamic and static correlation even for those systems with significant multiconfigurational character.

In our approach, a natural orbital functional (NOF) is firstly used for capturing all static correlation effects. Then, the total energy is approximated as $E_{\text{hf}} + E^{\text{dyn}} + E^{\text{sta}}$, where $E_{\text{hf}}$ is the Hartree-Fock energy obtained with natural orbitals. The dynamic energy correction ($E^{\text{dyn}}$) is derived from a properly modified second-order Møller–Plesset perturbation theory (MP2), while the non-dynamic correction ($E^{\text{sta}}$) is obtained from the pure static component of the new NOF. Let’s start with the NOF.

In NOF theory, the spectral decomposition of the one-particle reduced density matrix ($\Gamma = \sum_{i} n_i |\phi_i \rangle \langle \phi_i|$) is used to approximate the electronic energy in terms of the NOs and their occupation numbers (ONs), namely, $E = \sum_{i} n_i \mathcal{H}_{ii} + \sum_{ijkl} D[n_i, n_j, n_k, n_l] < kl | ij >$ (1)

Here, $\mathcal{H}_{ii}$ denotes the diagonal elements of the core-Hamiltonian, $< kl | ij >$ are the matrix elements of the two-particle interaction, and $D[n_i, n_j, n_k, n_l]$ represents the reconstructed two-particle reduced density matrix (2-RDM) from the ONs.

It is noteworthy that the resulting approximate functional $E[\{n_i, \phi_i\}]$ can solely be implicitly dependent on $\Gamma$ since the Gilbert’s theorem on the existence of the explicit functional $E[\Gamma]$ is valid only for the exact ground-state energy. In this vein, NOs are the orbitals that diagonalize the one-matrix corresponding to an approximate energy that still depends on the 2-RDM. Consequently, the energy is not invariant with respect to a unitary transformation of the orbitals, and it is more appropriate to speak of a NOF rather than a functional $E[\Gamma]$. A detailed account of the state of the art of the NOF theory can be found elsewhere.

The construction of a $N$-representable functional given by $\mathcal{H}$, i.e., derived from an antisymmetric $N$-particle wavefunction, is obviously related to the $N$ representability problem of the 2-RDM. The use of the (2,2)-positivity $N$-representability conditions for generating a reconstruction functional was proposed in reference 9. This particular reconstruction is based on the introduction of two auxiliary matrices $\Delta$ and $\Pi$ expressed in terms of the ONs to reconstruct the cumulant part of the 2-RDM 10. In a spin-restricted formulation, the energy functional for singlet states reads as

$E = 2 \sum_{pq} n_p \mathcal{H}_{pp} + \sum_{\pi \pi} \Pi_{\pi \pi} \mathcal{L}_{\pi \pi} + \sum_{\pi q} (n_q n_p - \Delta_{\pi q}) (2\mathcal{J}_{\pi q} - \mathcal{K}_{\pi q})$ (2)

where $\mathcal{J}_{\pi q}$, $\mathcal{K}_{\pi q}$, and $\mathcal{L}_{\pi q}$ are the direct, exchange, and exchange-time-inversion integrals. Appropriate
forms of matrices $\Delta$ and $\Pi$ lead to different implementations known in the literature as PNOFi (i=1-6) [3].

The conservation of the total spin allows to derive the diagonal elements $\Delta_{pp} = n_p^2$ and $\Pi_{pp} = n_p$ [12]. The $N$-representability D and $Q$ conditions of the 2-RDM impose the following inequalities on the off-diagonal elements of $\Delta$ [9],

$$\Delta_{qp} \leq n_q n_p, \quad \Delta_{qp} \leq h_q h_p \quad (3)$$

while to fulfill the G condition, the elements of the $\Pi$-matrix must satisfy the constraint [13]

$$\Pi_{qp}^2 \leq (n_q h_p + \Delta_{qp})(h_q n_p + \Delta_{qp}) \quad (4)$$

where $h_p$ denotes the hole $1-n_p$. Notice that for singlets the total hole for a given spatial orbital $p$ is $2h_p$.

