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Exploring the potential of natural orbital functionals

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In recent years, Natural Orbital Functional (NOF) theory has gained increasing significance in quantum chemistry, successfully addressing one of the field's most challenging problems: providing an accurate and balanced description of systems with strong electronic correlation. The quest for NOFs that strike the delicate balance between computational tractability and predictive accuracy represents a holy grail for researchers. Today, NOFs provide an alternative formalism to both density functional and wavefunction-based methods, with their appeal rooted in a wonderfully simple conceptual framework. This perspective outlines the basic concepts, strengths and weaknesses, and current status of NOFs, while offering suggestions for their future development.

1 Introduction

In recent decades, we have witnessed significant advances in hardware and software that have greatly enhanced our ability to simulate molecules and materials with increasing numbers of atoms. This progress has opened new avenues in scientific research, enabling the exploration of molecular dynamics, material properties, and chemical reactions on unprecedented scales. As a result, the fields of computational chemistry and materials science are undergoing a transformative phase, promising groundbreaking discoveries and innovations. Much of this success can be credited to the development of density functional approximations, which provide reasonable results at modest computational costs.

Density functional theory (DFT) was established¹ by Hohenberg and Kohn (HK), with practical implementations relying on the Kohn–Sham (KS) formulation.² In the KS approach, the unknown kinetic energy functional as a functional of the electron density is avoided by introducing a reference system of non-interacting electrons described by a single Slater determinant. This difference highlights issues, particularly from the correlation kinetic energy, posing a significant challenge in current density functionals. While local density and generalized gradient approximations are commonly used, they often fail to describe strong electron correlations. Hybrid-exchange functionals and range-separated interactions have been practical solutions to this problem, showing improved performance, although failures persist.^{3,4} Today, there is a plethora of empirical and non-empirical parametrized density functionals,⁵ but this extensive parametrization often limits

their applicability to specific systems and phenomena, deviating from a physically grounded modeling approach.^{6,7}

The exact solution of the time-independent non-relativistic Schrödinger equation can be achieved by the full configuration interaction (FCI) method, which accounts for all possible electronic configurations based on a one-particle basis, the spin-orbitals. However, FCI scales exponentially with the number of orbitals, making methods based on approximate wavefunctions more practical for solving the many-body problem, despite the progress made with the density matrix renormalization group technique.⁸ Currently, the coupled-cluster wavefunction with single, double, and perturbative triple excitations⁹ is considered the “gold standard” in quantum chemistry, with efficient and nearly linear-scaling implementations.^{10,11} Nevertheless, this method still demands significant computational resources as the system size increases and is unsatisfactory for systems with strong static correlation due to its single Hartree–Fock reference character.

There is no universal consensus on the distinction between static and dynamic electron correlation, and the transition between them is gradual. Static correlation generally involves a limited number of close-lying orbitals, usually the frontier orbitals near the Fermi level. The wavefunction in such cases is a mixture of configuration state functions, each with appreciable weight. In contrast, dynamic correlation involves a very large number of configurations, each with a small weight. The most interesting chemistry—such as systems with partially broken bonds, transition states for bond breaking, transition metal compounds, compounds of strongly electronegative first-row atoms, large conjugated systems, electronically excited states, *etc.*—requires a balanced treatment of both static and dynamic correlation. Presently, the most reliable approaches to address this are multireference methods, such as the complete active space self-consistent field (CASSCF)¹² and its

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combination with second-order perturbation theory (CASPT2).¹³ Unfortunately, multireference methods still suffer from high computational costs and sensitivity to active space selection, especially for a large number of strongly correlated orbitals. Furthermore, while incorporating dynamic correlation through perturbative corrections improves the accuracy of absolute energies, it does not improve the quality of the reference. Achieving results that include all electron correlation at once requires a comprehensive optimization process, which becomes computationally prohibitive for multireference-perturbative methods.

Reduced density matrix (RDM)-based methods offer alternative formalisms to both density functional and wavefunction-based approaches. It has long been known¹⁴ that the energy of a system with at most two-body interactions is an exact linear functional of the two-particle RDM (2RDM), the only functional we know with certainty. Today, realistic variational 2RDM calculations are possible,¹⁵ but they remain computationally expensive. A dramatic reduction in computational scaling can be achieved by further reducing the complexity of the fundamental variable, specifically by using the one-particle reduced density matrix (1RDM).

The existence of a functional of the 1RDM^{16–18} is already implicit in the original HK theorem.¹⁹ However, the existence of the functional alone does not allow us to determine its analytical expression in a general manner. While the Levy formulation¹⁷ can reveal the explicit form of the exact functional for certain model systems,^{20,21} it remains impractical for computational purposes. This limitation has driven the development of approximate functionals, most of which are formulated in the natural orbital (NO) representation,²² where the 1RDM is diagonal. The spectral decomposition of the 1RDM allows the functional to be expressed in terms of the NOs and their occupation numbers (ONs), thereby defining it as a natural orbital functional (NOF).

