Bohr model for many-electron atoms[1]

In the limit of infinitely many electrons, Bohr model energy obeys Thomas - Fermi law $\sim Z^{7/3}$, while the electron density resembles the Thomas - Fermi density function.

I. BOHR MODEL FOR AN ATOM WITH N ELECTRONS

For a given number of electrons N and nuclear charge Z ($Z = N$ for a neutral atom), the functional of energy is defined as

$$W = W_1 + W_2, \tag{1}$$

where

$$W_1 = \sum_{i=1}^{N} \left(\frac{n_i^2}{2r_i^2} - \frac{Z}{r_i} \right), \tag{2}$$

$$W_2 = \sum_{i<j} \frac{1}{r_{ij}}, \tag{3}$$

$$r_i = |\boldsymbol{r}_i|, \quad r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|. \tag{4}$$

In (2), n_i for $i = 1, 2, 3, \ldots, N$ is a principal quantum number of i-th electron. The energy W is minimized in respect to vectors $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N$.

II. BEHAVIOR OF THE PRINCIPAL QUANTUM NUMBER n_i AT LARGE i

In approximation of weakly interacting electrons, each electron is characterized by three quantum numbers and projection of spin, (n, l, m, σ_z), where $n = 1, 2, \ldots$ is a principal quantum number. For a given n, the angular momentum quantum number could be $l = 0, 1, 2, \ldots, n-1$. For any given l, the "magnetic" quantum number (projection of angular momentum on z-axis) could accept $2l+1$ values $m = -l, -l+1, \ldots, l$, while σ_z could accept two values $\pm 1/2$. In total, there are $2l^2 = 2 \times [1 + 3 + \ldots + (2l+1)]$ states for a given number l and $n(n+1)(2n+1)/3 = 2 + 8 + \ldots + 2n^2$ states for a given n. As a rule, the i-th electron is always placed to the lowest available unoccupied or partially occupied n-shell. Possible exceptions are few outer shells, where sometimes higher l subshells of n-shell remain unoccupied while some lower-l subshells of $n+1$ and $n+2$ shells start to fill. Therefore,

the first two electrons are placed on $n = 1$ shell, the next 8 with numbers between 3 and 10 are placed on $n = 2$ shell, and generally, with numbers between $(n-1)n(2n-1)/3+1$ and $n(n+1)(2n+1)/3$ to n-th shell. This could be summarized by a general formula for the sequence of integers n_i,

$$n_i = \{\nu_i\}, \tag{5}$$

where $\{x\}$ in equation (5) stands for the smallest integer larger or equal than x, and ν_i is a sequence of real numbers satisfying a cubic equation $\nu_i(\nu_i+1)(2\nu_i+1)/3 = i$. Explicitly,

$$\nu_j = \frac{1}{12}\left[-6 + \frac{3}{\mu_j}\left(1+\mathrm{i}\sqrt{3}\right) + \left(1-\mathrm{i}\sqrt{3}\right)\mu_j\right], \quad \mu_j = \left(3\sqrt{2916j^2-3} - 162j\right)^{1/3}, \tag{6}$$

where we temporarily changed index i to j in order to distinguish the index i from $\mathrm{i} = (-1)^{1/2}$.

Expanding ν_i for large i, $\nu_i = (3/2)^{1/3}\, i^{1/3} - 1/2 + O\left(i^{-1/3}\right)$ and approximating $\{x\}$ as $x + 1/2$ in equation (5), we obtain an approximate formula

$$n_i \approx \left(\frac{3}{2}\, i\right)^{1/3}. \tag{7}$$

The function n_i together with its almost everywhere exact approximation given by equation (5) and large-i approximation given by equation (7) are shown in Figure 1.

