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ON THEORY OF SPECTRUM OF HYDROGEN-LIKE ATOMS

Yu.M. Poluektov*, V.N. Savchenko**
National Science Center "Kharkov Institute of Physics and Technology"
1, Akademicheskaya St., 61108 Kharkov, Ukraine
*** V.N. Karazin Kharkov National University*
Svobody Sq. 4, 61022, Kharkiv. Ukraine
E-mail: yuripoluektov@kipt.kharkov.ua

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**.**

К ТЕОРИИ СПЕКТРА ВОДОРОДОПОДОБНЫХ АТОМОВ
Ю.М. Полуэктов*, В.Н. Савченко**
* ННЦ ХФТИ
ул. Академическая,1, Харьков, 61108
** ХНУ им. В.Н. Каразина
пл. Свободы 4, Харьков, 61022

Предложена достаточно простая модель водородоподобных атомов, основанная на том, что остов, состоящий из электронов заполненных оболочек, описывается моделью Томаса-Ферми, а внешний валентный электрон - волновой функцией. В рамках предложенной модели без использования подгоночных параметров вычислены поправка Ридберга для высоковозбужденных состояний с нулевым моментом и энергия однократной ионизации, проведено сравнение с экспериментальными данными. Развитая модель водородоподобных атомов может быть использована для дальнейшего развития теории взаимодействия бозе-эйнштейновских конденсатов с электромагнитным полем.
КЛЮЧЕВЫЕ СЛОВА: поправка Ридберга, щелочные металлы, спектр атома, теория Томаса-Ферми, атомарный бозе-эйнштейновский конденсат.

ДО ТЕОРІЇ СПЕКТРА ВОДНЬОПОДІБНИХ АТОМІВ
Ю.М. Полуектов*, В.М. Савченко**
* ННЦ ХФТІ
вул. Академічна, 1, Харків, 61108
** ХНУ ім. В.Н. Каразіна
пл. Свободи, 4, Харків, 61022

Запропонована достатньо проста модель водньоподібних атомів, заснована на тому, що остов, який складається з електронів, що знаходяться у заповнених оболонках, описується за допомогою моделі Томаса-Фермі, а зовнішній валентний електрон описується хвильової функцією. В межах даної моделі без використання підгоночних параметрів обчислені поправка Рідберга для високозбуджених станів з нульовим моментом, енергія одноразової іонізації водньоподібних атомів, та проведено порівняння з експериментальними даними. Запропонована модель водньоподібних атомів може бути використана для подальшого розвинення теорії взаємодії бозе-ейнштейнівських конденсатів з електромагнітним полем.
КЛЮЧОВІ СЛОВА: поправка Рідберга, лужні метали, спектр атома, теорія Томаса-Фермі, атомарний бозе-ейнштейновський конденсат.

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

$$H = -\frac{\hbar^2}{2\mu}\Delta + U(r), \tag{1}$$

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 $Z|e|$ 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

$$H = H_0 + V(r), \tag{2}$$

where

$$H_0 = -\frac{\hbar^2}{2\mu}\Delta - \frac{e^2}{r} \tag{3}$$

is Hamiltonian of hydrogen atom, and

$$V(r) = U(r) + \frac{e^2}{r}. \tag{4}$$

Potential energy can be stated as

$$U(r) = -|e|\Phi(r), \tag{5}$$

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

$$\Delta\Phi(r) = -4\pi Z|e|\delta(\mathbf{r}) + 4\pi|e|n(r). \tag{6}$$

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

$$4\pi\int_0^{r_0} dr\, r^2 n(r) = Z - 1. \tag{7}$$

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

$$-\frac{5}{3}c_0\frac{\hbar^2}{m}n^{2/3} - U(r) + \mu = 0, \tag{8}$$

where $c_0 = 3^{5/3}\pi^{4/3}/10 \approx 2,871$. Chemical potential μ introduced in equation (8) allows taking into consideration conservation of overall electron number $N = Z - 1 = 4\pi\int_0^{r_0} dr\, r^2 n(r)$. 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:

$$\chi(r_0) = 0, \qquad \chi(r) \to \frac{Ze^2}{r} \quad at \quad r \to 0$$
(11)

and equation

$$\chi(r) = \frac{5}{3} c_0 \frac{\hbar^2}{m} n^{\frac{2}{3}}.$$
(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 $x \equiv r/L$. Here L denotes characteristic length, proportional to Bohr radius $a_0 = \hbar^2/me^2$:

$$L = \frac{a_0}{2Z^{\frac{1}{3}}} \left(\frac{3\pi}{4} \right)^{\frac{2}{3}}.$$
(14)

