PHYSICAL REVIEW A **109**, L010801 (2024)

Letter

Tool for assessing the accuracy of approximate electronic wave functions

Jerzy Cioslowski[1,2,*] and Krzysztof Strasburger[3]

[1]*Institute of Physics, University of Szczecin, Wielkopolska 15, 70-451 Szczecin, Poland*
[2]*Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Straße 38, 01187 Dresden, Germany*
[3]*Department of Physical and Quantum Chemistry, Faculty of Chemistry, Wrocław University of Science and Technology,*
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

(Received 29 August 2023; revised 3 November 2023; accepted 29 November 2023; published 5 January 2024)

The authors propose a tool for assessing the accuracy of approximate electronic wave functions produced by diverse electronic structure calculations. The plots of $f_n = (\frac{\pi^2}{\nu_n})^{1/4} \frac{\langle \psi_n(\vec{r}) | [\Phi(\vec{r})]^{1/4} | \psi_n(\vec{r}) \rangle}{\langle \psi_n(\vec{r}) | \hat{T} | \psi_n(\vec{r}) \rangle}$ vs ν_n, where $\psi_n(\vec{r})$ is the nth natural (spin) orbital, ν_n is its occupation number, $\Phi(\vec{r})$ is the on-top two-electron density, and $\hat{T}$ is the kinetic energy operator, are found to vividly reveal inaccuracies of the underlying wave functions. As such, they provide synthetic yet detailed visual information well suited for accuracy assessments especially in the cases of approaches employing unstandardized basis sets and/or energy minimizations with unascertainable global convergence characteristics.

DOI: 10.1103/PhysRevA.109.L010801

Orbital-based formalisms of quantum chemistry are the workhorse of modern electronic structure calculations. These formalisms, which date back to the formulation of the Hartree equation [1] and its subsequent augmentation with the electron-exchange term by Fock [2] and Slater [3] almost a century ago, invariably involve the construction of an approximate electronic wave function or its equivalent (such as the reduced density matrix or the one-electron density) from one-electron functions (orbitals) given by linear combinations of the elements of some basis set. The finiteness of the cardinality of this set introduces the truncation error in the computed electronic properties that is independent of its intrinsic counterpart due to the approximations inherent to a given approach. In the case of modern implementations of the Kohn-Sham formalism [4], which are *de facto* semiempirical methods due to the plethora of adjustable parameters employed in their approximate functionals, the latter error is both dominant and not readily amenable to rigorous analysis, making the impact of the basis set quality on the overall accuracy less relevant. In contrast, highly sophisticated *ab initio* approaches, invoked when both accuracy and reliability are demanded, are characterized by small intrinsic errors, which brings the issue of the truncation error to the forefront.

The electron-electron coalescence cusp, whose presence in the exact electronic wave function Ψ [5] carries over to the related quantities such as the two-electron density $\rho_2(\vec{r}_1, \vec{r}_2)$ [6] and the one-electron reduced density matrix (the 1-matrix) ${}^1\Gamma(\vec{r}_1; \vec{r}_{1'})$ [7] (here and in the following the spin coordinates are suppressed for the sake of clarity), is poorly approximated by combinations of the Slater determinants constructed from finite numbers of orbitals. This flaw of the orbital-based formalisms is the root cause of the slow decay of the truncation error $\Delta E_{\mathcal{N}}$ in the electronic energy (and thus in all the other properties) with the basis-set size $\mathcal{N}$ [8]. In fact, the ratio $\frac{\Delta E_{\mathcal{N}}}{N}$, where N is the number of electrons, turns out to be inversely proportional to $\frac{\mathcal{N}}{N}$ [9]. At the first glance, this scaling of $\Delta E_{\mathcal{N}}$ with $\mathcal{N}$ appears to be very unfavorable due to the computational cost being typically proportional to $\mathcal{N}^{\lambda}$ (where $\lambda > 1$). However, this problem is mitigated in practical calculations with several numerical techniques, such as the computation of relative quantities (especially in the case of the electronic energy), the extrapolation to the complete-basis-set (CBS) limit [10] (note, however, the lack of solid theoretical foundations for this approach [11]), and the standardization of basis sets [12]. Among these three techniques, the last one is particularly important as it allows meaningful comparisons of the results obtained with different formalisms by different practitioners of quantum chemistry, *a priori* ballpark estimation of errors in the computed quantities with various rules of thumb concerning appropriateness of a given combination (colloquially called "the level of theory" [13]) of the formalism and the basis set for a given system or a class of systems, and the formulation of various composite methods that aim at error reduction without undue increase in computational cost [14]. Moreover, the aforementioned CBS extrapolations hinge upon the employment of systematically designed sequences of standard basis sets.

Unfortunately, this alleviation of the truncation error problem does not suffice when very high accuracy of electronic properties is sought. In such circumstances, the construction of approximate electronic wave functions from basis functions involving the interelectron distance(s) becomes indispensable. There are many variants of this explicitly correlated formalism [15–18] (which emerged concurrently [19] with its orbital-based counterpart) that differ in accuracy and computational cost. Among them, those employing the exponentially correlated Gaussians (ECGs) of Boys [20] and Singer [21] are

---

[*] To whom correspondence should be addressed: jerzy@wmf.univ.szczecin.pl

particularly suitable for few-electron systems [17,22], enabling predictions of electronic properties of atoms (such as Be [23], B [24], and C [25]), molecules (such as LiH [26], LiH$^-$ [27], BH [28], and H$_3$ [29]), and weakly bound species (such as He$_2$ [30]) with unprecedented accuracy. Since calculations involving ECGs readily lend themselves to efficient parallelization, the ongoing progress in the performance of computer hardware is certain to result in further extension of their range of applicability to other di- and triatomic molecules and their ions (especially within the nonrelativistic clamped-nuclei approximation).

