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Scaling in the correlation energies of atomic ions

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We show through numerical investigations that the ground-state correlation energies of atomic ions follow an unexpectedly simple scaling relation, $E_c \approx Z^{4/3} f_c(Z/N)$, where N is the number of electrons, Z is the atomic number, and f_c is a universal function, for which an analytic expression with a one-parameter fit can be provided. The relation agrees well with several sets of correlation energies obtained from different methods for atomic ions with $N = 2, \ldots, 18$ and $Z = 2, \ldots, 28$. Moreover, our relation gives a good agreement with neutral atoms up to $N \approx 90$. Our main result is readily applicable to estimating correlation energies of heavy elements, for which there are no available data in the literature. The simplicity of the relation may also have implications in the development of correlation functionals within density-functional theory.

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I. INTRODUCTION

Electronic correlation is a fundamental property of a many-particle quantum system that leads to important physical effects and applications in condensed-matter and material physics, e.g., in superconductivity, ultracold atoms, and semiconductor materials. On the other hand, theoretical treatment of correlation effects is particularly challenging in first-principles approaches such as density-functional theory (DFT) [1]. In the development of density functionals for the exchange and/or correlation [2], a common approach is to exploit the properties of a known system, such as the homogeneous electron gas or the exchange and/or correlation hole. These properties can then be combined with exact constraints arising from, e.g., the Lieb-Oxford lower bound for the exchange-correlation energy [3,4] or the limit of strictly correlated electrons [5,6]. Nevertheless, simple, scalable properties of the correlation energy are highly desirable.

In this paper we follow the standard definition for the electronic ground-state correlation energy [7–9]

$$E_c = E_{\mathrm{gs}} - E_{\mathrm{HF}}, \tag{1}$$

where E_{gs} is the total ground-state energy and E_{HF} is the Hartree-Fock (HF) total ground-state energy that, by definition, captures the electronic exchange through a single Slater determinant but misses the electron correlation (contribution of other determinants). It is noteworthy that in the DFT definition for E_c, the HF term is replaced by the exact-exchange term, where the HF orbitals are replaced by the Kohn-Sham orbitals. The energy difference between these definitions is practically negligible.

Our goal in this work is to find a scaling relation for E_c that works for a large set of atomic ions, as well as for neutral atoms, and is still as simple as possible. Our construction is guided by extensive sets of numerical data for ions and atoms (see below) as well as the Thomas-Fermi (TF) theory as the starting point. The TF theory has been previously used to find scaling relations for the total energies of atoms [10–13] and ionization potentials [14]. Regarding correlation energies, scaling relations have been derived for two-dimensional artificial atoms, i.e., quantum dots modeled by a harmonic-oscillator potential [15]. For neutral, conventional (three-dimensional) atoms, on the other hand, Kais *et al.* [16] have found that E_c behaves as $Z^{4/3}$ in the large-Z limit, a tendency that has been supported by several other studies [17–26].

To the best of our knowledge, a generic expression à la Thomas-Fermi [see Eq. (2)] for the correlation energy of both ions and neutral atoms is not yet available. In the following we show that such a relation can be found with a remarkable agreement with several sets of numerical data. This finding has predictive power, albeit not yet within chemical accuracy, and might also help in the development of simple, but efficient, density functionals for the electronic correlation.

II. SCALING RELATION

Our ansatz for the correlation energy follows a scaling relation of the form

$$E_c(N,Z) = Z^{\alpha} f_c(Z/N), \tag{2}$$

which is reminiscent of the scaling of the total energy for ions and neutral atoms [27]. The use of the combination Z/N instead of N/Z responds only to aesthetic criteria: since most of the available data correspond to the cationic domain ($Z > N$), we preferred to see the scaling behavior in an "extended domain," i.e., $0 < Z/N \leqslant \infty$. All of the results can be easily recovered in terms of N/Z.

To find the parameter α and the function f_c in Eq. (2), we analyze the results for the correlation energy reported in Refs. [28–30], which have been used as a benchmark by many authors. The results were obtained by removing the relativistic contribution from measured ground-state energies and therefore are often considered to be *exact* [31]. We use the values of the correlation energy of all the systems with $7 \leqslant N \leqslant 18$ and $N - 1 \leqslant Z \leqslant 28$ in Ref. [30], for which the scaling behavior is apparent. In addition, we include the results of He-like ions ($N = 2, N \leqslant Z \leqslant 28$) reported in Ref. [28]. In total, we consider more than 200 systems (see Fig. 2) that we label Cha1996 later on in the paper.

