# Resolution of the identity approximation applied to PNOF correlation calculations

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In this work, the required algebra to employ the resolution of the identity approximation within Piris Natural Orbital Functional (PNOF) is developed, leading to an implementation named DoNOF-RI. The arithmetic scaling is reduced from fifth-order to fourth-order, and the memory scaling is reduced from fourth-order to third-order, allowing significant computational time savings. After the DoNOF-RI calculation has fully converged, a restart with four-center electron repulsion integrals can be performed to remove the effect of the auxiliary basis set incompleteness, quickly converging to the exact result. The proposed approach has been tested on cycloalkanes and other molecules of general interest to study the numerical results as well as the speed-ups achieved by PNOF7-RI when compared with PNOF7.

Keywords: Resolution of the Identity, Density Fitting, 1RDM, PNOF, DoNOF

# I. INTRODUCTION

Recently [1], an open-source implementation of natural orbital functional (NOF) based methods has been made available to the scientific community. The associated computer program <u>DoNOF</u> is designed to solve the energy minimization problem of an approximate NOF which describes the ground-state of an N-electron system in terms of the natural orbitals (NOs) and their occupation numbers (ONs). Approximate NOFs have demonstrated [2] to be more accurate than density functionals for highly multi-configurational systems, and scale better with the number of basis functions than correlated wavefunction methods. A detailed account of the state of the art of the NOF-based methods can be found elsewhere [3–7].

A route [8] for the construction of an approximate NOF involves the employment of necessary N-representability conditions [9] for the two-particle reduced density matrix (2RDM) reconstructed in terms of the one-particle reduced density matrix (1RDM). Appropriate 2RDM reconstructions have led to different implementations known in the literature as PNOFi (i=1-7) [10–17]. This family of functionals provide an efficient way of including dynamic and static correlation with chemical accuracy in many cases [18, 19]. It has recently been shown [20, 21] that PNOF7 is an efficient method for strongly correlated electrons in one and two dimensions. In addition, the use of perturbative corrections allow to improve the dynamic correlation in order to achieve a complete method to describe electron correlated systems [22, 23]. In the current implementation, <u>DoNOF</u> computer code needs to transform the atomic orbital (AO) electron repulsion integrals (AO-ERIs) into molecular orbital (MO) electron repulsion integrals (MO-ERIs) in order to evaluate the Coulomb and exchange integrals required in PNOF. The optimization process involves searching for ONs, which requires the computation of Coulomb and exchange matrices in MO representation, and for NOs, which requires computing Coulomb and exchange matrices in AO representation for each MO. These procedures have overall fifth-order arithmetic scaling factor. While this scaling factor is lower compared to other procedures such as those based on configuration interaction and coupled cluster approaches, there is still room for improvement.

Resolution of the identity (RI), also known as density fitting [24–26], approximates the product of basis functions as a linear combination of an auxiliary basis set [27]. It usually reduces the arithmetic and memory scaling factors, and produces intermediate easy-to-handle arrays, as has been reported in other methodologies [28– 39] such as RI-MP2 [34, 40–44], DF-MP2 [45, 45], DF-MP2.5 [46, 47], DF-MP3 [46, 47], DF-LCCD [48], DF-CCSD [33, 49, 50], and DF-CCSD(T) [50, 51]. In particular, the use of the RI approximation in v2RDM-CASSCF calculations [52, 53] has been shown, leading to energy expressions and handling of the MO-ERIs in the optimization procedure different from those necessary in the PNOF family of functionals. Applying the RI approximation in PNOF correlation calculations allows faster calculations, decreasing the arithmetic scale factor of the integral transformation of AO-ERIs to MO-ERIs from fifth order to fourth order, as shown in this work.

The text is structured as follows. In the second section, the elemental theory of PNOF formulation is shown and

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the use of the RI approximation in the ONs and NOs optimization process is analyzed. In the third section, the details about the implementation are given. In the fourth section, the time savings due to the use of the RI approximation as well as the energy results in standard cycloalkanes test set up to nine carbon atoms are presented, another relevant molecules such as oxazole, borazine, coumarin, cyanuryc chloride, benzene, thiepine, and thieno[2,3-b]thiophene are also presented. Finally, conclusions are given in the fifth section.

