

## Thomas-Fermi scaling in the energy spectra of atomic ions

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(Received 23 June 2009; published 12 August 2009)

The energy spectra of atomic ions are re-examined from the point of view of Thomas-Fermi scaling relations. For the first ionization potential, which sets the energy scale for the true discrete spectrum, Thomas-Fermi theory predicts the following relation:  $E_{ioniz} = Z^2 N^{-2/3} g(N/Z)$ , where  $Z$  is the nuclear charge,  $N$  is the number of electrons, and  $g$  is a function of  $N/Z$ . This relation does not hold for neutral atoms, but works extremely well in the cationic domain,  $Z > N$ . We provide an analytic expression for  $g$ , with two adjustable parameters, which fits the available experimental data for more than 380 ions. In addition, we show that a rough fit to the integrated density of states with a single exponential:  $N_{states} = \exp(\Delta E/\Theta)$ , where  $\Delta E$  is the excitation energy, leads to a parameter,  $\Theta$ , exhibiting a universal scaling a la Thomas-Fermi:  $\Theta = Z^2 N^{-4/3} h(N/Z)$ , where  $h$  is approximately linear near  $N/Z = 1$ .

DOI: [10.1103/PhysRevA.80.024502](https://doi.org/10.1103/PhysRevA.80.024502)

PACS number(s): 32.30.-r, 31.15.-p, 32.10.Hq

Energy levels of atoms and ions have been measured since the earliest times of quantum mechanics. At present, there is a huge amount of very precise measurements, which can be found, for example, in the critical compilation by the NIST [1]. In these big volumes of data, sometimes universal relations remain hidden. In order to find them, you need a simple theory in which universality or scaling naturally appears.

Thomas-Fermi theory [2] was the first mean-field theory of atoms, the predecessor of more elaborated approaches, such as density functional theory [3]. It is based on a simple estimation of the kinetic energy, with the help of Pauli exclusion principle, and the introduction of self-consistency with the Poisson equation in order to take account of Coulomb interactions. Thomas-Fermi theory has proven to be a valuable tool for the qualitative and semiquantitative understanding of real [4–6] and artificial [7] atoms.

A very interesting aspect of Thomas-Fermi theory is the scaled form of physical magnitudes, which are very often respected by the exact quantum mechanical magnitudes. This aspect has not been completely exploited so far. Recently, we showed, for example, that the density of low-lying excited states of artificial (quantum dot) atoms can be parametrized in a universal (scaled) way [8], suggested by Thomas-Fermi theory. No similar parametrization for neutral atoms or ions is available yet.

In the present Brief Report, we focus on the energy spectra of atomic ions, and show that, in some sense, the excitation spectrum is “universal,” that is, may be described by scaled functions. In order to support the theoretical statements, we make extensive use of the NIST detailed compilation on atomic energy levels.

Let us start considering the first ionization potential of ions, which sets the energy scale for the true discrete spectrum. In atomic units, where atomic ions are characterized by only two free parameters: the nuclear charge,  $Z$ , and the number of electrons,  $N$ , the ground-state energy in the Thomas-Fermi approximation may be shown to satisfy the following scaled relation [5],

$$E_{gs}(N, Z) = Z^2 N^{1/3} f(N/Z), \quad (1)$$

where  $f$  is a universal function of the variable  $N/Z$ . The ionization potential can be obtained from Eq. (1). Indeed,

$$\begin{aligned} E_{ioniz}(N, Z) &= E_{gs}(N-1, Z) - E_{gs}(N, Z) \\ &\approx -\frac{\partial}{\partial N} E_{gs}(N, Z) \\ &\approx Z^2 N^{-2/3} g(N/Z), \end{aligned} \quad (2)$$

where  $g$  is also a universal function of its argument. It may be easily verified for free electrons in a Coulomb field that, in the  $N \rightarrow \infty, N/Z \rightarrow 0$  limit,  $g(0) = (3/2)^{1/3}/3 \approx 0.3816$  [9].

The law given by Eq. (2) does not hold for neutral atoms. The ionization potential of neutral atoms, apart from shell effects, has a very smooth dependence on  $Z$ , and is close to that of hydrogen, 0.5, in accordance to the fact that at long distances every singly ionized atom looks like a proton.

