THE ORDER OF FILLING WITH ELECTRONS OF SUCCESSIVE SUB-SHELLS OF A SHELL IN MANY-ELECTRONIC ATOMS

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Abstract: In the framework of the Thomas-Fermi (statistical) model of neutral heavy atoms, in this paper we investigate the electronic structure of the atoms from the Mendeleyev table, namely the order of filling with electrons of various sub-shells of a shell. Because exact solutions of the Thomas-Fermi equation do not exist, we will use three new approximate solutions, compatible with the boundary conditions. By means of an old and, in the same time, well-known method, we investigate the distribution of the electrons according to their angular momentum, that is to say, we calculate the minimum value of the atomic number \( Z \) for which the filling of \( s- \), \( p- \), \( d- \) and \( f- \) state is possible in atoms. For one of these trial functions (with a good confidence - in our opinion), the deduced values of the atomic number \( Z \), at which a given value of orbital angular momentum (quantum number \( \ell \)) can appear, are in enough good agreement with the reality.

1. INTRODUCTION

The statistical theory of the atom is very useful in dealing with a multitude of physical problems where a more fundamental quantum mechanical approach is either not feasible or not warranted (see [1]). The simplest physical formulation of the statistical theory is the so-called Thomas-Fermi (TF) model [2,3] which, expressed mathematically, is an ordinary nonlinear differential equation of the second order. The TF equation possesses a universal solution for all the heavy neutral atoms, but has to be solved separately for each degree of ionization of each atom. Dirac [4] has investigated the relationship between the statistical theory and quantum mechanics and has shown that the TF model is the semiclassical equivalent of the Hartree approximation, because they both share the same shortcoming of not considering the exchange effect between electrons of parallel spin. The exchange effect has been introduced into the TF model by Dirac [4] leading to the Thomas-Fermi-Dirac (TFD) model and into the Hartree approximation by Fock [5], leading to the Hartree-Fock (HF) approximation. The statistical theory has been further refined by Gombas [6] who has considered the correlation effect between electrons of antiparallel spin. The simplest form of quantum-mechanical equivalent of the Thomas-Fermi-Dirac-Gombas (TFDG) model is the unrestricted HF approximation.

In the framework of the TF model for heavy neutral atoms, in the present paper, mainly with didactic purpose, we investigate the electronic structure of the atoms in the periodic (Mendeleyev) table, namely the order of filling with electrons (satisfying the Pauli’s exclusion principle) of various sub-shells of a shell. As is well known, in the ground state, within a shell, the first to be occupied are the states with \( \ell = 0 \) (\( s- \) sub-shells), then the states with \( \ell = 1 \) (\( p- \) sub-shells). But, after that, this rule does not work more. The filling of the \( 3d- \) subshell does not begin from Potassium \((Z=19)\), as expected, but is shifted to the element Scandium \((Z=21)\), i.e. until the completion of the \( 4s- \) subshell. Also, the filling of the \( 4f- \) subshell does not start with Silver \((Z = 47)\), but begins only with Cerium \((Z = 58)\), which corresponds to the Lanthanide group.
We investigate how some new optimized approximate solutions of the TF equation (model) can explain these strange behaviours. More, we infer that the filling of the 5g-subshell ($\ell = 4$) could begin only with the element with $Z = 121$ or 122.

2. NEUTRAL ATOMS. THOMAS-FERMI THEORY.

In the TF theory one considers the inter-electronic repulsion, the electron-nuclear attraction and a contribution from the kinetic-energy which is proportional to the 5/3 power of the number density in electronic cloud [7].

