Analytic gradients for spin multiplets in natural orbital functional theory

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Analytic energy gradients with respect to nuclear motion are derived for non-singlet compounds in the natural orbital functional theory. We exploit the formulation for multiplets in order to obtain a simple formula valid for any many-electron system in its ground mixed state with a total spin $S$ and all possible spin projection $S_z$ values. We demonstrate that the analytic gradients can be obtained without resorting to linear response theory or involving iterative procedures. It is required a single evaluation, so integral derivatives can be computed on-the-fly along the calculation and thus improve the effectiveness of screening by the Schwarz inequality. Results for small and medium size molecules with many spin multiplicities are shown. The method has no spin-contamination effects. Our results are compared with experimental data and accurate theoretical equilibrium geometries.

Keywords: Analytic Energy Gradients, Equilibrium Geometries, Natural Orbital Functional, Spin Multiplets, Reduced Density Matrix

I. INTRODUCTION

Non-singlet systems are a non-trivial problem for reduced density matrix (RDM) based electronic structure methods. Most commonly used procedures focus on the high-spin component \cite{1,2} or break spin symmetry \cite{3}. In either of these cases, it is not possible to describe the degeneracy of the energy levels with respect to the spin projection ($S_z$). In fact, a single energy value is available if we focus only on the high-spin component, whereas the total spin $S$ is not a proper quantum number whenever the unrestricted formalism is used. The correct spin symmetry can be recovered by a posteriori projection \cite{6}, however, the latter applies only to the energy. Alternatively, Alcoba and co-workers have developed \cite{7} a purification procedure that simultaneously retrieves the $N$- and $S$-representability of the two-particle RDM (2RDM). Unfortunately, the latter implies an added complexity since different spin symmetries require explicit conditions to be imposed. An incorrect treatment of the spin symmetry may have dramatic consequences on the molecular equilibrium geometries. Consequently, it is of fundamental importance to compute energy gradients preserving the spin symmetry of the system.

Recently \cite{3}, a new formulation of the first-order RDM (1RDM) functional theory in its spectral representation, the so-called natural orbital functional (NOF) theory (NOFT), was proposed for multiplet states. Then the 1RDM is expressed by the natural orbitals (NOs) and their occupation numbers (ONs). This approach relies on considering the reconstruction of the ensemble 2RDM in terms of the ONs to describe a many-electron system in its ground mixed state with a total spin $S$ and all possible $S_z$ values. It turns out that the expected value of $S_z$ for the whole ensemble is zero, therefore the spin-restricted theory can be adopted although the total spin is non-zero. A particularly relevant consequence of considering the spin multiplet is that the energy derivatives of non-singlet compounds can be computed in complete analogy to their calculation in singlet states.

The efficient computation of analytic energy gradients is now under intense development in RDM based methods \cite{3,4}. In NOFT, the general formulation of analytic gradients was presented in Ref. \cite{13}, where equilibrium geometries of molecules in singlet states were efficiently calculated. In fact, it was demonstrated that the analytic gradients can be obtained by simple evaluation without resorting to linear response theory or involving iterative procedures. In this article, we demonstrate that the latter also applies to non-singlet compounds in NOFT as long as the entire multiplet is considered. Consequently, equilibrium geometries of molecular systems with any spin value can be easily obtained without spin contamination effects.

This article is organized as follows. We begin in section \textsuperscript{II} with a brief review of the analytic gradients with respect to nuclear displacements in the context of NOFT. Then, we expose the details of our approach for mixed quantum states with nonzero total spin. Computational aspects related to an efficient gradient computation are also discussed. Results for molecular systems involving many spin multiplicities are shown in section \textsuperscript{III}. The latter includes a comparison with respect to experimental data, as well as standard electronic structure methods such as Hartree-Fock (HF) or coupled-cluster including singles and doubles excitations with perturbative triples [CCSD(T)]. At the end we highlight the main conclusions of this paper.

