ON THEORY OF SPECTRUM OF HYDROGEN-LIKE ATOMS

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Simple model of hydrogen-like atoms is proposed. Model is based on consideration of electron core, which consists of electrons in complete shells, using Thomas-Fermi model. Outer-shell electron is described by wave function. The model has no fitting parameters. Calculations of Rydberg correction for high-excited states with zero angular momentum are done. Calculations of energy of single ionization of hydrogen-like atoms and comparison with experimental data are done. The developed model can be used for further research of interaction of Bose-Einstein condensate and electromagnetic field.

KEY WORDS: Rydberg correction, alkali metals, atomic spectrum, Thomas-Fermi theory, atomic Bose – Einstein condensate

DO TEORI SPECTRA VODYNOPODNYX ATOMOV

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Предложена достаточно простая модель водородоподобных атомов, основанная на том, что остов, состоящий из электронов заполненных оболочек, описывается моделью Томаса-Ферми, а внешний валентный электрон описывается волновой функцией. В рамках представленной модели без использования подгоночных параметров вычислены поправка Ридберга для высокозависимых состояний с нулевым моментом, энергия одноразовой ионизации водородоподобных атомов, та проведено сравнение с экспериментальными данными. Предложенная модель водородоподобных атомов может быть использована для дальнейшего развития теории взаимодействия бозе-ёйнштейновских конденсатов с электромагнитным полем.

КЛЮЧЕВЫЕ СЛОВА: поправка Ридберга, щелочные металлы, спектр атома, теория Томаса-Ферми, атомный бозе-ёйнштейновский конденсат

К ТЕОРИИ СПЕКТРА ВОДОРОДОПОДНОБНХ АТОМОВ

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Hydrogen atoms and ions, that contain one electron, like, for example, He⁺, Li++, in non-relativistic approximation are described precisely [1-5]. Strict analytic calculations for atoms and ions containing two electrons, such as H⁺, He, Li, are impossible, however these objects are simple enough to use different approximate methods, that provide sufficient accuracy [1-5]. Hartree - Fock self-consistent method usually is used to compute more complex atoms [6], but such calculations appear to be rather bulky, especially for atoms containing many electrons. Thomas-Fermi statistical method is widely used to investigate structure of many-electron atoms [7, 8]. Significance of this approach is simplicity, though it gives less accurate results and does not reproduce periodical dependence of atomic sizes and ionization potentials from atomic number.

Hydrogen-like atoms have simple enough energy spectrum similar to that of hydrogen atom. Atoms of alkali metals Li, Na, K, Rb, Cs, Fr, and so called Rydberg atoms, that have one electron in high-excited state [9], are considered as hydrogen-like atoms. Atoms of alkali metals drew attention in recent years, because they are used to obtain and investigate Bose-Einstein condensates in magnetic traps [10-12]. Phenomena in such condensates are theoretically described by Gross - Pitaevskii equation [13]. However, more consistent description of interaction of

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Bose-Einstein condensate with electromagnetic field should take into account inner structure of atoms in condensate. Generalization of Gross-Pitaevskii equation, that takes structure of hydrogen-like atoms into consideration, is proposed in [14]. Influence of inner structure of atom on Bose – Einstein condensation in ideal gas of hydrogen-like atoms is considered in works [15, 16]. Development of rather simple model, that allows description of inner structure of alkali atoms, is significantly important for further development of theory of interaction of Bose-Einstein condensate with electromagnetic field.

Investigation of Rydberg atoms is of interest for astrophysics and for usage of such atoms as detectors of long-wave radiation [9]. Research of so called “Rydberg matter”, which is metastable crystal consisting of high-excited atoms with the same principal quantum number [17], is of significant interest. Such matter should have density \(10^{16} - 10^{19}\) cm\(^{-3}\) and thus be condensed matter with gas density and unique properties.

The aim of the present work is to develop rather simple model of structure of hydrogen-like atoms, which would allow taking into account influence of finite size of electron core, which consists of electrons in filled shells, on energy levels of valence electron with sufficient accuracy. In the proposed model electrons in atomic core are described by Thomas-Fermi approach and valence electron – by single-particle wave function. Calculations of quantum defect, energy of low-lying levels and ionization energy are done. The model has no fitting parameters.