Taking into account (6), (11), (12) and (14) one gets Thomas-Fermi equation

$$x^{\frac{1}{2}} \frac{d^2 \psi(x)}{dx^2} = \psi^{\frac{3}{2}}(x)$$
(15)

with boundary conditions

$$\psi(0) = 1, \qquad \psi(x_0) = 0,$$
(16)

where $x_0 = r_0/L$. Radius r_0 can be obtained from condition of continuity of electric field in point r_0

$$-\frac{d\Phi}{dr}\bigg|_{r=r_0} = \frac{|e|}{r_0^2}.$$
(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

$$V(r) = \begin{cases} \dfrac{e^2}{r} - \dfrac{e^2}{r_0} - \chi(r), & при \quad r < r_0, \\ 0, & при \quad r > r_0. \end{cases}$$
(18)

Hydrogen functions are known $\Psi_{nlm} = R_{nl}(r) Y_{lm}(\Omega)$, where $\Omega \equiv (\vartheta, \phi)$ 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

$$E_{nl} = E_n^{(0)} + E_{nl}^{(1)},$$
(19)

where $E_n^{(0)} = -\left(\mu e^4 / 2\hbar^2 n^2 \right)$ are hydrogen energy levels. Under act of perturbation every level with given n splits into n levels, that are $2(2l+1)$ times degenerated. Correction to energy of the ground state is

$$E_{nl}^{(1)} = \int_0^{r_0} dr r^2 R_{nl}^2(r) \left(\frac{e^2}{r} - \frac{e^2}{r_0} - \chi(r) \right).$$
(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

$$\psi_0(x) = (1+z)^{-\lambda_1/2},$$
(21)

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where $z = \left(x/144^{1/3}\right)^{\lambda_2}$. 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

$$\psi(x) = \psi_0(x)\left[1 - \left(\frac{1+z}{1+z_0}\right)^{\frac{\lambda_1}{\lambda_2}}\right], \tag{22}$$

where $z_0 = \left(x_0/144^{1/3}\right)^{\lambda_2}$. Taking (17) into account, boundary radius is found from relation

$$q = \frac{Z-N}{Z} = -x_0\left.\frac{d\psi(x)}{dx}\right|_{x_0}, \tag{23}$$

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

$$\lambda_1\frac{z_0}{\left(1+z_0\right)^{\frac{\lambda_1}{2}+1}} = q. \tag{24}$$

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 1

Radius r_0 of singly ionized positive ions

Atom	Li	Na	K	Rb	Cs	Fr
r_0/a_0	2.555	4.483	5.100	5.742	6.074	6.419
r_{0*}/a_0	-	3.025	3.546	4.102	4.396	4.705

CALCULATION OF RYDBERG CORRECTION

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

$$E_{nl} = -\frac{Ry}{\left(n-\delta_l\right)^2}, \tag{25}$$

where $Ry = \mu e^4/2\hbar^2$ is Rydberg constant, and δ_l 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

$$\delta_l = -\frac{n^3}{2Ry}E_{nl}^{(1)}. \tag{26}$$

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]

$$R = \sqrt{\frac{2}{ra_0^2 n^3}}J_{2l+1}\left(\sqrt{\frac{8r}{a_0}}\right). \tag{27}$$

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

$$\delta_l = -\frac{1}{a_0^2 Ry}\int_0^{r_0}drrV(r)J_{2l+1}^2\left(\sqrt{\frac{8r}{a_0}}\right). \tag{28}$$

Results of computations with equation (28) and experimental values are stated in Table 2. Obtained values at $l = 0$

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 2

Values of Rydberg correction at $l = 0$

Atom	Li	Na	K	Rb	Cs	Fr
δ_0	0.148	0.832	1.402	2.482	3.403	4.823
$\delta_{0\,\exp}$	0.41	1.37	2.23	3.20	4.13	-

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

$$HR_n = ER_n,\tag{29}$$

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

$$R_n = \sum_{n'} C_{nn'} R_{n'0}^{(0)},\tag{30}$$

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

$$\sum_{n'} C_{nn'}\left(\left(E_{n'}^{(0)} - E\right)\delta_{n'n} + \langle n|\hat{V}|n'\rangle\right) = 0 \quad , n = 1, 2, 3\ldots .\tag{31}$$

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 3

Ionization energies of atoms of alkali metals

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

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.