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II. THEORY

A. Analytic gradients in NOFT

In the Born-Oppenheimer approximation, the total energy of an N-electron molecule can be cast as the sum of the nuclear ($E_{\text{nuc}}$) and electronic ($E_{\text{el}}$) energies,

$$E = E_{\text{nuc}} + E_{\text{el}} = \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} + E_{\text{el}}. \quad (1)$$

$Z_A$ represents the atomic number of nucleus $A$, and $R_{AB}$ is the distance between nuclei $A$ and $B$. $E_{\text{el}}$ is an exactly and explicitly known functional of the 1RDM ($\Gamma$) and 2RDM ($\Delta$),

$$E_{\text{el}} = \sum_{ik} \Gamma_{ki} \mathcal{H}_{ki} + \sum_{ijkl} D_{kl} \langle kl | ij \rangle, \quad (2)$$

resulted from a non-relativistic Hamiltonian without spin coordinates, namely,

$$\hat{H} = \sum_{ik} \mathcal{H}_{ki} \hat{a}_k^\dagger \hat{a}_i + \frac{1}{2} \sum_{ijkl} \langle kl | ij \rangle \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_j \hat{a}_i. \quad (3)$$

$\mathcal{H}_{ki}$ are matrix elements of the one-electron part of the Hamiltonian involving the kinetic and potential energy operators, whereas $\langle kl | ij \rangle$ are the two-electron integrals of the Coulomb interaction. $\hat{a}_i^\dagger$ and $\hat{a}_i$ are the familiar fermion creation and annihilation operators associated with the complete orthonormal spin-orbital set $\{|i\rangle\}$. In this context, the ground state is a multiplet, i.e., an ensemble of states that allows all possible spin projections. For a given $S$, there are $(2S+1)$ energy degenerate eigenvectors $|SM_s\rangle$, so the ground state is defined by the N-particle density matrix statistical operator of all equiprobable pure states:

$$\mathcal{D} = \frac{1}{2S+1} \sum_{S=-S}^{S} |SM_s\rangle \langle SM_s| \quad (4)$$

From Eq. (3), it follows that matrix elements of the RDMs are

$$\Gamma_{ki} = \frac{1}{2S+1} \sum_{M_s=-S}^{S} \langle SM_s | \hat{a}_k^\dagger \hat{a}_i | SM_s \rangle \quad (5)$$

$$D_{kl}ij = \frac{1}{2(2S+1)} \sum_{M_s=-S}^{S} \langle SM_s | \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_j \hat{a}_i | SM_s \rangle \quad (6)$$

The Löwdin’s normalization is used, therefore, the traces of the 1RDM and 2RDM are equal to the number of electrons and the number of electron pairs, respectively.

To construct an approximate NOF, we employ the representation where the 1RDM is diagonal ($\Gamma_{ki} = n_i \delta_{ki}$). Restriction on the ONs to the range $0 \leq n_i \leq 1$ represents a necessary and sufficient condition for ensemble N-representability of the 1RDM [16]. We further assume that all NOs $\{\phi_i(x) = \langle x|i \rangle\}$ are real and expand them in a fixed basis set,

$$\phi_i(x) = \sum_v C_{vi} \zeta_v(x) \quad (7)$$

In Eq. (8), $x \equiv (r, s)$ stands for the combined spatial and spin coordinates, $r$ and $s$, respectively. Accordingly, the electronic energy (9) can be rewritten as

$$E_{\text{el}} = \sum_{\mu \nu} \Gamma_{\mu \nu} \mathcal{H}_{\mu \nu} + \sum_{\mu \nu \eta} D_{\mu \nu \eta} \langle \mu | \nu \eta \rangle, \quad (8)$$

where $\Gamma_{\mu \nu}$ and $D_{\mu \nu \eta}$ are the RDMs in the atomic orbital (AO) representation,

$$\Gamma_{\mu \nu} = \sum_{ij} n_i C_{\nu i}, \quad D_{\mu \nu \eta} = \sum_{ijkl} D_{kl} i C_{\mu k} C_{\nu l} C_{\eta i} C_{\delta j}. \quad (9)$$

Then, the derivative of the total energy (10) with respect to the coordinate $x$ of nucleus $A$ is given by

$$\frac{dE}{dx_A} = \sum_{\mu \nu \eta} \frac{\partial \mathcal{H}_{\mu \nu}}{\partial x_A} + \sum_{\mu \nu \eta \delta} \frac{\partial D_{\mu \nu \eta}}{\partial x_A} - \sum_{\mu \nu \eta \delta} \lambda_{\mu \nu} \frac{\partial S_{\mu \nu}}{\partial x_A} \quad (11)$$

The first term of Eq. (11) is the derivative of the nuclear energy, the second represents the negative Hellmann-Feynman force, while the third contains the explicit derivatives of two-electron integrals. The last term in Eq. (11), known as the density force [17] arises from the implicit dependence of the orbital coefficients $\{C_{\nu i}\}$ on geometry. Recall that the implicit dependence of ONs on geometry does not contribute to analytic gradients.