Introducing the dimensionless variable $x$ by

$$ x = 4 \left( \frac{2Z}{9\pi^2} \right)^{\frac{1}{3}} \left( \frac{r}{a_B} \right) = \frac{r}{a}, \quad a = 0.8853414 Z^{-\frac{1}{3}} a_B, \quad a_B = \frac{\hbar^2}{m e_0^2}, \quad (1) $$

where $r$ is the distance from the nucleus, $a_B$ is the Bohr radius and $Z$–the atomic number, the TF theory leads to the universal nonlinear differential equation [8]

$$ \sqrt{x} \frac{d^2 \phi(x)}{dx^2} = \phi^{3/2}(x), \quad (2) $$

which, for a neutral atom, is to be solved with the boundary conditions

$$ \phi(0) = 1, \quad \phi(\infty) = 0, \quad \phi'(\infty) = 0. \quad (3) $$

Between the electric potential $\phi(r)$ inside a heavy atom, at the distance $r$, and the dimensionless function $\phi(x)$ of the TF theory there are the relation

$$ \phi(r) = \frac{Ze}{4\pi e_0 r} \phi(x) = \frac{Ze_0}{4\pi e_0} \frac{\phi(x)}{r}, \quad (4) $$

with $e_0 = e/\sqrt{4\pi\epsilon_0}$.

Now, it is important to see that neither the equation (2) nor the boundary conditions (3) for the dimensionless function $\phi(x)$, involve the atomic number $Z$. It is therefore sufficient to integrate the equation (2) once for all atoms. But, of course, the equation can be applied only to heavy atoms, i.e. with large and (at least) medium atomic $Z$ numbers.

Going back to the dimensional distance $r$, we find that the function $\phi(x)$ yields the potential distribution for each $Z$ in the following manner

$$ \phi(r) = \left( \frac{Ze}{4\pi e_0 r} \right) \left( 12950781.1 r^{5/3} (r/a_B) \right). \quad (5) $$

Since for the same values of $x$ the value of $\phi(x)$ is the same for all atoms, the corresponding values of $r$ for different atoms are conversely proportional to $Z^{1/3}$. Hence, in heavy atoms, the bulk of the electrons is concentrated closer to the nucleus than in lighter atoms.

Therefore, this nonlinear differential equation of the TF model, deceptively simple-looking, is a fundamental equation in atomic physics which describe the screened electrostatic Coulomb potential around a heavy charged nucleus and its concomitant cloud of electrons. Unfortunately, for the TF equation does not exist exact analytical solutions (satisfying all the boundary conditions) and, in this situation, numerical results and different semi-analytical approaches have been given during more than three quarters of century.

We will see at once that the TF differential nonlinear equation (2) can be replaced by an equivalent variation principle. Choosing the Lagrangian function

$$ L(\phi, \phi', x) = \frac{1}{2} \phi'^2 + \frac{2}{5} \phi^{5/2}/\sqrt{x}, \quad (6) $$
the following functional (action integral) can be constructed

\[ S(\phi) = \int_0^{+\infty} L(\phi(x), \phi'(x), x) \, dx . \]  

(7)

Then, we can observe that the variation principle

\[ \delta S = 0 \quad \text{or} \quad S(\phi) = \text{extremal} \]

(8)
is the equivalent of equation (2), because the substitution of the Lagrangian (6) into the Euler-Lagrange equation

\[ \frac{d}{dx} \left( \frac{\partial L}{\partial \phi'} \right) = \frac{\partial L}{\partial \phi} \]

(9)
results in the TF equation (2).

The problem is now the selection of a trial function (ansatz) \( \phi(x) \) with a specified dependence on the independent dimensionless variable \( x \), which satisfies the boundary conditions in equation (3). Obviously, a large class of functions is admissible and, therefore, in a didactical activity, in choosing one, we must resort to some forms which permits, if is possible, computational simplicity in connection with the integral from the equation (7).

In order to allow for some flexibility in the trial functions, it is also assumed to depend on a number of unknown (free) parameters \( q_j, j = 1,2,3,...,n \). Therefore we can write

\[ \phi = \phi_n(x; q_1, q_2, ... , q_n) . \]

By means of the Lagrangian (6), this ansatz is inserted in the action integral (7) which, then, can be integrated to become a specific function only of the unknown (flexibility) parameters \( q_j \). Therefore we can write

\[ S = S_n(q_1, q_2, ..., q_n) . \]

Optimization with respect to the parameters yields a system of algebraic equations \( \partial S_n / \partial q_j = 0, j = 1,2,...,n \), which, when solved, determines the stationary (optimized) solution within the set of trial functions and a concomitant approximation for the true solution of the TF equation (2).

