Analytic gradients for natural orbital functional theory

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The analytic energy gradients with respect to nuclear motion are derived for natural orbital functional (NOF) theory. The resulting equations do not require to resort to linear-response theory, so the computation of NOF energy gradients is analogous to gradient calculations at the Hartree-Fock level of theory. The structures of 15 spin-compensated systems, composed by first- and second-row atoms, are optimized employing the conjugate gradient algorithm. As functionals, two orbital-pairing approaches were used, namely, the fifth and sixth Piris NOFs (PNOF5 and PNOF6). For the latter, the obtained equilibrium geometries are compared with coupled cluster singles and doubles (CCSD) calculations and accurate empirical data.

I. INTRODUCTION

Since in 1958 Bratoz\textsuperscript{1} derived for first time the analytic gradient for the restricted Hartree-Fock (HF) case, the development and applications of analytical gradients has been of great interest for chemistry and physics\textsuperscript{2}. Energy gradients are primarily employed to locate and characterize critical points on the energy surface in electronic structure theory, especially minima and saddle points, and calculate rovibrational spectroscopic constants and energy levels. The direct analytical calculation of energy derivatives from the wavefunction is computationally more complex than the numerical calculation, but offers greater speed and accuracy. In fact, that is why it has been invested much effort in the development of analytic energy derivatives for many well-known electronic structure methods, such as configuration interaction (CI)\textsuperscript{3}\textsuperscript{4}, density cumulant functional theory (DCFT)\textsuperscript{5}, Moller-Plesset perturbation theory (MP2)\textsuperscript{6}, or coupled cluster (CC) theory including different number of excitations, as recently Gauss and Stanton did for the full singles, doubles and triples (CCSDT) method\textsuperscript{7}.

From the very beginning there have been many attempts to use the Hellmann-Feynman theorem for calculating energy gradients\textsuperscript{8}\textsuperscript{10}, since this approach allows to compute them by using exclusively one-electron operators. It is important to note that the theorem is only valid if all parameters entering the involved density matrices are invariant with respect to nuclear distortion. Unfortunately, this condition is met solely in the complete basis set limit because the location of atomic orbitals (AO) is not important. To achieve accurate results, calculations require the contribution from two-electron terms, which are in turn the bottleneck of the analytic energy gradient computation. In this work, the method proposed in Ref.\textsuperscript{11} has been followed to compute efficiently derivatives of the two-electron integrals.

By reconstructing the second-order reduced density matrix (2-RDM)\textsuperscript{D} from the knowledge of the first-order reduced density matrix (1-RDM)\textsuperscript{Γ}, in its spectral representation, the electronic energy functional can be explicitly written in terms of the natural orbitals (NOs) and corresponding occupation numbers (ONs), leading to the natural orbital functional (NOF) theory (NOFT)\textsuperscript{12}\textsuperscript{14}. In the last decade, Piris and collaborators have proposed\textsuperscript{15}\textsuperscript{16} a series of NOFs known in the literature as PNOFi (i=1,...,6), which have been able to reproduce, in many cases, a degree of accuracy comparable to those provided by high-level standard electronic structure methods\textsuperscript{17}\textsuperscript{22}. In the present article, we develop the analytic energy gradients for the NOFT, and in particular for PNOF. To our knowledge, this is the first direct analytical calculation of the energy derivatives with respect to nuclear motion in NOFT. Perhaps the only precedent is the derivation of analytical gradients in the IBCS theory, which can be considered as a NOFT\textsuperscript{23}.

No iterative procedure is needed in order to evaluate the derivative expressions, therefore, the presented here theory is analogous to the gradient computation at the HF level of theory. Our methodology allows the calculation of analytic energy gradients corresponding to a correlated method at low computational cost, in comparison with standard wavefunction based methods that must resort to linear-response theory in order to evaluate the energy derivatives with respect to nuclear distortions.

This paper is organized as follows. The basic equations involving NOFT are introduced in section\textsuperscript{II A} followed by the development of general expressions for the energy gradients with respect to nuclear motion in section\textsuperscript{II B} and analytic gradients for PNOF in section\textsuperscript{II C}. The next section\textsuperscript{III} is dedicated to discussing the computational aspects related to energy gradient calculations. In section\textsuperscript{IV} we compare the optimized structures of 15 spin-compensated systems at the PNOF5 and PNOF6 levels of theory with respect to the corresponding coupled cluster singles and doubles (CCSD) results, by using the correlation consistent triple-zeta (cc-pVTZ) basis set developed by Dunning and coworkers\textsuperscript{24}. Accurate empirical geometries\textsuperscript{25} are included in order to carry out a statistical analysis.
II. THEORY

A. Natural Orbital Functional Theory

In the Born-Oppenheimer approximation, the total energy of an $N$-electron molecule can be cast as the sum of the nuclear and electronic energies,

$$E = E_{\text{nuc}} + E_{\text{el}} = \sum_{A < B} \frac{Z_A Z_B}{R_{AB}} + E_{\text{el}},$$

(1)

being the electronic energy ($E_{\text{el}}$), an exactly and explicitly known functional of the 1- and 2-RDMs,

$$E_{\text{el}} = \sum_{ik} \Gamma_{ki} \mathcal{H}_{ki} + \sum_{ijkl} D_{ijkl} \langle kl|ij \rangle.$$  

(2)

In Eq. (2), $\mathcal{H}_{ki}$ are the one-electron matrix elements of the core-Hamiltonian, whereas $\langle kl|ij \rangle$ are the two-electron integrals of the Coulomb interaction. In the following, all representations used are assumed to refer to the basis in which the one-matrix $\Gamma$ is diagonal. $E_{\text{el}}$ can be then expressed in terms of the NOs and their ONs.