This perspective is intended for a general audience, emphasizing the fundamental and practical aspects of NOF approximations. Rather than delving into detailed computational procedures and specific system results, it provides insights into the current state of the field and outlines future directions. For a comprehensive historical overview of the formulation and evolution of NOFs, readers are referred to the recent review article by the author.²³

2 The method behind approximate NOFs

The Hamiltonian operator of an N -electron system consists of both one- and two-electron components. Consequently, the energy of an electronic system can be determined by accessing the 1RDM and 2RDM, represented as Γ and D , respectively:

$$E_{\text{el}} = \sum_{ik} H_{ki} \Gamma_{ki} + \sum_{ijkl} \langle kl|ij \rangle D_{kl,ij} \quad (1)$$

Here, H_{ki} represents the matrix elements of the one-particle part of the Hamiltonian, which includes the kinetic energy and

potential energy operators, while $\langle kl|ij \rangle$ denotes the two-particle interaction matrix elements. The non-interacting part of the energy already exhibits an explicit dependence on Γ , highlighting a key advantage of the 1RDM formulation: the kinetic energy is explicitly defined and does not require the construction of a functional, as is necessary with a density functional. Therefore, the main objective in 1RDM functional theory (1RDMFT) is to reconstruct the electron–electron potential energy (V_{ee}), which is the portion of the energy that explicitly depends on D , in terms of Γ .

Assuming we can determine the universal functional $V_{\text{ee}}[\Gamma]$, it becomes necessary to impose certain restrictions on the allowable 1RDMs to ensure a physically valid ground-state energy.²⁴ These restrictions require that the 1RDM originate from an N -particle quantum state that is antisymmetric with respect to the exchange of identical electrons, a property known as N -representability. A crucial aspect of N -representability is its connection to either a pure or ensemble state. In 1963, Coleman established²⁵ the conditions for ensuring the ensemble N -representability of Γ , and these are relatively straightforward to implement. In contrast, the more recent systematic approach to deriving pure-state N -representability conditions for the 1RDM,^{26,27} has proven extremely complex to implement.

For a considerable time, it was widely believed that pure and ensemble universal functionals were equivalent within their shared domain of pure-state N -representable 1RDMs.^{18,28} However, recent research²⁹ has shown that the ensemble functional is actually the lower convex envelope of the pure functional. Fortunately, the equivalence of pure and ensemble energy functionals on the set of ν -representable 1RDMs was confirmed recently.³⁰ Consequently, we can focus on physical electronic systems in their ground states under an external potential $v(\mathbf{r})$, where pure and ensemble functionals are indistinguishable, and consider only ensemble constraints during the energy minimization process to satisfy N -representability conditions.

Disappointingly, analytically determining $V_{\text{ee}}[\Gamma]$ remains a formidable challenge. Despite significant efforts, this goal has yet to be achieved, necessitating the use of approximations for V_{ee} . To approximate the unknown energy functional, one can use the exact functional form (1) in the NO representation, with a 2RDM constructed using a reconstruction functional $D[n_i, n_j, n_k, n_l]$, namely,

$$E_{\text{el}}[n_i, \phi_i] = \sum_i n_i H_{ii} + \sum_{ijkl} D[n_i, n_j, n_k, n_l] \langle kl|ij \rangle \quad (2)$$

where n_i denotes the ON of the NO ϕ_i . The restriction of the ONs to the range $0 \leq n_i \leq 1$ is both a necessary and sufficient condition for the ensemble N -representability of the 1RDM²⁵ within Löwdin normalization, where the traces of Γ and D correspond to the total number of electrons and electron pairs, respectively.

The approximate functional (2) clearly retains dependence on the 2RDM,³¹ meaning it is necessary to ensure not only the N -representability of the 1RDM but also the N -representability of the functional itself.³² Specifically, the reconstructed $D[n_i, n_j, n_k, n_l]$ must satisfy the same N -representability conditions as an



unreconstructed D (ref. 33) to guarantee the existence of a compatible N -electron system for the functional.