III. EQUILIBRIUM LOCATIONS OF ELECTRONS AND ELECTRON DENSITY

If number of electrons is large, we could assume that electrons with numbers between i and $i+\delta i$ are smeared over a sphere of radius r_i. Coulomb force acting on i-th electron from other electrons inside the sphere of radius r_i is $F_{\mathrm{Coulomb}} = \frac{Z-i+1}{r_i^2}$, and the centrifugal force which originates from the potential $\frac{1}{2}n_i^2/r_i^2$ is $F_{\mathrm{c}} = n_i^2/r_i^3$. From the condition of equilibrium $F_{\mathrm{Coulomb}} = F_{\mathrm{c}}$ and using large-i approximation for the function n_i, equation (7), we find

$$r_i = \frac{1}{Z-i+1}\left(\frac{3}{2}\, i\right)^{2/3}. \tag{8}$$

The corresponding electron density is given by a parametric formula

$$\rho(r_i) = \left(4\pi r_i^2\, \frac{dr_i}{di}\right)^{-1} = \frac{(Z-i+1)^4}{3\pi i(2Z+i+2)}, \tag{9}$$

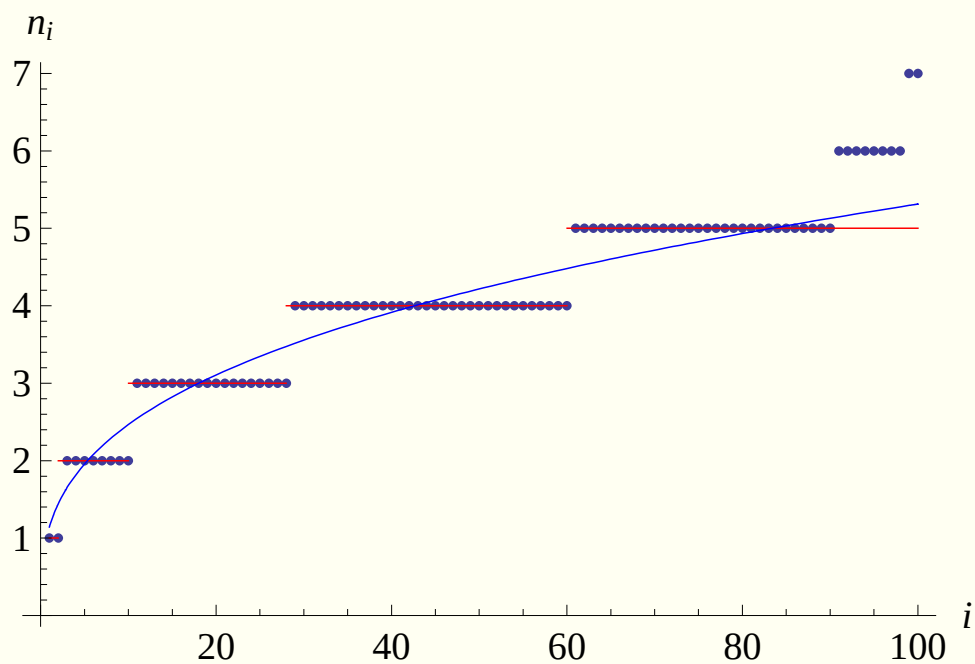

FIG. 1. Principal quantum number of i-th electron for an element Fermium (Fm, $Z = 100$). Dots - according to its commonly accepted shell structure $1s^2\,2s^2 2p^6\,3s^2 3p^6 3d^{10}\,4s^2 4p^6 4d^{10} 4f^{14}\;\; 5s^2 5p^6 5d^{10} 5f^{12}\,6s^2 6p^6\,7s^2$, red stepwise line - equation (5), smooth line - equation (7).

where r_i is given by equation (8). The parameter i changes in the interval $[0, Z+1)$ while r_i changes between zero and infinity.

The electron density for an element Fermium ($Z = 100$) is plotted on Fig. 2. The density obtained from Thomas-Fermi theory,

$$\rho_{\mathrm{T-F}}(r) = \frac{Z^2}{4\pi b^3}\left(\frac{\chi(x)}{x}\right)^{3/2}, \tag{10}$$

where

$$x = Z^{1/3} b^{-1} x, \quad b = \frac{1}{2}\left(\frac{3\pi}{4}\right)^{2/3}, \tag{11}$$

and $\chi(x)$ is a solution of a differential equation

$$\chi''(x) = \frac{Z^2}{4\pi b^3}\left(\frac{\chi(x)}{x}\right)^{3/2} \tag{12}$$

with boundary conditions $\chi(0) = 1$ and $\chi(\infty) = 0$ is plotted too.