In Eq. (11), $S_{\mu \nu} = \langle \mu | \nu \rangle$ is the overlap matrix in the AO representation, whereas the Lagrange multipliers $\lambda_{\mu \nu}$ are calculated as

$$\lambda_{\mu \nu} = \sum_{ij} C_{\mu j} \lambda_{ji} C_{\nu i}, \quad (12)$$

$$\lambda_{ji} = n_i \mathcal{H}_{ji} + 2 \sum_{klm} D_{kl} \langle kl | jm \rangle \quad (13)$$

It is worth noting that all derivatives in Eq. (11) have an explicit dependence on the nuclear coordinate $x_A$. Consequently, the analytic gradients $dE/dx_A$ can be obtained by a single evaluation since NOs and ONs corresponding to perturbed geometries are not required. Following Ref. [18], two-electron integral derivatives $\partial \langle \mu | \nu \eta \rangle / \partial x_A$ remain the bottleneck of gradient evaluation, so they are computed on-the-fly in order to efficiently apply the Schwarz’ screening [18] with corresponding savings of storage and computing times. Additionally, the present implementation in the DoNOF computer program [19] allows to carry out the geometry optimization procedure ruled by Eq. (11) using the conjugate gradient or L-BFGS algorithms.
B. Natural Orbital Functional for Multiplets

To construct an approximate NOF, the second term of the electronic energy, which is an explicit functional of the 2RDM, must be reconstructed from the 1RDM. In our case, we reconstruct the ensemble 2RDM from the ONs. We neglect any explicit dependence of $D$ on the NOs themselves given that the energy functional already has a strong dependence on the latter via the one- and two-electron integrals. In the following, the reconstruction $D[n_i, n_j, n_k, n_l]$ leading to spin-multiplets is briefly described. For further details, the reader should consult Ref. [8].

In this work, we shall use the static version of our latest functional, namely PNOF7s. This functional approximation was introduced [20] to provide the reference NOF in the second-order Möller-Plesset perturbation method (NOF-MP2) that allows the inter-pair dynamic correlation to be recovered. It is worth noting that PNOF7s satisfies electron pairing restrictions [21], but only takes into account the inter-pair static electron correlation, thus preventing the ONs and NOs from experiencing spurious inter-pair correlation in the dynamic correlation domains characteristic of molecular equilibrium regions.

Consider $N_1$ single electrons determine the spin $S$ of the system, and the rest of electrons ($N_{11} = N - N_1$) are spin-paired, so that all spins corresponding to $N_{11}$ electrons provide a zero spin. Next, focus on the mixed state of highest multiplicity: $2S + 1 = N_1 + 1, S = N_1/2$. For the ensemble of pure states $\{|SM_s\rangle\}$, we have that

$$\langle \hat{S}_z \rangle = \frac{1}{N_1 + 1} \sum_{M_s=-N_1/2}^{N_1/2} M_s = 0. \quad (11)$$

Eq. (11) implies that the expected value of $\hat{S}_z$ for the whole ensemble is zero. This result is of transcendental importance for the present work. In fact, the spin-restricted theory can be adopted although the total spin of the system is non-zero. Consequently, we can use a single set of orbitals for $\alpha$ and $\beta$ spins. All the spatial orbitals will be then doubly occupied in the ensemble, so that occupancies for particles with $\alpha$ and $\beta$ spins are equal: $n^\alpha_p = n^\beta_p = n_p$. On the other hand, the RDMs [3] and Lagrange multipliers [10] become

$$\Gamma_{\mu\nu} = 2 \sum_p n_p C_{\mu p} C_{\nu p},$$
$$D_{\mu\nu ij} = 2 \sum_{pqrst} (D^\alpha_{pqrst} + D^\beta_{pqrst}) C_{\mu p} C_{\nu q} C_{ir} C_{jt},$$
$$\lambda_{\mu\nu} = 2 \sum_{pq} C_{\mu p} \lambda_{\nu q} C_{pq},$$
$$\lambda_{qp} = n_p \mathcal{H}_{qp} + 4 \sum_{rtu} (D^{\alpha}_{rtpu} + D^{\beta}_{rtpu}) \langle rt|qu \rangle. \quad (12)$$