It has often been assumed, incorrectly, that approximate functionals do not encounter N -representability issues because the 1RDM conditions were believed to be sufficient. Although some functionals, like Müller's,³⁴ appear well-formulated and accurate for certain systems, they often violate fundamental N -representability conditions. This has exposed that many currently used approximate functionals^{35–37} fail to meet functional N -representability criteria.^{38–40}

Two procedures can be envisioned to derive $E_{\text{el}}[\{n_i, \phi_i\}]$: the so-called top-down and bottom-up methods.⁴¹ In the top-down approach, an approximate N -particle wavefunction is proposed in the NO representation, with the expansion coefficients explicitly expressed in terms of the ONs. This method directly yields an approximate functional that is N -representable by construction. Although this approach is straightforward, its success has been limited to a single case beyond the Hartree–Fock approximation: PNOF5.^{42,43}

In contrast, the bottom-up approach involves proposing $D[n_i, n_j, n_k, n_l]$ without relying on an N -particle state. The functional is then constructed by incrementally incorporating the set of N -representability conditions³³ into the proposed 2RDM reconstruction. Since the complete set of N -representability conditions for the 2RDM involves higher-order RDMs, only those conditions directly related to the 2RDM itself can be effectively applied. Specifically, the (2,2)-positivity conditions are used, which require the two-electron density matrix, the electron–hole density matrix, and the two-hole density matrix to be positive semidefinite. Consequently, we can never be entirely certain that the functional is fully N -representable, with the exception of PNOF5, which was derived using this method before its generating wavefunction was identified. However, the other functionals obtained *via* the bottom-up method can be considered approximately N -representable, as only some of the necessary N -representability conditions are imposed. The more conditions imposed on the 2RDM, the closer the resulting energy (2) is to the exact energy.

Given the implicit dependence of approximate functionals on the 2RDM, it is more accurate to classify $E_{\text{el}}[\{n_i, \phi_i\}]$ as a NOF rather than as a 1RDM functional. Ultimately, these functionals are only comprehended within the NO representation, including even the well-established functional derived from the Löwdin–Shull wavefunction⁴⁴ with a chosen phase combination, which accurately describes closed-shell two-electron systems. In this context, NOFs can be regarded as approximate energy expressions derived from an approximate quantum state, with certainty when using the top-down method and with high confidence when employing the bottom-up method. A significant consequence of this is that energy is not invariant under unitary transformations of the orbitals, resulting in the absence of a generalized Fockian when working with approximate functionals.⁴⁵ This property can only be guaranteed by the exact 1RDM functional, which can be defined in any representation, not just that of the NOs.

A systematic application of the bottom-up approach, using an explicit two-index approximation⁴⁶ of the two-particle

cumulant,^{47,48} has resulted in the development of a series of JKL -only functionals known as PNOF*i* ($i = 1–7$),^{49–55} where J , K , and L represent Coulomb, exchange, and exchange-time-inversion integrals, respectively.⁵⁶ These functionals have been particularly successful in capturing static electron correlation,⁵⁷ especially those based on electron pairing,⁵⁸ which closely match results from accurate wavefunction-based methods for small systems by also accounting for dynamic electron correlation within intrapair interactions.

The missing dynamic electron correlation can be addressed through perturbative corrections.^{59–62} However, while this approach primarily improves energies relative to reference NOF values, it does not enhance the quality of the NOs and ONs. Fully correlated NOs and ONs requires a more comprehensive strategy, such as the global NOF (GNOF).⁶³ GNOF achieves a balanced description of dynamic and static correlations, and its strong agreement with accurate wavefunction-based methods in both relative and absolute energies further underscores its reliability.

Minimizing a NOF requires adhering to the orthonormality constraints for the NOs, while the ONs must meet both ensemble N -representability conditions and Löwdin normalization. For NOFs based on electron pairing, additional conditions are imposed, which inherently ensure normalization. This setup results in a constrained optimization problem, typically tackled by optimizing the energy separately with respect to ONs and NOs, since simultaneous optimization of all variables has been shown to be inefficient for approximations.⁶⁴ Currently, open-source codes like DoNOF^{65,66} efficiently handle this problem and support GPU acceleration *via* implementations in modern programming languages such as Python and Julia. These codes provide various features, including geometry optimization, natural and canonical representations of molecular orbitals, computation of ionization potentials and electric moments, perturbative corrections for dynamic correlation, NOF-based *ab initio* molecular dynamics, and excited state calculations.

3 Assessment and future directions

NOFs can accurately treat strongly correlated systems,^{67–71} while requiring less computational effort than multiconfigurational wavefunction-based methods and coupled cluster theories. Unlike multireference methods such as CASPT2, NOFs are not sensitive to the selection of the active space or prone to instabilities due to changes in active space orbitals. In typical NOF calculations, all electrons are correlated across all available orbitals within a given basis set, an approach that is currently unfeasible for large systems using existing wavefunction-based methods.