However, the scaling law, Eq. (2), is quickly reestablished in the cationic domain,  $Z > N$ . We show in Fig. 1 the ionization potential of more than 380 atomic ions, taken from the NIST compilation [1]. All of the systems with  $N > 10$  are considered, for which the scaled behavior is apparent. The nuclear charge,  $Z$ , spans the range from 12 (Mg) to 80 (Hg), although, as it can be seen from the table of available levels [10], most of the data correspond to the interval  $12 < Z < 37$ .

The function  $g(x)$  should go to zero in the  $x \rightarrow 1$  limit, in accordance to the fact that, in the leading approximation, the anionic instability border is located at  $N/Z = 1$  [11]. We fitted the experimental data with a two-point Padé approximant [12] interpolating between the  $x \rightarrow 0$  and  $x \rightarrow 1$  limits,

$$g(x) = \frac{(p_0 + p_1 x)(1 - x)}{1 + q_1 x}, \quad (3)$$

where  $p_0 = g(0)$ , and the fitting parameters are:  $p_1 = 2.6555$ ,  $q_1 = 11.4399$ . The fit gives a very good qualitative description of the data. The three points at  $N/Z \approx 0.5$ , lying a little farther, correspond to the Xe XXVII, Xe XXVIII, and Xe

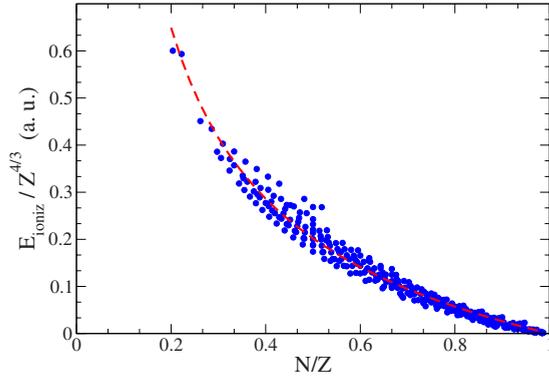


FIG. 1. (Color online) Scaling in the ionization potential of ions with more than ten electrons. The curve  $(N/Z)^{-2/3}g$ , where  $g$  is given by Eq. (3), is also drawn (dashed line).

XXIX ions, for which it seems that there is an overestimation in the reported values [13].

We stress that the fit given by the function  $g$  captures the general behavior of  $E_{ioniz}$  as a function of  $N$  and  $Z$ . Effects not included in Thomas-Fermi theory, such as shell or subshell filling, spin-orbit interactions, etc., could lead to relatively large (of the order of 10% or even larger) deviations from the universal behavior, as seen in Fig. 1.

Next, we attempt a global universal description of the excitation spectrum. Excitation energies,  $\Delta E$ , cover the range  $(0, E_{ioniz})$ . In the spectrum, we shall distinguish between intrashell and intershell excitations, which exhibit different behaviors.

In quality of example, we show in Fig. 2 the Ar-like series, from the Ar I atom ( $N=Z=18$ ) to the Mn VIII ion ( $N=18, Z=25$ ). The y axis represents the total (accumulative) number of states for excitation energies below  $\Delta E$ . The degeneracy of multiplets is explicitly taken into account. In the x axis, the excitation energy is scaled by  $Z^2$ .

First, we notice that from Ar I to Ca III the spectrum is restructured. This corresponds to reestablishing the  $Z \rightarrow \infty$  sequence of Hartree-Fock orbitals:  $1s, 2s, 2p, 3s, 3p, 3d, \dots$ , in place of the neutral atom sequence [14].

From Ca III on, it is evident that the low-lying spectrum goes to a definite limit as  $Z$  increases. These are intrashell excitations (in the  $N=18$  system, the  $n=3$  shell is open). This means that intrashell excitation energies scale as  $\Delta E \sim Z^2$ , independently of the degree of ionization,  $N/Z$ . We notice that from  $Z \rightarrow \infty$  perturbation theory one would expect intrashell excitations to be of the order of  $Z$ , thus the observed behavior is stressing that the lowest excitations have a non-perturbative character.

Larger excitation energies correspond to intershell transitions, which are of the same order of  $E_{ioniz}$  and, thus, exhibit the characteristic dependence on  $Z$ ,  $N$ , and  $N/Z$ .