To achieve the gradients [9], we obviously need specific approximations for the 2RDM spin-components. Let us divide the orbital space into two subspaces: $\Omega = \Omega_1 \oplus \Omega_2$. $\Omega_1$ is composed of $N_{11}/2$ mutually disjoint subspaces $\Omega_g$. Each of which contains one orbital $|g\rangle$ with $g \leq N_{11}/2$, and $N_g$ orbitals $|p\rangle$ with $p > N_{11}/2$, namely,

$$\Omega_g = \{ |g\rangle, |p_1\rangle, |p_2\rangle, \ldots, |p_{N_g}\rangle \}. \quad (13)$$

Taking into account the spin, the total occupancy for a given subspace $\Omega_g$ is 2, which is reflected in the following sum rule:

$$\sum_{p \in \Omega_{11}} n_p = n_g + \sum_{i=1}^{N_g} n_{p_i}, \quad g = 1, 2, \ldots, \frac{N_{11}}{2}. \quad (14)$$

In general, $N_g$ may be different for each subspace, but it should be sufficient for the description of each electron pair. In this work, $N_g$ is equal to a fixed number for all subspaces $\Omega_g \in \Omega_1$. The maximum possible value of $N_g$ is determined by the basis set used in calculations. From [14], it follows that

$$2 \sum_{p \in \Omega_{11}} n_p = 2 \sum_{g=1}^{N_{11}/2/N_1} \left( n_g + \sum_{i=1}^{N_g} n_{p_i} \right) = N_{11}. \quad (15)$$

Here, the notation $p \in \Omega_{11}$ represents all the indexes of $|p\rangle$ orbitals belonging to $\Omega_{11}$. It is important to recall that orbitals belonging to each subspace $\Omega_g$ vary along the optimization process until the most favorable orbital interactions are found. Therefore, orbitals do not remain fixed in the optimization process, they adapt to the problem. Similarly, $\Omega_l$ is composed of $N_l$ mutually disjoint subspaces $\Omega_g$. In contrast to $\Omega_{11}$, each subspace $\Omega_g \in \Omega_l$ contains only one orbital $g$ with $2n_g = 1$. It is worth noting that each orbital is completely occupied individually, but we do not know whether the electron has $\alpha$ or $\beta$ spin: $n^\alpha_g = n^\beta_g = n_g = 1/2$. It follows that

$$2 \sum_{p \in \Omega_l} n_p = 2 \sum_{g=1}^{N_{ll}/2/N_l+1} n_g = N_{ll}. \quad (16)$$

Taking into account Eqs. (15) and (16), the trace of the 1RDM is verified equal to the number of electrons:

$$2 \sum_{p \in \Omega} n_p = 2 \sum_{p \in \Omega_{11}} n_p + 2 \sum_{p \in \Omega_l} n_p = N_{11} + N_l = N. \quad (17)$$

To guarantee the existence of an $N$-electron system compatible with a NOF, we must observe the N-representability conditions [22] on the reconstructed 2RDM [23]. In electron-pairing-based NOFs, the employment of these constraints leads to divide the matrix elements of $D$ into intra- and inter-subspace contributions. The intra-subspace blocks only involve intrapair
correlation-consistent polarized valence triple-zeta (cc- 
NOF-based methods for quantum chemistry. The 
out using DoNOF [19], our open-source implementation 
Chemistry Comparison and Benchmark Database [25].

Hereafter, we set 
geometries for multiplets by unconstrained optimizations 
with respect to nuclear coordinates. Consequently, we em-

Then, we are in position to calculate PNOF7s equilibrium 
geometries using these methods.