**MODEL DEFINITION**

Hamiltonian of valence electron in hydrogen-like atom can be set as

\[
H = \frac{\hbar^2}{2\mu} \Delta + U(r),
\]

where \(\mu = mM/(m + M)\) is reduced mass, \(m\) is electron mass, \(M\) is overall mass of atomic nucleus and electron core, \(U(r)\) is potential energy of electron in the field, produced by nucleus with charge \(Ze\) and electron core with total charge \(-(Z-1)e\). Hamiltonian of hydrogen-like atom (1) can be stated as sum of Hamiltonian of hydrogen atom and additional potential related to finite size of electron core

\[
H = H_0 + V(r),
\]

where

\[
H_0 = -\frac{\hbar^2}{2}\Delta - \frac{e^2}{r}
\]

is Hamiltonian of hydrogen atom, and

\[
V(r) = U(r) + \frac{e^2}{r}.
\]

Potential energy can be stated as

\[
U(r) = -\frac{Ze}{r} \Phi(r),
\]

where \(\Phi(r)\) is potential, created by nucleus with charge \(Ze\) and electron core with full charge \(-(Z-1)e\), that satisfy Poisson equation

\[
\Delta \Phi(r) = -4\pi Z|e|\delta(r) + 4\pi|e|n(r).
\]

In (6) \(n(r)\) is particle number density, which satisfies normalization condition

\[
4\pi \int_0^{r_0} dr^2 n(r) = Z - 1.
\]

Here \(r_0\) is boundary radius, where particle number density comes zero. As it is known [7, 8], neutral atom has \(r_0 = \infty\), and for positively charged ion, as in our case of nucleus and electron core, \(r_0\) is finite quantity.

In order to obtain electron core potential Thomas-Fermi approach is used. In this approach equation for electron density distribution is derived from condition of equality zero of variation of energy, which consists of kinetic energy, own electron potential energy and energy in external field [7, 8]. Thus, one has the equation

\[
-\frac{5}{3} \epsilon_0 \frac{\hbar^2}{m} n^{3/2} - U(r) + \mu = 0,
\]

where \(\epsilon_0 \approx 3^{10} \pi^{10}/10 \approx 2,871\). Chemical potential \(\mu\) introduced in equation (8) allows taking into consideration conservation of overall electron number \(N = Z - 1 = 4\pi \int_0^{r_0} dr^2 n(r)\). From condition of turning electronic density
\[ n(r_0) = 0 \] into zero one concludes connection of chemical potential with electron core radius
\[ \mu = U(r_0) = -\frac{e^2}{r_0}. \] (9)

It is sufficient to use following function in further considerations
\[ \chi(r) = U(r_0) - U(r). \] (10)

This function is divergent from zero in \( 0 < r \leq r_0 \) range, is nonnegative everywhere and satisfies boundary conditions:
\[ \chi(r_0) = 0, \quad \chi(r) \to \frac{Ze^2}{r} \quad \text{at} \quad r \to 0 \] (11)

and equation
\[ \chi(r) = \frac{5}{3} c_0 \frac{\hbar^2}{m} n^\frac{3}{2}. \] (12)

In the sequel it is suitable to introduce dimensionless function \( \psi(x) \)
\[ \chi(r) = \frac{Ze^2}{r} \psi(x), \] (13)

which depends from dimensionless variable \( x = r/L \). Here \( L \) denotes characteristical length, proportional to Bohr radius \( a_0 = \hbar^2/me^2 \):
\[ L = \frac{a_0}{2Z^{\frac{3}{2}} \left( \frac{3\pi}{4} \right)^{\frac{3}{2}}}. \] (14)

Taking into account (6), (11), (12) and (14) one gets Thomas-Fermi equation
\[ x^{\frac{3}{2}} \frac{d^2\psi(x)}{dx^2} = \psi^{\frac{3}{2}}(x) \] (15)

with boundary conditions
\[ \psi(0) = 1, \quad \psi(x_0) = 0, \] (16)

where \( x_0 = r_0/L \). Radius \( r_0 \) can be obtained from condition of continuity of electric field in point \( r_0 \)
\[ \frac{d\Phi}{dr} \bigg|_{r=r_0} = \frac{k}{r^2}. \] (17)