NOFs effectively address a broader spectrum of systems^{72–76} than density functionals, which are limited by their single-reference nature, frequently achieving chemical accuracy.^{63,77} They are particularly effective in complex scenarios such as bond-breaking and bond-forming reactions,^{78–81} as well as in transition metal chemistry.^{82,83} PNOFs based on electron pairing have been especially successful in capturing static electron



techniques and leverage innovative optimization methods. Additionally, to further reduce the scaling of orbital optimization, solving the problem in the atomic orbital basis, as is usually done in self-consistent field methods, is essential.

Another difficulty to consider in any functional theory is spin. Since the electronic Hamiltonian commutes with the total spin squared (S^2) and one of its components, typically S_z , its eigenvectors must also be eigenvectors of these spin operators. Some methodologies to address this challenge use spin-unrestricted approaches, which bypass the requirement for approximate functionals to fully exhibit all symmetries. In these methodologies, the number of spin-up and spin-down electrons is fixed, but spin contamination is allowed. Relaxing the constraint on total spin conservation can improve size consistency and accuracy in energy predictions for molecular dissociations, among other scenarios. Nevertheless, spin-unrestricted methodologies often involve non-physical interpretations.

In the absence of an external field, total spin invariance implies that the ground state of a many-electron system forms a multiplet, a mixed quantum state encompassing all possible S_z values. One approach to addressing the spin issue is to focus solely on the high-spin component of the multiplet. Extensions of NOF theory to high-spin multiplet states have been reported,⁹⁶⁻⁹⁸ demonstrating some positive outcomes for atoms and molecules. However, no approximation currently exists that can accurately describe each component of the multiplet individually.

A more comprehensive strategy, without focusing on the specifics of each component, is to treat the multiplet as a whole.^{99,100} This approach centers on the mixed-spin state with the highest multiplicity ($2S + 1 = N_{\uparrow} + 1$), corresponding to the quantum number $S = N_{\uparrow}/2$, where $N_{\uparrow}$ denotes the number of unpaired electrons. A key feature of this formulation is the zero average spin projection across the ensemble, which enables 2RDM reconstructions that conserve spin and allows for the application of the machinery developed for singlet states. The results from this approach, which contrasts with conventional methods that emphasize the high-spin component or break spin symmetry, are promising.¹⁰¹ However, in some systems, additional correlation for unpaired electrons is still necessary,^{82,83} and simulating individual states remains crucial, especially in cases where the multiplet components are no longer degenerate.

In the context of NOF calculations, the general formulation of analytic energy gradients with respect to nuclear motion facilitates the efficient computation of equilibrium geometries.^{100,102} These gradients can be obtained through straightforward evaluation, eliminating the need for linear response theory or iterative procedures. However, calculating the analytic Hessian requires knowledge of NOs and ONs at the perturbed geometry, which can only be obtained by solving coupled-perturbed equations.¹⁰³ Consequently, computing second-order energy derivatives is significantly more demanding in terms of storage and computational time compared to evaluating gradients, making numerical differentiation of analytical gradients more efficient than direct analytical evaluation of the

opening in various systems,^{117,118} although some inaccuracies persist in photoemission spectra. Conversely, NOF-EKT offers an unsatisfactory description of electron affinities, though these can be estimated using the inverse of the IP of the corresponding anionic species, computed at the experimental geometry of the neutral species.¹¹⁵ On the other hand, neutral excitations within the extended random-phase approximation (ERPA)¹¹⁹ have recently led to the development of various NOF-ERPA methods,¹²⁰ which have produced very promising results, comparable to high-level CI methods but at significantly lower computational costs, and substantially outperform those obtained with time-dependent density functional theory. The accuracy of vertical excitation calculations is expected to improve in parallel with advancements in ground-state NOFs, as well as with enhanced implementations to better handle cases involving degeneracy of ONs.

A promising research direction is the extension of NOFs to periodic systems. Previously, some attempts were made using very basic functionals for polymers¹²¹ and solids,^{122,123} where translational symmetry allowed NOs to be represented as Bloch states. Other studies have focused on model systems such as the Hubbard model¹²⁴ or systems consisting solely of hydrogen atoms.^{68–70} The most significant achievement to date is demonstrating the viability of NOFs in cases where density functionals struggle, particularly in treating strong correlations, including Mott insulators. Consequently, there is a heightened focus on developing NOF-based methods that can effectively tackle the design and analysis of strongly correlated materials.¹²⁵

One unresolved issue is the treatment of dispersion interactions. Although some attempts have been made in the past,⁵⁰ *JKL*-only functionals face significant challenges with these systems. Employing non-*JKL* functionals with more complex dependencies seems necessary,¹²⁶ but this approach increases the computational cost of NOFs and detracts from their inherent simplicity. Current alternatives include incorporating perturbative corrections,⁶¹ using empirical treatments similar to those in DFT, or potentially improving functionals through machine learning. The latter has already shown promise in 1RDM-based electronic structure calculations,¹²⁷ in DFT,^{128,129} and in 1RDMFT for bosons.¹³⁰ By training on *ab initio* data, more accurate approximations could be achieved. Nevertheless, a key challenge for these functionals is generalization. Alternatively, machine learning could be employed as a phenomenological predictive tool, directly forecasting observables from large datasets or computational results by establishing intricate connections. However, this approach does not facilitate the rationalization of structure–property relationships from first principles, highlighting the important distinction that prediction does not equate to understanding.¹³¹