# II. THEORY

The ground-state electronic energy of an approximate NOF is given by the expression

$$E = 2\sum_{p} n_{p} H_{pp} + \sum_{pqrs} D[n_{p}, n_{q}, n_{r}, n_{s}](pq|rs)$$
(1)

where  $H_{pp}$  denotes the one-electron matrix elements of the kinetic energy and outer potential operators, (pq|rs) are the MO-ERIs in chemists' notation, and  $D[n_p, n_q, n_r, n_s]$  represents the reconstructed 2RDM from the ONs  $\{n_p\}$ . Restrictions on the ONs to the range  $0 \le n_p \le 1$  represent the necessary and sufficient conditions for ensemble N-representability of the 1RDM under the normalization condition,  $2\sum_p n_p = N$ .

It is worth noting that any explicit dependence of D on the NOs  $\{\phi_p\}$  themselves is neglected. Accordingly, NOs are the MOs that diagonalize the 1RDM of an approximate ground-state energy, so it is more appropriate to speak of a NOF rather than a functional of 1RDM due to the explicit dependence on the 2RDM [54].

It is clear that the construction of an N-representable functional given by Eq. (1) is related to the Nrepresentability problem of D. Using its ensemble Nrepresentability conditions to generate a reconstruction functional leads to PNOF [8]. 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 2RDM [55]. For the sake of simplicity, let us address only singlet states in this work. The generalization of our results to spin-multiplet states [23] is straightforward. Consequently, energy expression of Eq. (1) becomes

$$E = 2\sum_{p} n_p H_{pp} + \sum_{qp} \Pi_{qp} L_{pq} + \sum_{qp} (n_q n_p - \Delta_{qp}) (2J_{pq} - K_{pq})$$
(2)

where  $J_{pq}$ ,  $K_{pq}$ , and  $L_{pq}$  are Coulomb, exchange, and exchange-time-inversion integrals [56]. Note that  $L_{pq} = K_{pq}$  for real MOs as developed in this work. Therefore, only two-index  $J_{pq}$  and  $K_{pq}$  integrals are necessary due to our approximation for the 2RDM. Appropriate forms of matrices  $\Delta$  and  $\Pi$  lead to different implementations known as PNOFi (i=1-7). Remarkable is the case of PNOF5 which turned out to be strictly pure N-representable [57].

In the current implementation, minimization of the energy  $E[\{n_p\}, \{\phi_p\}]$  is performed under orthonormality requirement for real NOs, whereas ONs conform to the ensemble N-representability conditions. The solution is established by optimizing the functional of Eq. (2) with respect to the ONs and to the NOs, separately [58].

In  $\underline{\text{DoNOF}}$  [1], the Coulomb integrals are built according to the equation

$$J_{pq} = \sum_{\mu\nu} P^{p}_{\mu\nu} J^{q}_{\mu\nu}$$
(3)  
$$= \sum_{\mu} C_{\mu p} \sum_{\nu} C_{\nu p} \sum_{\sigma} C_{\sigma q} \sum_{\lambda} C_{\lambda q}(\mu\nu|\sigma\lambda)$$

where the indices  $\mu$ ,  $\nu$ ,  $\sigma$ ,  $\lambda$  label AOs of dimension  $N_b$ , and  $(\mu\nu|\sigma\lambda)$  is an AO-ERI. Hence,  $J^q$  is the Coulomb matrix in AO basis for the MO  $\phi_q$ , and  $P^p$  is computed by means of the MO coefficient matrix, C, as

$$P^p_{\mu\nu} = C_{\mu p} C_{\nu p} \quad . \tag{4}$$

Similarly, the integrals are defined as

$$K_{pq} = \sum_{\mu\sigma} P^{p}_{\mu\sigma} K^{q}_{\mu\sigma}$$
(5)  
$$= \sum_{\mu} C_{\mu p} \sum_{\sigma} C_{\sigma p} \sum_{\nu} C_{\nu q} \sum_{\lambda} C_{\lambda q}(\mu \nu | \sigma \lambda)$$

where  $\mathbf{K}^q$  is the exchange matrix in AO basis for the MO  $\phi_q$ .