The procedure for the minimization of the energy (3) relies on the corresponding functional $\Lambda [N, \{n_i\}, \{\phi_i\}]$ is given by

$$\Lambda = E_{\text{el}} - \mu \left( \sum_i n_i - N \right) - \sum_{ki} \lambda_{ki} \left( \langle \phi_k|\phi_i \rangle - \delta_{ki} \right).$$

(5)

By making stationary with respect to the NOs and ONs, we obtain the following system of Eqs.:  

$$\frac{\partial E_{\text{el}}}{\partial n_i} = \mathcal{H}_{ki} + \frac{\partial V_{ee}}{\partial n_i} = \mu,$$  

(6)

$$\frac{\partial E_{\text{el}}}{\partial \phi_i^*} = n_i \mathcal{H}_{\phi_i} + \frac{\partial V_{ee}}{\partial \phi_i^*} = \sum_k \lambda_{ki} \phi_k.$$  

(7)

Eq. (6) is obtained holding the orbitals fixed, whereas the set of the orbital Euler Eqs. (7) is satisfied for a fixed set of occupancies. At present, the procedure of solving simultaneously Eqs. (6) and (7) is carried out by the iterative diagonalization method developed by Piris and Ugalde [31], which has proven to be a powerful tool for attaining the solutions in NOFT.

B. Analytic gradients in NOFT

Assume all NOs are real and expand them in a fixed basis set, $\phi_i (x) = \sum_j c_{ij} \zeta_j (x)$, then, the electronic energy can be rewritten as

$$E_{\text{el}} = \sum_{\mu \nu} \Gamma_{\mu \nu} C_{\mu \nu} + \sum_{\mu \nu \delta} D_{\mu \nu \delta} \langle \mu \eta | \nu \delta \rangle,$$  

(8)

where $\Gamma_{\mu \nu}$ and $D_{\mu \nu \delta}$ are respectively the 1- and 2-RDM given in the atomic orbital (AO) representation,

$$\Gamma_{\mu \nu} = \sum_{\mu} n_i C_{\mu \nu},$$

$$D_{\mu \nu \delta} = \sum_{ijkl} D_{ijkl} C_{\mu i} C_{\nu j} C_{\nu \delta} C_{\mu \delta}.$$  

(9)

Then, the derivative of the total energy (1) with respect to the coordinate $x$ of nucleus $A$ is given by

$$\frac{dE}{dx_A} = \frac{\partial E_{\text{el}}}{\partial x_A} + \frac{\partial E_{\text{nuc}}}{\partial x_A} + \sum_{\mu \nu} \frac{\partial E_{\text{el}}}{\partial C_{\mu \nu}} \frac{\partial C_{\mu \nu}}{\partial x_A} + \sum_{i} \frac{\partial E_{\text{el}}}{\partial n_i} \frac{\partial n_i}{\partial x_A},$$  

(10)

where $\partial E_{\text{el}}/\partial x_A$ and $\partial E_{\text{nuc}}/\partial x_A$ represent the derivative of all terms with explicit dependence on the nuclear coordinate $x_A$, whereas the last two terms in Eq. (10)
arise from the implicit dependence of the orbital coefficients and ONs on geometry, respectively.

The electronic energy \((\text{5})\) presents explicit dependence on the nuclear motion via one- and two-electron integrals, due to the dependence of the AOs on the geometry, namely,

\[
\frac{\partial E_{\text{el}}}{\partial x_{\mu}} = \sum_{\mu \nu} \Gamma_{\mu \nu} \frac{\partial H_{\mu \nu}}{\partial x_{\mu}} + \sum_{\mu \nu \rho} D_{\mu \nu \rho} \frac{\partial (\mu \rho | \nu \delta)}{\partial x_{\mu}}. \tag{11}
\]

The first term in Eq. (11) is the negative Hellmann-Feynman force \([31, 32]\). The second term, which contains the derivatives of the two-electron integrals, is the bottleneck for calculating the analytical gradient.