By minimizing the rms deviation of the data as a function of α we find that the minimum deviation is obtained for $\alpha \approx 1.32$, as visualized in Fig. 1. This is very close to the expected value of 4/3 [see Eq. (2)], which we adopt as our value in

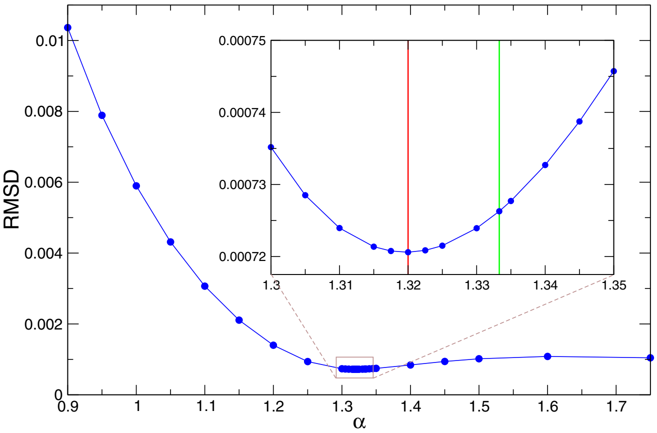

FIG. 1. (Color online) The rms deviation of the scaling relation from the set of data for atomic ions in Refs. [28–30] as a function of the parameter α in Eq. (2). The best fit is obtained with $\alpha \approx 1.32 \approx 4/3$.

the following. For the function f_c, on the other hand, we first introduce a two-parameter form $f_c = \gamma(\frac{Z}{N})^\delta$. One of these parameters can be removed by using the known case of the simplest hydride anion $^1\text{H}^-$ (with $Z = 1$ and $N = 2$) as a constraint. For this system $E_c(^1\text{H}^-) \approx 0.039751$ (Ref. [32]), leading to $\gamma = E_c(^1\text{H}^-)/2^\delta$. Finally, the parameter δ is found through fitting, and the scaling relation becomes

$$E_c(N,Z) = Z^{4/3}\frac{0.0165663}{(Z/N)^{1.26274}}. \qquad (3)$$

We point out that the limit $Z/N \to \infty$ correctly leads to zero correlation. On the other hand, the limit $Z/N \to 0$ is never reached because it is beyond the instability threshold given by $Z_c \lesssim N - 1$.

In Fig. 2 we show the sign-reversed scaled correlation energy according to Eq. (3) as a function of Z/N (solid line) together with the data in Refs. [28–30] (symbols). The overall agreement between our scaling relation and the data is obvious due to the fitting procedure, but the good agreement through a wide range of Z/N is surprising in view of the simple form of Eq. (3). Let us recall that at $Z/N \sim 1$ the systems are close to the instability threshold that characterizes the anionic domain ($Z < N$). On the other hand, in the cationic domain ($Z > N$) the TF theory is more valid [33]. This explains why the largest deviations from the scaling in Fig. 2 occur around the vertical line of neutral atoms ($Z/N = 1$).

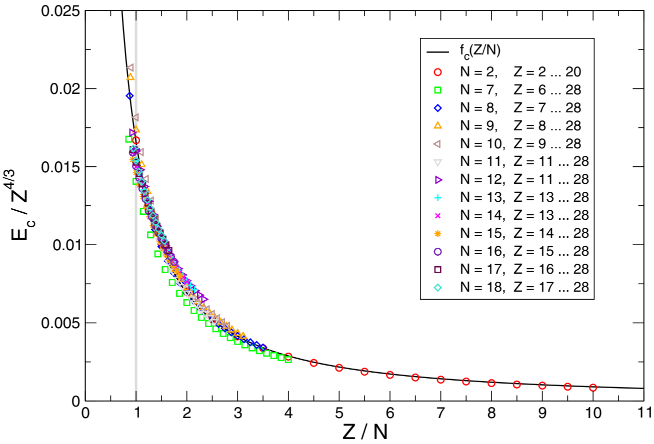

FIG. 2. (Color online) Sign-reversed scaled correlation energies for atomic ions with $N = 2, 1 \leqslant Z \leqslant 20$ [28] and $7 \leqslant N \leqslant 18, N - 1 \leqslant Z \leqslant 28$ [30]. The solid line represent the function $f_c(Z/N)$, and the vertical gray line indicates the position of neutral atoms.

