

PCCP

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

**Analytical Density-Scaling Rules: a
Comment on “Scaling Properties of
Information-Theoretic Quantities in Density
Functional Reactivity Theory” by Rong *et. al.* [*Phys. Chem. Chem. Phys.*, 2015, 17,
4977]**

Hugo J. Bohórquez

Quantum Biochemistry & Biomathematics, FIDIC, Cra. 50 No. 26-00, Of. 102,
Bogotá D. C., Colombia

PBX: (57+1+)315 8919 x122;

PBX: (57-1)3244671 x108

hugo.j.bohorquez@fdic.org.co

Abstract

The scaling properties of density functionals are key for fundamentally understanding the density functional theory. Accordingly, the dependence of density functionals with the number of particles is of paramount relevance. The numerical exploration by Rong *et al.* addressed the N -scaling for a set of quantum information quantities; they found linear relationships between each one of them and the electronic population for atoms, molecules, and atoms in molecules. A main motivation for their computational work was that the theoretical scaling of these quantities is unknown; however, these scaling properties can be analytically determined. Here I reveal the derivation of the N -scaling rules for the quantities studied by Rong *et al.* by following the procedure introduced in *Comp. Theor. Chem.*, 2015, 1053, 38. In addition, a new atomic scaling rule explains the linear relation between atomic populations and atomic values of the same quantum information quantities.

Density scaling has been a major subject of research in the development of the density functional theory (DFT)[1] which states that all ground-state properties of the system can be expressed as unique functionals of the density ρ . [2] In general, a density functional $f[\rho]$ is homogeneous of degree β with respect to density scaling if the functional satisfies the following condition,

$$f[\zeta\rho] = \zeta^\beta f[\rho] \quad (1)$$

A special case is the scaling induced by the density per particle $\sigma = \rho/N$, which leads to

$$f[\rho] = N^\beta f[\sigma] \quad (2)$$

by taking $\zeta = 1/N$ in Eq. 1. This N -scaling rule is useful for systematically studying the role of the total number of particles in density functionals.[3, 4, 5] In a recent paper, Rong *et al.*[6, 7] observed a linear scaling with N for different information functionals: Shannon entropy S_S , [8] Fisher information I_F , [9] and Ghosh-Berkowitz-Parr (GBP) entropy S_{GBP} . [10] The underlying argument in favor of their computational survey is the assumption that a dependence of these quantities with the number of electrons is theoretically unknown. However, as shown in the present comment, one can theoretically explain the N -dependence for all of them by assuming that the ground-state density ρ is known; no further assumptions are necessary—except for the N -scaling proof of GBP entropy which is circumscribed to the Khon-Sham approximation.[11]

From the Shannon entropy of ρ , $S_S[\rho] = -\int \rho \ln \rho$, the following equation emerges

$$S_S[\rho] = N\Delta S[\sigma; N] \quad (3)$$

where $\Delta S = S_\sigma - S_N$ is the Kullback-Leibler information divergence[12] between the density per particle distribution σ and the constant distribution $p = 1/N$ —for which Shannon entropy takes the maximum value of $S_N \equiv \ln N$. [13] For any neutral atom after fluorine (i. e. $N > 9$), $\ln N$ is the dominant term in ΔS which implies $S_\sigma < S_N$ and consequently $S_S < 0$ —as Table 1 in Rong *et al.* shows.[6, 7] Hence, for large N values $-NS_N$ is the dominant term in S_S . Notice

that from the atomic data reported by Rong *et al.* one can find a correlation coefficient of $R^2 = 0.92$ between S_S and N which is greater—about 15%—than the one between S_σ versus N ($R^2 = 0.80$) they reported.[7] Both of these linear correlations, however, obviate the periodic trends of the data sets. Indeed S_σ versus N appreciably deviates from linearity within each row of the periodic table, as Sen *et al.*[14] show in their Fig. 1 for the neutral atoms from He to Ac ($2 \leq N \leq 89$).