Regarding the contribution from the NO coefficients, combining Eq. (7) with the chain rule, is not difficult to obtain the next formula:

\[
\frac{\partial E_{\text{el}}}{\partial C_{\mu j}} = 2 \sum_{i} S_{\mu i} C_{vi} \lambda_{ij}, \tag{12}
\]

where \(S_{\mu i}\) is the overlap matrix \((\mu | i)\). At the same time, the response of NO coefficients to nuclear motion can be computed from the orthonormality relation \(\text{14}\) in the AO representation \((C! SC = 1)\) \([32]\) indeed,

\[
2 \sum_{\mu \nu} \frac{\partial C_{\mu j}}{\partial x_{\mu}} S_{\mu i} C_{vi} = - \sum_{\mu i} C_{\mu i} \frac{\partial S_{\mu i}}{\partial x_{\mu}} C_{vi}. \tag{13}
\]

Combining then Eqs. (12) and (13), and taking into account the contribution from different indexes, we obtain the total contribution from the NO coefficients to the gradient, which is known as the density force:

\[
\sum_{\mu j} \frac{\partial E_{\text{el}}}{\partial C_{\mu j}} = - \sum_{\mu j} \lambda_{\mu j} \frac{\partial S_{\mu i}}{\partial x_{\mu}} C_{vi}, \tag{14}
\]

where

\[
\lambda_{\mu j} = \sum_{i} C_{\rho j} \lambda_{ij} C_{vi}. \tag{15}
\]

The last term of Eq. (10) does not bring any contribution to the gradient, since deriving the normalization condition \((\sum_{i} n_{i} = N)\) of the ONs, one obtains

\[
\sum_{i} \frac{\partial n_{i}}{\partial x_{\mu}} = 0. \tag{16}
\]

Hence, combining (16) and (6), brings about a contribution to the gradient equal to zero:

\[
\sum_{i} \frac{\partial E_{\text{el}}}{\partial n_{i}} \frac{\partial n_{i}}{\partial x_{\mu}} = \mu \sum_{i} \frac{\partial n_{i}}{\partial x_{\mu}} = 0. \tag{17}
\]

Finally, bringing together Eqs. (11) and (14) with the nuclear contribution \(\frac{\partial E_{\text{nuc}}}{\partial x_{\mu}}\), we obtain the expression for NOF analytic gradients, namely,

\[
\frac{dE}{dx_{\mu}} = \sum_{\mu \nu} \Gamma_{\mu \nu} \frac{\partial H_{\mu \nu}}{\partial x_{\mu}} + \sum_{\mu \nu \rho} D_{\mu \nu \rho} \frac{\partial (\mu \rho | \nu \delta)}{\partial x_{\mu}} + \frac{\partial E_{\text{nuc}}}{\partial x_{\mu}} \tag{18}
\]

The spin orbitals are direct products \(|\phi_{\mu} = |\varphi_{\rho} \otimes |\sigma\rangle\), so \(|\phi_{\mu}(x)\rangle\) may be split into two subsets: \(|\varphi_{\rho}(x)\alpha(s)\rangle\) and \(|\varphi_{\beta}(x)\beta(s)\rangle\). Given a set of \(2R\) spin orbitals \(|\phi_{i}(i = 1, ..., 2R)\rangle\), we have two sets of \(R\) orthonormal spatial functions, \(|\tau_{\rho}(x)\rangle\) and \(|\tau_{\beta}(x)\rangle\), such that in general the first set is not orthogonal to the second one. Nevertheless, the original set

\[
\phi_{2p-1}(x) = \varphi_{\rho}^{\alpha}(x) \alpha(s), \quad p = 1, ..., R
\]

\[
\phi_{2p}(x) = \varphi_{\beta}^{\alpha}(x) \beta(s), \quad p = 1, ..., R
\]

continues being orthonormal via the orthogonality of the spin functions

\[
\int d\sigma \varphi^{\ast}(s) \beta(s) = \int d\sigma \varphi^{\ast}(s) \alpha(s) = 0. \tag{19}
\]

Since we deal herein only with singlet states, the spin restricted formulation is employed, in which a single set of orbitals is used for \(\alpha\) and \(\beta\) spins: \(|\varphi_{\rho} (x)\rangle = |\varphi_{\beta} (x)\rangle\). Similarly as we did above for the spin NOs, let us expand the spatial NOs \(|\varphi_{\rho}\rangle\) as a linear combination of atomic orbitals: \(|\varphi_{\rho}(x)\rangle = \sum_{\nu} C_{\nu \rho} \chi_{\nu}(x)\rangle\). Consequently, in Eq. (18), entering magnitudes become

\[
\Gamma_{\mu \nu} = 2 \sum_{\nu \rho} n_{\nu} C_{\nu \rho} C_{\nu \nu}
\]

\[
D_{\mu \nu \rho \delta} = 2 \sum_{\rho \nu \tau \tau} C_{\mu \nu \rho} C_{\mu \nu \delta} C_{\nu \tau} C_{\tau \nu} C_{\tau \mu} \tag{20}
\]

\[
\lambda_{\mu \nu} = 2 \sum_{\nu \rho} C_{\rho \mu} \rho \nu C_{\nu \rho}. \tag{21}
\]

C. Analytic gradients for PNOF

In this work, we use a particular reconstruction of the 2-RDM in terms of the 1-RDM proposed by Piris \([15]\). Thus, the electronic energy for a system with an even number \(N\) of electrons is given by the \(J\)KKL-only NOF

\[
E_{el} = 2 \sum_{\rho \nu} n_{\rho} H_{\rho \nu} + \sum_{\rho \nu} \Pi_{\rho \nu} L_{\rho \nu} + \sum_{\rho \nu} (n_{\rho} n_{\nu} - \Delta_{\rho \nu}) (2J_{\rho \nu} - K_{\rho \nu}). \tag{21}
\]