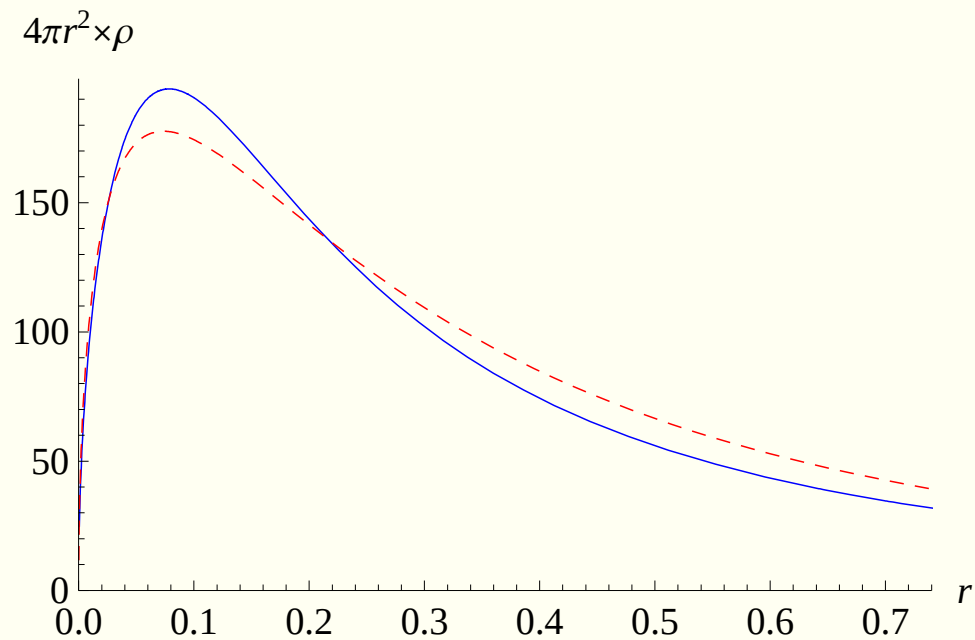

FIG. 2. Radial electron density, ρ multiplied by $4\pi r^2$, for an element Fermium (Fm, $Z = 100$). Solid line - according to Bohr model in the limit of large Z, equation (9), dashed line - from Thomas-Fermi theory, equation (10).

IV. ENERGY

The energy of i-th electron is one-half of its Coulomb energy,

$$E_i = \frac{1}{2}\,\frac{Z-i+1}{r_i} \approx \frac{1}{2}(Z-i+1)^2\left(\frac{3}{2}\,i\right)^{-2/3}. \tag{13}$$

The total energy is

$$E_{\rm tot} = \sum_{i=1}^{N} E_i \approx \frac{1}{2}\left(\frac{3}{2}\right)^{-2/3}\int_0^Z (Z-i)^2 i^{-2/3}\,di = \frac{3}{7}\left(\frac{3}{2}\right)^{4/3} Z^{7/3}, \tag{14}$$

where we replaced $Z-i+1$ by $Z-i$ since both Z and i are large.

According to Thomas-Fermi theory, the energy grows as $0.76875\,Z^{7/3}$ for large Z which is slightly different from the behavior $0.73589\,Z^{7/3}$ according to equation (14). The difference between Bohr model and Thomas-Fermi (asymptotically exact result) is $100\% \times (0.73589/0.76875 - 1) = -4.27\%$, in agreement with Fig. 3.

The growth of the total binding energy of all electrons is shown on Fig. 4, together with the predicted large Z behavior.