At the center core of such calculations is the minimization of the Rayleigh quotient with respect to (in general) $\frac{N(N+1)}{2}$ exponents and $3N$ origin-shift coordinates of each ECG. Since thousands of ECGs are typically used, this quotient is an extremely complicated function of these variational parameters that has a large number of local minima. Consequently, its computed approximate minimizer is inherently ill-defined, depending strongly on the initial guess, the minimization method, and the number of function evaluations. Although, from a practical point of view, "it is only necessary to find a wave function that is sufficiently low lying in energy" [17], the infeasibility of locating the global minimum hinders the evaluation of the overall accuracy of the electronic properties produced by a given ECG calculation. This is so because, unlike in the case of the orbital-based formalisms, in which standardized basis sets are usually employed and the electronic wave function (or its equivalent) results from global minimization of some energy expression (often followed by additional mathematical operations involving the minimizer) and/or of the norm of the residual error vector, these properties are derived from sets of variational parameters corresponding to the vicinities of local minima that are approached at random. Consequently, as the lowering of the electronic energy cannot be regarded as a reliable indicator of the improvement in the overall accuracy, the juxtaposition of the computed data against their experimentally determined counterparts appears to be the only reliable way of comparing the quality of different ECG calculations. However, such an approach is not without its own challenges that stem from uncertainties in empirical data and the necessity of their adjustment to account for the contributions (such as those due the nuclear motion, the relativistic effects, and the QED phenomena) not included in the calculations.

In principle, bracketing of the ground-state energy offered by combining rigorous lower bounds with their variational counterparts discussed above can provide some information about the quality of the underlying approximate wave function. However, a practical application of this accuracy measure has several disadvantages. First of all, except for those obtained from the Weinstein formalism, the lower bounds are *de facto* properties of the basis sets whose linear combinations are the approximate wave functions rather than properties of the wave functions themselves [31]. Second, these bounds are usually quite loose, resulting in estimates of energy errors that are far too large. Third, these estimates are just single numbers that may not reflect the deficiencies of the wave functions affecting electronic properties other than energy.

The above observations underscore the necessity of development of a theoretical tool enabling a comprehensive yet concise accuracy assessment of ECG-based predictions of electronic properties. Such a tool, whose importance is particularly clear in light of the anticipated increase in the number of these predictions due to the continuous advances in the performance of computer hardware, should (i) rely solely on the quantities derivable from the electronic wave function under examination, (ii) be universally applicable to a broad spectrum of quantum-chemical methods (despite, for the reasons spelled out above, being developed with the ECG-based approaches in mind), (iii) be robust, i.e., yielding equally useful information for wave functions of both high and low accuracy, (iv) be sensitive enough to readily reveal differences among wave functions corresponding to barely different energies, and (v) produce synthetic yet sufficiently detailed output (preferably graphical) that lends itself to simple interpretation, thus facilitating rapid comparison and identification of individual wave functions.

Consider the ratio

$$f_n = \left(\frac{\pi^2}{\nu_n}\right)^{1/4} \frac{\langle \psi_n(\vec{r}) | [\Phi(\vec{r})]^{1/4} | \psi_n(\vec{r}) \rangle}{\langle \psi_n(\vec{r}) | \hat{T} | \psi_n(\vec{r}) \rangle}, \tag{1}$$

where $\hat{T}$ is the kinetic energy operator, $\psi_n(\vec{r})$ is the nth natural (spin) orbital (NO), ν_n is its occupation number [32], and $\Phi(\vec{r}) = \rho_2(\vec{r}, \vec{r})$ is the on-top two-electron density. When derived from exact Ψ, these quantities are known to asymptotically obey the zero-energy Schrödinger equation [33]

$$\hat{T}\,\psi_n(\vec{r}) - \left(\frac{\pi^2}{\nu_n}\right)^{1/4} [\Phi(\vec{r})]^{1/4}\,\psi_n(\vec{r}) = 0 \tag{2}$$

at the limit of $n \to \infty$ (where n orders the occupation numbers nonascendingly) provided that $\Phi(\vec{r})$ does not vanish for all $\vec{r}$. This asymptotic behavior implies f_n rapidly tending to one as $\nu_n \to 0$ [33,34]. Thus, as any deviation from this trend (called "a feature" in the following text) is indicative of inaccuracies in a given approximate electronic wave function, the plot of f_n vs ν_n (the latter conveniently displayed in a logarithmic scale) constitutes an accuracy fingerprint of such Ψ.

The quantities that enter Eq. (1) are readily computable from any N-electron wave function. The first step in the evaluation of f_n involves the computations of $\rho_2(\vec{r}_1, \vec{r}_2)$ and $^1\Gamma(\vec{r}_1; \vec{r}_{1'})$, which are particularly straightforward for Ψ given by a linear combination of ECGs. Diagonalization of the latter (in a suitable basis of one-electron functions whose adequacy can be easily assessed by examining the effect of its augmentation on the accuracy fingerprint) affords the NOs and their occupation numbers, from which the expectation values of $[\Phi(\vec{r})]^{1/4}$ and $\hat{T}$ can be calculated for each $\psi_n(\vec{r})$. For the latter, the respective integrals are amenable to analytical evaluation, whereas one has to resort to a numerical quadrature for the former. However, since $[\Phi(\vec{r})]^{1/4}$ varies rather slowly with $\vec{r}$, the estimate

$$\langle \psi_n(\vec{r}) | [\Phi(\vec{r})]^{1/4} | \psi_n(\vec{r}) \rangle \approx \sum_j [\Phi(\vec{R}_j)]^{1/4} \int_{\Omega_j} |\psi_n(\vec{r})|^2\, d^3\vec{r}, \tag{3}$$