In Eq. (21), \(J_{\rho \nu} = \langle \rho | \rho \nu \rangle\) and \(K_{\rho \nu} = \langle \rho | \rho \nu \rangle\) are the usual direct and exchange integrals, respectively, whereas \(L_{\rho \nu} = \langle \rho | \rho \nu \rangle\) is the exchange and time-inversion integral \([33]\). \(\Delta\) and \(\Pi\) are the auxiliary matrices introduced in reference \([15]\), which exclusively depend on the ONs.
The so-called (2,2)-positivity conditions \[28\] for the \(\mathcal{N}\)-representability of the 2-RDM provide bounds for the off-diagonal terms of matrices \(\Delta\) and \(\Pi\) \[32\], whereas the conservation of the total spin allows to determine the diagonal elements as \(\Delta_{pp} = n_p^2\) and \(\Pi_{pp} = n_p\) \[33\].

For real orbitals, \(\mathcal{L}_{pq}\) reduces to \(\mathcal{K}_{pq}\), so the energy functional \[21\] becomes a \(\mathcal{J}K\-only\) NOF,

\[
E_{el} = 2\sum_p n_p H_{pp} + 2\sum_{pq} (n_q n_p - \Delta_{qp}) J_{pq} - \sum_{pq} (n_q n_p - \Delta_{qp} - \Pi_{qp}) K_{pq}.
\]

(22)

Accordingly, the analytical gradients for PNOF are given by Eq. \[18\] together with the 1- and 2-RDM defined in \[20\], where the latter is now expressed as

\[
\mathcal{D}_{\mu \nu \delta} = \sum_{pq} \left[ 2(n_q n_p - \Delta_{qp}) C_{\mu \nu} C_{\nu \delta} - (n_q n_p - \Delta_{qp} - \Pi_{qp}) C_{\mu \delta} C_{\nu \gamma} C_{\nu \gamma} C_{\nu \gamma} \right].
\]

(23)

Note that the four-index summation appearing in Eq. \[20\] for the 2-RDM is reduced to only two in Eq. \[23\], due to the two-index nature of the PNOF reconstruction that leads to a \(\mathcal{J}K\-only\) NOF \[13\].

**Orbital pairing approaches**

Recently, the electron-pairing approach has been exploited in PNOF theory. Two approximations with pairing restrictions have been proposed so far, namely, the independent-pair model (PNOF5) \[37\] and an interacting-pair approximation (PNOF6) \[38\]. Extended versions of both approaches have been proposed \[39, 40\], too. For them, the orbital space \(\Omega\) is partitioned into \(F = N/2\) subspaces \(\{\Omega_g\}\). The subspaces are considered mutually disjoint (\(\Omega_g \cap \Omega_{g'} = 0\)), i.e., each orbital belongs only to one subspace \(\Omega_g\). Each subspace contains one orbital \(g\) below the Fermi level \((F)\), and \(N_g\) coupled orbitals above it, which is reflected in additional sum rules for the ONs in each \(\Omega_g\), namely,

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

(24)

Note that \(N_g = 1\) corresponds to the simplest formulations, PNOF5 or PNOF6, whereas \(N_g > 1\) leads to different extended formulations of both. Taking into account the spin, each subspace contains solely an electron pair, and the normalization condition \((2\sum_p n_p = N)\) is automatically fulfilled. Moreover, we look for orbitals belonging to each subspace \(\Omega_g\), which yield the minimum energy for the functional of Eq. \[22\]. However, the actual orbitals that satisfy the pairing conditions \[24\] are not constrained to remain fixed along the orbital optimization process. Consequently, the pairing scheme of the orbitals is allowed to vary along the optimization process till the most favorable orbital interactions are found.

In accordance to these new constraints, we may associate new Lagrange multipliers \(\{\lambda_g\}\) with the \(F\) pairing conditions \[24\], instead of the chemical potential \(\mu\). It has been suggested \[11\] that the smallest \(\lambda_g\) can be then identified as the chemical potential of an open system. The auxiliary functional \(\Lambda\) \[43\] may be in turn redefined by the formula

\[
\Lambda = E_{el} - 2\sum_{g=1} F\sum_{p \in \Omega_g} \left( n_p - 1 \right) - 2\sum_{qp} \lambda_{pq} \left( \langle \varphi_q | \varphi_p \rangle - \delta_{qp} \right).
\]

(25)

The partial derivative \((\partial E/\partial n_p)\), holding the spatial NOs \(\{\varphi_g\}\) fixed, are now given by the expressions

\[
\frac{\partial E_{el}}{\partial n_p} = 2H_{pp} + \frac{\partial V_{el}}{\partial n_p} = 2\mu_g, \forall p \in \Omega_g.
\]

(26)

Regarding the analytical gradient equation for orbital pairing approaches, the Eq. \[18\] fulfills independently for each orbital subspace \(g\) due to relation \[24\],

\[
\sum_{p \in \Omega_g} \frac{\partial n_p}{\partial x_A} = 0,
\]

(27)

thereby the contribution to the gradient becomes zero for each subspace

\[
\sum_{p} \frac{\partial E_{el}}{\partial n_p} \frac{\partial n_p}{\partial x_A} = 2\sum_{g} \mu_g \sum_{p \in \Omega_g} \frac{\partial n_p}{\partial x_A} = 0.
\]

(28)

In consequence, the analytical energy gradients \[18\] remain unmodified for orbital pairing approaches.