Exact solution of Schrödinger equation for hydrogen atom is known. Influence of finite size of electron core (4) is considered with the use of perturbation theory. In terms of function (10) perturbation (4) takes the following form
\[ V(r) = \begin{cases} \frac{e^2}{r} - \frac{e^2}{r_0} - \chi(r), & \text{при } r < r_0, \\ 0, & \text{при } r > r_0. \end{cases} \] (18)

Hydrogen functions are known \( \Psi_{nlm} = R_{nlm}(\Omega) \), where \( \Omega = (\theta, \phi) \) are angular variables, and radial functions are normalized by condition \( \int_0^\infty dr r^2 R_{nl}^2(r) = 1 \). Every level is degenerated \( 2n^2 \) times. Perturbation partially splits the levels.

Using perturbation theory for degenerated states [2], one finds energy levels
\[ E^{(0)}_{nl} = E^{(0)}_n + E^{(1)}_{nl}, \] (19)

where \( E^{(0)}_n = -(\mu e^4/2\hbar^2n^2) \) are hydrogen energy levels. Under act of perturbation every level with given \( n \) splits into \( 2(2l+1) \) times degenerated. Correction to energy of the ground state is
\[ E^{(1)}_{nl} = \int_0^\infty dr r^2 R_{nl}^2 \left( \frac{e^2}{r} - \frac{e^2}{r_0} - \chi(r) \right). \] (20)

Solution of equation (15) is needed in order to obtain this correction.

**APPROXIMATE SOLUTION OF THOMAS-FERMI EQUATION**

Approximate solution of equation(15), obtained by Sommerfeld [7, 8], for neutral atom
\[ \psi_0(x) = (1 + z)^{-\frac{1}{2}}, \] (21)
where \( z = \left( x / 144^{1/3} \right)^{1/6} \). Here \( \lambda_1 = 7.772 \), \( \lambda_2 = 0.772 \), and \( \lambda_1 \lambda_2 = 6 \). For positively charged ion solution of (15) has the form

\[
\psi(x) = \nu \left( 1 - \frac{x}{1 + x \lambda_1} \right)^{-1/2},
\]

where \( z_0 = \left( x_0 / 144^{1/3} \right)^{1/6} \). Taking (17) into account, boundary radius is found from relation

\[
q = \frac{Z - N}{Z} = -x_0 \frac{d\psi(x)}{dx} \bigg|_{r_0},
\]

where \( N = Z - 1 \) is number of electrons in core. Substitution (22) into (23) gives the equation for obtaining \( z_0 \)

\[
\lambda_1 \frac{z_0}{(1 + z_0)^{1/2}} = q.
\]

In the primary formulation, which is stated above, Thomas-Fermi theory took into consideration energy of self electric field of electrons. However, only energy of interaction of charged particles should be taken into account in quantum-mechanical description (see discussion in [18, 19]). Approximate way to eliminate self-field energy in Thomas-Fermi approach was proposed by Fermi and Amaldi [7].

Results of numeric calculations of electron core radii for atoms of alkali metals are stated in Table 1. Symbol * marks results obtained taking into account Fermi-Amaldi correction. We should state that, strictly speaking, for lithium atom, which consists a few electrons, given model is non-applicable. Specifically, it appears in the fact, that equation for electron core radius for lithium atom with Fermi-Amaldi correction doesn’t have solutions. Note, that elimination of self-field energy leads to decrease of core radius.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
</tr>
<tr>
<td>( r/a_0 )</td>
</tr>
<tr>
<td>( r_0/a_0 )</td>
</tr>
</tbody>
</table>

**CALCULATION OF RYDBERG CORRECTION**

Energy of high-excited levels of hydrogen-like atoms can be described by equation

\[
E_{nl} = -\frac{Ry}{\left(n - \delta_0 \right)^2},
\]

where \( Ry = \mu e^4 / 2\hbar^2 \) is Rydberg constant, and \( \delta_0 \) is quantum defect or Rydberg correction, which usually has positive sign. Taking quantum defect into account leads to splitting of energy levels, which are degenerated by principal quantum number in hydrogen atom. Rydberg correction is connected with first order correction to energy (20) by the following equation

\[
\delta_0 = -\frac{n^3}{2Ry} E_{nl}^{(1)}.
\]