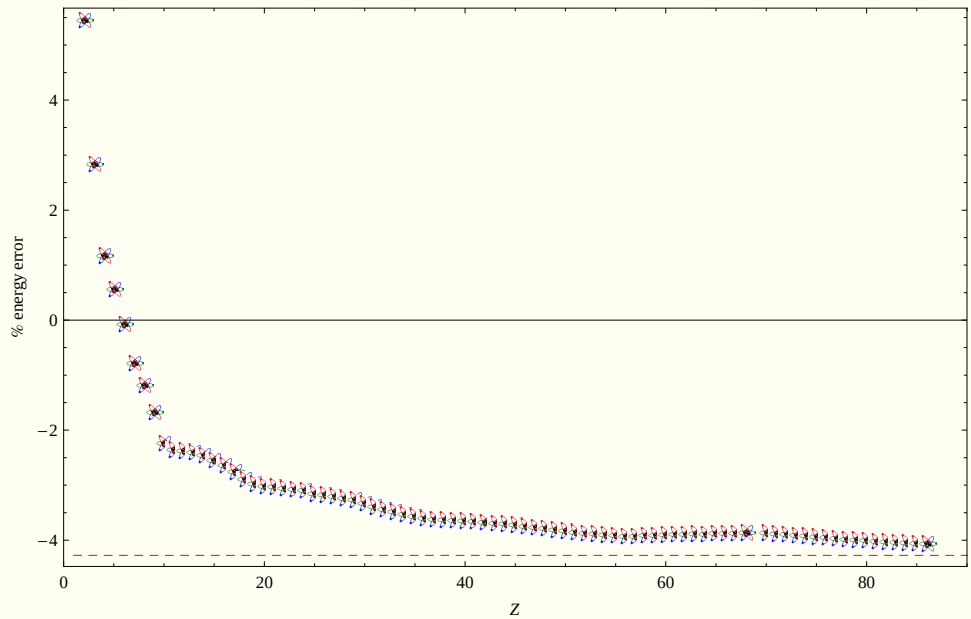

FIG. 3. Accuracy of Bohr model as a function of Z. Dashed line is large-Z asymptotics -4.27%.

V. COMBINING BOHR MODEL AND THOMAS - FERMI THEORY

According to statistical Thomas - Fermi theory, the energy behaves at large Z as

$$E \sim E^{(Z\to\infty)} = -0.76875 Z^{7/3} + 0.5 Z^2 - 0.2699 Z^{5/3}, \tag{15}$$

see for example [2].

Bohr energy has a similar functional behavior at large Z, but with slightly different coefficients,

$$E_{\rm Bohr} \sim E_{\rm Bohr}^{(Z\to\infty)} = C_0 Z^{7/3} + C_1 Z^2 + C_2 Z^{5/3}, \tag{16}$$

where $C_0 = -0.73589$ according to equation (14). Ab initio calculation of coefficients C_1 and C_2 is a formidable task because it requires taking into account many effects like polarization of an electron core by outer electrons. Here, we just used a least-square fit of the difference $\delta(Z) = (E_{\rm Bohr} - C_0 Z^{7/3}) - (E + 0.76875\, Z^{7/3})$ by a linear combinations of functions Z^2 and $Z^{5/3}$, $-0.0534\, Z^2 - 0.0199\, Z^{5/3}$ and found that

$$C_1 = 0.5 - 0.0534 = 0.4466, \quad C_2 = -0.2699 - 0.0199 = -0.2898. \tag{17}$$

It is interesting that coefficients in equations (15) and (16) differ only by few percents. The difference

$$\epsilon_{\rm TF} = E^{(Z\to\infty)} - E_{\rm Bohr}^{(Z\to\infty)} = -0.03286 Z^{7/3} + 0.0534 Z^2 + 0.0199 Z^{5/3} \tag{18}$$