**III. COMPUTATIONAL ASPECTS**

The Eq. \[18\] implies that we do not require an iterative procedure for evaluating the derivative of the total energy with respect to the coordinate \(x_A\). The gradient can be efficiently computed by first calculating the quantities \(\Gamma_{uv}, D_{\mu \nu \delta},\) and \(\lambda_{uv},\) subsequently contracting by derivatives of the integrals.

In contrast to what happens in other post-HF theories, our methodology allows the calculation of analytic energy gradients by the simple evaluation without resorting to the linear-response theory. Our gradient computation is therefore analogous to that which is performed at the HF level of theory with the corresponding savings of computational time. Indeed, the PNOF analytic gradient reduces to the HF expression after removing \(\Delta\) and \(\Pi\) matrices in Eq. \[23\], i.e., the two-electron cumulant matrix \[13\]. Consequently, as it happens in the HF case, the bottleneck of gradient evaluation is the computation of the two-electron contribution, since 12 gradient components arise from each two-electron integral \[11\]. In this sense, our approach is similar to the projected Hartree-Fock method that recovers a significant portion of static correlation too \[12\].
Overall, the calculation scales nominally as $M^5$ (M being the number of basis set functions) due to the pq-linkage in the auxiliary matrices of the PNOF $D_{pq\Pi \Sigma}$, given by Eq. (23). However, in case of pairing approximations, the auxiliary matrices could contain a lot of zeros corresponding to neglecting ONs of the higher NOs in energy. For instance, in case of simplest pairing, PNOF5 or PNOF6, the number of involved NOs with non-zero occupancies is equal to the the number of electrons $N$, therefore, the summations by $p$ and $q$, in Eq. (23), are up to $N$ instead of $M$, and the scaling reduces from $M^5$ to $N \cdot M^4$. Obviously, factorized PNOF auxiliary matrices $\Delta$ and $\Pi$, i.e., $\Delta_{qp} = \Delta_{q} \Delta_{p}$ and $\Pi_{qp} = \Pi_{q} \Pi_{p}$, could reduce the scaling to $M^4$. In this case, we could make the summations by $p$ and $q$ before contracting by derivatives of the integrals, in a similar way to what one does in the HF approximation.

In practice, the scaling is also reduced by applying a previous screening of two-electron integrals based on Schwarz’ inequality [13], especially in the case of large systems where the smallness of most two-electron integrals allows to skip their evaluation. In any case, the basis set employed determines the computational time instead of the number of geometrical degrees of freedom.

In the present implementation, as there is no constraint regarding the nuclear coordinates of the system, we use the well-known nonlinear conjugate gradient (CG) method [14] to locate ground state equilibrium geometries. This algorithm associates conjugacy properties with the steepest descent method, so that both efficiency and reliability are achieved, as reflected in the results reported in the next section. The main advantage is that the method requires only gradient evaluations and does not use much storage, because the search direction is acquired from linear combinations of the gradient obtained in the previous iteration. Its main drawback is that the search direction is not necessarily correct. Herein, the studied systems are simple molecules with starting configurations close to the optimized geometries, therefore we have no doubt that they are equilibrium geometries. For diatomic molecules herein studied, the harmonic frequency analyses have already been done in previous works [18, 39, 15]. Nevertheless, to be sure of having reached a minimum in the other systems, it is required to compute the Hessian (matrix of second derivatives) in addition to the gradient. Note that it is possible to avoid the problems inherent to the analytic calculation of the Hessian, such as storage issues, solving coupled perturbed equations, or computing the large amount of two-electron integral second derivatives, by a numerical differentiation of analytic gradients [16].

IV. RESULTS

In this section, we carry out a NOF study of the ground-state equilibrium geometries for a selected set of spin-compensated molecules. This set includes the following 15 systems: HF, H$_2$O, NH$_3$, CH$_4$, N$_2$, CO, HOF, HNO, H$_2$CO, HNNH, H$_2$CCH$_2$, HCCH, HCN, HNC, and O$_3$. As functionals, two orbital-pairing approaches were used, namely, PNOF5 and PNOF6. Both functionals, including their extended versions, take into account most of the non-dynamical effects, but also the important part of dynamical electron correlation corresponding to the intrapair interactions [17–21, 37, 38]. PNOF5 does not describe correlation between electron pairs at all, while PNOF6 includes mostly non-dynamic interpair correlation.