III. EQUILIBRIUM GEOMETRIES

In this section, we study the equilibrium geometries of 
32 molecules in their multiplet ground states. We have 
cluded exclusively doublets and triplets spin states. All 
results corresponding to NOF calculations were carried 
out using DoNOF [19], our open-source implementation 
of NOF-based methods for quantum chemistry. The 
correlation-consistent polarized valence triple-zeta (cc-
pVTZ) basis set developed by Dunning and co-workers 
was shown [15] to be suitable for PNOF geometry 
optimizations in singlet states. Consequently, we em-
ploy the cc-pVTZ basis set in all multiplet calculations. 
Experimental data as well as HF, MP2, and CCSD(T) 
geometries were obtained from the NIST Computation-

Table I: Mean signed (Δ) and unsigned (Δabs) errors for the 
bond distances (Å) of polyatomic molecules regarding exper-
imental data. See appendix for the equilibrium distance data.

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performed for all systems using numerical differentiation 
of analytic gradients [14]. In all cases it was verified that 
a minimum of the geometry had been reached.

Table I shows the mean signed (Δ) and unsigned (Δabs) 
errors corresponding to the equilibrium bond distances 
obtained for 24 molecular dimers at the PNOF7s, HF, 
MP2, and CCSD(T) levels of theory. Bond distance 
errors were calculated as the differences between theoreti-
cal data. See appendix for the equilibrium distance data. 

Table II shows the mean signed (Δ) and unsigned (Δabs) 
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PNOF7s $\Delta_{abs}$ gets larger as the system increases in polyatomic molecules. Recall that in NOF7 based on electron pairs [21], the intrapair electron correlation is appropriately captured, but a significant part of the correlation between electron pairs is lost. In the case of PNOF7s, the static interpair correlation is well described, but not the dynamic one. The lack of interpair dynamic correlation becomes significant when the number of electron pairs increases, so a worsening in the description of the geometries is expected.

The dynamic correlation can be incorporated using perturbation corrections, which led to the NOF-MP2 method [20, 26]. Recently, it has been shown that a more accurate description of the potential energy surface (PES) can be obtained (e.g., see Fig. 4 in Ref. [19]) using NOF-MP2. Unfortunately, obtaining the energy gradients corresponding to methods based on the MP2 formulation implies additional complexity [24], since it is necessary to iteratively solve coupled perturbed equations [28]. Therefore, the analytic gradients of the NOF-MP2 method are beyond the scope of this work.

Overall, the PNOF7s mean signed and unsigned errors obtained for bond distances are $\Delta = 0.000$ Å and $\Delta_{abs} = 0.014$ Å, respectively. Therefore, the conclusions previously obtained [14] for spin compensated systems hold in the present study. On the one hand, bond distances obtained at the PNOF7s/cc-pVTZ level of theory are in good agreement with the experimental data and, on the other, PNOF7s produces slightly larger errors than the CCSD(T) method. In fact, the absolute error corresponding to CCSD(T) reads as $\Delta_{abs} = 0.013$ Å. However, we must recall that CCSD(T) requires solving coupled perturbed equations to compute the energy gradients and introduces spin contamination effects due to the use of the spin unrestricted approach in the case of non-zero spin systems.

|         | PNOF7s | HF     | MP2   | CCSD(T) |
|---------|--------|--------|-------|---------|
| $\Delta$ | -0.15  | 1.28   | 0.15  | 0.36    |
| $\Delta_{abs}$ | 1.41   | 2.21   | 1.25  | 1.16    |

Table III shows the mean signed $(\Delta)$ and unsigned $(\Delta_{abs})$ errors in bond angles corresponding to the 8 studied polyatomic molecules. The data used to calculate these errors can be found in Table 3 of the Appendix. Despite imposing no symmetry on PNOF7s calculations, it is worth noting that DoNOF maintains the point group symmetry of the starting HF molecular equilibrium geometries. According to the values reported in Table III, bond angles obtained using PNOF7s are in good agreement with those obtained at the MP2 and CCSD(T) levels of theory, and thereby imply a significant improvement with respect to HF results. In contrast to the results obtained for bond lengths, PNOF7s produces a non-negligible mean signed error of $\Delta = -0.15$ degrees, with a slight tendency to underestimate bond angles. Nevertheless, together with the mean signed errors obtained for the bond distances, Table III shows that the cc-pVTZ basis set conforms to PNOF7s in order to obtain accurate equilibrium geometries.