From Eqs. (3) - (5), we observe that the four-index transformation of the ERIs generally scales as  $N_b^5$ . In the occupancy optimization, this operation is carried out once for fixed orbitals, however, in the orbital optimization it is necessary to perform this transformation every time orbitals change, which is a time-consuming process.

It is worth noting that the last members of the PNOF family, namely PNOF5-PNOF7, use electron-pairing constraints [7]. Until now, only these NOFs can provide the correct number of electrons in the fragments after a homolytic dissociation [19, 59]. Moreover, the constrained nonlinear programming problem for the ONs can be transformed into an unconstrained optimization with the corresponding saving of computational time. In the case of electron-pairing approaches, we can additionally reduce the number of orbitals in calculations, and use just orbitals in the pairing scheme, which we will represent as  $N_{\Omega}$  ( $N_{\Omega} \leq N_b$ ). From now on we will focus on the electron-pairing-based PNOFs.

In Table I, we show the conventional algorithm used to compute the Coulomb  $(\mathbf{J})$  and exchange  $(\mathbf{K})$  integrals in MO representation, and the Coulomb  $(\mathbf{J}^q)$  and exchange  $(\mathbf{K}^q)$  matrices in AO representation for each orbital  $\phi_q$ . In the last columns, the memory and arithmetic scaling of the steps are reported. We see that the evaluation of

	Step	Operation	Scaling	
			Memory	Arithmetic
Common	0 1	Evaluation of $(\mu\nu \sigma\lambda)$ $P^p_{\mu\nu} = C_{\mu p}C_{\nu p}$	$\begin{array}{c} N_b^4 \\ N_b^2 N_\Omega \end{array}$	$\begin{array}{c} N_b^4 \\ N_b^2 N_\Omega \end{array}$
$J_{pq}$	2 3	$J^{q}_{\mu\nu} = \sum_{\sigma\lambda} P^{q}_{\sigma\lambda}(\mu\nu \sigma\lambda)$ $J_{pq} = \sum_{\mu\nu} P^{p}_{\mu\nu} J^{q}_{\mu\nu}$	$N_b^2 N_\Omega$ $N_\Omega^2$	$N_b^4 N_\Omega$ $N_b^2 N_\Omega^2$
$K_{pq}$	2 3	$\begin{split} K^q_{\mu\sigma} &= \sum_{\nu\lambda} P^q_{\nu\lambda} (\mu\nu   \sigma\lambda) \\ K_{pq} &= \sum_{\mu\sigma} P^p_{\mu\sigma} K^q_{\mu\sigma} \end{split}$	$N_b^2 N_\Omega$ $N_\Omega^2$	$N_b^4 N_\Omega$ $N_b^2 N_\Omega^2$

Table I: Algorithm used to compute J and K in the occupancy optimization, and  $J^q$  and  $K^q$  in the orbital optimization.

the AO-ERIs  $(\mu\nu|\sigma\lambda)$ , labeled as step zero, has an arithmetic scaling of  $N_b^4$ . In the current implementation, they are evaluated and stored at the beginning, consequently, this step does not contribute significantly to the computational time. However, its storage represents the highest memory demand with a memory scaling of  $N_b^4$ .