Let us stress that for both the intra- and the intershell regimes, locally the number of states increases exponentially with energy differences. This behavior is quite general [8]. It was first observed in nuclear systems, where it is known as the ‘‘constant-temperature approximation’’ [15]. In Fig. 2, dashed lines represent fits to the intra- and intershell excitations in the Mn VIII ion. The discontinuity of the slopes signals that the mechanisms of formation of these states are different [16].

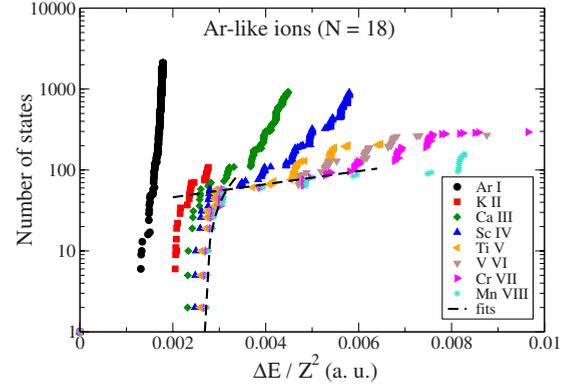


FIG. 2. (Color online) The excitation spectra of Ar-like ions showing the  $Z^2$  dependence of intrashell excitations, and the exponential increase of  $N_{states}$  with  $\Delta E$ .

A rough characterization of the spectrum can be given in terms of a single exponential,

$$N_{states} \approx \exp(\Delta E/\Theta), \quad (4)$$

where we expect the temperature parameter,  $\Theta \sim Z^2$ . The dependence of  $\Theta$  on  $N$  can be extracted from the  $Z \rightarrow \infty$  asymptote. In this limit and for closed shell ions, the gap and the number of electrons are expressed in terms of the principal quantum number of the last occupied shell as:  $\Delta E_1 \approx Z^2/n^3$ , and  $N \approx 2n^3/3$ , respectively. The available number of levels at energies  $\Delta E_1$  is  $N_{states} \sim [2(n+1)^2]! / \{[2n^2]![2(2n+1)]!\} \sim \exp(an+bn \ln n) \sim \exp(cn)$ , where  $a$ ,  $b$ , and  $c$  are numerical coefficients. The last expression comes from the fact that  $\ln n$  is a slowly varying function. Comparison with Eq. (4) leads to  $\Theta \sim Z^2 N^{-4/3}$ .

In the spirit of Thomas-Fermi scaling, we assume for  $\Theta$  the relation,

$$\Theta = Z^2 N^{-4/3} h(N/Z), \quad (5)$$

where  $h$  is a universal function. We fit the excitation spectra of ions with  $N > 10$  with a function given by Eq. (4). We study all of the ions with at least 100 measured lines, and use the first 100 lines to perform the fit. The results are shown in Fig. 3.

Although Eq. (4) gives a rough global characterization (the exponential dependence holds locally, with different slopes in different sectors of the spectrum), and there could be experimental problems such as missing lines, etc., the data show scaling, with a function  $h$  approximately linear,

$$h \approx 0.165(1 - N/Z). \quad (6)$$

Due to the reasons mentioned above, the observed dispersion of points is natural.

Similarly to the ionization potential, the parameter  $\Theta$  for neutral atoms takes in mean a constant value,  $\Theta \approx 0.045$ , with strong fluctuations related to shell effects. The reason for such a behavior is also the proximity of the anionic instability border.

In conclusion, we verified that Thomas-Fermi theory offers a fresh view to the energy spectra of atomic ions. The energy spectrum can be described in a ‘‘universal’’ way in

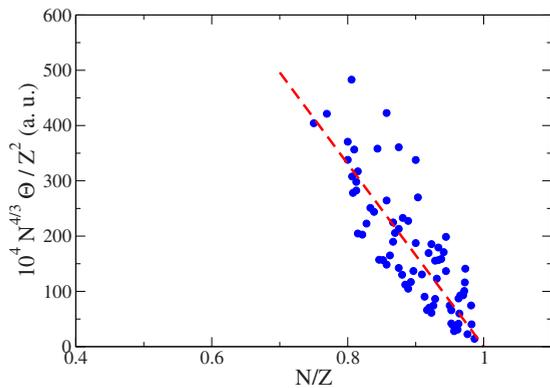


FIG. 3. (Color online) Scaling of the temperature parameter,  $\Theta$ . Ions with  $N > 10$  and at least 100 measured lines are included in the plot.

terms of scaling functions. One of these functions describes the first ionization potential, which is the natural scale for the excitation spectrum. On the other hand, if the excitation spectrum is fitted by a single exponential, the temperature parameter is shown to approximately exhibit also a scaling relation *a la* Thomas-Fermi.