IV. CLOSING REMARKS

In this work, it has been demonstrated that the analytic energy gradients of non-singlet compounds in their ground state can be obtained analogously to singlets by using the NOF approach for multiplets. The latter describes a mixed quantum state with all possible spin projections, so the energy degeneration with respect to these projections is adequately accounted for. No spin contamination effects are introduced. The previously developed formulæ to compute gradients for singlets are valid for non-zero values of total spin. Thus, the NOF gradients are easily computed by a single evaluation and without solving coupled perturbed equations.

Geometry optimization was performed for 32 molecules with spin multiplicities equal to 2 and 3. In all cases, it was confirmed that all the harmonic vibrational frequencies were positive, so it was corroborated that we had reached a minimum in the potential energy surfaces. In most cases, PNOF7s geometries are comparable to those obtained at MP2 and CCSD(T) levels of theory, so a significant improvement with respect to HF results is obtained. Since the mean signed error is nearly zero, the cc-pVTZ basis set appears to be suitable for calculating equilibrium geometries with PNOF7s.

In view of the results shown throughout this work, PNOF7s is an efficient method to calculate the equilibrium geometries of non-singlet systems without introducing spin contamination effects. Furthermore, approximate NOFs deal with static correlation from the outset and do not require prior knowledge of the system or parameterization techniques. This makes PNOF7s a method of choice to be used in problems related to energy gradients and systems where an accurate description of the non-dynamic correlation effects is needed.

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[1] P. Leiva and M. Piris, Int. J. Quantum Chem. **107**, 1 (2007).
[2] M. Piris, J. M. Matxain, X. Lopez, and J. M. Ugalde, J. Chem. Phys. **131**, 021102 (2009).
[3] D. R. Rohr and K. Pernal, J. Chem. Phys. **135** (2011).
[4] R. Quintero-Monsebaiz, I. Mitxelena, M. Rodríguez-Mayorga, A. Vela, and M. Piris, J. Phys. Condens. Matter **91**, 109 (2019).
[5] D. R. Alcoba, A. Torre, L. Lain, G. E. Massacesi, O. B. Oña, and E. Ríos, J. Chem. Phys. **150**, 164106 (2019).
[6] T. M. Henderson and G. E. Scuseria, Phys. Rev. A **96**, 022506 (2017).
[7] D. R. Alcoba, C. Valdemoro, L. M. Tel, and E. Pérez-Romero, Phys. Rev. A **77**, 042508 (2008).
[8] M. Piris, Phys. Rev. A **100**, 032508 (2019).
[9] E. Maradzike, G. Gidofalvi, J. M. Turney, H. F. Schaefer, and A. E. DePrince, J. Chem. Theory Comput. **13**, 4113 (2017).
[10] J. W. Mullinax, E. Maradzike, L. N. Koulias, M. Mostafanejad, E. Epifanovsky, G. Gidofalvi, and A. E. DePrince, J. Chem. Theory Comput. **15**, 6164 (2019).
[11] A. J. Valentine and D. A. Mazziotti, Chem. Phys. Lett. **685**, 300 (2017).
[12] A. W. Schlimgen and D. A. Mazziotti, J. Chem. Phys. **149**, 164111 (2018).
[13] A. Y. Sokolov, J. J. Wilke, A. C. Simmonett, and H. F. Schaefer, J. Chem. Phys. **137**, 054105 (2012).
[14] I. Mitxelena, M. Piris, and J. M. Ugalde, in *State of The Art of Molecular Electronic Structure Computations: Correlation Methods, Basis Sets and More*, edited by L. U. Ancarani and P. E. Hoggan (Academic Press, 2019), vol. 79 of *Advances in Quantum Chemistry*, pp. 155 – 177.
[15] I. Mitxelena and M. Piris, J. Chem. Phys. **146**, 014102 (2017).
[16] A. J. Coleman, Rev. Mod. Phys. **35**, 668 (1963).
[17] P. Pulay, Mol. Phys. **17**, 197 (1969).
[18] H. Horn, H. Weiss, M. Häser, M. Ehrig, and R. Ahlrichs, J. Comput. Chem. **12**, 1058 (1991).
[19] M. Piris and I. Mitxelena (submitted to Comput. Phys. Commun.).
[20] M. Piris, Phys. Rev. A **98**, 022504 (2018).
[21] M. Piris, in *Theoretical and Quantum Chemistry at the Dawn of the 21st Century*, edited by T. Chakraborty and R. Carbó-Dorca (Apple Academic Press, New Jersey, 2018), chap. 22, pp. 593–620.
[22] D. A. Mazziotti, Phys. Rev. Lett. **108**, 263002 (2012).
[23] M. Piris, in *Many-body approaches at different scales: a tribute to N. H. March on the occasion of his 90th birthday*, edited by G. G. N. Angilella and C. Amovilli (Springer, New York, 2018), chap. 22, pp. 283–300.
[24] T. H. Dunning Jr., J. Chem. Phys. **90**, 1007 (1989).
[25] R. D. Johnson III, ed., *NIST Computational Chemistry Comparison and Benchmark Database*, vol. 17b (2015).
[26] M. Piris, Phys. Rev. Lett. **119**, 063002 (2017).
[27] Z. Ni, Y. Wang, W. Li, P. Pulay, and S. Li, J. Chem. Theory Comput. **15**, 3623 (2019).
[28] A. El Azhary, G. Rauhut, P. Pulay, and H.-J. Werner, J. Chem. Phys. **108**, 5185 (1998).
[29] R. M. Parrish, L. A. Burns, D. G. A. Smith, A. C. Simmonett, A. E. DePrince, E. G. Hohenstein, U. Bozkaya, A. Y. Sokolov, R. Di Remigio, R. M. Richard, et al., J. Chem. Theory Comput. **13**, 3185 (2017).
Appendix: Theoretical and experimental equilibrium geometries