The most significant achievements of NOFs have so far been in describing ground states, while developing a robust theoretical framework for accurately addressing excited states, both charged ($E_v^{N\pm 1} - E_0^N$) and neutral ($E_v^N - E_0^N$), remains an ongoing challenge. Research has mainly focused on the energies of vertical excitations, with only a few studies addressing adiabatic transitions for charged excitations. For neutral excitations, the problem remains unresolved, as a description of the excited state independent of the ground state is still needed. Progress has been made using time-dependent theory within the adiabatic linear response framework^{105–107} and extending 1RDMFT to ensemble states with fixed weights w .^{108,109} However, both approaches still require more efficient minimization schemes to achieve significant success.

Current vertical excitation calculations rely on the ground state and vary depending on the excitation operator used to generate either charged or neutral states. Charged excitations are typically addressed using the extended Koopmans' theorem (EKT),^{110,111} while neutral excitations employ Rowe's excitation operator formalism.¹¹² In both methods, the coefficients defining these excited states are derived from the first- and second-order RDMs of the ground state. NOF-EKT provides satisfactory results for lower ionization potentials (IPs), but its accuracy diminishes for higher IPs.^{113–116} Recent advancements have improved IP accuracy and effectively addressed band gap

4 Conclusions

- 16 T. L. Gilbert, *Phys. Rev. B: Solid State*, 1975, **12**, 2111–2120.
- 17 M. Levy, *Proc. Natl. Acad. Sci. U. S. A.*, 1979, **76**, 6062–6065.
- 18 S. M. Valone, *J. Chem. Phys.*, 1980, **73**, 1344–1349.
- 19 R. A. Donnelly and R. G. Parr, *J. Chem. Phys.*, 1978, **69**, 4431–4439.
- 20 A. J. Cohen and P. Mori-Sánchez, *Phys. Rev. A*, 2016, **93**, 042511.
- 21 T. S. Müller, W. Töws and G. M. Pastor, *Phys. Rev. B*, 2018, **98**, 045135.
- 22 P. O. Löwdin, *Phys. Rev.*, 1955, **97**, 1474–1489.
- 23 M. Piris, *Adv. Quantum Chem.*, 2024, **90**, 1–52.
- 24 A. J. Coleman, in *Reduced-Density-Matrix Mechanics: with applications to many-electron atoms and molecules*, ed. D. A. Mazziotti, John Wiley and Sons, Hoboken, New Jersey, USA, 2007, ch. 1, vol. 134, pp. 1–9.
- 25 A. J. Coleman, *Rev. Mod. Phys.*, 1963, **35**, 668–687.
- 26 A. a. Klyachko, *J. Phys.: Conf. Ser.*, 2006, **36**, 72–86.
- 27 M. Altunbulak and A. Klyachko, *Commun. Math. Phys.*, 2008, **282**, 287–322.
- 28 T. T. Nguyen-Dang, E. V. Ludeña and Y. Tal, *J. Mol. Struct.: THEOCHEM*, 1985, **120**, 247–264.
- 29 C. Schilling, *J. Chem. Phys.*, 2018, **149**, 231102.
- 30 O. V. Gritsenko and K. Pernal, *Phys. Rev. A*, 2019, **100**, 012509.
- 31 R. A. Donnelly, *J. Chem. Phys.*, 1979, **71**, 2874–2879.
- 32 M. Piris, in *Many-Body Approaches Differ. Scales a Tribut. to N. H. March Occas. His 90th Birthd.*, ed. G. G. N. Angilella and C. Amovilli, Springer, New York, 2018, ch. 22, pp. 261–278.
- 33 D. a. Mazziotti, *Phys. Rev. Lett.*, 2012, **108**, 263002.
- 34 A. M. K. Müller, *Phys. Lett. A*, 1984, **105**, 446–452.
- 35 S. Sharma, J. K. Dewhurst, N. N. Lathiotakis and E. K. U. Gross, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 201103(R).
- 36 M. A. L. Marques and N. N. Lathiotakis, *Phys. Rev. A*, 2008, **77**, 032509.
- 37 D. R. Rohr, K. Pernal, O. V. Gritsenko and E. J. Baerends, *J. Chem. Phys.*, 2008, **129**, 164105.
- 38 M. Rodríguez-Mayorga, E. Ramos-Cordoba, M. Via-Nadal, M. Piris and E. Matito, *Phys. Chem. Chem. Phys.*, 2017, **19**, 24029–24041.
- 39 I. Mitxelena, M. Piris and M. Rodríguez-Mayorga, *J. Phys.: Condens. Matter*, 2017, **29**, 425602.