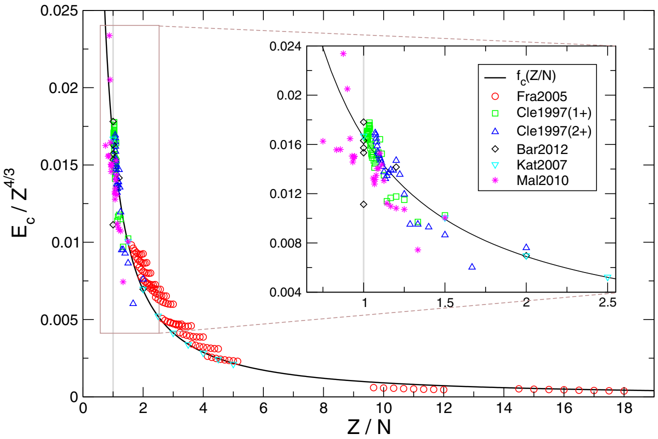

FIG. 3. (Color online) Sign-reversed scaled correlation energies for atomic ions computed with different methods (see the main text for details). The solid line shows $f_c(Z/N)$ from the scaling relation in Eq. (3), and the vertical gray line indicates the position of neutral atoms.

III. TESTING THE RELATION FOR OTHER CALCULATIONS

In order to corroborate the scaling relation using Eq. (3), we next consider additional independent results for the correlation energy obtained with different methods. The sets of data included are (1) the results of Ref. [30] extrapolated to highly charged cations by Fraga and García de la Vega [34] (Fra2005), which includes data of positive ions with $N = 2,3$ and $7 \leqslant N \leqslant 18$, with $Z = 29, \ldots, 36$ in all the cases, (2) quantum Monte Carlo (QMC) calculations for both positive and negative singly charged ions from Li through Ar [35] (Mal2010), (3) Fadeev random phase approximation calculations [36] (Bar2012) for light atoms and ions up to Ar, which includes He, Be^{2+}, Be, Ne, Mg^{2+}, Mg, and Ar^{14+}, (4) He isoelectronic series ($2 \leqslant Z \leqslant 10$) computed by Katriel *et al.* [37] (Kat2007), and (5) virial-constrained effective Hamiltonian (VCEH) results for singly charged ions [$3 \leqslant Z \leqslant 55$; Cle1997(1+)] and doubly charged ions [$4 \leqslant Z \leqslant 30$; Cle1997(2+)] [26].

All the results are shown in Fig. 3 (symbols) together with our scaling relation in Eq. (3) (solid line). We can find the same trend as in Fig. 2 (i.e., the overall qualitative agreement is good), but the closer we get to the anionic domain ($Z/N < 1$), the larger the deviations are.

Finally, we focus in more detail on the most challenging regime in the agreement above, i.e., the case of neutral atoms with $Z/N = 1$. Again, we consider several sets of data in the literature: (1) the results of Refs. [28–30] for $2 \leqslant Z \leqslant 18$, which are also included in Fig. 2 (Cha1996), (2) the results

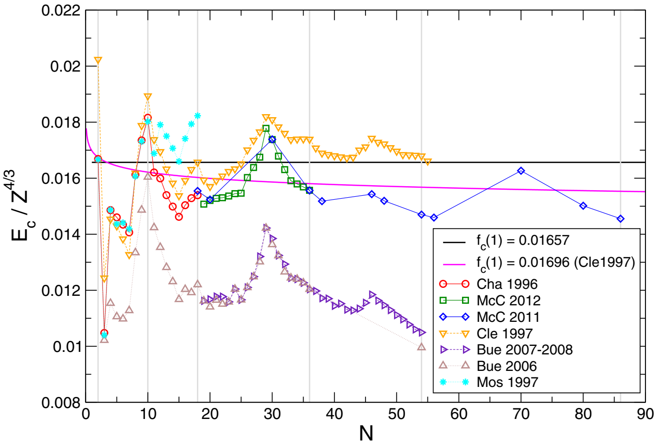

FIG. 4. (Color online) Sign-reversed correlation energies of neutral atoms as a function of the electron number N (symbols) computed with different methods (see the text). The horizontal solid line shows our scaling relation in Eq. (3), i.e., $f_c(Z/N = 1) = 0.0165663$. The vertical gray lines indicate the positions of noble atoms with filled shells.

