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HYDROGEN-LIKE ATOMS AND SPECTRA: SPECIAL QUANTUM STATES AND MAXIMUM RELATIVE INTENSITY LINE OF ITS MULTIPLET

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Using the quantum model of the hydrogen-type atom, we compute the wave-functions and the expressions of Dirac energy both in Bohr approximation as well as in fine structure approximation. Based on this quantum model (QM), we identify some special quantum states called maximum localization sub-shells. Then, we present numerical values of the radial distributions and the electron density functions, as well as the average radii ordered sequences of sub-shells. Analyzing the NIST atomic database, we observe that the transition between these special quantum states explains the occurrence of the maximum relative intensity line of the corresponding fine structure multiplet. Thus, using NIST database, the QM-results are validated for the α-Lyman, α-Balmer, .., and α-Pfund spectral H-lines in fine structure approximation.

Keywords: astrophysics, hydrogen spectra, fine structure approximation, quantum states, average radii of sub-shells.

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1. **Introduction**

The work of Schrödinger (1926), Dirac (1928), Born and Jordan, and others paved the way for development of Quantum Mechanics [13, 3].

Quantum and Atomic Physics [1] and their applications in Astrophysics and Astrochemistry ([14, 15] can successful explain spectra of various cosmic sources such as galaxies, stars and interstellar clouds ([16, 2, 12]), as well as Astroseismology [11].

The atomic models are the basis for understanding atomic-scale processes and phenomena in different types of gases and plasma [10]. Historically speaking, there are several atomic models: the planetary model, the Bohr's model [7], the quantum model (QM) in fine structure approximation [4, 6] and in hyperfine structure approximation [9], respectively.

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Furthermore, according to Kramida's work, the accuracy of reference wavelengths of the H-Lyman and H-Balmer series lines are useful for wavelength calibration of various laboratory discharge lamps or in diagnosis and modeling of solar spectra [2]. The intensity of certain spectral lines of the emitting plasma, correlated to the electron density, may be useful for plasma diagnosis.

The main goal of this paper is to analyze the quantum states of H-likes atoms and to correlate them to the experimental line spectra. Useful information about certain quantum states involved in transitions can be found by analyzing hydrogen atom different models for the first six levels and their corresponding of αLy, αBa, .., αPf lines measured in the H-absorption spectra [5].

The corresponding quantum states are analyzed using a computer based model and thus the numerical values of some observables are calculated and interpreted.

The structure of our paper is as follows:

In section 2, the mathematical framework of the hydrogen-like atom (H-like atom), both in Bohr approximation as well as in fine structure (*fs*) approximation, is described.

In section 3, for the first four hydrogen levels, the values of maximum localization density, the electron density depending on an angular factor, several maximum localization-radii and also average radii of sub-shells are calculated and tabulated. Thus, we identify some special quantum states which are correlated with the relative intensity of fine structure multiplets lines for the hydrogen αLy, αBa, .., αPf lines, according with NIST atomic database.

Finally, we give a synthesis consisting of two sets of results: the QM-analysis which helped us in identifying of the special quantum states in order to explain the profile of fine structure multiplets, and also the number values of the maximum localization-radii and sub-shells average-radii for the first four H levels.

2. METHODOLOGY

QM: The H-like atomic model

For the construction of QM, we need some key equations and quantum concepts.

The physical model of a H-like atom is made by a spherical nucleus with an electric charge of *+Ze* and an electron orbiting around it. This system can be mathematical described by the Schrödinger's equation [1] expressed in SI units:

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2+V(r)\right]\cdot\psi_{n\ell m}(r,\theta,\varphi)=E_n\cdot\psi_{n\ell m}(r,\theta,\varphi) \tag{1}$$

where $r>0$, $\theta\in(0,\pi)$, and $\varphi\in[0,2\pi)$ are the spherical coordinates and $V(r)$ is the atemporal potential-function which describes the interactions between the components' system. Due to the spherical symmetry of the atom, this potential can be considered to depend only of the radial coordinate r.

The simplest approximation takes in consideration only the coulombian interaction between electron and nucleus which is described by the Coulomb potential. In our case of H-like atom, the potential expresion is:

$$V(r) = \frac{-Ze^2}{4\pi\varepsilon_0 r} \tag{2}$$

where e is the electron charge and ε_0 is the permittivity of vacuum. According to the literature, in this approximation, the solution of Schrödinger's equation from eq. 1 provides the energy eigenvalues: [1]

$$E_n = E_1/n^2 \tag{3}$$

where $E_1 = -13.6eV$, and the principal quantum number $n = 1, 2, 3, ..$ which quantifies the total energy of the electron. In the same approximation, the space components of wave-functions are:

$$\psi_{n\ell m}(r, \theta, \varphi) = R_{n\ell}(r) \cdot Y_\ell^m(\theta, \varphi) \tag{4}$$

One can observe that the space-wave-function is indexed by 3 indices representing the following quantum numbers $(n, l.m)$ where the quantum number of the orbital angular momentum $\ell = 0, 1, 2, .., n-1$ and the magnetic quantum number $m = -\ell, .., 0, .., \ell$.

