Atomic number scaling of electron spectra in the free atoms

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Abstract. The atomic number scaling of electron binding energies in the free atoms is found. It is demonstrated in the calculations by the different theoretical models and in the experimental data. Hence the simple way to estimate an inner binding energy level in a free atom is proposed.

1. Introduction

The atomic number \(Z\) scaling of the properties is known to be in the Thomas–Fermi (TF) statistical model. It means particularly that the self-consistent potential by the model may be calculated through the same function for all the elements. In the paper it is shown that one electron spectra, i.e. binding energies, in the TF-potential exhibit the scaling properties too. The two unique functions may be used to estimate inner energy levels. It is also shown that the found binding energy dependence on the atomic number proves to be true for the most part of spectrum in the quantum-mechanical model and experimental data. The features of the one-electron spectra in the spherically symmetric self-consistent attraction potentials have been under study in the paper [1] (see reviews [2, 3] too). Specifically the potentials with the Coulomb singularity have been there considered. The screening of the Coulomb potential is known to lead to a removal of the orbital momentum degeneracy. It has been shown in [1], that a corresponding splitting \(\varepsilon_{nl} - \varepsilon_{n0}\) depends on the orbital momentum \(l\) quadratically (here \(n\) is a principal quantum number). In addition an analysis of the energy levels calculated in the nonrelativistic Hartree–Fock model for some heavy elements has confirmed the same dependence even for not small orbital momentum values. That is the basis of the proposed method to estimate electron binding energies in atoms.

In the paper we joint together the square energy dependence on \(l\) and the TF atomic number scaling in considering a free atom and obtain the atomic number scaling of the coefficients in the square law. Then we verify this law by analyzing the level energies calculated in the different theoretical models and taken from experiments.
Figure 1. The functions \( e(\sigma) \) and \( d(\sigma) \) by the TF-model: \( \log |e(\sigma)| - \nabla \), \( \log d(\sigma) - \triangle \) with their quintic polynomial interpolated curves (see table 1 for the coefficients).

2. Semiclassical binding energies in the TF-model
To determine one-electron energy levels \( \varepsilon_{nl} \), the semiclassical approach is applied and the Bohr–Zommerfeld quantization condition is used:

\[
S_{\varepsilon}(\lambda) = \int_{R_{\varepsilon\lambda}'}^{R_{\varepsilon\lambda}} p_{\varepsilon\lambda}(r) dr = \pi \left( n - l - \frac{1}{2} \right) = \pi (n - \lambda). \quad (1)
\]

Here \( S_{\varepsilon}(\lambda) \) and \( p_{\varepsilon\lambda}(r) = \sqrt{p_{\varepsilon\lambda}^2(r) - \lambda^2/r^2} \) are the radial action and momentum of an electron with the energy \( \varepsilon \) and orbital momentum \( \lambda = l + 1/2 \), \( p_{\varepsilon\lambda}^2(r) = 2[\varepsilon - U(r)] \), \( U(r) \) is a self-consistent potential, the integration region is restricted by turning points \( R_{\varepsilon\lambda}', R_{\varepsilon\lambda} \).

The energy of \( s \)-level \( \varepsilon_{n0} \) is determined from the condition

\[
S_{\varepsilon_{n\lambda}}(0) = \pi n. \quad (2)
\]

The expansion \( S_{\varepsilon}(\lambda) \) in energy and orbital momentum near this level and equations (1), (2) have resulted in the next relation [1–3]

\[
\varepsilon_{nl} = \varepsilon_{n0} - \frac{S''_{\varepsilon_{n0}}(0)}{2T_{\varepsilon_{n0}}} \lambda^2. \quad (3)
\]

Here \( T_{\varepsilon} = \partial S_{\varepsilon}/\partial \varepsilon \) is a classical time, \( S''_{\varepsilon_{n0}}(0) \) is a second derivation of a radial action \( S_{\varepsilon}(\lambda) \) in \( \lambda \) at the point \( \lambda = 0 \), a value \( \varepsilon_{n0} \) is computed from the equation (2).
### Table 1. Quintic polynomial fit data $c_k \left(f(\sigma) = \sum_{k=0}^{5} c_k \sigma^k\right)$ for functions $\log |e(\sigma)|$ and $\log d(\sigma)$ by TF model.