of McCarthy and Thakkar for $2 \leqslant Z \leqslant 55$ [38] (McC2011), (3) the results of McCarthy and Thakkar for $18 \leqslant Z \leqslant 36$ [39] (McC2012), (4) VCEH results of Clementi and Corongiu for $2 \leqslant Z \leqslant 55$ [26] (Cle1997), (5) variational QMC results for $3 \leqslant Z \leqslant 36$ and $Z = 54$ in Ref. [40] (Bue2006), (6) variational QMC results for $19 \leqslant Z \leqslant 54$ in Refs. [41,42] tabulated in [38] (Bue2007-08), and (7) results from Ref. [43] for $2 \leqslant Z \leqslant 18$ (Mos1997).

The results are collected in Fig. 4. Overall, the data seems to follow the $Z^{4/3}$ trend as expected. In addition, the horizontal line resulting from our scaling relation with $f_c(Z/N = 1) = 0.0165663$ agrees relatively well with most of the data sets, especially at large N. The sets of QMC results in Refs. [40–42] (Bue2006 and Bue2007-08) fall considerably below the scaling. However, it is important to know that QMC calculations always give an upper bound for the total energy, and since $E_{\rm HF} \geqslant E_{\rm gs}$, QMC, especially variational QMC, can underestimate the absolute value of the correlation energy. This is in line with our observation; in other words, the deviation between Bue2006 and Bue2007-08 from the scaling relation and the other data sets is most likely due to the nature of the variational QMC method.

The local deviations in the data from the scaling relation are due to fine details, such as the shell structure, which are not captured by the TF theory or our scaling relation. In the small-N regime, local extrema in the data sets match the positions of noble atoms (gray vertical lines) with $N = 2, 10, 18$. The maximum deviation in the considered range of N is, however, rather moderate and indicates that Eq. (3) can be used to obtain good estimations for the correlation energy of atomic systems. In general, the fact that E_c scales is unexpected because, by definition, the electronic correlation is beyond the mean-field properties [7,8,44–53].

Finally, we point out that the relative fraction of the correlation energy with respect to the total energy χ also follows a simple scaling relation:

$$\chi = \left| \frac{E_c}{E_{\rm gs}} \right| = \frac{Z^{4/3} f_c(Z/N)}{Z^{7/3} f_{\rm gs}(Z/N)} = Z^{-1} f_\chi(Z/N). \qquad (4)$$

This quantity gives important information about the degree of correlation in a specific system. An approximate expression for $f_\chi(Z/N)$ can be obtained by replacing $f_c(Z/N)$ in Eq. (4) by Eq. (3) and $f_{\rm gs}(Z/N)$ by a known relation for the total energy such as the one reported in Ref. [27]. However, further elaboration of this term is left to future studies.

IV. SUMMARY

In summary, we have found a simple scaling relation for the correlation energy of atomic ions including neutral atoms. The relation has been found by applying an ansatz based on the Thomas-Fermi theory and numerical fitting to an accurate set of data, together with an exact constraint for the ^{1}H$^-$ hydride anion. The obtained scaling relation has been tested against a large set of data for the correlation energy obtained using a variety of methods. The overall agreement is good for both ions and neutral atoms. In the latter case the observed deviations have been analyzed. Our relation can thus provide useful estimates for the correlation energies of heavy elements and their corresponding ions, for which there are no available data in the literature. However, in the absence of further data one needs to be cautious when applying the present approximation because the correlation energy is a subtle quantity. Our result may also have implications for the development of correlation functionals for density-functional calculations [17,54] and may also supplement the recently developed density-functional theory for strictly correlated electrons [5] and related approaches.

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