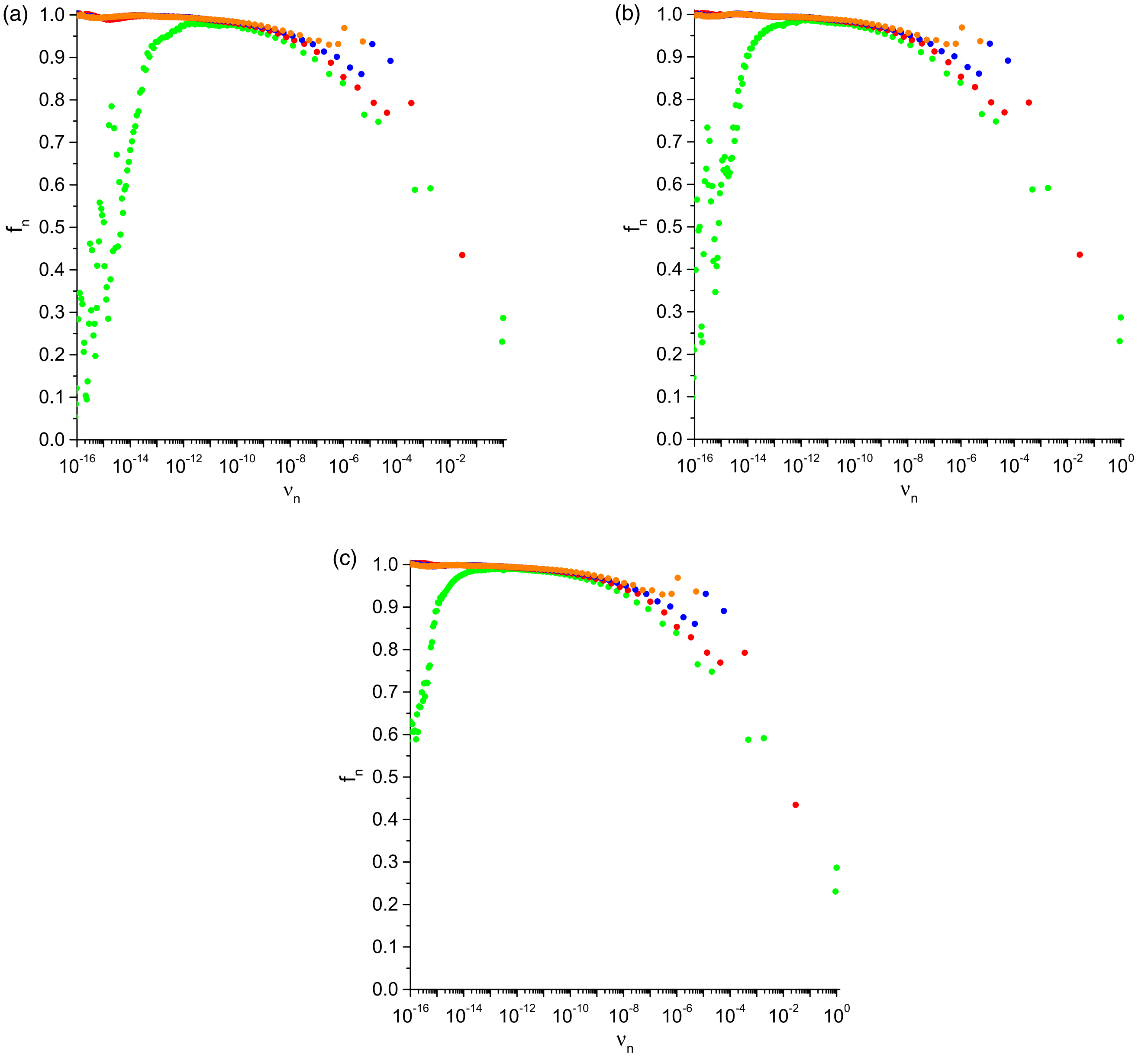

FIG. 1. The accuracy fingerprints of the approximate ground-state electronic wave functions of the Be atom computed with (a) 2745, (b) 4023, and (c) 5896 ECGs. The quantities corresponding to the *s*-, *p*-, *d*-, and *f*-type NOs are denoted by green, red, blue, and orange dots, respectively.

where $\vec{R}_j = \frac{\int_{\Omega_j} \vec{r}\, d^3\vec{r}}{\int_{\Omega_j} d^3\vec{r}}$ is the center of Ω_j, converges rapidly to the exact value with the diminishing sizes of the domains $\{\Omega_j\}$ such that $\bigcup_j \Omega_j = \mathbb{R}^3$ (note that three significant digits in the computed properties suffice for the purpose of their plotting).

It transpires from the above considerations that, being directly derivable from approximate electronic wave functions of any accuracy computed with a broad spectrum of quantum-chemical methods [including those that are not explicitly wave-function-based, for which, if available, $\rho_2(\vec{r}_1, \vec{r}_2)$ and ${}^1\Gamma(\vec{r}_1; \vec{r}_{1'})$ can be used instead of Ψ], the accuracy fingerprints meet the first three of the aforementioned five requirements expected to be satisfied by the interpretive tool sought in the present study. The conformity with the remaining two requirements is convincingly demonstrated with the help of the following numerical examples.

The first of these examples concerns the approximate ${}^1S_g$ ground-state electronic wave functions of the Be atom obtained with 2745, 4023, and 5896 [35] ECGs (which correspond to the respective energies of $-14.667\,356\,431$, $-14.667\,356\,476$, and $-14.667\,356\,500$ hartree that are 77, 32, and 8 nhartree above the best literature value of $-14.667\,356\,508$ hartree [23]). Inspection of their accuracy fingerprints displayed in Fig. 1 gives rise to several interesting observations. First of all, the deficiencies of the wave functions in question are manifest almost exclusively in the *s*-type NOs, hinting perhaps at the predominance of inaccuracies in the reproduction of the electron-nucleus cusp over those pertaining to its electron-electron counterpart. Second,