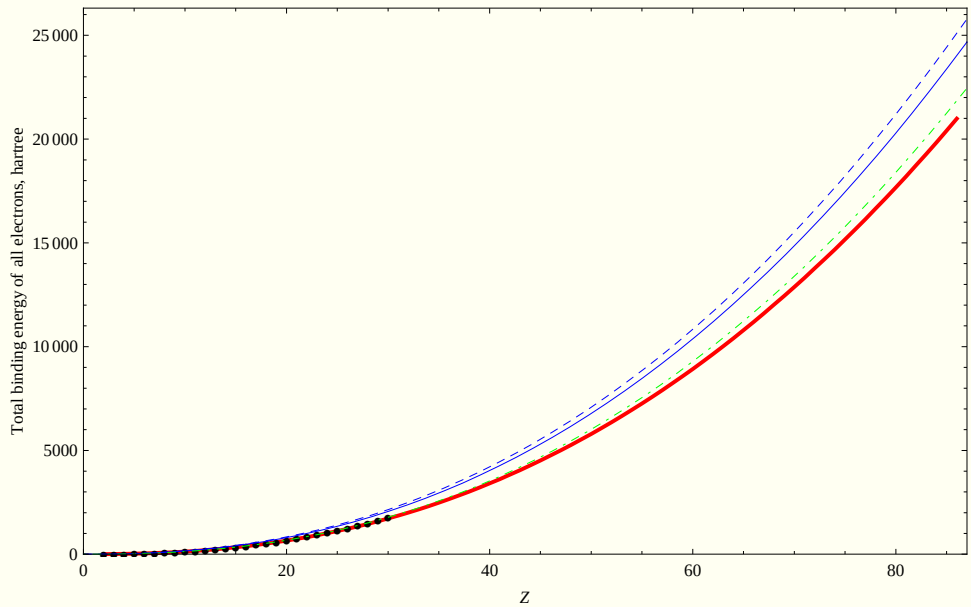

FIG. 4. Total binding energy vs. Z. Dots are exact energies, thick line is Bohr model energy, solid line - its large-Z asymptotics $0.73589\, Z^{7/3}$, dashed line - Thomas-Fermi formula $0.76875\, Z^{7/3}$, dot-dashed line - three-term refined Thomas-Fermi, equation (15)

may be considered as Thomas - Fermi correction to the Bohr energy. The function

$$E_{\mathrm{Bohr-TF}} = E_{\mathrm{Bohr}} + \epsilon_{\mathrm{TF}} \tag{19}$$

has the same asymptotical behavior at large Z as exact energy and reflects electronic shell structure that the statistical Thomas - Fermi theory lacks. Errors of Bohr, Thomas - Fermi, and combined energy given by equation (19) are shown in Fig. 5. The combined approximation oscillates around the exact quantum-mechanical energy with decreasing amplitude as Z increases. It outperforms Bohr energy for large Z due to correct asymptotical behavior. It outperforms Thomas - Fermi energy for small Z presumably because it takes into account electronic shell structure which is more pronounced for few-electron atoms.

VI. IONIZATION POTENTIALS

E_{I} for a given Z is defined as a difference of energies between a positive ion with $Z-1$ electrons and a neutral atom (with Z electrons). Ionization potentials are plotted on Fig. 6. Bohr model shows shell effect in dependence of $E_{\mathrm{I}}(Z)$ because quantum numbers in this model are based on electronic occupancy numbers over different shells. A generalized full-