We use HF geometries as starting points to PNOF optimizations. For comparison, we have included high-quality empirical equilibrium structures obtained from least-squares fits involving experimental rotational constants and theoretical vibrational corrections [22]. Furthermore, the corresponding CCSD [7] values are included. All calculations are carried out using the correlation-consistent polarized triple-zeta (cc-pVTZ) basis set developed by Dunning and coworkers [24], which are suitable in correlated calculations [23].

Tables II and III show respectively the errors in bond lengths and bond angles obtained for the selected set of molecules at PNOF5, PNOF6 and CCSD levels of theory, along with the empirical equilibrium structures. Note that reported NOF results involve the simplest coupling ($N_g = 1$) in our calculations, so each orbital below the Fermi level is coupled with a single orbital above it.

A survey of both tables II and III reveals that both NOFs employed here, PNOF5 and PNOF6, provide ground-state equilibrium structures comparable to those of the CCSD. For PNOF5, the corresponding mean absolute errors $\Delta_{abs}$ are 0.75 degs and 0.8 pm for bond angles and bond lengths, respectively, which are slightly above 0.47 degs and 0.6 pm obtained by using the CCSD method. PNOF6 performs relatively worse for bond distances ($\Delta_{abs} = 1.2$ pm), but it provides the best bond angles ($\Delta_{abs} = 0.33$ degs), even better than the behavior of CCSD. The slight differences with respect to CCSD are mainly due to the HNC, HOF and O$_3$ molecules, for which the largest errors are observed.

It is worth noting that the systems studied in the current work can be well described by independent-pair approximations since they do not present delocalized electrons. For the latter, it is well-known that approaches like PNOF5 predict symmetry-breaking artifacts [15, 25]. On the other hand, the $\mathcal{FKE}$-only functional PNOF6 includes interactions between the electron pairs, but to the detriment of the correlation energy that recovers, which is smaller than that obtained with PNOF5 in the presented herein systems [37, 38]. That is why calculated bond distances decreases when going from PNOF5 to PNOF6, as happens when going to a lower-energy correlation method in wavefunction-based theories.

We note that the independent-pair approximation (PNOF5) underestimates some inter-atomic distances, while overestimates in other cases, with a slight ten-
Table I: Errors in the equilibrium bonds (in pm) at PNOF5, PNOF6, and CCSD levels of theory calculated by using the cc-pVTZ basis set with respect to empirical structural data. $\Delta$ and $\Delta_{abs}$ correspond to the mean signed error and mean absolute error, respectively.

| Molecule | Bond | PNOF5 | PNOF6 | CCSD  | EMP   |
|----------|------|-------|-------|-------|-------|
| HF       | H—F  | -0.2  | -0.3  | -0.3  | 91.7  |
| H$_2$O   | O—H  | 0.1   | -0.5  | -0.2  | 95.8  |
| NH$_3$   | N—H  | 0.6   | -0.3  | -0.3  | 101.2 |
| CH$_4$   | C—H  | 1.5   | -0.5  | -0.1  | 108.6 |
| N$_2$    | N—N  | -0.7  | -1.4  | -0.4  | 109.8 |
| CO       | C—O  | -1.1  | -1.5  | -0.3  | 112.8 |
| HNO      | N—O  | 0.0   | -1.3  | -0.9  | 120.9 |
|          | H—N  | -0.7  | -2.1  | -0.3  | 105.2 |
| H$_2$CO  | C—O  | 0.2   | -1.1  | -0.5  | 120.5 |
|          | C—H  | 0.4   | -1.1  | -0.4  | 110.1 |
| HNNH     | N—N  | -0.1  | -1.2  | -0.7  | 124.6 |
|          | N—H  | 0.1   | -1.6  | -0.4  | 102.9 |
| H$_2$CCH$_2$ | C—C | 0.9   | -0.3  | -0.4  | 133.1 |
|          | C—H  | 1.1   | -0.7  | -0.4  | 108.1 |
| HCCH     | C—C  | -0.1  | -1.0  | -0.4  | 120.4 |
|          | C—H  | 0.7   | -0.7  | -0.4  | 106.1 |
| HCN      | C—N  | -0.5  | -1.3  | -0.4  | 115.3 |
|          | C—H  | 0.5   | -0.8  | -0.6  | 106.5 |
| HNC      | C—N  | -2.3  | -1.3  | -0.4  | 116.9 |
|          | N—H  | -1.3  | -1.0  | -0.4  | 99.5  |
| HOF      | O—F  | 3.6   | 2.4   | -1.9  | 143.4 |
|          | H—O  | -0.3  | -1.9  | -0.5  | 96.8  |
| O$_3$    | O—O  | 2.6   | -3.5  | -3.6  | 127.2*|

$\Delta$

$\Delta_{abs}$

0.2

0.8

1.2

0.6

*Geometry extracted from Ref. [47].