According to Eq. 2, Fisher information I_F is homogeneous of degree one under the density scaling i.e. $I_F = NI_\sigma$. However, Rong *et al.* reported that $I_\sigma \propto N$, which necessarily implies $I_F \propto N^2$. One can derive this N -dependence of $I_F[\rho]$ from the analytic properties of the von Weizsäcker kinetic energy T_W because it is proportional to Fisher information

$$T_W[\rho] = \frac{1}{8} \int \frac{|\nabla\rho|^2}{\rho} = \frac{1}{8} I_F[\rho] \quad (4)$$

T_W can be written in different equivalent forms; one of them is particularly useful for revealing its dependence with the number of particles. Given the quantity $\tilde{\mathbf{p}} = -\nabla\rho/2\rho$ then

$$T_W[\rho] = \int \frac{|\tilde{\mathbf{p}}|^2}{2} \rho \quad (5)$$

i.e. T_W is the expectation value of the single-particle kinetic energy given by the local value $|\tilde{\mathbf{p}}|^2/2$. [15, 16] This quantity has an extreme value at the nuclear position by Kato's cusp condition,[17] which can be expressed by

$$\int \frac{|\tilde{\mathbf{p}}|^2}{2} \delta(\mathbf{r}) = \frac{Z^2}{2} \quad (6)$$

Therefore the integrand in Eq. 5 has an absolute maximum at the nucleus because $Z^2\rho(\mathbf{0})/2 > |\tilde{\mathbf{p}}|^2\rho(\mathbf{r})/2$ for $|\mathbf{r}| > 0$. At large distances from the nucleus the limiting value of $|\tilde{\mathbf{p}}|^2/2$ is the ionisation potential I_Z [18]

$$\frac{|\tilde{\mathbf{p}}|^2}{2} \Big|_{|\mathbf{r}| \rightarrow \infty} \rightarrow I_Z \quad (7)$$

Hence the integrand in Eq. 5 for the outermost electron shells rapidly vanishes due

to the exponential decay of the electron density;[16, 19] as a result, the integral for the electrons in the first electron shell dominates over the remaining terms by nearly an order of magnitude.[20, 19] Accordingly, $Z^2/2$ is the leading term determining the Weizsäcker kinetic energy (Eq. 5) i.e. $T_W[\rho] \propto Z^2$. Z is a limiting value for the electron velocity near the nucleus that is useful for determining kinematic relativistic corrections.[21] The number of electrons in a neutral atom is equal to the atomic number, $N = Z$, and therefore

$$T_W[\rho] \propto N^2 \quad (8)$$

The correlation between $T_W[\rho]$ and N^2 is $R^2 = 0.9998$, according to the data reported by Rong et al. This dependence of T_W with N cannot be intuitively anticipated because it depends on the particular behaviour of the von Weizsäcker kinetic energy T_W for fermions.[22] Because $T_W = NI_\sigma/8$ then Eq. 8 finally leads to

$$I_\sigma[\sigma] \propto N \quad (9)$$

Hence the Fisher information associated with the density per particle $I_\sigma[\sigma]$ scales linearly with the number of electrons N —in agreement with Rong *et al.*. An early numerical exploration by Nagy and Sen already reported an almost linear trend between I_σ and N through the numerical fit $I_\sigma = 5.8325N^{1.0801}$ from the data set by Romera using Koga–Roothaan Hartree–Fock atomic wave functions.[23, 24] Therefore, one can explore the theory behind the Weizsäcker kinetic energy for an analytical derivation of the linear and the quadratic scaling of I_σ and I_F with N , respectively.

With reference to the relation between S_{GBP} and its equivalent for the density per particle S_{GBP}^σ , Rong *et al.* conjectured that $S_{GBP} \approx NS_{GBP}^\sigma$ “since the density-scaling and N -scaling properties for the kinetic energy density $t(\mathbf{r}, \rho)$ are unknown, it is unclear whether there exists any explicit relationship between the two quantities”. [6] Such a statement may be motivated by the fact that an exact expression for the orbital-free kinetic energy density functional is unknown. Yet the explicit theoretical relationship between S_{GBP}^σ and S_{GBP} is readily possible

within the limits of the non-interacting kinetic energy approximation. Certainly, it provides the scaling properties of the constituent quantities of S_{GBP} that yields to the total scaling rules—by following the same strategy used for determining the scaling properties of the topology of the electron density.[5] From the definition of the GBP entropy

$$S_{GBP}[\rho] = \frac{3}{2}k \int \rho \left\{ c + \ln \frac{t(\mathbf{r}, \rho)}{t_{TF}(\mathbf{r}, \rho)} \right\} \quad (10)$$