For neutral atoms, the scaling is broken because of the proximity of the anionic instability border. We shall further study this border seeking for positive uses of its presence.

There are still many interesting points requiring further investigation. Intra- and intershell excitations could be more detailed described by means of constant-temperature approximations. Alternative characterizations of the spectrum could also be employed. We have in mind, for example, the first moment, which is a magnitude with dimensions of energy. The energy region closer to the ionization potential could also be studied. In this region, we expect the dependence  $N_{states} \sim (E_{ioniz} - \Delta E)^{-3/2}$ , coming from the existence of Rydberg states. A very interesting possibility is to write down an interpolation formula to spectroscopic accuracy for the ionization potential, which takes our  $g$  function as the starting point, but includes also shell-filling effects, spin-orbit interactions, etc. Research along these lines is in progress.

The authors are grateful to the participants of the Theory Seminar at the ICIMAF for discussions and remarks. Support by the Caribbean Network for Quantum Mechanics, Particles and Fields (ICTP, Trieste, Italy), and by the Programa Nacional de Ciencias Básicas (Cuba) is acknowledged.

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- [1] Yu. Ralchenko, A. E. Kramida, J. Reader, and NIST ASD Team, NIST Atomic Spectra Database (version 3.1.5). Available online: <http://physics.nist.gov/asd3>. National Institute of Standards and Technology, Gaithersburg, MD.
- [2] L. H. Thomas, Proc. Cambridge Philos. Soc. **23**, 542 (1927); E. Fermi, Rend. Accad. Naz. Lincei **6**, 602 (1927).
- [3] W. Kohn, A. D. Becke, and R. G. Parr, J. Phys. Chem. **100**, 12974 (1996).
- [4] D. A. Kirzhnits, Yu. E. Lozovik, and G. V. Shpatakovskaya, Sov. Phys. Usp. **18**, 649 (1975).
- [5] E. H. Lieb, Rev. Mod. Phys. **53**, 603 (1981).
- [6] L. Spruch, Rev. Mod. Phys. **63**, 151 (1991).
- [7] E. H. Lieb, J. P. Solovej, and J. Yngvason, Phys. Rev. B **51**, 10646 (1995).
- [8] A. Odriazola, A. Delgado, and A. Gonzalez, Phys. Rev. B **78**, 205320 (2008).
- [9] This limit should be understood in the sense that  $Z$  is large enough in order that Coulomb attraction by the nucleus prevails over electron-electron repulsion. But, of course,  $Z < Z_c$  should be guaranteed in order to avoid instabilities against electron-positron pairs production. For pointlike nuclei,  $Z_c \approx 137$ , see L. D. Landau and E. M. Lifshits, *Quantum Electrodynamics* (Nauka, Moscow, 1989) (in Russian); whereas for finite nuclei,  $Z_c \approx 173$ , see W. Greiner and J. Reinhardt, *Quantum Electrodynamics* (Springer, Berlin, 1992).
- [10] A table of available levels can be found online at [http://physics.nist.gov/cgi-bin/ASD/levels\\_pt.pl](http://physics.nist.gov/cgi-bin/ASD/levels_pt.pl)
- [11] E. H. Lieb, I. M. Sigal, B. Simon, and W. Thirring, Phys. Rev. Lett. **52**, 994 (1984).
- [12] G. A. Baker, Jr. and P. Graves-Morris, *Padé Approximants* (Addison-Wesley, Reading, Massachusetts, 1981).
- [13] Indeed, these values are taken from E. B. Saloman, J. Phys. Chem. Ref. Data **33**, 765 (2004); which seem to be a few percent larger than the calculations of T. A. Carlson *et al.*, At. Data Nucl. Data Tables **2**, 63 (1970). We thank Yu. Ralchenko for this remark.
- [14] L. D. Landau and E. M. Lifshits, *Quantum Mechanics (in Russian)* (Nauka, Moscow, 1989).
- [15] T. Ericson, Adv. Phys. **9**, 425 (1960); A. Gilbert and A. G. W. Cameron, Can. J. Phys. **43**, 1446 (1965).
- [16] A. Gonzalez and R. Capote, Phys. Rev. B **66**, 113311 (2002).