| $k$ | $\log |e(\sigma)|$ | $\log d(\sigma)$ |
|-----|-------------------|-------------------|
| 0   | 2.920595188918E+00 | 1.211170422361E+00 |
| 1   | -4.506251788322E+00 | -2.377270691365E+00 |
| 2   | 3.264808776975E+00  | 1.742055800053E+00  |
| 3   | -1.387317303526E+00 | -7.51668523350E-00  |
| 4   | 2.830731359676E-00  | 1.545198111561E-00  |
| 5   | -2.267624662588E-02 | -1.24600226676E-02  |

To verify equation (3) the electron energy spectrum has been at first calculated by the TF free atom model. According to the model a semi-consistent potential $U_{TF}(r)$ in an atom $Z$ is written through the TF function $\varphi(x)$ which does not depend on $Z$ [4]:

$$U_{TF}(r) = -Z\varphi(x)/r, \quad r = cxZ^{-1/3}, \quad c = 0.88534,$$

$$\sqrt{x}\varphi'' = \varphi^{3/2}, \quad \varphi(0) = 1, \quad \varphi(\infty) = 0.$$

The necessary functions for a calculation with equation (3) are

$$S_e(0) = \int_0^{R_e} \sqrt{2 \left( \varepsilon + \frac{Z}{r} \varphi(x) \right)} \, dr = \sigma(e)Z^{1/3},$$

$$\sigma(e) = \sqrt{2c} \int_0^{X_e} \frac{\varphi(x)/x + ce}{\sqrt{\varphi(x)/x + ce}} \, dx, \quad e = \varepsilon Z^{-4/3}.$$  

Similarly

$$T_e(0) = \tau(e)Z^{-1}, \quad S''_{\varepsilon_n}(0) = -\delta(e)Z^{-1/3},$$

$$\tau(e) = \varepsilon^{3/2} \int_0^{X_e} \frac{dx}{\sqrt{2}\sqrt{\varphi(x)/x + ce}},$$

$$\delta(e) = \frac{1}{\sqrt{2c}} \int_0^{X_e} \left[ \frac{1}{\sqrt{\varphi(x)/x + ce}} - \frac{1}{\sqrt{1/x + ce}} \right] \, dx - \frac{2}{c} \left[ \frac{1}{X_e + ce} \right].$$

Here the reduced values $\varepsilon$, $\sigma$, $\tau$, $\delta$ correspond to the electron energy, action, time, second derivation $S''_{\varepsilon_n}(0)$ in $\lambda$ for a hydrogen atom ($Z = 1$) and $R_e = cX_eZ^{-1/3}$.

As a result we get

$$\varepsilon_{nl} = Z^{1/3}\varepsilon_n + Z^{2/3}d(e_n)\lambda^2, \quad d(e_n) = \frac{\delta(e_n)}{2\varepsilon(e_n)},$$

where the s-state reduced energy $e_n$ is determined from equation (4) as

$$Z^{1/3}\sigma(e_n) = \pi n, \quad \varepsilon_{n0} = e_nZ^{4/3}.$$
Table 2. The electron binding energies in the mercury ($Z = 80$) and radon ($Z = 86$) atoms by the TF-model from the equation (11) and Bohr–Zommerfeld condition (1).