The first step corresponds to the evaluation of  $\boldsymbol{P}$  matrix, as shown in Eq. (4), which has low arithmetic and memory scaling factors of  $N_b^2 N_{\Omega}$ . The second step corresponds to the evaluation of  $\boldsymbol{J}^q$  and  $\boldsymbol{K}^q$  matrices for each MO in AO basis. This is the bottleneck of the current implementation with an arithmetic scaling factor of  $N_b^4 N_{\Omega}$  and memory scaling of  $N_b^2 N_{\Omega}$ . Finally, in the third step,  $\boldsymbol{J}$  and  $\boldsymbol{K}$  integrals in MO representation are computed with an arithmetic scaling factor of  $N_b^2 N_{\Omega}^2$ . The memory scaling of this step is  $N_{\Omega}^2$ , which is not significant compared to the other steps.

As mentioned above, energy minimization is made up of two independent optimization procedures, an outer one that involves the optimization of the ONs for fixed orbitals, and an inner one that involves the optimization of the NOs for fixed occupancies, as shown in Fig. 1. Both optimizations are iterative procedures in which many inner iterations are performed per each outer iteration until convergence. In the next subsections, the introduction of the RI approximation in each optimization procedure applied to PNOFi (i=5-7) is analyzed. For further reference, to emphasize the specific functional used, the calculations within this approach will be labeled as PNOFi-RI (i=5-7), while the global implementation will be named DoNOF-RI.

#### Occupancy Optimization with RI

In <u>DoNOF</u> [1], bounds on  $\{n_p\}$  are imposed automatically by expressing the ONs through new auxiliary variFigure 1: General scheme of the energy optimization. A guess for ONs and NOs is considered, then an iterative procedure composed of two independent optimizations, with respect to ONs and NOs respectively, is performed. For a more detailed description, see the reference [1].



ables  $\{\gamma_p\}$ . In this way, the constrained minimization problem with respect to ONs for a fixed set of NOs is transformed into an unconstrained minimization problem with respect to auxiliary  $\gamma$ -variables.

Since the orbitals do not change, J and K can be computed once and stored along the occupancy optimization process of an outer iteration. The RI approximation can be used to reduce the arithmetic scaling factors of Jand K integrals. In this approximation, the four-center AO-ERI,  $(\mu\nu|\sigma\lambda)$ , is expressed using three-center ERIs,  $(\mu\nu|k)$ , and two-center ERIs, (k|l), according to the equation

$$(\mu\nu|\sigma\lambda) = \sum_{k} (\mu\nu|k) \sum_{l} G_{kl}^{-1}(l|\sigma\lambda) \quad , \tag{6}$$

where k, l represent functions of the auxiliary basis of dimension  $N_{aux}$ , and G is a metric matrix defined as  $G_{kl} = (k|l)$ . In a symmetric approach,  $\mathbf{G}^{-1/2}$  would be computed through eigenvalue decomposition or singular value decomposition, and multiplied by the three-center AO-ERIs, however, the metric matrix may be numerically ill conditioned [38], having small or even negative eigenvalues. Although this problem might be surpassed truncating eigenvalues below a certain tolerance, the overall process is slow and may affect the numerical stability. Recently, a modified Cholesky decomposition has been applied to factorize the metric matrix and correct the numerical problems if required [38, 60]. In this approach, the metric matrix is expressed as [61]

$$G = \mathbf{P} \mathbf{L} \mathbf{D} \mathbf{L}^T \mathbf{P}^T \quad , \tag{7}$$

where **P** is a permutation matrix, **L** is a lower triangular matrix, and **D** is a block diagonal matrix with blocks of dimension  $1 \times 1$  and  $2 \times 2$  [62]. The eigenvalue spectrum

of the **D** matrix is analyzed block by block to correct negative and very small eigenvalues, giving a corrected matrix,  $\tilde{\mathbf{D}}$  [63]. In PNOF correlation calculations a symmetric approach results convenient, thus the **G** matrix is expressed as

$$\mathbf{G} = \mathbf{P} \mathbf{L} \tilde{\mathbf{D}}^{1/2} \tilde{\mathbf{D}}^{1/2} \mathbf{L}^T \mathbf{P}^T \quad , \tag{8}$$

the process of decomposing the **D** matrix in its eigenvectors and eigenvalues is fast due to the small dimension of its blocks. Once the eigenvalues have been corrected, its square root can be evaluated directly. Then, a **b** tensor is found by solving the following linear equation system

$$\mathbf{P}\mathbf{L}\tilde{\mathbf{D}}^{1/2}\mathbf{b}^T = (\mu\nu|k) \ . \tag{9}$$