Table II: Errors in the equilibrium bond angles (in degs) at PNOF5, PNOF6, and CCSD levels of theory calculated by using the cc-pVTZ basis set with respect to empirical structural data. $\Delta$ and $\Delta_{abs}$ correspond to the mean signed error and mean absolute error, respectively.

| Molecule | Bond angle | PNOF5 | PNOF6 | CCSD  | EMP   |
|----------|------------|-------|-------|-------|-------|
| H$_2$O   | H—O—H     | 0.23  | 0.04  | -0.47 | 104.51|
| NH$_3$   | H—N—H     | 0.45  | -0.89 | -0.89 | 107.25|
| HOF      | H—O—F     | -0.27 | -0.22 | 0.43  | 97.94 |
| HNO      | H—N—O     | -0.53 | 0.21  | 0.00  | 108.27|
| H$_2$CO  | H—C—O     | -0.09 | 0.07  | 0.29  | 121.63|
| HNNH     | H—N—N     | 0.82  | 1.07  | -0.04 | 106.36|
| H$_2$CCH$_2$ | H—C—C | -0.15 | 0.00  | 0.03  | 121.43|
| O$_3$    | O—O—O     | -3.44 | 0.09  | 1.57  | 116.70*|

$\Delta$

-0.37

0.75

0.05

0.33

0.12

0.47

$\Delta_{abs}$

0.12

0.47

*Geometry extracted from Ref. [47].

The tendency to the latter as evidenced by the mean signed value $\Delta$ given in Table I. It is worth to note that this trend has been observed when perturbative triples are included in CC theory [25] for the used basis set. On the other hand, the inclusion of the interactions between electron pairs by PNOF6, underestimates the bond distances in all studied cases, as CCSD consistently does, with the exception of the O—F length in the HOF molecule. In the case of bond angles, PNOF5 behaves similarly, but here the trend is slightly to underestimate, whereas PNOF6 reports practically equal values to experimental data ($\Delta = 0.05$ degs), according to the results reported in Table II. Obviously, more sample molecules are needed in order to come to a conclusion.
The case of ozone is remarkable, since none of the methods used in this work give a satisfactory result for the O—O bond length in comparison with the experimental value. Although, we should note that PNOF6 corrects the O—O—O bond angle obtained by using PNOF5, so the interactions between electron pairs seem to play an important role in O₃. Interestingly, for the employed cc-pVTZ basis set, CCSD(T) is able to correct the CCSD value and yield a bond distance of 127.6 pm [7] with an error of 0.4 pm, despite O₃ being a typical two-configuration system.

One of the possible ways to improve the results obtained herein is the inclusion of more orbitals in the description of the electron pairs. For simplicity, consider each orbital g is coupled to a fixed number of orbitals (N_g = N_c), which gives rise to the functionals PNOF5(N_c) or PNOF6(N_c) as appropriate. Taking into account that molecules studied here only comprise atoms of the first and second rows of the periodic table, the inclusion of 5 more orbitals in each subspace [PNOF5(5)] is suitable to improve our results. Our results for bond lengths and angles are reported in Tables III and IV respectively.

By inspection of Table III one concludes that better description of the intrapair electron correlation shortens calculated bond lengths. Accordingly, the performance of PNOF5 improves when the extended approach is employed, whereas in the case of PNOF6, which tends to underestimate bond distances, calculated geometries are slightly worse if more orbitals are included in the description of electron pairs. Table IV shows that the mean absolute errors differ approximately in 0.1 degs for bond angles, so the use of extended versions of both functionals does not affect systemically our results.

Let us highlight some molecules for which the better description of the intrapair correlation yields better geometrical parameters. In the case of methane, the C—H distance shortens from 110.1 pm to 108.2 pm, which closely compares to the experimental value of 108.6 pm. Similarly, the error in HNC bond lengths reduces from 2.3 pm and 1.3 pm to 1.3 pm and 0.6 pm, respectively, for the C—N and N—H bonds. It is worth noting that the only case for which PNOF6 overestimates a bond distance, the O—F bond in HOF molecule, is corrected using PNOF6(5), namely, this bond distance shortens from 145.9 pm to 143.4 pm, in outstanding agreement with the empirical value reported in Table I.

V. CONCLUSION

For first time, we have developed the direct analytical calculation of the energy derivatives with respect to nuclear motion in NOFT. Since the energy gradients give much information on potential energy surfaces and other properties, the study carried out in this work significantly extends the usefulness of NOFT, which have recently shown high accuracy calculating dissociation energies [20, 21], electrostatic moments [22], ionization potentials [48], etc.

It is well known that analytical gradients allow to speed up calculations and avoid numerical errors. The equations obtained herein allow computing analytic gradients of a correlated method without solving coupled equations as is the case in most post-HF methods, for example, in coupled cluster theories, so there is no need for iterative process to calculate the energy gradient in NOFT.

By using the nonlinear conjugate gradient method, we have optimized the structures of 15 spin-compensated molecules at the PNOF5 and PNOF6 levels of theory, employing the cc-pVTZ basis set of Dunning. In comparison with the CCSD method, the mean absolute error in bond distances obtained with PNOF5 differs only in 0.2 pm, although the difference increases to 0.6 pm when PNOF6 is employed. Bond angles calculated by using PNOF6 are the most accurate with mean signed error and mean absolute error equal to 0.05 and 0.33 degress, respectively. The present article proves the ability of both PNOF5 and PNOF6 to yield geometrical structures at lower computational cost than other post-HF methods.