Since the perturbation in our case is always negative the first order correction is also negative. Thus, Rydberg correction is positive. Under the condition \( r \ll na_0 \) solution for radial part of wave function is expressed in terms of Bessel function [1]

\[
R = \sqrt{\frac{2}{na_0^2}} J_{2l+1} \left( \frac{8r}{a_0} \right).
\]

Obtaining matrix element of perturbation with function (27) and substituting it into (26), one finds equation for Rydberg correction

\[
\delta_l = -\frac{1}{a_0^2 Ry} \int_0^\infty dr V(r) J_{2l+1}^2 \left( \frac{8r}{a_0} \right).
\]
appeared to be understated in comparison with experimental values [5]. However, accuracy of calculations, as one should suppose, increases with atom number. Calculated values of Rydberg correction at $l = 1, 2, 3$ appear to be significantly understated [20], what is conditioned by neglecting electric polarization of electron core by valence electron in present model.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>Fr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^0$</td>
<td>0.148</td>
<td>0.832</td>
<td>1.402</td>
<td>2.482</td>
<td>3.403</td>
<td>4.823</td>
</tr>
<tr>
<td>$\delta_{\text{exp}}$</td>
<td>0.41</td>
<td>1.37</td>
<td>2.23</td>
<td>3.20</td>
<td>4.13</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2

IONIZATION ENERGY OF HYDROGEN-LIKE ATOMS

In order to obtain ionization energy let’s consider solutions for energy levels with azimuthal quantum number $l = 0$. Let $R_n$ be radial part of solution of Schrödinger equation for valence electron

$$HR_n = ER_n, \quad (29)$$

where $H$ is stated by equation (1). Solution $R_n$ can be expanded into series in hydrogen radial functions with $l = 0$:

$$R_n = \sum C_n R_n^{(0)}, \quad (30)$$

where $R_n^{(0)}$ are radial functions for hydrogen atom. From Schrödinger equation (29) and series (30) one concludes infinite set of equations for expansion coefficients (30)

$$\sum C_n \left( \left( E_n^{(0)} - E \right) \delta_n + \left( n \left| \vec{V} \right| n' \right) \right) = 0, \quad n = 1, 2, 3, \ldots \quad (31)$$

System of equations (31) has nontrivial solution if determinant equals zero. Calculations considered a few lowest levels. Number of levels taken into account is determined from condition, that adding one more level changes energy less than on 1%. Results of such calculations are stated in Table 3. The last line of the table states the energy levels neglecting size of electron core.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>Fr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of levels taken into account</td>
<td>4</td>
<td>10</td>
<td>13</td>
<td>16</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>Calculated energy, eV</td>
<td>4.61</td>
<td>4.49</td>
<td>3.51</td>
<td>3.50</td>
<td>3.11</td>
<td>3.08</td>
</tr>
<tr>
<td>Experimental value, eV</td>
<td>5.32</td>
<td>5.14</td>
<td>4.34</td>
<td>4.18</td>
<td>3.89</td>
<td>-</td>
</tr>
<tr>
<td>Point-like core, eV</td>
<td>3.40</td>
<td>1.51</td>
<td>0.85</td>
<td>0.54</td>
<td>0.38</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Taking into account finite size of electron core significantly improves agreement between theoretical calculations and experimental values, especially for massive atoms.

CONCLUSION

Simple enough model of hydrogen-like atoms, which are atoms of alkali metals and Rydberg atoms, is described in the present paper. In this model electron core, which consists of electrons in filled shells, is described by Thomas-Fermi approach, while outer-shell valence electron is described by wave function, which satisfies Schrödinger equation. Radii of electron cores, which are radii of singly ionized ions, are calculated. Rydberg corrections for high-excited states are calculated. Obtained values for s-states are in good agreement with experiment. Also, energies of single ionization of hydrogen-like atoms are calculated and compared with experimental data. It is shown, that taking into account finite size of electron core significantly improves agreement between theory and experiment. The theory allows further modification, related, in particular, with taking into considerations polarization of the core by valence electron. Core polarization should significantly influence on valence electron states with $l > 0$. Performed calculations lead to conclusion, that present model can be used, in particular, for describing many-particle systems of alkali metals, Bose-Einstein condensates and Rydberg matter.
REFERENCES


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