|   | Hg         |          |          | Rn         |          |          |
|---|------------|----------|----------|------------|----------|----------|
|   | $n$ | $l$ | $\varepsilon_{nl}$ (1) | $\varepsilon_{nl}$ (11) | $\Delta \varepsilon / \varepsilon$ (%) | $\varepsilon_{nl}$ (1) | $\varepsilon_{nl}$ (11) | $\Delta \varepsilon / \varepsilon$ (%) |
| 1 | 0   | 2.73E+03 | 2.73E+03 | 0.0 | 3.18E+03 | 3.18E+03 | 0.0 |
| 2 | 0   | 4.55E+02 | 4.55E+02 | 0.0 | 5.38E+02 | 5.38E+02 | 0.0 |
| 3 | 0   | 1.08E+02 | 1.08E+02 | 0.0 | 1.31E+02 | 1.31E+02 | 0.0 |
| 3 | 1   | 9.80E+01 | 9.74E+01 | 0.6 | 1.20E+02 | 1.20E+02 | 0.0 |
| 3 | 2   | 8.24E+01 | 7.94E+01 | 4.0 | 1.03E+02 | 9.98E+01 | 4.0 |
| 4 | 0   | 2.43E+01 | 2.43E+01 | 0.0 | 3.11E+01 | 3.11E+01 | 0.0 |
| 4 | 1   | 2.02E+01 | 2.00E+01 | 1.0 | 2.64E+01 | 2.62E+01 | 0.8 |
| 4 | 2   | 1.37E+01 | 1.24E+01 | 10.0 | 1.89E+01 | 1.75E+01 | 7.4 |
| 4 | 3   | 4.93E+00 | 1.01E+00 | — | 8.56E+00 | 4.42E+00 | — |
| 5 | 0   | 3.97E+00 | 3.97E+00 | 0.0 | 5.59E+00 | 5.59E+00 | 0.0 |
| 5 | 1   | 2.62E+00 | 2.50E+00 | 7.5 | 3.93E+00 | 3.81E+00 | 3.0 |
| 5 | 2   | 7.14E-01 | -1.12E-01 | — | 1.50E+00 | 6.35E-01 | — |
| 6 | 0   | 2.59E-01 | 2.59E-01 | 0.0 | 4.70E-01 | 4.70E-01 | 0.0 |
| 6 | 1   | 1.33E-01 | 5.81E-02 | — | 1.33E-01 | 5.81E-02 | — |
| 7 | 0   | 1.40E-03 | 1.40E-03 | 0.0 | 1.40E-03 | 1.40E-03 | 0.0 |

However it is more suitable to use another argument instead of $e$ and apply the two functions $e(\sigma)$ and $d(\sigma)$. Then the equation (9) may be rewritten as

$$
\varepsilon_{nl} = Z^{4/3} e(\sigma_n) + Z^{2/3} d(\sigma_n) \lambda^2, \quad \sigma_n = \pi n Z^{-1/3}.
$$

The two functions, $e(\sigma)$ and $d(\sigma)$, are independent on the atomic number $Z$. Their interpolated logarithm curves by the quintic polynomials are represented in figure 1 and there are their polynomial coefficients in table 1. So one can use equation (11) with the interpolated functions $e(\sigma)$ and $d(\sigma)$ to estimate electron binding energies in the free atom TF model.

The comparative results of $\varepsilon_{nl}$ calculations from the equation (11) and the Bohr–Zommerfeld condition (1) and their relative difference for mercury and radon atoms are represented in table 2. The comparison shows a rather good fitting of equation (11) within the limits of 10% for inner energy levels but it fails for the highest ones.

The above semiclassical consideration suggests the electron energy level dependence (11) on the atomic number $Z$ and orbital momentum $l$. There are two scaling laws:

- atomic number scaling $Z^{4/3}$ for the $s$-state energies;
- atomic number scaling $Z^{2/3}$ and $\lambda^2$-dependence for the states with $l > 0$.

We verify them by comparison with more exact quantum mechanical models—two versions of the local density functional theory (LDA and ScRLDA), as well as with experimental data.

3. Analysis of the theoretical and experimental electron binding energies

Now one needs to solve an opposite problem. There are electron energies data $\{\varepsilon_{nl}\}$, calculated by any model or taken from the experiment, and it is necessary to evolve from them the dependence and scaling in question.
We suppose the equation (11) to be true for all the available data and consider at first the $s$-states $\{\varepsilon_{n0}\}$, $1 \leq n \leq n_{\text{max}}$ solely. Here $n_{\text{max}} = n_{\text{max}}(Z)$ is a maximal principal number for the element with an atomic number $Z$. The reduced value $e_n = \varepsilon_{n0}/Z^{4/3}$ corresponds to the value $\sigma_n = \pi n/Z^{1/3}$. That is one of the discrete values of a function $e(\sigma)$ (if the function exists, that is not evident).
**Figure 4.** The dependence of the deviation value \( d \) (12) on \( \sigma = \pi n Z^{-1/3} \) by the ScRLDA \([5]\) for atoms \( Z = 10, 11, 18, 19, 21, 30, 36, 37 \) solely—different markers in (a) and all of them (open triangles) with their common cubic polynomial interpolation (sold line, see table 3 for the coefficients)—(b).