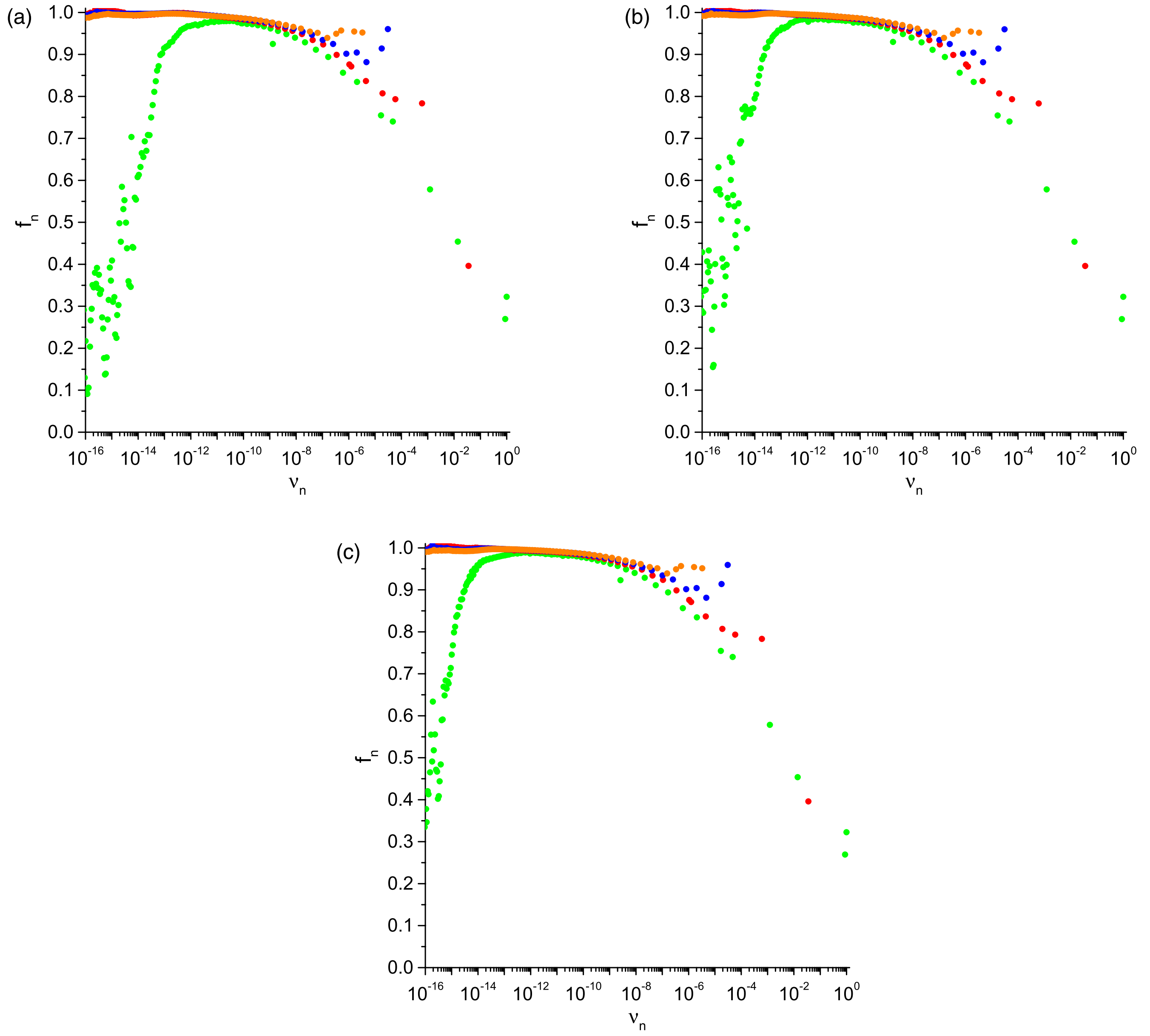

FIG. 2. The accuracy fingerprints of the approximate ground-state electronic wave functions of the Li$^-$ anion atom computed with (a) 2745, (b) 4023, and (c) 5896 ECGs. The quantities corresponding to the *s*-, *p*-, *d*-, and *f*-type NOs are denoted by green, red, blue, and orange dots, respectively.

the features in the accuracy fingerprints that reflect these deficiencies are rich in detail, which implies the feasibility of rapid comparisons of wave functions originating from different sources by means of simple superimpositions of the relevant plots. Such comparisons are expected to be particularly useful in the cases of calculations (partially) converged to distinct local minima with close energy values or in the situations where relative quality of the results of calculations carried out by different researchers (possibly with different methods) has to be ascertained. Third, although the magnitudes of the occupation numbers at the onsets of these features become progressively smaller with the increasing numbers of ECGs, the features themselves do not evolve in a systematic manner, signaling the random and incomplete nature of the minimization process involved in the computation of the underlying approximate wave functions.

The above observations carry over to the analogous accuracy fingerprints pertaining to the ^1S_g ground state of the Li$^-$ anion (Fig. 2), for which the calculations employing 2745, 4023, and 5896 [35] ECGs yield the respective energies of $-7.500\,776\,566$, $-7.500\,776\,603$, and $-7.500\,776\,622$ hartree (note that the last of these values is lower than its best literature counterpart of $-7.500\,776\,613$ hartree computed with 10 000 ECGs [36]). An interesting aspect of these accuracy fingerprints is the presence of the *s*-type NO with the occupation number of ca. 10^{-9} that stands out from the otherwise regular dependencies of f_n on ν_n as a solitary persistent feature in the midsections of the plots. This NO is an instance of solitonic natural orbitals (SoNOs) that occasionally appear