Let’s divide the orbital space $\Omega$ into $N/2$ mutually disjunct subspaces $\Omega_g$, so each orbital belongs only to one subspace. Consider each subspace contains one orbital $g$ below the Fermi level ($N/2$), and $N_g$ orbitals above it, which is reflected in additional sum rules for the ONs:

$$\sum_{p \in \Omega_g} n_p = 1; \quad g = 1, 2, \ldots, N/2 \quad (5)$$

Taking into account the spin, each subspace contains solely an electron pair, and the normalization condition for $\Gamma$ ($\sum n_p = N$) is automatically fulfilled. It is important to note that orbitals satisfying the pairing conditions [9] are not required to remain fixed throughout the orbital optimization process [14].

The simplest way to comply with all constraints leads to an independent pair model (PNOF5) [15,16]:

$$\Delta_{qp} = n_q^2 \delta_{qp} + n_q h_p (1-\delta_{qp}) \delta_{q\Omega_g} \delta_{p\Omega_g}$$

$$\Pi_{qp} = n_p \delta_{qp} + \Pi_{qp}^g (1-\delta_{qp}) \delta_{q\Omega_g} \delta_{p\Omega_g}$$

$$\Pi_{qp}^g = \begin{cases} -\sqrt{n_q n_p}, & p = q \text{ or } q = g \\ \sqrt{n_q n_p}, & p, q > N/2 \end{cases} \quad (6)$$

$$\delta_{q\Omega_g} = \begin{cases} 1, & q \in \Omega_g \\ 0, & q \notin \Omega_g \end{cases}$$

Interestingly, an antisymmetrized product of strongly orthogonal geminals (APSG) with the expansion coefficients explicitly expressed by the ONs also leads to PNOF5 [16,17]. This demonstrates that the functional is strictly $N$-representable. In addition, PNOF5 is size-extensive and size-consistent, inherent properties to singlet-type APSG wavefunctions.

To go beyond the independent-pair approximation, let’s maintain $\Delta_{qp} = 0$ and consider nonzero the $\Pi$-elements between orbitals belonging to different subspaces. From Eq. (3), note that provided the $\Delta_{qp}$ vanishes, $|\Pi_{qp}| \leq \Phi_q \Phi_p$ with $\Phi_q = \sqrt{n_q h_q}$. Assuming the equality, one can generalize the sign convention [9], namely $\Pi_{qp} = \Phi_q \Phi_p$ if $q, p > N/2$, and $\Pi_{qp}^g = -\Phi_q \Phi_p$, otherwise. Thus, the energy $\Phi$ becomes

$$E = \sum_{g=1}^{N/2} E_g + \sum_{f \neq g} E_{fg}$$

$$E_g = \sum_{p \in \Omega_g} \left[ n_p (2\mathcal{H}_{pp} + J_{pp}) + \sum_{q \in \Omega_g, q \neq p} \Pi_{qp}^g \mathcal{L}_{pq} \right]$$

$$E_{fg} = \sum_{p \in \Omega_f} \sum_{q \in \Omega_g} \left[ n_q n_p (2J_{pq} - \mathcal{K}_{pq}) + \Pi_{qp}^g \mathcal{L}_{pq} \right] \quad (7)$$

This new approach will henceforth refer to as PNOF7. The first term of the Eq. (7) is the sum of the pair energies described accurately by the two-electron functional $E^g$. In the second term, $E^{fg}$ correlates the motion of the electrons in different pairs with parallel and opposite spins. It is clear that the main weaknesses of the approach (7) is the absence of the interpair dynamic electron correlation since $\Pi_{qp}^g$ has significant values only when the ONs differ substantially from 1 and 0. Consequently, PNOF7 is expected to be able to recover the complete intra-pair, but only the static inter-pair correlation.

The performance of the PNOF7 has been tested by the dissociation of a dozen diatomic molecules. The selected systems comprise different types of bonding, which span a wide range of values for binding energies and bond lengths. However, in all cases the correct dissociation limit implies an homolytic cleavage of the bond with high degree of degeneracy effects. For simplicity, we consider $N_g$ equal to a fixed number that corresponds to the maximum value allowed by the basis set used.