The most explicit approximate solution of the TF equation has been given by Sommerfeld [9]. He noted that a particular exact solution of the TF equation can be found in the form

\[ \phi(x) = \frac{\phi_0}{x^\alpha} . \]  

(10)

By inserting this ansatz into the TF equation (2), one readily find \( \alpha = 3 \) and \( \phi_0 = 144 \). The solution

\[ \phi(x) = \frac{144}{x^3}, \]  

(11)
known as the exact Sommerfeld’s solution, fulfils the boundary condition at \( x \to \infty \), but not the boundary condition \( \phi(0) = 1 \).

In order to remedy this shortcoming, Sommerfeld employed several transformations of the equation and an asymptotic saddle point analysis to find the beautifully simple approximate solution

\[ \phi(x) = \left[ 1 + \left( \frac{x}{x_0} \right)^{3/\lambda} \right]^{-\lambda}, \]

(12)
where \( \lambda = 3.886 \) and \( x_0 = \frac{3}{\sqrt[3]{144}} = 5.2414828 \). Clearly, this solution satisfies both boundary conditions and approaches the exact particular solution as \( x \to \infty \) . However, it tends to underestimate the true solution for small and moderate values of \( x \) (in particular in the region \( x \leq x_0 \)), i.e. in the important region where \( \phi(x) \) rapidly decays to less than 7 per cent of its original value. On the other hand, it is also important to compare this \( \phi(x) \) with the exact solution given by the equation (11), which neglects the boundary condition at \( x = 0 \). This last
function, which diverges when \( x \to 0 \), grossly overestimates the true variation in the region \( x \leq x_0 \). Really, already for \( x = x_0 \), the solution is more than a factor of 14 larger than the correct solution.

Naturally, the choice of a trial function - in order to describe a physical behaviour - is a crucial step, not a commonplace. This assertion can be motivated by the fact that the trial function must be flexible enough to contain the basic physics of the problem and still simple (if possible) to allow the integration of the Lagrangian in the action functional (7) and, then, the sequence of all steps of the optimization method described early.

Eight years ago, Desaix, Anderson and Lisak (DAL) [10] proposed three new approximate solutions of the TF equation (2), with one, two or three free parameters, all inspired by Sommerfeld’s solution (12). They investigate the screening of the Coulomb potential inside heavy neutral atoms and concluded that, in the main region of the screening potential, the most accurate (the best, but yet approximate) solution is the trial function with three free parameters, determined by the variational approach previously described.

The first DAL choice of a trial function is

\[
\phi^{(1)}_a(x) = \left[1 + (kx)^{3/\alpha}\right]^{-\alpha},
\]

with only one free variational parameter \( \alpha \), and where \( k = (144)^{-1/3} \). The optimization condition \( dS^{(1)}_a/d\alpha = 0 \) leads to the optimal value \( \alpha = 3.584 \). In fact, this trial function has the same shape as the approximate Sommerfeld’s solution (12), but with \( \alpha = 3.886 \) (determined by variational method) instead of \( \lambda = 3.886 \) (determined by another method by Sommerfeld).

The second DAL trial function is obtained using the same analytical expression as before, i.e. \( \phi^{(2)}_a(x) = \phi^{(1)}_a(x) \), but considering \( k \) also as a free parameter. The optimization conditions \( \partial S^{(2)}_a / \partial \alpha = 0, \partial S^{(2)}_a / \partial k = 0 \) leads to \( \alpha = 3.362 \) and \( k = 0.2521 \) respectively.