and taking the Kohn-Sham orbitals ϕ_i for an N -electron system,[11] the expression of the electron density is $\rho = \sum_i^N |\phi_i|^2 \equiv \sum_i^N \rho_i$ that leads to a proof of the scaling rule for $S_{GBP}[\rho]$ restricted to the non-interacting kinetic energy—whose positive-definite expression is $t_s(\mathbf{r}, \rho) = \frac{1}{2} \sum_i^N |\nabla \rho_i^{1/2}(\mathbf{r})|^2$. By replacing ρ by $N\sigma$ we have $\sigma = \sum_i^N \rho_i/N \equiv \sum_i^N \sigma_i$ and consequently $\rho_i = N\sigma_i$. Therefore,

$$t_s(\mathbf{r}, \sigma) = \frac{N}{2} \sum_i^N |\nabla \sigma_i^{1/2}(\mathbf{r})|^2 \quad (11)$$

which shows the linear scaling of the non-interacting kinetic energy density in terms of σ with the number of particles N or $t_s(\mathbf{r}, \rho) = t_s(\mathbf{r}, N\sigma) = Nt_s(\mathbf{r}, \sigma)$; while this proof is valid for the Kohn-Sham approximation, it can be extended to the general case by considering the results by Liu *et al.* who state that the kinetic-energy component of the correlation energy density also scales linearly with the number of electrons or $t_c(\mathbf{r}, \rho) = Nt_c(\mathbf{r}, \sigma)$. [25] Therefore, by considering both the KS approximation t_s and the kinetic-energy component of the correlation t_c , one can deduce that the kinetic energy density is homogeneous of degree one under the density scaling:

$$t(\mathbf{r}, \rho) = t(\mathbf{r}, N\sigma) = Nt(\mathbf{r}, \sigma) \quad (12)$$

Alternatively, this general result can be deduced from previous theoretical works by e.g., Nagy and March,[26] or from the recent work from Della Sala *et al.*,[27] according to which the kinetic energy density can be formally written as a function times the electron density, or $t(\mathbf{r}, \rho) = \rho f(\mathbf{r})$. In this way, its respective density per particle expression linearly depends on the number of particles i.e. $t(\mathbf{r}, N\sigma) = N\sigma f(\mathbf{r})$. Additional arguments and formal requirements for the density scaling

of the kinetic energy density can be found in Liu and Parr,[1] or in the work by Borgoo and Tozer.[4] On the other hand, the Thomas-Fermi kinetic energy density ($t_{TF}(\mathbf{r}, \rho) = c_K \rho^{5/3}$) scales with the $(5/3)^{th}$ power of N : [11]

$$t_{TF}(\mathbf{r}, \rho) = t_{TF}(\mathbf{r}, N\sigma) = N^{5/3} t_{TF}(\mathbf{r}, \sigma) \quad (13)$$

Then, after replacing Eqs. 12 and 13 into Eq. 10, we find the exact scaling rule for $S_{GBP}[\rho]$

$$S_{GBP}[\rho] = N \Delta S'[\sigma; N] \quad (14)$$

with the entropy difference $\Delta S' = S_{GBP}^\sigma - k S_N$. Equation 14 states that S_{GBP} and S_{GBP}^σ obey a similar N -dependence to that one of S_σ (Eq. 3). In this case, however, the dominant term is positive because S_{GBP}^σ grows faster than $k \ln N$ by more than one order of magnitude—making $S_{GBP} > 0$ for every atom. This result fully explains the correlation $R^2 = 0.99$ between S_{GBP} and N reported by Rong *et al.*.

Finally, Rong *et al.* also found strong linear relationships of the theoretical information quantities for atoms as a function of their respective electron populations via Bader's zero-flux,[28] Becke's fuzzy atom,[29] and Hirshfeld's stockholder partitions.[30] Along similar lines, I recently disclosed the utility of atomic values for revealing inevident scaling properties in kinetic energy density functionals.[31] Furthermore, the density per particle definition $\sigma = \rho/N$ imposes a scaling invariance on topological density functionals.[5] By following a similar approach one can derive a general scaling rule—applicable to any partition scheme—which governs the atomic values. Indeed, *perfect* N linear scaling has some interesting consequences on the atomic scaling properties. Specifically, by assuming that a given functional A is homogeneous of degree one with respect to the number of particles, i.e. that obeys $A[\rho] = A[N\sigma] = NA[\sigma]$, the following equation holds