Using RI, the Coulomb and exchange integrals can be expressed as

$$J_{pq} = \sum_{l} b_{pp}^{l} b_{qq}^{l} , \qquad (10)$$

$$K_{pq} = \sum_{l} b_{pq}^{l} b_{pq}^{l} , \qquad (11)$$

where the change of indices in **b** denotes contractions from AOs  $(\mu, \nu)$  to MOs (p, q) according to

$$b_{p\nu}^{l} = \sum_{\mu} C_{\mu p} b_{\mu \nu}^{l} , \qquad (12)$$

$$b_{pq}^{l} = \sum_{\nu} C_{\nu q} b_{p\nu}^{l}$$
 (13)

An equivalent **b** tensor is employed in RI implementations that use  $\mathbf{G}^{-1/2}$ , particularly, the equations are similar to those used in RI-MP2 [34, 40–44] to build other MO-ERIS.

The memory and arithmetic scaling factors of the Eqs. (6)-(13) with the RI approximation are shown in Table II. The zero step corresponds to the evaluation of the  $(\mu\nu|k)$ AO-ERIs, and the first step corresponds to solve the linear equation system for the b tensor with a memory scaling factor of  $N_b^2 N_{aux}$  and arithmetic scaling factor of  $N_b^2 N_{aux}^2$ . Assuming that enough memory is available to store the b tensor in AO representation, this step can be performed only once at the beginning of the calculation; hence, although the first step has the largest memory scaling, it does not pose a problem through the iterative process. The second step is the contraction of an index of the **b** tensor from AO to MO with memory scaling of  $N_b N_{aux} N_{\Omega}$  and arithmetic scaling of  $N_b^2 N_{aux} N_{\Omega}$ , being the most demanding step per outer iteration; in the third step the remaining atomic orbital is contracted with arithmetic scaling of  $N_b N_{aux} N_{\Omega}^2$  and memory scaling of  $N_{aux}N_{\Omega}^2$  respectively. Finally, in step four, the **b** tensor is used to build the Coulomb and exchange integrals with arithmetic scaling of  $N_{aux}N_{\Omega}^2$  and memory scaling of  $N_{\Omega}$ . The overall procedure has a fourth-order arithmetic scaling of  $N_b^2 N_{aux} N_{\Omega}$ .

Table II: Algorithm used to compute J and K in the occupancy optimization with RI. Formal memory scaling is shown. However, to optimize memory usage, the contraction of b tensor for J and K (steps 2, 3, and 4) are carried out simultaneously for each l, such that the dimension of the auxiliary basis does not affect the memory scaling.

	Step	Operation	Scaling	
			Memory	Arithmetic
	0	Evaluation of $(\mu\nu k)$	$N_b^2 N_{aux}$	$N_b^2 N_{aux}$
Common	1	Solve $\mathbf{PL}\tilde{\mathbf{D}}^{1/2}\mathbf{b}^T$	$N_b^2 N_{aux}$	$N_b^2 N_{aux}^2$
	2	$b_{p\nu}^l = \sum_{\mu} C_{\mu p} b_{\mu \nu}^l$	$N_b N_{aux} N_{\Omega}$	$N_b^2 N_{aux} N_{\Omega}$
	3	$b_{pq}^l = \sum_{\nu} C_{\nu q} b_{p\nu}^l$	$N_{aux}N_{\Omega}^2$	$N_b N_{aux} N_{\Omega}^2$
$J_{pq}$	4	$J_{pq} = \sum_{l} b_{pp}^{l} b_{qq}^{l}$	$N_{\Omega}^2$	$N_{aux}N_{\Omega}^2$
$K_{pq}$	4	$K_{pq} = \sum_{l} b_{pq}^{l} b_{pq}^{l}$	$N_{\Omega}^2$	$N_{aux}N_{\Omega}^2$

#### Orbital Optimization with RI

In the inner optimization procedure of the current implementation (see Fig. 1), the energy minimization is performed with respect to real MOs under the requirement of orthonormality, and considering a fixed set of ONs. In general, an approximate NOF is not invariant with respect to an orthogonal transformation of the orbitals. Consequently, orbital optimization cannot be reduced to a pseudo-eigenvalue problem like in the Hartree-Fock approximation.