The present study demonstrates the efficiency of computing energy gradients in NOFT, therefore its calculation in periodic solids is now affordable. The extension of NOFT to periodic systems has been done in the past [44, 51], so we expect to achieve a computational efficiency close to that obtained in HF methodologies [52].

Finally, a comment about the optimization algorithm is mandatory. The nonlinear conjugate gradient method is often used to solve unconstrained optimization problems such as the energy minimization studied in this article. Its main advantage is that it requires only gradient evaluations and does not use much storage. Its main drawback is that the search direction is not necessarily down. To be sure of having reached a minimum or a transition state, or to improve our implementation with a Newton-like algorithm, we require computing the Hessian (matrix of second derivatives) in addition to the gradient. A work in this direction is underway.

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Table III: Errors in the equilibrium bonds (in pm) at PNOF5, PNOF5(5), PNOF6, and PNOF6(5) levels of theory calculated by using the cc-pVTZ basis set with respect to empirical structural data. **Δ** and **Δ**\(_{abs}\) correspond to the mean signed error and mean absolute error, respectively.

| Molecule | Bond   | PNOF5 | PNOF5(5) | PNOF6 | PNOF6(5) |
|----------|--------|-------|----------|-------|----------|
| HF       | H–F    | -0.2  | -0.5     | -0.3  | -1.2     |
| H\(_2\)O | O–H    | 0.1   | -0.3     | -0.5  | -0.9     |
| NH\(_3\) | N–H    | 0.6   | 0.1      | -0.3  | -1.3     |
| CH\(_4\) | C–H    | 1.5   | -0.4     | -0.5  | -0.2     |
| N\(_2\)  | N–N    | -0.7  | -0.9     | -1.4  | -2.2     |
| CO       | C–O    | -1.1  | -1.4     | -1.5  | -1.8     |
| HNO      | N–O    | 0.0   | -0.5     | -1.3  | -1.8     |
| H\(_2\)CO| C–O    | 0.2   | -0.1     | -1.1  | -1.4     |
| H\(_2\)CCH\(_2\)| C–C | 0.9 | 0.6 | -0.3 | -0.8 |
| HCN      | C–N    | -0.5  | -0.8     | -1.3  | -2.0     |
| HNC      | C–N    | -2.3  | -1.3     | -1.3  | -1.7     |
| HOF      | O–F    | 3.6   | 3.3      | 2.4   | 0.1      |
| H\(_2\)O| H–O    | 2.6   | 1.4      | -3.5  | -3.8*    |

**Δ**

| Molecule | Bond        | PNOF5 | PNOF5(5) | PNOF6 | PNOF6(5) |
|----------|-------------|-------|----------|-------|----------|
| H\(_2\)O| H–O–H      | 0.23  | 0.43     | 0.04  | 0.76     |
| NH\(_3\)| H–N–H      | 0.45  | -0.54    | -0.89 | 0.46     |
| HOF     | H–O–F      | -0.27 | -0.25    | -0.22 | 0.58     |
| HNO     | H–N–O      | -0.53 | 0.07     | 0.21  | 0.31     |
| H\(_2\)CO| H–C–O    | -0.09 | 0.21     | 0.07  | 0.15     |
| HNNH    | H–N–N      | 0.82  | 1.01     | 1.07  | 1.01     |
| H\(_2\)CCH\(_2\)| H–C–C | -0.15 | 0.02 | 0.00 | 0.21 |
| O\(_3\) | O–O–O      | -3.44 | -2.99    | 0.09  | 0.38*    |

**Δ**\(_{abs}\)

* For this molecule 3 orbitals are considered in each subspace.

Table IV: Errors in the equilibrium bond angles (in degs) at PNOF5, PNOF5(5), PNOF6, and PNOF6(5) levels of theory calculated by using the cc-pVTZ basis set with respect to empirical structural data. **Δ** and **Δ**\(_{abs}\) correspond to the mean signed error and mean absolute error, respectively.

| Molecule | Bond angle | PNOF5 | PNOF5(5) | PNOF6 | PNOF6(5) |
|----------|------------|-------|----------|-------|----------|
| H\(_2\)O| H–O–H     | 0.23  | 0.43     | 0.04  | 0.76     |
| NH\(_3\)| H–N–H     | 0.45  | -0.54    | -0.89 | 0.46     |
| HOF     | H–O–F     | -0.27 | -0.25    | -0.22 | 0.58     |
| HNO     | H–N–O     | -0.53 | 0.07     | 0.21  | 0.31     |
| H\(_2\)CO| H–C–O    | -0.09 | 0.21     | 0.07  | 0.15     |
| HNNH    | H–N–N     | 0.82  | 1.01     | 1.07  | 1.01     |
| H\(_2\)CCH\(_2\)| H–C–C | -0.15 | 0.02 | 0.00 | 0.21 |
| O\(_3\) | O–O–O     | -3.44 | -2.99    | 0.09  | 0.38*    |

**Δ**\(_{abs}\)

* For this molecule 3 orbitals are considered in each subspace.

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