$$A[\rho] = N \sum_i^M A[\sigma]_i = A[\sigma] \sum_i^M N_i \quad (15)$$

where $A[\sigma]_i = \int_{\Omega_i} A(\sigma, \mathbf{r})$ is the atomic value of the observable A corresponding

to the atomic region Ω_i , $A[\sigma] = \sum_i^M A[\sigma]_i$, with $N = \sum_i^M N_i = \sum_i^M \int_{\Omega_i} \rho$, and M the total number of atoms. Therefore

$$A[\sigma]_i = \frac{A[\sigma]}{N} N_i \quad (16)$$

For a stationary state of a molecular system for which $A[\sigma]$ and N are constants, Eq. 16 reveals that every atomic value $A[\sigma]_i$ scales linearly with its respective electronic population N_i . Accordingly, a plot of $A[\sigma]_i$ vs N_i should be linear with a proportionality factor close to the property per particle $A[\sigma]/N$. For the special case $A = \rho$, Eq. 16 correctly yields the atomic shape function value given by $\sigma_i = N_i/N$ previously defined. Notice that discrepancies with respect to Eq. 16 may be attributed either to an imperfect linear scaling with the number of electrons N , or to numerical errors, or both simultaneously. Rong *et al.* correctly obtained the trend given by Eq. 16 for two information properties—Fisher information and the GBP entropy—and for three partitioning schemes. Equation 16 suggests that by knowing *any* atomic value $A[\sigma]_i$ and its respective electronic population N_i one can determine the total value of the functional $A[\sigma]$ —given the perfect linear scaling of A with N , even if N is unknown because it can be determined from Kato's theorem as demonstrated in Ref. [5]. These observations seem to be consistent with the extension of the theorem of Hohenberg and Kohn to sub domains, according to which the ground state particle density of an arbitrary subdomain uniquely determines the ground state properties of the total system.[32]

In summary, in this comment I put forward the claim that one can derive analytically all the scaling rules numerically obtained by Rong *et al.* and hence their findings can be generalised. The theoretical approach shown here yields to a better understanding of the role of the number of particles N as a privileged scaling parameter for density functionals evaluated for atoms and atoms in molecules.

Acknowledgements

The author wants to express his gratitude to Professor C. Cárdenas for his insightful suggestions about the manuscript and to FIDIC for the financial support.

References

- [1] Shubin Liu and Robert G Parr. Additional functional relations in the density functional theory of finite interacting electronic systems. *Chem. Phys. Lett.*, 278(4):341–344, 1997.
- [2] Pierre Hohenberg and Walter Kohn. Inhomogeneous electron gas. *Phys. Rev.*, 136(3B):B864, 1964.
- [3] Alex Borgoo, Andrew M Teale, and David J Tozer. Effective homogeneity of the exchange–correlation and non-interacting kinetic energy functionals under density scaling. *J. Chem. Phys.*, 136(3):034101, 2012.
- [4] Alex Borgoo and David J Tozer. Density scaling of noninteracting kinetic energy functionals. *J. Chem. Theory Comput.*, 9(5):2250–2255, 2013.
- [5] Hugo J Bohórquez. Scale-invariance of the topological equations of the density per particle. *Comp. Theor. Chem.*, 1053:38–43, 2015.
- [6] Chunying Rong, Tian Lu, Paul W. Ayers, Pratim K. Chattaraj, and Shubin Liu. Scaling properties of information-theoretic quantities in density functional reactivity theory. *Phys. Chem. Chem. Phys.*, 17:4977–4988, 2015.
- [7] Chunying Rong, Tian Lu, Paul W. Ayers, Pratim K. Chattaraj, and Shubin Liu. Correction: Scaling properties of information-theoretic quantities in density functional reactivity theory. *Phys. Chem. Chem. Phys.*, 17:11110–11111, 2015.
- [8] CE Shannon. A mathematical theory of communication, Bell Telephone System Tech. *Publ. Monograph B-1598*, pages 1–80, 1948.
- [9] Ronald Aylmer Fisher. Theory of statistical estimation. In *Mathematical Proceedings of the Cambridge Philosophical Society*, volume 22, pages 700–725. Cambridge Univ Press, 1925.
- [10] Swapan K Ghosh, Max Berkowitz, and Robert G Parr. Transcription of ground-state density-functional theory into a local thermodynamics. *Proc. Natl. Acad. Sci. U.S.A.*, 81(24):8028–8031, 1984.