In <u>DoNOF</u> [1], the optimal NOs are obtained by iterative diagonalizations of a symmetric matrix  $F^{\lambda}$  determined by the Lagrange multipliers  $\{\lambda_{pq}\}$  associated to the orthonormality conditions. A remarkable advantage of this procedure is that the orthonormality constraints are automatically satisfied. Unfortunately, the diagonal elements cannot be determined from the symmetry property of  $\lambda$ , so this procedure does not provide a generalized Fockian in the conventional sense. Nevertheless,  $\{F_{pp}^{\lambda}\}$ may be determined with the help of an aufbau principle [58].

Thus, the orbital optimization requires to calculate  $\{\lambda_{pq}\}$ in each step of the inner iterations in order to determine the symmetric matrix  $F^{\lambda}$ . Since orbitals change in each step,  $J^q$  and  $K^q$  must be recomputed in each inner iteration. Many inner iterations are performed per outer iteration, so the computation of these matrices in the orbital optimization is the most important contribution to the computational time of the present algorithm.

The RI approximation can also be applied in this case, using the procedure shown in Table III. The zero and first steps evaluate the  $(\mu\nu|k)$  AO-ERIs and the **b** tensor in AO basis, both are common steps shared with the oc-

Table III: Algorithm used to compute  $J^q$  and  $K^q$  in the orbital optimization with RI. Formal memory scaling is shown. However, to optimize memory usage, the contraction of b tensor for  $J^q$  (steps 2, 3, and 4) and  $K^q$  (steps 2 and 3) are carried out simultaneously for each l, such that the dimension of the auxiliary basis does not affect the memory scaling.

	Step	Operation	Scaling	
			Memory	Arithmetic
Common	0	Evaluation of $(\mu\nu k)$	$N_b^2 N_{aux}$	$N_b^2 N_{aux}$
	1	Solve $\mathbf{PL}\tilde{\mathbf{D}}^{1/2}\mathbf{b}^T$	$N_b^2 N_{aux}$	$N_b^2 N_{aux}^2$
	2	$b_{q\nu}^l = \sum_{\mu} C_{\mu q} b_{\mu\nu}^l$	$N_b N_{aux} N_{\Omega}$	$N_b^2 N_{aux} N_{\Omega}$
$J^q_{\mu u}$	3	$b_{qq}^l = \sum_{\nu} C_{\nu q} b_{q\nu}^l$	$N_{aux}N_{\Omega}$	$N_b N_{aux} N_{\Omega}$
	4	$J^q_{\mu\nu} = \sum_l b^l_{qq} b^l_{\mu\nu}$	$N_b^2 N_\Omega$	$N_b^2 N_{aux} N_{\Omega}$
$K^q_{\mu\nu}$	3	$K^q_{\mu\nu} = \sum_l b^l_{q\mu} b^l_{q\nu}$	$N_b^2 N_\Omega$	$N_b^2 N_{aux} N_{\Omega}$

cupancy optimization and performed at the beginning of the calculation. In the second step, an index of the **b** tensor is contracted from AO to MO with arithmetic scaling of  $N_b^2 N_{aux} N_{\Omega}$ . In the third step of the Coulomb procedure, an additional contraction is performed for the **b** tensor. Finally, in the last steps of both the Coulomb and exchange procedures, the intermediate tensors are multiplied to compute  $J^q$  and  $K^q$ . The algorithm reduces the arithmetic scaling factor of orbital optimization to the fourth-order  $(N_b^2 N_{aux} N_{\Omega})$ , as in the previous case. Hence, an overall reduction of the arithmetic scaling factor from fifth-order to the fourth-order, and of the memory scaling factor from fourth-order to the third-order is achieved due to the RI approximation.