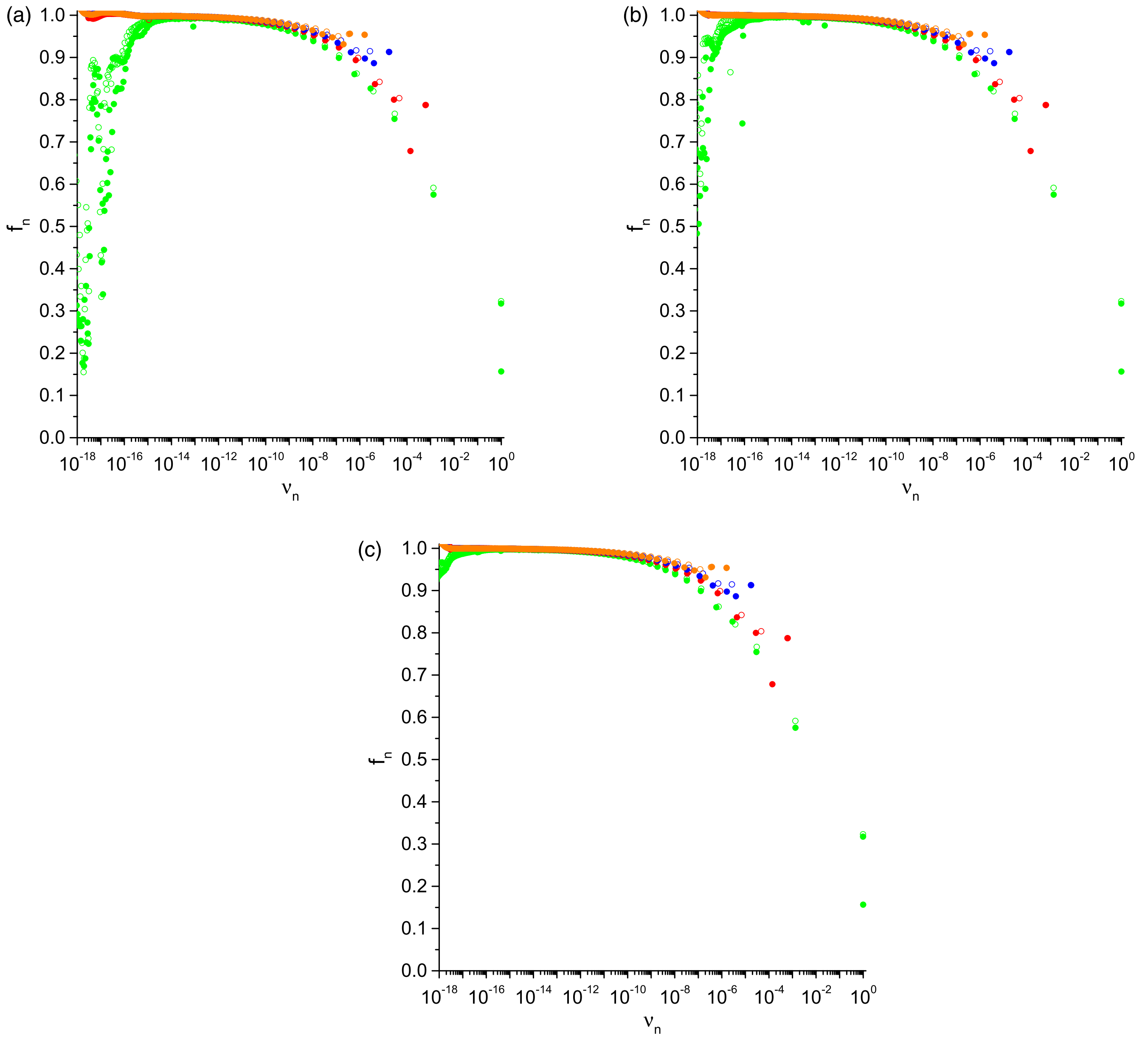

FIG. 3. The accuracy fingerprints of the approximate ground-state electronic wave functions of the Li atom computed with (a) 1873, (b) 2745, and (c) 4023 ECGs. The quantities corresponding to the *s*-, *p*-, *d*-, and *f*-type NOs are denoted by green, red, blue, and orange dots (solid/hollow for the NOs with the α/β spin components), respectively.

in strongly correlated systems [34]. Although the values of f_n computed for these SoNOs deviate significantly from 1, their appearance in the accuracy fingerprints is largely irrelevant in the context of the present study.

The example involving the ^2S_g ground state of the Li atom, for which the energies of −7.478 060 322 652, −7.478 060 323 725, and −7.478 060 323 881 hartree (which are 1258, 185, and 29 phartree above their best literature counterpart of −7.478 060 323 910 147 hartree [37]) are obtained with 1873, 2745, and 4023 [35] ECGs, respectively, demonstrates the applicability of the concept of the accuracy fingerprints to approximate wave functions of spin-polarized systems. In this instance, the NOs can be marked for not only their angular momenta but also their spin components (Fig. 3). As in the previous cases of Be and Li^-, it turns out that the features indicating the deficiencies of the corresponding wave functions are largely confined to the *s*-type NOs with both the α and β spin components. Not surprisingly, the presence of these features does not correlate with the magnitude of the energy error as some of those absent in the accuracy fingerprint pertaining to 1873 ECGs appear upon the number of the basis functions being increased to 2745, only to vanish again for the wave function computed with 4023 ECGs.

The capability of the accuracy fingerprints to discriminate among approximate wave functions yielding essentially identical variational energies is vividly illustrated with the results of a numerical experiment in which the optimized exponents of the 4023 ECGs employed in the construction of the most accurate of the three aforedescribed ground-state wave functions of the lithium atom are scaled by either