Representative potential energy curves (PECs) of these molecules are depicted in Fig. (see supplementary material for absolute energies). PNOF7 produces qualitatively correct PECs with right dissociation limits for all cases, even in the case of the highest degeneracy ($N_2$). In Table I selected electronic properties, including equilibrium bond lengths ($R_e$), dissociation energies ($D_e$), and harmonic vibrational frequencies ($\omega_e$) can be found. In this work, the experimental bond lengths

![Figure 1: Potential Energy Curves (cc-pVTZ)](image-url)
and spectroscopic data reported are taken from the National Institute of Standards and Technology (NIST) Database [18], whereas the experimental dissociation energies result from a combination of Refs. [18] and [19]. The correlation-consistent valence triple-ζ basis set (cc-pVTZ) developed by Dunning [20] was used throughout, except for the anionic species (OH\(^-\) and CN\(^-\)) where the augmented basis set (aug-cc-pVTZ) was used.

Table I shows that 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 values deteriorate especially for the dissociation energies. This is related to a better description of the asymptotic region with respect to the equilibrium where the dynamic correlation prevails. It is therefore mandatory to add the inter-pair dynamic electron correlation to improve these results.

The second-order Møller–Plesset [2] perturbation theory (MP2) is the simplest and cheapest way of properly incorporating dynamic electron correlation effects. The Hartree-Fock (HF) wavefunction is taken as the start-

ging point in MP2, so let’s consider an Slater determinant formed by the NOs as the zeroth-order wavefunc-
tion, and define the zeroth-order Hamiltonian \(H^{(0)}\) by the expansion \(\sum_i \varepsilon_i |\phi_i\rangle \langle \phi_i|\). Here, \(\varepsilon_i\) is the \(i\)-th diagonal element of the Fock matrix \(\mathbf{F}\) in the NO representation. The first-order energy correction leads to an energy \((\tilde{E}_{hf})\) that differs from the true HF energy since NOs are used instead of the canonical HF orbitals. Besides, the Fock matrix is no longer diagonal, therefore single excitations in addition to doubles contribute to the MP2 energy correction, namely,

\[
E^{(2)} = 2 \sum_{g=1}^{N/2} \sum_{p>N/2} \frac{|F_{pq}|^2}{\varepsilon_g - \varepsilon_p} + \sum_{g,f=1}^{N/2} \sum_{p,q>N/2} \frac{(g|p|f)(q|g|f) - (p|q|f)(g|f)}{\varepsilon_g + \varepsilon_f - \varepsilon_p - \varepsilon_q}
\]

(8)

where \(M\) is the number of basis functions.

In general, MP2 lacks non-dynamic correlation, which is well recovered by PNOF7, but we cannot simply add these contributions since double counting occurs. With this in mind, new dynamic \((E^{dyn})\) and static \((E^{sta})\) energy functionals have to be defined from the MP2 and PNOF7, respectively, so that the total energy of the system will be given by

\[
E = \tilde{E}_{hf} + E^{corr} = \tilde{E}_{hf} + E^{sta} + E^{dyn}
\]

(9)

Henceforth, the energy obtained with the Eq. (9) is called NOF-MP2. From Eq. (7), it is evident that we must differentiate between intra- and inter-pair contributions for both functionals. In accordance, one has

\[
E^{corr}_{intra} = \sum_{g=1}^{N/2} \left( E^{sta} + E^{dyn} \right)_{fg}
\]

\[
E^{corr}_{inter} = \sum_{f \neq g} \left( E^{sta} + E^{dyn} \right)_{fg}
\]

(10)

hence \(E^{corr} = E^{corr}_{intra} + E^{corr}_{inter}\) as well. To avoid double counting, we are going to consider the amount of static electron correlation in each orbital as a function of its occupancy:

\[
\Lambda_p = 1 - |1 - 2n_p|
\]

(11)

Note that \(\Lambda_p\) goes from zero for empty or fully occupied orbitals to one if the orbital is half occupied. Using this function, let’s define the static and dynamic g-th intra-
Taking into account the square root that already appears given by Ec. (12) and those of PNOF7, which in this results obtained with the new intra-pair energy functionals it is remarkable the excellent agreement between the re-
fig introduce the following functionals for the archetypal 2-electron singlet, $H_g$