Table IV: Comparison of the energies (Hartrees) obtained with PNOF7, PNOF7-RI using aug-cc-pVDZ/GEN-A2\* for the cycloalkanes test. Mean diff:  $2.2 \times 10^{-4}$ 

Molecule	$E_{PNOF7}$	$\Delta E_{PNOF7-RI}{}^{a}$
Cyclopropane $(C_3H_6)$	-117.228991	$1.5 \times 10^{-4}$
Cyclobutane $(C_4H_8)$	-156.328758	$1.9 \times 10^{-4}$
Cyclopentane $(C_5H_{10})$	-195.449913	$2.5 \times 10^{-4}$
Cyclohexane $(C_6H_{12})$	-234.549938	$2.2 \times 10^{-4}$
Cycloheptane $(C_7H_{14})$	-273.630436	$2.3 \times 10^{-4}$
Cyclooctane $(C_8H_{16})$	-312.714209	$2.4 \times 10^{-4}$
Cyclononane $(C_9H_{18})$	-351.799073	$2.9 \times 10^{-4}$

 $^a\mathrm{Positive}$  differences mean that PNOF7-RI energy is above than the PNOF7 energy.

### **III. COMPUTATIONAL DETAILS**

The proposed PNOFi-RI (i=5-7) algorithm was implemented in a modified version of the DoNOF software [1] using Cartesian Gaussian basis functions and MPI parallelization, leading to a new implementation labeled as DoNOF-RI.

We assume that there is enough memory available to compute at the beginning all the required AO-ERIs as well as the **b** tensor on the atomic basis, and store them for use along the calculation. Operations of optimization procedures correspond only to arithmetic manipulations and not to AO-ERI evaluations. Four-center AO-ERIs,  $(\mu\nu|\sigma\lambda)$ , have been screened to discard those lower than  $10^{-9}$ . This approach has been taken to reduce the arithmetic scaling when four center ERIs are used [24, 64– 66]. All results shown in this article were calculated using 24 threads of an Intel Xeon Gold 5118 CPU. Basis sets were taken from the basis set exchange [67–69] www.basissetexchange.org website.

# IV. RESULTS

Single point energy calculations were performed to study the numerical stability and speed-up achieved with the DoNOF-RI implementation. The structures were optimized with Psi4 software [70] using M06-2X [71] and augcc-pVDZ/aug-cc-pVDZ-jkfit [72] basis set. Initial auxiliary variables  $\{\gamma_p^0\}$  corresponding to a Fermi–Dirac distribution of  $\{n_p^0\}$  were employed. For NOs, the guess MOs were taken from a Hartree-Fock calculation.

Figure 2 presents the computational times of an outer iteration for occupancy optimization (top panel) as well as for orbital optimization (bottom panel) from cyclopropane to cyclononane employing aug-cc-pVDZ basis set [73, 74] and GEN-A2<sup>\*</sup> auxiliary basis set [75-77], which generates auxiliary basis functions according to the basis set. In both plots, blue bars represent the elapsed time obtained with PNOF7 and yellow bars correspond to computed time with PNOF7-RI, the speed-up achieved by PNOF7-RI with respect to PNOF7 is presented over each pair of bars. The different sizes of the blue bars compared to the yellow bars makes evident the different arithmetic scaling factors between PNOF7 and PNOF7-RI. For the smallest cycloalkane tested,  $C_3H_6$ , an outer iteration of PNOF7-RI is 12 times faster than the equivalent iteration in PNOF7, in the other hand, for the largest cycloalkane tested, C<sub>9</sub>H<sub>18</sub>, PNOF7-RI is 83 and 37 times faster for occupancy and orbital optimization respectively. Speed-ups for occupancy and orbital optimization behave accordingly to the described arithmetic scaling factors, since the final steps of the integral evaluation for the orbital optimization shown in Table III have slightly higher arithmetic scaling factors than the final steps of the integral evaluation in the occupancy optimization described in Table II.