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REFERENCES

1.   Bethe H., Salpeter E. Quantum Mechanics of One- and Two-electron Atoms. – M.: Fizmatgiz, 1960.
2.   Landau L.D., Lifshits E.M. Kvantovaya Mekhanika. – M.: Nauka, 1989.
3.   Condon E.U., Shortley G.H. Theory of Atomic Spectra. – M.: Inostrannaya Literatura, 1949.
4.   Sobelman I.I. Vvedenie v Teoriyu Atomnykh Spektrov. – M.: Nauka, 1977.
5.   Elyashevich M.A. Atomnaya i Molekulyarnaya Spektroskopiya. – M.: Fizmatgiz, 1962.
6.   Hartree D. The Calculation of Atomic Structures. – M.: Inostrannaya Literatura, 1960.
7.   Gombas P. The Statistical Theory of Atom and its Application. – M.: Inostrannaya Literatura, 1951.
8.   Theory of Inhomogeneous Electron Gas. Edited by S. Lundqvist and N.H. March. – M.: Mir, 1987.
9.   Smirnov B.M. Highly Exited Atomic States // Uspekhi Fiz. Nauk. - 1980. – Vol. 131. - P. 577. [Sov. Phys. Usp. – 1980. - Vol. 23. - P. 450.]
10. Anderson M.H., Ensher J.R., Matthews M.R., Wieman C.E., Cornell E.A. Observation of Bose-Einstein Condensation in a Dilute Atomic Vapor // Science. – 1995. **-** Vol. 269. - P. 198.
11. Davis K.B., Mewes M.-O., Andrews M.R., van Druten N.J., Durfee D.S., Kurn D.M., Ketterle W. Bose-Einstein Condensation in a Gas of Sodium Atoms // Phys. Rev. Lett. - 1995. - Vol. 75. - P. 3969.
12. Bradley C.C., Sackett C.A., Tollett J.J., Hulet R.G. Evidence of Bose-Einstein Condensation in an Atomic Gas with Attractive Interactions // Phys. Rev. Lett. – 1995. - Vol. 75. - P. 1687.
13. Pitaevskii L.P. Bose-Einstein Condensation in Magnetic Traps. Introduction to the Theory // Uspekhi Fiz. Nauk. - 1998. **-** Vol. 168. - P. 641. [Phys. Usp. – 1998. **-** Vol. 41. - P. 569.]
14. Poluektov Yu.M. Polarization Properties of Atomic Gas in a Coherent State // Fizika Nizkikh Temperatur. - 2011. **-** Vol. 37. - P. 1239.
15. Slyusarenko Yu.V., Sotnikov A.G. On the influence of the internal structure of the atom on Bose–Einstein condensation in an ideal gas of hydrogenlike atoms // Fizika Nizkikh Temperatur. – 2007. - Vol. 33. - P.41.
16. Slyusarenko Yu.V., Sotnikov A.G. Green-function method in the theory of ultraslow electromagnetic waves in an ideal gas with Bose-Einstein condensates // Phys. Rev. A. – 2008**.** - Vol. 78. – P.053622.
17. Holmlid L., Manykin E.A. Rydberg matter – a long-lived excited state of matter // Zhurnal Eksp. i Teor. Fiziki. – 1997. - Vol. 111. - P. 1601. [Journal of Exp. and Theor. Phys. – 1997. – Vol. 84. - P. 875.]
18. Vlasov A.D. The Schrödinger Atom // Uspekhi Fiz. Nauk. - 1993. **-** Vol. 163. - P. 97. [Phys. Usp. – 1993. - Vol. 36 (2).- P. 94.]
19. Pitaevskii L.P. On the Problem of the «Schrödinger Atom» // Uspekhi Fiz. Nauk. - 1993**.** - Vol. 163. - P. 119. [Phys. Usp. - 1993. - Vol. 36 (2). - P. 760.]
20. Kondratev V.N. Struktura Atomov i Molekul. – M.: Fizmatgiz, 1959.

Poluektov Yuri Matveevich - D.Sc. in physics and mathematics. Currently working as a Leading Researcher at Institute of theoretical physics at National Science Center "Kharkov Institute of Physics & Technology". His research interests are in the physics of many-particle systems, superconductivity, quantum fluids.

Savchenko Vladimir Nikolayevich - sixth year student in the department of Physics and Technology of V.N. Karazin Kharkov National University.