Finally, the third DAL choice, the ansatz with three free variation parameters is

\[
\phi^{(3)}_a(x) = \left[1 + (kx)^{\beta}\right]^{\alpha},
\]

with \( k, \alpha, \beta \) as unknown parameters. Calculating the corresponding Lagrangian (6) and the action integral (7) with the help of the well-known integral

\[
\int_0^{+\infty} x^{\mu-1} \frac{dx}{(1+x)^\nu} = \frac{\Gamma(\mu)\Gamma(\nu-\mu)}{\Gamma(\nu)},
\]

the following dependence with gamma (\( \Gamma \)) functions can be obtained

\[
S^{(3)}_a(\alpha, \beta, k) = \frac{k \alpha^2}{2} \frac{\Gamma(2-1/\beta)\Gamma(2\alpha+1/\beta)}{\Gamma(2\alpha+2)} + \frac{2}{5\beta^2} \frac{\Gamma(5\alpha/2-1/2\beta)\Gamma(1/2\beta)}{\Gamma(5\alpha/2)}. \tag{16}
\]

From the algebraic system \( \partial S^{(3)}_a / \partial \alpha = 0, \partial S^{(3)}_a / \partial \beta = 0, \partial S^{(3)}_a / \partial k = 0 \), DAL deduced \( k = 0.4835, \alpha = 2.098 \) and \( \beta = 0.9238 \).

By comparing the numerical values for \( x \in [0 \div 40] \), obtained from the optimized trial functions \( \phi^{(1,2,3)}_a \) with a numerical solution [11] of the TF equation (2), DAL concluded that \( \phi^{(3)}_a(x) \) is the most accurate (the best) approximate solution in the main region of the screening potential, even if the asymptotic behaviour of this function is wrong (\( \phi \propto 1/x^{\alpha\beta} \) with \( \alpha \beta = 1.938 \) instead of 3).
In order to compare our results from the next section with the one which are presented in *Quantum mechanics* and *Statistical physics* textbooks (see, for example, [7], [8] and [12]), or in the literature [13]-[16], we introduce also the well-known ansatz \( \phi(x) = \exp(-\gamma x) \) which satisfies the boundary conditions (3). The optimized value of the free parameter \( \gamma \) can be obtained from the equation \( \frac{dS(\gamma)}{d\gamma} = 0 \), where

\[
S(\gamma) = \frac{\gamma}{4} + \frac{2}{5} \sqrt{\frac{2\pi}{5\gamma}}
\]  

and the final result is

\[
\gamma = \left(\frac{2}{5}\right)(4\pi)^{1/3} = 0.9299579.
\]

### 3. THE APPEARANCE IN ATOMS OF ELECTRONS WITH A GIVEN VALUE OF \( \ell \)

The TF model for neutral atoms can be used efficiently enough to study such exotic questions as the value of \( Z \) for which an orbital angular momentum quantum number \( \ell \), of an individual electron, a \( d \)-, or an \( f \)-state, for example, first appear.

It is well known that the angular momentum \( \vec{L} \) for the electron is

\[
\vec{L} = \vec{r} \times \vec{p} \quad \text{or} \quad L = r p \sin \theta = r p_n,
\]

where \( p_n \) is the projection of momentum \( \vec{p} \) on the plane which is orthogonal on \( \vec{r} \). We have obviously

\[
p_n^2 = \frac{L^2}{r^2} \leq P^2, \tag{20}
\]

where \( P \) is the maximal value of the momentum \( p \) in the atom. Because in the statistical model of the atom (TF-model) the boundary energy is equal to zero we have

\[
P^2 = 2m_e \phi(r) = \hbar^2 (3\pi^2 n(r))^{2/3}, \tag{21}
\]

where

\[
n(r) = \frac{8\pi}{3h^3} (2m_e \phi(r))^{3/2} \tag{22}
\]

is the density of electronic gas (i.e. the number of electrons in unit spatial volume. From the last two relations we obtain

\[
p^2 = \frac{2m_e^2 \phi(x)}{r}. \tag{23}
\]

In the place of \( L^2 \) in the equation (20) we can put \( \hbar^2 \ell(\ell + 1) \). But, since the present theory corresponds wholly to *quasi-classical approximation*, a rather better result is obtained with the quasi-classical eigenvalue of \( L^2 \). It can be shown that the quasi-classical eigenvalue of \( L^2 \) is \( \hbar^2 (\ell + 1/2)^2 \) and note that \( (\ell + 1/2)^2 \) differs from \( \ell(\ell + 1) \) by only 1/4.