Molecule  $\Delta E_{PNOF7-RI}$ aSpeed-up<sup>b</sup>  $E_{PNOF7}$ Oxazole  $(C_3H_3NO)$ -244.980370 $8.8 \times 10^{-4}$ 23 $7.0 \times 10^{-4}$ Borazine  $(B_3H_3N_3)$ -241.48794419 $1.7{\times}10^{-3}$ Coumarin  $(C_9H_6O_2)$ -494.72476119 $8.0{\times}10^{-3}$ Cyanuric Chloride  $(C_3Cl_3N_3)$ 1655.966373 23 $6.7{\times}10^{-4}$ Benzene  $(C_6H_6)$ -231.05874728 $2.4 \times 10^{-3}$ Thiepine  $(C_6H_6S)$ 37 -628.585882Thieno[2,3-b]thiophene (C<sub>6</sub>H<sub>4</sub>S<sub>2</sub>) 1239.953451  $7.1 \times 10^{-3}$ 27

Table V: Comparison of the energies (Hartrees) obtained with PNOF7, PNOF7-RI using cc-pVTZ/GEN-A2\* for molecules of general interest. Mean diff:  $3.1 \times 10^{-3}$ 

 $^a\mathrm{Positive}$  differences mean that the PNOF7-RI energy is above than the PNOF7 energy.

<sup>b</sup>Global speed-up per outer iteration

Figure 2: Analysis of occupancy (top panel) and orbital optimizations (bottom panel) for PNOF7 and PNOF7-RI computing time using aug-cc-pVDZ/GEN-A2\*. Achieved speedup is presented over each pair of bars.



(a) Outer occupancy optimization cycle.



(b) Outer orbital optimization cycle.

Although a significant reduction of computational time has been achieved, it is important to analyze the numerical impact of the RI approximation applied to PNOF7 on the final energy values. For this purpose, the NO's and ON's of the converged PNOF7-RI calculation have been used to restart the calculation using four center ERIs, namely, a PNOF7 calculation. The results are presented in Table IV, where the PNOF7 energy and PNOF7-RI energy difference for each cycloalkane is tabulated. It can be seen that PNOF7-RI allows achieving a general accuracy between three and four decimal places, with a mean difference of  $2.2 \times 10^{-4}$  Hartrees. In all cases a restart of the PNOF7-RI calculation converged to the PNOF7 energy in at most two outer iterations, allowing for a PNOF7 result in a reduced amount of time.

The described restarting procedure using ccpVTZ/GEN-A2\* basis sets for molecules of general interest has been performed. The results are shown in Table V, where the PNOF7 energy is shown with the corresponding deviation of the PNOF7-RI result. The minimum error of  $6.7 \times 10^{-4}$  corresponds to the benzene molecule, and the maximum error of  $1.7 \times 10^{-3}$ corresponds to the coumarin molecule. The global times of an outer iteration of PNOF7-RI and PNOF7 were compared and the result can be seen in the column labeled as speed-up, where it is shown that PNOF7-RI is 37 times faster than PNOF7 for the case of the thiepine, as well as important speed-ups for the other cases. Overall, the results prove that DoNOF-RI allows to compute medium size molecules of general interest.

# V. CONCLUSIONS

The resolution of the identity approximation has proved to be significant to decrease the arithmetic and memory scaling factors of the PNOFi (i=5-7) functionals, leading to the DoNOF-RI implementation. The generality of the algorithm proposed here makes it applicable to all approximate natural orbital functionals known so far. While having an acceptable deviation of the final energy value, the solution for the natural orbitals and occupation numbers can be used as a start guess for a regular PNOF calculation with convergence in few iterations. Consequently, DoNOF-RI provides a way of reaching accurate results in a reduced amount of time, allowing PNOFi (i=5-7) functionals to be used to study systems of general interest.

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