- 40 I. Mitxelena, M. Piris and M. Rodríguez-Mayorga, *J. Phys.: Condens. Matter*, 2018, **30**, 089501.
- 41 E. V. Ludeña, F. J. Torres and C. Costa, *J. Mod. Phys.*, 2013, **04**, 391–400.
- 42 K. Pernal, *Comput. Theor. Chem.*, 2013, **1003**, 127–129.
- 43 M. Piris, J. M. Matxain and X. Lopez, *J. Chem. Phys.*, 2013, **139**, 234109.
- 44 P. O. Löwdin and H. Shull, *Phys. Rev.*, 1956, **101**, 1730–1739.
- 45 M. Piris and J. M. Ugalde, *J. Comput. Chem.*, 2009, **30**, 2078–2086.
- 46 M. Piris, *Int. J. Quantum Chem.*, 2006, **106**, 1093–1104.
- 47 D. A. Mazziotti, *Chem. Phys. Lett.*, 1998, **289**, 419–427.
- 48 W. Kutzelnigg and D. Mukherjee, *J. Chem. Phys.*, 1999, **110**, 2800–2809.
- 49 P. Leiva and M. Piris, *J. Chem. Phys.*, 2005, **123**, 214102–214107.
- 50 M. Piris, X. Lopez and J. M. Ugalde, *J. Chem. Phys.*, 2007, **126**, 214103–214105.
- 51 M. Piris, J. M. Matxain, X. Lopez and J. M. Ugalde, *J. Chem. Phys.*, 2010, **132**, 031103.
- 52 M. Piris, J. M. Matxain, X. Lopez and J. M. Ugalde, *J. Chem. Phys.*, 2010, **133**, 111101.
- 53 M. Piris, X. Lopez, F. Ruipérez, J. M. Matxain and J. M. Ugalde, *J. Chem. Phys.*, 2011, **134**, 164102.
- 54 M. Piris, *J. Chem. Phys.*, 2014, **141**, 044107.
- 55 M. Piris, *Phys. Rev. Lett.*, 2017, **119**, 063002–063005.
- 56 M. Piris, *J. Math. Chem.*, 1999, **25**, 47–54.
- 57 I. Mitxelena, M. Piris and J. M. Ugalde, in *State Art Mol. Electron. Struct. Comput. Correl. Methods, Basis Sets More*, ed. P. Hoggan and U. Ancarani, Academic Press, 2019, ch. 7, vol. 79 of Advances in Quantum Chemistry, pp. 155–177.
- 58 M. Piris, in *Quantum Chemistry at the Dawn of the 21st Century. Series: Innovations in Computational Chemistry*, ed. R. Carbó-Dorca and T. Chakraborty, Apple Academic Press, 2018, ch. 22, pp. 593–620.
- 59 M. Piris, *J. Chem. Phys.*, 2013, **139**, 064111.
- 60 M. Piris, F. Ruipérez and J. Matxain, *Mol. Phys.*, 2014, **112**, 711–718.
- 61 M. Piris, *Phys. Rev. A*, 2018, **98**, 022504–022506.
- 62 M. Rodríguez-Mayorga, I. Mitxelena, F. Bruneval and M. Piris, *J. Chem. Theory Comput.*, 2021, **17**, 7562–7574.
- 63 M. Piris, *Phys. Rev. Lett.*, 2021, **127**, 233001.
- 64 E. Cancès and K. Pernal, *J. Chem. Phys.*, 2008, **128**, 134108.
- 65 M. Piris and I. Mitxelena, *Comput. Phys. Commun.*, 2021, **259**, 107651.
- 66 J. F. H. Lew-Yee, M. Piris and J. M. del Campo, *J. Chem. Phys.*, 2021, **154**, 064102.
- 67 I. Mitxelena, M. Rodríguez-Mayorga and M. Piris, *Eur. Phys. J. B*, 2018, **91**, 109.
- 68 I. Mitxelena and M. Piris, *J. Phys.: Condens. Matter*, 2020, **32**, 17LT01.
- 69 I. Mitxelena and M. Piris, *J. Chem. Phys.*, 2020, **152**, 064108.
- 70 I. Mitxelena and M. Piris, *J. Chem. Phys.*, 2022, **156**, 214102.
- 71 I. Mitxelena and M. Piris, *J. Chem. Phys.*, 2024, **160**, 204106–204108.
- 72 X. Lopez, F. Ruipérez, M. Piris, J. M. Matxain and J. M. Ugalde, *ChemPhysChem*, 2011, **12**, 1061–1065.
- 73 J. J. M. Matxain, F. Ruipérez, I. Infante, X. Lopez, J. J. M. Ugalde, G. Merino and M. Piris, *J. Chem. Phys.*, 2013, **138**, 151102.
- 74 M. Piris and N. H. March, *J. Phys. Chem. A*, 2015, **119**, 10190–10194.
- 75 J. M. Mercero, R. Grande-Aztatzi, J. M. Ugalde and M. Piris, *Adv. Quantum Chem.*, 2023, **88**, 229–248.
- 76 J. F. H. Lew-Yee and J. M. Campo, *AIP Adv.*, 2023, **13**, 065213.
- 77 X. Lopez, M. Piris, J. M. Matxain and J. M. Ugalde, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12931–12934.
- 78 X. Lopez, F. Ruipérez, M. Piris, J. M. Matxain, E. Matito and J. M. Ugalde, *J. Chem. Theory Comput.*, 2012, **8**, 2646–2652.
- 79 X. Lopez, M. Piris, F. Ruipérez and J. J. M. Ugalde, *J. Phys. Chem. A*, 2015, **119**, 6981–6988.