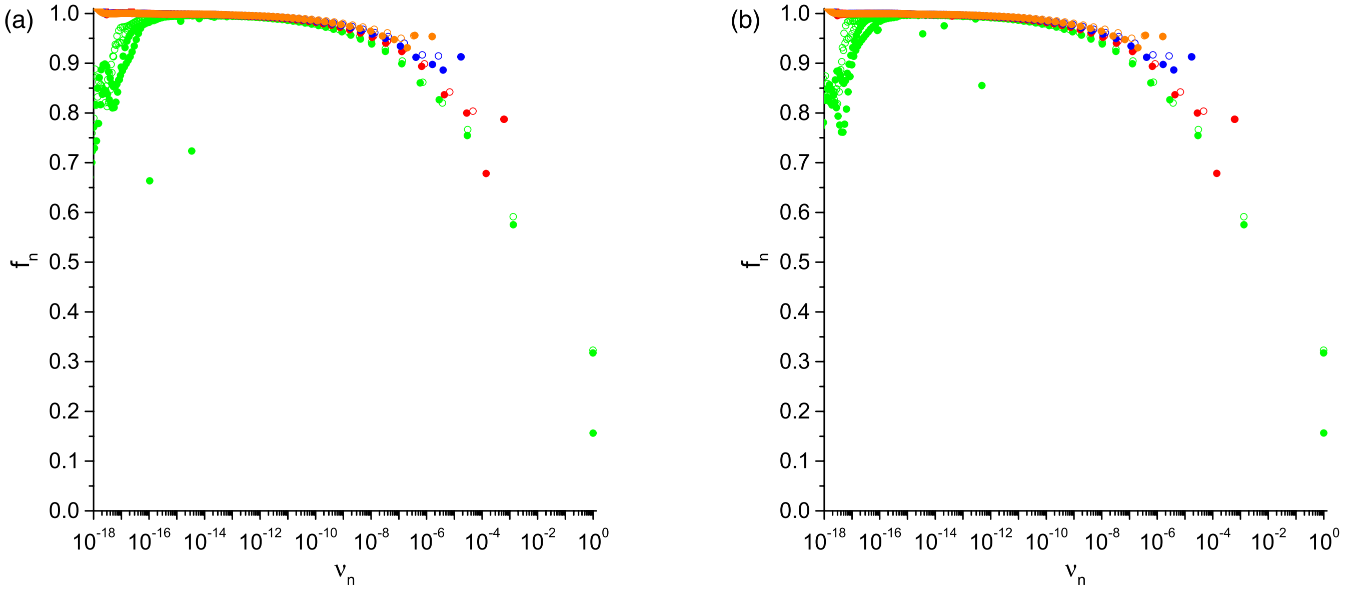

FIG. 4. The accuracy fingerprints of the approximate ground-state electronic wave functions of the Li atom computed from 4023 ECGs with the optimized exponents scaled by (a) 0.90893 and (b) 1.10395. The quantities corresponding to the *s*-, *p*-, *d*-, and *f*-type NOs are denoted by green, red, blue, and orange dots (solid/hollow for the NOs with the α/β spin components), respectively.

0.908 93 or 1.103 95 in order to simulate incomplete energy minimizations. Such a scaling results in the variational energies matching within 0.1 phartree that corresponding to the wave function computed with 2745 ECGs. Inspection of the plots displayed in Fig. 4 and their comparison with that presented in Fig. 3(b) reveal well-pronounced dissimilarities among the accuracy fingerprints of the approximate wave functions arising from a smaller basis of optimized ECGs and from its larger unoptimized counterparts. In addition to distinct features in the leftmost regions of the plots, there are prominent differences within the 10^{-16}–10^{-12} range of the occupation numbers, where the three features present at ca. 2.52×10^{-17}, 8.17×10^{-17}, and 8.73×10^{-17} in the accuracy fingerprint pertaining to the 2745 optimized ECGs [Fig. 3(b)] are replaced by those at 1.06×10^{-16} and 3.44×10^{-15} [for the 4023 ECGs with the exponents scaled down; Fig. 4(a)] and at 3.58×10^{-15}, 2.11×10^{-14}, and 4.84×10^{-13} [for the 4023 ECGs with the exponents scaled up; Fig. 4(b)]. One is tempted to regard the earlier (i.e., at greater occupation numbers) onset of these features as the indicator of the incomplete energy minimizations simulated by scaling of the optimized exponents.

The usefulness of the accuracy fingerprints in the detection of inaccuracies in approximate electronic wave functions obtained with the orbital-based methods is convincingly demonstrated by the case of the ^1S_g ground state of the helium atom. A juxtaposition of the plot pertaining to the approximate wave function obtained from benchmark calculations [38] against that produced by the full configuration interaction (FCI) method employed in conjunction with the cc-pV6Z basis set [12] reveals two interesting facts (Fig. 5). First of all, although within the FCI formalism the number of the NOs equals the cardinality of the basis set, several of the respective occupation numbers are reproduced surprisingly well. On the other hand, the corresponding values of f_n are severely overestimated for all n due to the very inaccurate on-top two-electron density. In contrast to those encountered in the previous numerical examples, this deficiency is manifested at the rightmost region of the plot.

In summary, the plots of the values of a certain quantity derived from the properties of natural (spin) orbitals vs their occupation numbers can be regarded as accuracy fingerprints that encode deficiencies of approximate electronic

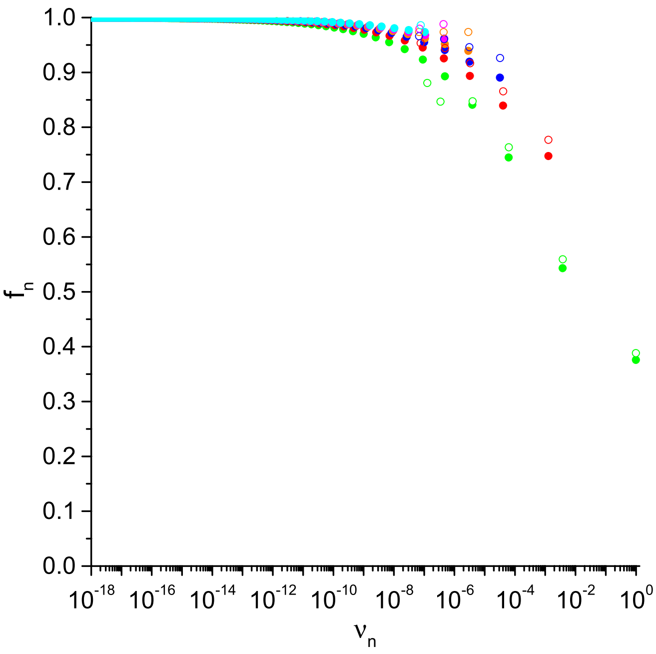

FIG. 5. A juxtaposition of the accuracy fingerprints pertaining to the approximate ground-state electronic wave functions of the He atom obtained from benchmark (solid dots) and FCI/cc-pV6Z (hollow dots) calculations. The quantities corresponding to the *s*-, *p*-, *d*-, *f*-, *g*-, and *h*-type NOs are denoted by green, red, blue, orange, magenta, and cyan dots, respectively.