- [11] Walter Kohn and Lu Jeu Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, 140(4A):A1133, 1965.
- [12] S. Kullback. *Information Theory and Statistics*. Peter Smith, 1978.
- [13] Mehran Kardar. *Statistical Physics of Particles*. Cambridge University Press, 2007.
- [14] KD Sen, F De Proft, A Borgoo, and P Geerlings. N-derivative of Shannon entropy of shape function for atoms. *Chem. Phys. Lett.*, 410(1):70–76, 2005.
- [15] Shunlong Luo. Statistics of local value in quantum mechanics. *Int. J. Theor. Phys.*, 41(9):1713–1731, 2002.
- [16] Hugo J Bohórquez and Russell J Boyd. On the local representation of the electronic momentum operator in atomic systems. *J. Chem. Phys.*, 129(2):024110, 2008.
- [17] W. A. Kato. On the eigenfunctions of many-particle systems in quantum mechanics. *Commun. Pure. Appl. Math.*, 10(2):151–177, 1957.
- [18] Maria Hoffmann-Ostenhof and Thomas Hoffmann-Ostenhof. Schrödinger inequalities and asymptotic behavior of the electron density of atoms and molecules. *Phys. Rev. A*, 16(5):1782–1785, Nov 1977.
- [19] Hugo J Bohórquez and Russell J Boyd. Is the size of an atom determined by its ionization energy? *Chem. Phys. Lett.*, 480(1):127–131, 2009.
- [20] Nicolás A Cordero, Norman H March, and Julio A Alonso. Ionization potentials of neutral atoms and positive ions in the limit of large atomic number. *Phys. Rev. A*, 75(1):012505, 2007.
- [21] Pekka Pyykko. Relativistic effects in structural chemistry. *Chemical Reviews*, 88(3):563–594, 1988.
- [22] Elliott H Lieb. Density functionals for coulomb systems. *Int. J. Quantum Chem.*, 24(3):243–277, 1983.

- [23] A Nagy and KD Sen. Atomic Fisher information versus atomic number. *Phys. Lett. A*, 360(2):291–293, 2006.
- [24] Toshikatsu Koga, Katsutoshi Kanayama, Tadanori Watanabe, Takashi Imai, and Ajit J Thakkar. Analytical Hartree–Fock wave functions for the atoms Cs to Lr. *Theor. Chem. Acc.*, 104(5):411–413, 2000.
- [25] S Liu, RC Morrison, and RG Parr. Approximate scaling properties of the density functional theory Tc for atoms. *J. Chem. Phys.*, 125(17):174109, 2006.
- [26] A Nagy and NH March. Exact potential-phase relation for the ground state of the C atom. *Phys. Rev. A*, 40(2):554, 1989.
- [27] Fabio Della Sala, Eduardo Fabiano, and Lucian A. Constantin. Kohn-Sham kinetic energy density in the nuclear and asymptotic regions: Deviations from the von Weizsäcker behavior and applications to density functionals. *Phys. Rev. B*, 91:035126, Jan 2015.
- [28] Richard FW Bader and PM Beddall. Virial field relationship for molecular charge distributions and the spatial partitioning of molecular properties. *J. Chem. Phys.*, 56(7):3320–3329, 1972.
- [29] Axel D Becke. A multicenter numerical integration scheme for polyatomic molecules. *J. Chem. Phys.*, 88(4):2547–2553, 1988.
- [30] FL Hirshfeld. Bonded-atom fragments for describing molecular charge densities. *Theor. Chim. Acta*, 44(2):129–138, 1977.
- [31] Hugo J. Bohórquez and Andrés Reyes. The Pauli Energy Grows Exponentially With The Electronic Localization. *Mol. Phys.*, 112(3-4):416–421, 2014.
- [32] Jürg Riess and Walter Münch. The theorem of Hohenberg and Kohn for subdomains of a quantum system. *Theor. Chim. Acta*, 58(4):295–300, 1981.