- 80 M. Piris, X. Lopez and J. M. Ugalde, *Chem.—Eur. J.*, 2016, **22**, 4109–4115.
- 81 X. Lopez and M. Piris, *Theor. Chem. Acc.*, 2019, **138**, 89.
- 82 J. M. Mercero, J. M. Ugalde and M. Piris, *Theor. Chem. Acc.*, 2021, **140**, 74.
- 83 J. F. H. Lew-Yee, J. M. del Campo and M. Piris, *J. Chem. Theory Comput.*, 2023, **19**, 211–220.
- 84 E. Ramos-Cordoba, X. Lopez, M. Piris and E. Matito, *J. Chem. Phys.*, 2015, **143**, 164112.
- 85 J. M. Matxain, M. Piris, F. Ruipérez, X. Lopez and J. M. Ugalde, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20129–20135.
- 86 F. Ruipérez, M. Piris, J. M. Ugalde and J. M. Matxain, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2055–2062.
- 87 M. Piris and N. H. March, *Phys. Chem. Liq.*, 2016, **54**, 797–801.
- 88 J. F. H. Lew-Yee, M. Piris and J. M. Campo, *J. Chem. Phys.*, 2023, **158**, 084110.
- 89 Y. Lemke, J. Kussmann and C. Ochsenfeld, *J. Chem. Theory Comput.*, 2022, **18**, 4229–4244.
- 90 N. G. Cartier and K. J. Giesbertz, *J. Chem. Theory Comput.*, 2024, **20**, 3669–3682.
- 91 M. Vladaj, Q. Marécat, B. Senjean and M. Saubanère, *J. Chem. Phys.*, 2024, **161**, 074105.
- 92 L. Franco, I. Bonfil-Rivera, J. F. H. Lew-Yee, M. Piris, J. M. del Campo and R. A. Vargas-Hernandez, *J. Chem. Phys.*, 2024, **160**, 244107.
- 93 R. Shepard, *Adv. Chem. Phys.*, 1987, **69**, 63–200.
- 94 U. Bozkaya, J. M. Turney, Y. Yamaguchi, H. F. Schaefer and C. D. Sherrill, *J. Chem. Phys.*, 2011, **135**, 104103–104117.
- 95 I. A. Elayan, R. Gupta and J. W. Hollett, *J. Chem. Phys.*, 2022, **156**, 094102.
- 96 P. Leiva and M. Piris, *Int. J. Quantum Chem.*, 2007, **107**, 1–11.
- 97 M. Piris, J. M. Matxain, X. Lopez and J. M. Ugalde, *J. Chem. Phys.*, 2009, **131**, 021102.
- 98 R. Quintero-Monsebaiz, I. Mitxelena, M. Rodríguez-Mayorga, A. Vela and M. Piris, *J. Phys.: Condens. Matter*, 2019, **31**, 165501–165508.
- 99 M. Piris, *Phys. Rev. A*, 2019, **100**, 32508.
- 100 I. Mitxelena and M. Piris, *J. Chem. Phys.*, 2020, **153**, 044101.
- 101 R. Quintero-Monsebaiz, L. I. Perea-Ramírez, M. Piris and A. Vela, *Phys. Chem. Chem. Phys.*, 2021, **19**, 2953–2963.
- 102 I. Mitxelena and M. Piris, *J. Chem. Phys.*, 2017, **146**, 014102–014107.
- 103 I. Mitxelena and M. Piris, *J. Math. Chem.*, 2018, **56**, 1445–1455.
- 104 A. Rivero-Santamaría and M. Piris, *J. Chem. Phys.*, 2024, **160**, 071102.
- 105 K. Pernal, K. Giesbertz, O. V. Gritsenko and E. J. Baerends, *J. Chem. Phys.*, 2007, **127**, 214101.
- 106 K. Giesbertz, E. Baerends and O. V. Gritsenko, *Phys. Rev. Lett.*, 2008, **101**, 033004.
- 107 R. van Meer, O. V. Gritsenko and E. J. Baerends, *J. Chem. Phys.*, 2017, **146**, 044119.