wave functions in a manner suitable for detailed visual inspection. Consequently, they provide simple yet effective means for assessing the numerical quality of such wave functions, solving a problem whose importance to quantum-chemical calculations employing unstandardized basis sets and/or energy minimizations with unascertainable global convergence characteristics has not been fully recognized thus far. When employed in conjunction with ECG-based approaches, the accuracy fingerprints are expected to be particularly useful as tools for monitoring both the gradual construction of basis sets and the optimization of their variational parameters, comparing both the wave functions that belong to different local energy minima and those obtained with different numerical runs, and identifying possible pathways to accuracy improvement. For electronic states with nontrivial point-group symmetries, the visual information carried by these fingerprints can be further enhanced by marking the NOs according to the pertinent irreducible representations.

Acknowledgments. The research described in this Letter has been funded by the National Science Center (Poland) under Grant No. 2018/31/B/ST4/00295. The support from Max-Planck-Institut für Physik Komplexer Systeme (MPI PKS), Dresden, is also acknowledged by one of the authors (J.C.). The majority of the calculations reported in this Letter have been carried out at Wrocław Center for Networking and Supercomputing (WCSS) [39].

Appendix: details of calculations. Since the methodology of the ECG-based electronic structure calculations has been repeatedly reviewed [17,22], only the details specific to the present work are presented here. Single functions of the spin coordinates $\{\sigma_i\}$, namely, $[\alpha(\sigma_1)\,\beta(\sigma_2) - \beta(\sigma_1)\,\alpha(\sigma_2)]\,\alpha(\sigma_3)$ for the ^2S_g state of Li and $[\alpha(\sigma_1)\,\beta(\sigma_2) - \beta(\sigma_1)\,\alpha(\sigma_2)]\,[\alpha(\sigma_3)\,\beta(\sigma_4) - \beta(\sigma_3)\,\alpha(\sigma_4)]$ for the ^1S_g states of Be and Li$^-$, have been employed. The ECG basis sets have been constructed in an iterative manner that commences with those comprising $K_1 = 1$, $K_2 = 2$, and $K_3 = 3$ functions. For each $J > 3$, the sets of K_{J-2} and K_J ECGs with the variational parameters already optimized by separate minimizations of the respective Rayleigh quotients have been merged and the resulting parameters of the set of $K_{J+1} = K_{J-2} + K_J$ ECGs have been employed as the initial guess for the *de novo* optimization.

The NOs and their corresponding occupation numbers have been obtained from the 1-matrices (which are themselves given by linear combinations of the ECG-type functions) derived from the computed approximate wave functions. These matrices have been projected onto basis sets composed of nucleus-centered Gaussian primitives $\{x^{k_i}\, y^{l_i}\, z^{m_i}\, e^{-\zeta_i r^2}\}$ with k_i, l_i, and m_i equal to either 0 or 1, the sum $k_i + l_i + m_i$ assuming the values of 0, 1, 2, and 3 for the s-, p-, d-, and f-type NOs, respectively. The projections have involved computation of the matrix elements of the 1-matrices in the bases of these primitives, their transformation to orthonormal bases, and diagonalization of the resulting matrices. In principle, the optimal values of the exponents $\{\zeta_i\}$ could be determined for each of the NO types by maximization of the overlap between the original and projected matrices. However, as such maximizations are prohibitively expensive, $\{\zeta_i\}$ have been restricted to the elements of two even-tempered sequences of exponents whose parameters have been optimized for the 1-matrices derived from the wave functions constructed with either 406 (Li) or 129 (Be and Li$^-$) ECGs. For the s- and p-type orbitals, the resulting sets of exponents have been augmented with modified even-tempered sequences covering the range of the greatest values of $\{\zeta_i\}$ in order to circumvent the problem of excessive linear dependencies among basis functions. In the case of Li, the final calculations of the NOs and their occupation numbers have been carried out in the extended precision of 96 decimal digits with 160 (320 for the s-type NOs) Gaussian primitives, whereas in the cases of Be and Li$^-$, 100 (200 for the s-type NOs) Gaussian primitives have been used in conjunction with the quad-double precision (equivalent to ca. 64 decimal digits). Appropriate numerical libraries [40] have been employed in all of these calculations.

[1] D. R. Hartree, The wave mechanics of an atom with a non-Coulomb central field. Part I. Theory and methods, Math. Proc. Cambridge Philos. Soc. **24**, 89 (1928).

[2] V. A. Fock, Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems, Z. Phys. **61**, 126 (1930).

[3] J. C. Slater, Note on Hartree's method, Phys. Rev. **35**, 210 (1930).

[4] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. **140**, A1133 (1965).

[5] T. Kato, On the eigenfunctions of many-particle systems in quantum mechanics, Commun. Pure Appl. Math. **10**, 151 (1957).

[6] E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry* (Academic, New York, 1976).

[7] J. Cioslowski, Off-diagonal derivative discontinuities in the reduced density matrices of electronic systems, J. Chem. Phys. **153**, 154108 (2020).

[8] R. N. Hill, Rates of convergence and error estimation formulas for the Rayleigh-Ritz variational method, J. Chem. Phys. **83**, 1173 (1985).

[9] J. Cioslowski and K. Strasburger, A universal power law governing the accuracy of wave function-based electronic structure calculations, J. Phys. Chem. Lett. **13**, 8055 (2022).