Equations (20) - (23) lead to

\[
8m_e^2 \phi(x) \geq \frac{\hbar^2 (2\ell + 1)^2}{x}. \tag{24}
\]

From this inequality and from the boundary conditions (3), it is clear that for \( x \to 0 \) (\( r \to 0 \)) and for \( x \to \infty \) (\( r \to \infty \)) the right hand side is greater than the left hand side. Consequently, the electrons from the neutral atoms can have the value \( \ell \) of the orbital quantum number only if \( x \in [x_1, x_2] \), where \( x_{1,2} \) are the roots of the equation.
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\[ \phi(x) = \frac{D_\ell}{x}, \quad (25) \]

where

\[ D_\ell = \frac{(2\ell + 1)^2 a_B}{8aZ}. \quad (26) \]

To have a well determinate value of \( \ell \), it is necessary to put \( x_1 = x_2 \). In this case we must to have not only the continuity of the functions from the two parts of the relation (25), but also the continuity of its derivatives

\[ \phi'(x) = D\ell'\left(\frac{1}{x}\right)' = -\frac{D\ell}{x^2} \quad (27) \]

and this means that

\[ \phi'(x) = -\frac{\phi(x)}{x}. \quad (28) \]

From the last relation we determine the solution \( x_1 = x_2 = \xi \), and consequently

\[ D_\ell = \xi \phi(\xi) = \frac{(2\ell + 1)^2 a_B}{8aZ} = \frac{(2\ell + 1)^2 Z^{-2/3}}{7.0827312}. \quad (29) \]

Finally we have

\[ Z = (0.05305165D_\ell^{-3/2})(2\ell + 1)^3. \quad (30) \]

This relation together with the optimized trial functions presented in the previous section, enable us to construct the following table.

<table>
<thead>
<tr>
<th>Trial function ((D_\ell - \text{value}))</th>
<th>Values of (Z) for sub-shells</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\phi(x) = \exp(-\gamma x)) ((0.3955872))</td>
<td>(\ell = 0) (s – state)</td>
</tr>
<tr>
<td>Sommerfeld- Eq.(12) ((0.4418033))</td>
<td>0.21</td>
</tr>
<tr>
<td>DAL - (\phi_a^{(1)}(x)) ((0.5354422))</td>
<td>0.14</td>
</tr>
<tr>
<td>DAL - (\phi_a^{(2)}(x)) ((0.4667175))</td>
<td>0.17</td>
</tr>
<tr>
<td>DAL - (\phi_a^{(3)}(x)) ((0.4836229))</td>
<td>0.16</td>
</tr>
<tr>
<td>Empirical values</td>
<td>(1)(H)</td>
</tr>
</tbody>
</table>

From the columns of the table we observe that, for \(\ell = 2\) (d- state) and for \(\ell = 3\) (f-state) the best results (percentage uncertainty of 0.96% and 1.62% respectively) are afforded by the DAL function \(\phi_a^{(2)}(x)\), and, for \(\ell = 1\)(p-state), by the Sommerfeld solution (percentage uncertainty of 2.4%) and then (percentage uncertainty of 10.2%) by DAL function \(\phi_a^{(2)}(x)\). In fact, these functions are of the Sommerfeld kind (i.e. like equation (12)) but with the free parameters (two in this case) determined by using the variational optimization method.
Another strange finding is the great difference between the values from the lines of Sommerfeld function and DAL $\Phi_a^{(1)}(x)$ - function. If we compare equation (12) with equation (13) and the parameter $k$ with $1/x_0$, we see that we have the same function but with $\lambda = 3.886$ and $\alpha = 3.584$ respectively. The conclusion is that the values of $Z$ calculated with the equation (30) are very sensitive when we pass from $\lambda$ to $\alpha$.

Why, with respect to our question of the sub-shell filling with electrons, the best function $\Phi_a^{(3)}(x)$ - in DAL opinion - give less good agreements with the reality? I think that the answer is: because of its wrong $x$-dependence for large $x$ (when $x \rightarrow \infty$, $\Phi_a^{(3)}(x) \propto x^{-\alpha \beta}$, with $\alpha \beta = 1.938$ instead of 3, as in (11), (12), (13) and $\Phi_a^{(2)}(x)$).

REFERENCES


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