- 108 C. Schilling and S. Pittalis, *Phys. Rev. Lett.*, 2021, **127**, 023001.
- 109 J. Liebert, F. Castillo, J.-P. Labbé and C. Schilling, *J. Chem. Theory Comput.*, 2022, **18**, 124–140.
- 110 D. W. Smith and O. W. Day, *J. Chem. Phys.*, 1975, **62**, 113–114.
- 111 O. W. Day, D. W. Smith and R. C. Morrison, *J. Chem. Phys.*, 1975, **62**, 115–119.
- 112 D. J. Rowe, *Rev. Mod. Phys.*, 1968, **40**, 153–166.
- 113 K. Pernal and J. Cioslowski, *Chem. Phys. Lett.*, 2005, **412**, 71–75.
- 114 P. Leiva and M. Piris, *J. Mol. Struct.: THEOCHEM*, 2006, **770**, 45–49.
- 115 M. Piris, J. M. Matxain, X. Lopez and J. M. Ugalde, *J. Chem. Phys.*, 2012, **136**, 174116.
- 116 E. N. Zarkadoulas, S. Sharma, J. K. Dewhurst, E. K. U. Gross and N. N. Lathiotakis, *Phys. Rev. A*, 2012, **85**, 032504.
- 117 S. Di Sabatino, J. Koskelo, J. A. Berger and P. Romaniello, *Phys. Rev. B*, 2022, **105**, 235123.
- 118 S. Di Sabatino, J. Koskelo, J. A. Berger and P. Romaniello, *Phys. Rev. B*, 2023, **107**, 035111.
- 119 K. Chatterjee and K. Pernal, *J. Chem. Phys.*, 2012, **137**, 204109.
- 120 J. F. H. Lew-Yee, I. A. Bonfil-Rivera, M. Piris and J. M. del Campo, *J. Chem. Theory Comput.*, 2024, **20**, 2140–2151.
- 121 M. Piris and P. Otto, *Int. J. Quantum Chem.*, 2005, **102**, 90–97.
- 122 S. Sharma, J. K. Dewhurst, S. Shallcross and E. K. U. Gross, *Phys. Rev. Lett.*, 2013, **110**, 116403–116405.
- 123 Y. Shinohara, S. Sharma, S. Shallcross, N. N. Lathiotakis and E. K. U. Gross, *J. Chem. Theory Comput.*, 2015, **11**, 4895–4899.
- 124 M. Saubanère and G. M. Pastor, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **84**, 035111.
- 125 J. Schmidt, C. L. Benavides-Riveros and M. A. L. Marques, *Phys. Rev. B*, 2019, **99**, 224502.
- 126 L. M. Mentel, X. W. Sheng, O. V. Gritsenko and E. J. Baerends, *J. Chem. Phys.*, 2012, **137**, 204117.
- 127 X. Shao, L. Paetow, M. E. Tuckerman and M. Pavanello, *Nat. Commun.*, 2023, **14**, 6281.
- 128 B. Kalita, L. Li, R. J. McCarty and K. Burke, *Acc. Chem. Res.*, 2021, **54**, 818–826.
- 129 J. T. Margraf and K. Reuter, *Nat. Commun.*, 2021, **12**, 344.
- 130 J. Schmidt, M. Fadel and C. L. Benavides-Riveros, *Phys. Rev. Res.*, 2021, **3**, L032063.
- 131 R. Hoffmann and J. P. Malrieu, *Angew. Chem., Int. Ed.*, 2020, **59**, 12590–12610.
- 132 S. E. Smart and D. A. Mazziotti, *Phys. Rev. Lett.*, 2021, **126**, 070504.
- 133 S. E. Smart and D. A. Mazziotti, *Phys. Rev. A*, 2022, **105**, 1–11.
- 134 M. Rodríguez-Mayorga, K. J. H. Giesbertz and L. Visscher, *SciPost Chemistry*, 2022, **1**, 004.
- 135 J. F. H. Lew-Yee, J. M. del Campo and M. Piris, 2024, 1–10, in preparation.