**Table 3.** Cubic polynomial fit data \( c_k \) \( (f(\sigma) = \sum_{k=0}^{3} c_k \sigma^k) \) for functions \( \lg |e(\sigma)| \) and \( \lg d(\sigma) \) from electron binding energies by ScRLDA \([5]\) and experimental data \([6]\).

| k  | \( \lg |e(\sigma)| \) \([5]\) | \( \lg d(\sigma) \) \([5]\) | \( \lg |e(\sigma)| \) \([6]\) |
|----|-----------------|-----------------|-----------------|
| 0  | 1.899780777361E+000 | 2.598720034646E+000 | 1.926367607010E+000 |
| 1  | -1.556421245297E+000 | -2.982727637721E+000 | -1.613571106323E+000 |
| 2  | 3.23454221748E−001 | 9.332931754418E−001 | 3.63589520815E−001 |
| 3  | -4.88500898881E−002 | -1.16835850612E−002 | -5.48169107828E−002 |

The value \( d \) for every \( n \) and \( l > 0 \) is calculated from the equation

\[
d = \frac{\varepsilon_{nl} - \varepsilon_{n0}}{Z^{2/3} \lambda^2}
\]

and corresponds to the value \( \sigma_n = \pi n Z^{-1/3} \). That is the discrete value of a function \( d(\sigma) \) (if the function exists, it is also not evident).

We used the available data from the paper \([5]\). There are specifically tables of orbital energy eigenvalues for all the atoms with \( 1 \leq Z \leq 92 \), as computed in the local-density approximation (LDA) and scalar-relativistic local-density approximation (ScRLDA). The experimental data were taken from the paper \([6]\), in which one can find all the references.

We applied a visual method to show the existing functional dependencies and represented all results of our analysis in figures 2–5.

Since the TF model is the most valid for many-electron atoms \( (Z \geq 10) \) with complete \( l \)-shells we start with rare gases. Figure 2 shows for neon, argon, krypton, xenon and radon the results for energy eigenvalues calculated in the LDA model \([5]\) without relativistic effects account. One can see in figure 2a an initial rather long common part for all the elements but the lightest atoms neon and argon deviate from the unit curve. The dependence \( d(\sigma) \) in figure 2b is a one-valued
Figure 5. The dependence of the $s$-state reduced binding energies $e = \varepsilon_{n0} Z^{-4/3}$ on $\sigma = \pi n Z^{-1/3}$ taken from the experimental data [6] or rare gases solely (solid markers): argon (up triangle), krypton (diamond), xenon (circle), radon (square)—(a) and for rare gases (down triangles), mercury (diamond) and uranium (circle) with cubic interpolated polynomial curve—(b).

function for inner binding energies only. Thus the scaling and square law in the LDA electron spectra appears partly.

One can see the better results in figures 3, 4 for energy eigenvalues calculated in the ScRLDA model [5] with a scalar account for relativistic effects. There is no splitting of the eigenvalues because of spin-orbital interaction in the model and it is possible to evolve the function $d(\sigma)$ too (see figure 4).

Figure 3a collects the $e(\sigma)$ results for all the rare gases from neon to radon. The approximate common curve has been interpolated with a cubic polynomial, the coefficients being in the table 3. In figure 3b there are results for many other elements together with the rare gases. One can see again the long common part of the curve for all the atoms.

Figure 4 verifies the square-law dependence on $\lambda$ and atomic number scaling of equation (11) for atoms with $Z < 40$, because the function $d(\sigma)$ (see equation (12)) is a unique coefficient for all the considered atoms in the square dependence on $\lambda$. Thus one can use our cubic polynomial interpolation (see table 3) to estimate the many electron energy levels for these elements. Of course this estimation does not pretend to have a spectroscopic precision.

Since there are a splitting of the experimental [6] electron energy levels with non-zero $l$ through a spin-orbital interaction it is possible to evolve only a function $e(\sigma)$ from the data. Figure 5 represents the corresponding results for rare gases: argon, krypton, xenon, radon solely (a) and for mercury and uranium together with the common rare gases data (b). The interpolated cubic polynomial fits all of the data rather well, the highest levels of mercury and uranium only deviating.

4. Conclusions
We have found that the more exact models and experimental data justify (better than rough models) the approximate atomic number scaling (11) for the most part of electron energy spectra. Therefore the scaling property may be a test for a theoretic model whether all principle effects were accounted for (the example is LDA as compared to ScRLDA). The scaling property may be used for the energy eigenvalue estimations as initial values in more exact computations.
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