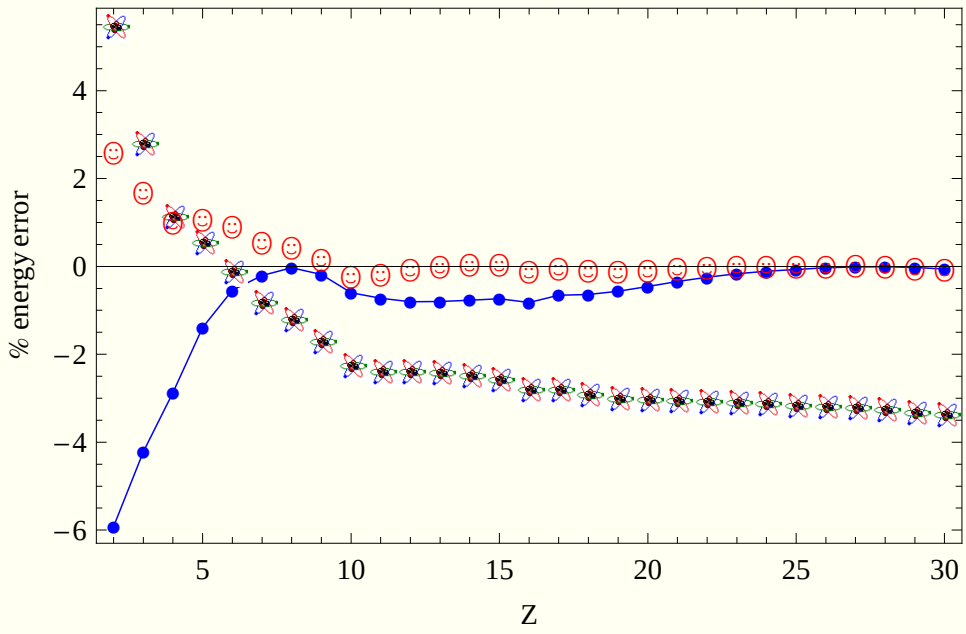

FIG. 5. Relative errors of Bohr energy (atomic symbols), Thomas-Fermi energy given by equation (15) (filled circles) and combined energy given by equation (19) (happy smileys).

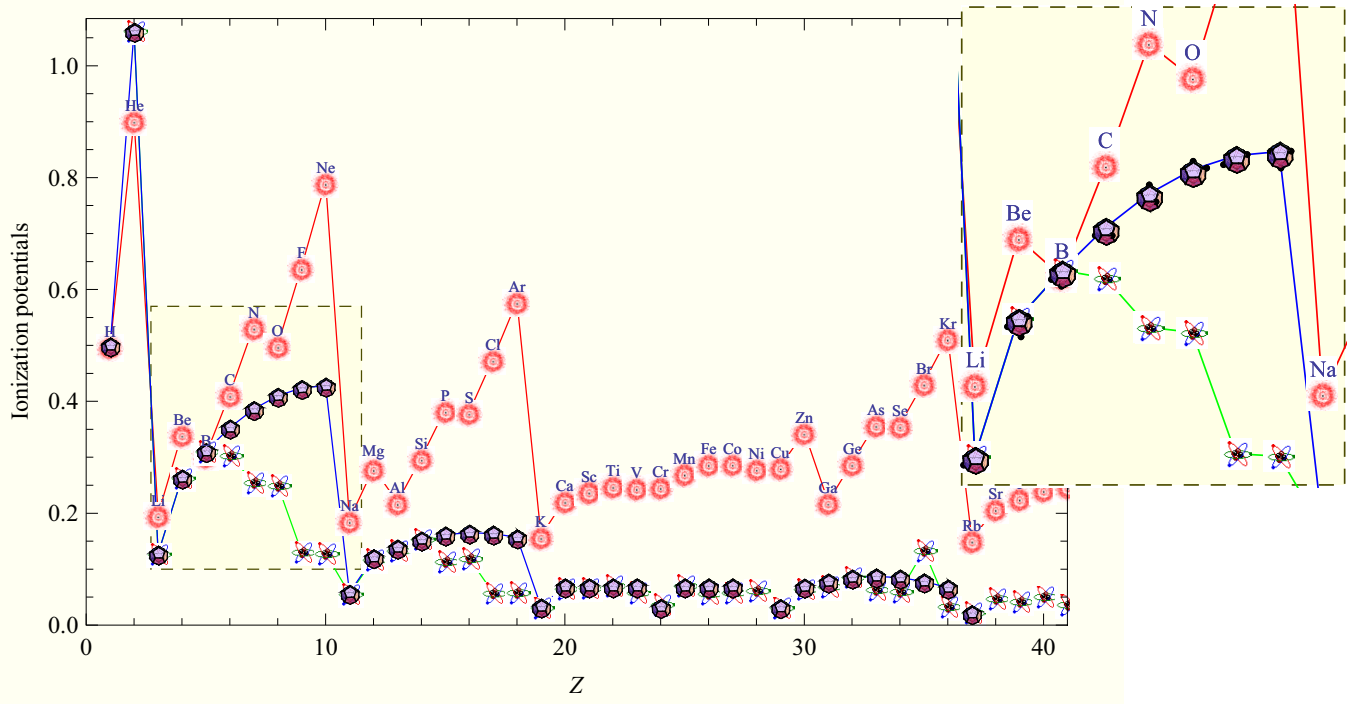

FIG. 6. Ionization potential as a function of Z. Fuzzy dots are exact results, atomic symbols - Bohr model, and dodecahedrons are results of a full-dimensional Bohr model, see Section VII. Enlarged area around the element Boron is shown to the right.

dimensional Bohr model (see next Section VII) shows maxima of the ionization potential corresponding to magic numbers 2, 10 and 18, but the maxima are somehow languid in comparison with sharp maxima of the accurate $E_{\rm I}(Z)$. Generally, Bohr model is not accurate for ionization energies, except for an element Boron (almost Bohr-on), where it gives good accuracy of 2%.