Table 1: Equilibrium bond distances (Å) of molecular dimers calculated at PNOF7s/cc-pVTZ level of theory. HF, MP2, CCSD(T) and experimental data from Ref. [25].

| Dimer  | 2S+1 | PNOF7s | HF   | MP2  | CCSD(T) | EXP  |
|--------|------|--------|------|------|---------|------|
| BeH    | 2    | 1.340  | 1.339| 1.342| 1.350   | 1.343|
| BO     | 2    | 1.188  | 1.182| 1.212| 1.213   | 1.204|
| BS     | 2    | 1.600  | 1.601| 1.613| 1.623   | 1.609|
| CF     | 2    | 1.272  | 1.254| 1.273| 1.278   | 1.272|
| CH     | 2    | 1.123  | 1.106| 1.114| 1.123   | 1.120|
| CN     | 2    | 1.159  | 1.150| 1.126| 1.174   | 1.172|
| CP     | 2    | 1.550  | 1.608| 1.518| 1.570   | 1.562|
| ClO    | 2    | 1.595  | 1.595| 1.593| 1.596   | 1.570|
| MgCl*  | 2    | 2.190  | 2.216| 2.203| 2.203   | 2.199|
| MgF*   | 2    | 1.750  | 1.748| 1.767| 1.763   | 1.750|
| MgH    | 2    | 1.725  | 1.737| 1.731| 1.744   | 1.723|
| NF     | 3    | 1.344  | 1.292| 1.312| 1.320   | 1.317|
| NH     | 3    | 1.047  | 1.021| 1.031| 1.039   | 1.036|
| NS     | 2    | 1.509  | 1.536| 1.423| 1.508   | 1.494|
| NO     | 2    | 1.142  | 1.116| 1.137| 1.153   | 1.151|
| OH     | 2    | 0.969  | 0.951| 0.962| 0.971   | 0.970|
| O₂     | 3    | 1.224  | 1.159| 1.224| 1.212   | 1.208|
| PH     | 3    | 1.426  | 1.414| 1.420| 1.429   | 1.422|
| PO     | 2    | 1.473  | 1.447| 1.497| 1.495   | 1.476|
| S₂     | 3    | 1.910  | 1.872| 1.911| 1.916   | 1.889|
| SH     | 2    | 1.344  | 1.334| 1.340| 1.346   | 1.340|
| SO     | 3    | 1.442  | 1.452| 1.501| 1.501   | 1.481|
| Si₂    | 3    | 2.223  | 2.223| 2.259| 2.180   | 2.246|
| SiF    | 2    | 1.607  | 1.596| 1.622| 1.620   | 1.601|

* HF, MP2, and CCSD(T) geometries obtained using PSI4 [29].