[10] W. Klopper, K. L. Bak, P. Jørgensen, J. Olsen, and T. Helgaker, Highly accurate calculations of molecular electronic structure, J. Phys. B: At., Mol. Opt. Phys. **32**, R103 (1999).

[11] J. Cioslowski and K. Strasburger, Angular-momentum extrapolations to the complete basis set limit: Why and when they work, J. Chem. Theory Comput. **17**, 3403 (2021).

[12] B. P. Pritchard, D. Altarawy, D. Brett, T. D. Gibson, and T. L. Windus, A new basis set Exchange: An open, up-to-date resource for the molecular sciences community, J. Chem. Inf. Model. **59**, 4814 (2019).

[13] J. A. Pople, Two-dimensional chart of quantum chemistry, J. Chem. Phys **43**, S229 (1965).

[14] For a review, see A. Karton, A computational chemist's guide to accurate thermochemistry for organic molecules, WIREs Comput. Mol. Sci. **6**, 292 (2016).

[15] C. Hättig, W. Klopper, A. Köhn, and D. P. Tew, Explicitly correlated electrons in molecules, Chem. Rev. **112**, 4 (2012).

[16] S. Ten-no, Explicitly correlated wave functions: Summary and perspective, Theor. Chem. Acc. **131**, 1070 (2012).

[17] J. Mitroy, S. Bubin, W. Horiuchi, Y. Suzuki, L. Adamowicz, W. Cencek, K. Szalewicz, J. Komasa, D. Blume, and K. Varga, Theory and application of explicitly correlated Gaussians, Rev. Mod. Phys. **85**, 693 (2013).

[18] M. B. Ruiz, J. S. Sims, and B. Padhy, High-precision Hy-CI and E-Hy-CI studies of atomic and molecular properties, Adv. Quantum Chem. **83**, 171 (2021).

[19] E. A. Hylleraas, Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium, Z. Phys. **54**, 347 (1929).

[20] S. F. Boys, The integral formulae for the variational solution of the molecular many-electron wave equation in terms of Gaussian functions with direct electronic correlation, Proc. R. Soc. London A **258**, 402 (1960).

[21] K. Singer, The use of gaussian (exponential quadratic) wave functions in molecular problems. I. General formulae for the evaluation of integrals, Proc. R. Soc. London A **258**, 412 (1960).

[22] S. Bubin, M. Pavanello, W.-C. Tung, K. L. Sharkey, and L. Adamowicz, Born-Oppenheimer and non-Born-Oppenheimer, atomic and molecular calculations with explicitly correlated Gaussians, Chem. Rev. **113**, 36 (2013).

[23] I. Hornyák, L. Adamowicz, and S. Bubin, Ground and excited ^1S states of the beryllium atom, Phys. Rev. A **100**, 032504 (2019).

[24] M. Puchalski, J. Komasa, and K. Pachucki, Explicitly correlated wave function for a boron atom, Phys. Rev. A **92**, 062501 (2015).

[25] K. Strasburger, Explicitly correlated wave functions of the ground state and the lowest quintuplet state of the carbon atom, Phys. Rev. A **99**, 052512 (2019).

[26] K. Strasburger and J. Cioslowski, Partial-wave decomposition of the one-electron properties of the LiH molecule computed with explicitly correlated basis sets, Mol. Phys. **120**, e2048107 (2022).

[27] S. Bubin and L. Adamowicz, Nonrelativistic molecular quantum mechanics without approximations: Electron affinities of LiH and LiD, J. Chem. Phys. **121**, 6249 (2004).

[28] S. Bubin, M. Stanke, and L. Adamowicz, Non-Born-Oppenheimer calculations of the BH molecule, J. Chem. Phys. **131**, 044128 (2009).

[29] M. Pavanello, W.-C. Tung, and L. Adamowicz, How to calculate H_3 better, J. Chem. Phys. **131**, 184106 (2009).

[30] M. Przybytek, W. Cencek, B. Jeziorski, and K. Szalewicz, Pair potential with submillikelvin uncertainties and nonadiabatic treatment of the halo state of the helium dimer, Phys. Rev. Lett. **119**, 123401 (2017).

[31] R. T. Ireland, P. Jeszenszki, E. Mátyus, R. Martinazzo, M. Ronto, and E. Pollak, Lower bounds for nonrelativistic atomic energies, ACS Phys. Chem. Au **2**, 23 (2022), and the references cited therein.

[32] P.-O. Löwdin, Quantum theory of many-particle systems. I. Physical interpretations by means of density matrices, natural spin-orbitals, and convergence problems in the method of configurational interaction, Phys. Rev. **97**, 1474 (1955).

[33] J. Cioslowski and K. Strasburger, From Fredholm to Schrödinger via eikonal: A new formalism for revealing unknown properties of natural orbitals, J. Chem. Theory Comput. **17**, 6918 (2021).

[34] J. Cioslowski, F. Prątnicki, and K. Strasburger, Solitonic natural orbitals in Coulombic systems, J. Chem. Phys. **156**, 034108 (2022).

[35] These numbers are the elements of the so-called Narayana's cows sequence; see N. J. A. Sloane, The Online Encyclopedia of Integer Sequences, http://oeis.org/A000930.

[36] S. Bubin, J. Komasa, M. Stanke, and L. Adamowicz, Isotope shift in the electron affinity of lithium, J. Chem. Phys. **131**, 234112 (2009).

[37] L. M. Wang, Z.-C. Yan, H. X. Qiao, and G. W. F. Drake, Variational energies and the Fermi contact term for the low-lying states of lithium: Basis-set completeness, Phys. Rev. A **85**, 052513 (2012).

[38] J. Cioslowski and F. Prątnicki, Universalities among natural orbitals and occupation numbers pertaining to ground states of two electrons in central potentials, J. Chem. Phys. **151**, 184107 (2019).

[39] http://wcss.pl.

[40] https://www.davidhbailey.com/dhbsoftware.