VII. FULL-DIMENSIONAL BOHR MODEL

Bohr energies for large atoms could be lowered by minimizing in infinitely-dimensional space instead of three dimensional. The results are shown on Fig. 7. Atomic symbols -

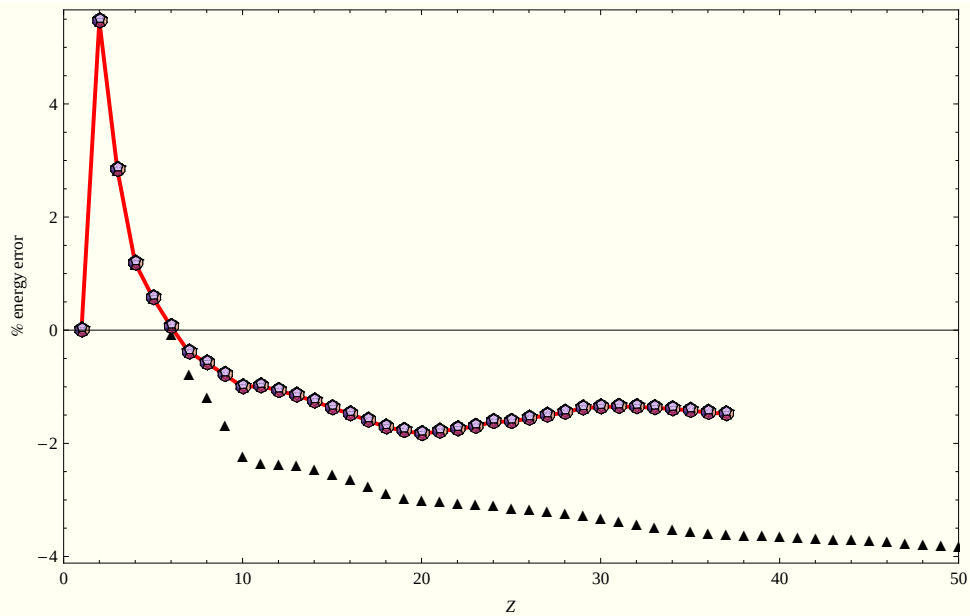

FIG. 7. Accuracy of Bohr model as a function of Z. Triangles are results of the Bohr model based on a minimization of classical configurations in three dimensional space, and dodecahedrons in $Z-1$ dimensional space.

errors of $3D$-model, and blue dots - infinitely-D model. For atoms with 2 or 3 electrons, $3D$ and infinitely-D models are the same because two electrons and a nucleus always lye in $2D$ space, and 3 electrons and nucleus in $3D$ space. In fact, results are the same even for 3 and 4 electrons, but differ by $\sim 0.1\%$ for 5 electrons. For more than 5 electrons, energies of infinitely-D model are visibly below $3D$ model because extra dimensions allow existence of more stable configurations. It seems that infinitely-D model is roughly two times more accurate than $3D$ model. It is also interesting, that in infinitely-D model configurations are

more symmetric and may be more easily calculated.

The method is better to be called $(N-1)$-dimensional, or "full dimensional" Bohr model, because in classical mechanics a configuration of N electrons could be always considered as $(N-1)$-dimensional simplex. So, it is completely different from infinite D limit of quantum mechanics, where all angles are almost 90 degrees. In the case of 5 and 6 electrons the model is essentially 3-dimensional too, because different shells are weakly correlated. Since carbon has only 4 electrons in outer shell, they could form a tetrahedron of maximum dimensionality 3, so the energy is almost the same as in $3D$ model.

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[1] The most recent version of these notes is available through Internet at address http://www.asergeev.com/files/tamu/tfermi.pdf.

[2] B.-G. Englert and J. Schwinger. Phys. Rev. A **32**, 47 (1985).