Table 2: Equilibrium bond distances (Å) of polyatomic molecules calculated at PNOF7s/cc-pVTZ level of theory. HF, MP2, CCSD(T) and experimental data from Ref. [25].

| Molecule | 2S+1 | Bond   | PNOF7s | HF   | MP2  | CCSD(T) | EXP  |
|----------|------|--------|--------|------|------|---------|------|
| CH₂      | 3    | rCH    | 1.091  | 1.070| 1.074| 1.078   | 1.085|
|          |      | rHH    | 1.997  | 1.954| 1.968| 1.982   | 2.008|
| CH₃      | 2    | rCH    | 1.082  | 1.071| 1.074| 1.079   | 1.079|
|          |      | rHH    | 1.874  | 1.855| 1.861| 1.869   | 1.869|
| HCO      | 2    | rCH    | 1.107  | 1.108| 1.117| 1.121   | 1.080|
|          |      | rCO    | 1.151  | 1.151| 1.182| 1.182   | 1.198|
|          |      | rHO    | 2.019  | 2.019| 2.031| 2.038   | 1.969|
| NH₂*     | 2    | rNH    | 1.023  | 1.009| 1.019| 1.024   | 1.024|
|          |      | rHH    | 1.606  | 1.596| 1.594| 1.598   | 1.607|
| NO₂      | 2    | rNO    | 1.154  | 1.155| 1.201| 1.199   | 1.193|
|          |      | rOO    | 2.144  | 2.145| 2.212| 2.209   | 2.198|
| OOH      | 2    | rOO    | 1.351  | 1.309| 1.315| 1.336   | 1.333|
|          |      | rOH    | 0.972  | 0.945| 0.972| 0.972   | 0.971|
|          |      | rHO    | 1.842  | 1.804| 1.804| 1.831   | 1.832|
| PH₂      | 2    | rPH    | 1.420  | 1.412| 1.415| 1.423   | 1.428|
|          |      | rHH    | 2.066  | 2.060| 2.036| 2.045   | 2.046|
| SiH₃     | 2    | rSiH   | 1.476  | 1.479| 1.478| 1.484   | 1.468|
|          |      | rHH    | 2.434  | 2.434| 2.437| 2.449   | 2.412|

* HF, MP2, and CCSD(T) geometries obtained using PSI4 [29].
Table 3: Equilibrium bond angles (degrees) of polyatomic molecules calculated at PNOF7s/cc-pVTZ level of theory. HF, MP2, CCSD(T) and experimental data from Ref. [25].

| Molecule | 2S + 1 | Angle | PNOF7s | HF   | MP2  | CCSD(T) | EXP |
|----------|--------|-------|--------|------|------|---------|-----|
| CH\(_2\) | 3      | HCH   | 132.4  | 131.8| 132.8| 133.5   | 135.5|
| CH\(_3\) | 2      | HCH   | 120.0  | 120.0| 120.0| 120.0   | 120.0|
| HCO      | 2      | HCO   | 117.0  | 126.7| 124.0| 124.4   | 119.5|
| NH\(_2\)* | 2    | HNH   | 103.4  | 104.5| 102.9| 102.6   | 103.4|
| NO\(_2\) | 2      | ONO   | 136.6  | 136.5| 134.1| 134.2   | 134.1|
| OOH      | 2      | OOH   | 103.7  | 105.2| 103.1| 103.9   | 104.3|
| PH\(_2\) | 2      | HPH   | 93.4   | 93.7 | 92.0 | 91.9    | 91.5 |
| SiH\(_3\) | 2    | HSiH  | 111.1  | 110.7| 111.1| 111.2   | 110.5|

* HF, MP2, and CCSD(T) geometries obtained using PSI4 [29].