In Eq. (13), $2\Phi_g$ plays the same role of $\sqrt{\Lambda_p}$ in Eq. (12), hence, $C_g^\Phi = 1 - 4\Phi_g^2 = 1 - 4n_p h_p$. Again, fully occupied and empty orbitals contribute nothing to static correlation, this time inter-pair, whereas orbitals with half occupancies yield a maximal contribution. The opposite occurs for dynamic correlation. It is worth noting that $C_g^\Phi$ is not considered if the orbital is below $N/2$.

Table II: Comparison of $R_e$ (Å), $D_e$ (kcal/mol), and $\omega_e$ (cm$^{-1}$) calculated at the NOF-MP2/cc-pVTZ level of theory with the experimental values. (a) aug-cc-pVTZ was used.

| Molecule | $R_e$ | $R_{e}^{\text{exp}}$ | $D_e$ | $D_{e}^{\text{exp}}$ | $\omega_e$ | $\omega_{e}^{\text{exp}}$ |
|----------|-------|----------------|------|----------------|------|----------------|
| Be$_2$(a) | 2.303 | 2.460 | 2.6 | 2.7 | 543 | - |
| OH$^-$ (a) | 0.967 | 0.964 | 121.6 | - | 3820 | 3770 |
| HF | 0.924 | 0.917 | 139.4 | 141.1 | 4151 | 4138 |
| LiF | 1.614 | 1.564 | 140.7 | 139.0 | 955 | 911 |
| N$_2$ | 1.084 | 1.098 | 224.2 | 228.3 | 2764 | 2359 |
| CN$^-$ (a) | 1.180 | 1.177 | 238.6 | 240.7 | 1961 | 2035 |
| CO | 1.129 | 1.128 | 255.1 | 259.3 | 2092 | 2170 |
| NO$^+$ | 1.060 | 1.063 | 261.1 | - | 2403 | 2377 |
| F$_2$ | 1.397 | 1.412 | 34.5 | 39.2 | 949 | 917 |

The included Beryllium dimer requires special attention. PNOF7 predicts a metastable minimum with a negative $D_e$, whereas NOF-MP2 recovers sufficient dynamic correlation to be able of predicting a stable Be$_2$ molecule. The obtained equilibrium distance is still underestimated, but the dissociation energy approaches the experimental value. For weaker bonds, e.g. He$_2$, NOF-MP2 does not predict bound due to a better description of the dissociated atoms with respect to the equilibrium region. In these cases, neglecting static correlation and using HF-MP2 leads to a binding PEC. The alternative is to include higher-order perturbative corrections.

The size-consistency of the NOF-MP2, i.e. the ability of the method to reproduce the additivity of the energy for a system composed of independent subsystems, has been numerically addressed too. It has been checked that total energies of spin-compensated dimers (He$_2$, Be$_2$, and HeNe) at an internuclear separation of 100 Å differ from the double value of the total energies of the corresponding atoms less than $10^{-5}$ Hartrees ($< 0.01$ kcal/mol).

Preliminary calculations on systems with more than two atoms confirm that the results are promising. The absolute energies obtained with the NOF-MP2 method improve over the PNOF7 values by recovering an important part of the dynamic correlation and getting closer to the values obtained by accurate wavefunction-based methods (see supplementary material).

In summary, a new size-consistent method for singlet states has been proposed that scales formally as $O(M^5)$. The resulting working formulas allow for static and dynamic correlation to be achieved in one shot, as is the case in the standard single-reference perturbation theory. Note that the NOF-MP2 method is not limited to PNOF7 NOs, it can also be used with NOs obtained from an approximation able of recovering non-dynamic electron correlation. In addition, the number of orbitals involved in the optimization can be easily reduced by establishing a cutoff in the value of the ONs, since the dynamic correlation for which the orbitals with small ONs are responsible will be properly recovered by $E^{dyn}$. With efficient approaches, based on recent developments of NOF and MP2 theories, NOF-MP2 could become a valuable tool for treating large systems with hundreds of atoms.

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