Returning to wave-functions, the radial components are:

$$R_{n\ell}(r) = -\sqrt{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} e^{\frac{-Zr}{na_\mu}} \left(\frac{2Zr}{na_\mu}\right)^\ell L_{n+\ell}^{2\ell+1}\left(\frac{2Zr}{na_\mu}\right) \tag{5}$$

with associated Laguerre's polynomials, electron mass m_e, reduce mass μ, $a_\mu = \frac{m_e}{\mu} a_0$, and a_0 the first Bohr radius. The harmonic components are:

$$Y_\ell^m(\theta, \varphi) = (-1)^m \sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}} P_\ell^m(cos\theta) e^{im\varphi}, m \geq 0 \tag{6}$$

and

$$Y^{*m}_\ell(\theta, \varphi) = (-1)^{|m|} Y_\ell^{|m|}(\theta, \varphi), m < 0 \tag{7}$$

with associated Legendre's polynomials.

For a quantum state described by 3 quantum numbers (n, ℓ, m), we compute the electron localization probability density by formula:

$$|\psi_{n\ell m}(r, \theta, \varphi)|^2 \tag{8}$$

The average radius formula of various quantum states becomes:

$$\langle r \rangle_{n\ell} = \frac{n^2 a_\mu}{Z}\left[1 + \frac{1}{2}\left(1 - \frac{\ell(\ell+1)}{n^2}\right)\right] \tag{9}$$

In order to identify some significant states, two important tools for quantum spectral analysis are used: the radial distribution function defined as:

$$DML_{n\ell}(r) = (rR_{n\ell}(r))^2 \tag{10}$$

and the electron density in angular factor function defined as:

$$Del_{\ell m}(cos(\theta)) = |Y_\ell^m(\theta,\varphi)|^2 \tag{11}$$

Remark 1: The atomic orbitals present a geometrical symmetry in spherical coordinates (θ,φ)(see eqs. (5) and (11)).

So, in order to simplify our presentation, we take only the positive values of m, namely the convention $m = |m|$.

In the approximation of Dirac theory which includes relativistic effects as a perturbation of the Coulomb potential [1], the Dirac energy is:

$$E_{nj} = E_n\left[1 + \frac{(Z\alpha)^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right] \tag{12}$$

with the total angular momentum quantum number $j = 1/2, 3/2, .., n - 1/2$. According to Bransden & Joachain 1990, ch 5, we specify:

Definition: The transitions $n\ell j \to n'\ell' j'$ between the fs components of the levels $n\ell$ and $n'\ell'$ form a set of spectral lines known as a multiplet of lines.

Remark 2: In Dirac's theory, for a fixed n, two states having the same value of j but with values of $\ell = j \mp 1/2$ have the same energy.

3. **RESULTS**

In astrophysics analysis, the H-Lyman, H-Balmer, and H-Paschen series lines from measured solar spectra are already presented by Brown and Kramida [2, 9]. Above all, Kramida in his work explains that the spectra of the other chemical elements are determined based on the H-spectrum. So, the study of H-spectra constitutes a fundamental aspect.

3.1. QM: Identification of ML-quantum states

Using the model already presented above and according to the eq. (10) and (11) for the first four H shells, we calculate the probability density function $DML_{n\ell}$ and the electron density $Del_{\ell m}$, respectively. The results are presented in table 1 and for each level (n,ℓ), the maximum values of these functions are marked as bold.

The left panel of table 1 shows us that the $DML_{n\ell}$ of each quantum state (n,ℓ) has the radius variable r as an argument. As a consequence, for level $(n, n-1)$ there is a maximum localization radius (ML-radius).

Proposition 1.1: For any orbital $(n, n-1)$, the maximum localization radius r corresponds to the n-th Bohr radius, namely n^2a_0.

Calculating the average radius for $n = 1$ as in the eq (9), we obtain $\langle r\rangle_{1s} = 1.5a_0$. Because the value of DML_{10} is maximum, the quantum state (1,0,0) is a significant state. Then, using values from table 1, we see that radial

n	ℓ	$\mathrm{DML}_{n\ell}(r \cdot a_0)$	$\langle r\rangle_{n\ell} \cdot a_0$	$r \cdot a_0$	$\ell_B = n-1$	m	$\mathrm{Del}_{\ell m}(w)$	w=cos(θ)
1	**0**	**0.54100**	1.5	**1**	0	**0**	**0.080**	w
2	0	0.19000	6	5.24	1	**0**	**0.238**	**1**
	1	**0.19500**	5	**4**		1	0.119	0
3	0	0.10150	13.5	13.07	2	**0**	**0.397**	**1**
	1	0.10170	12.5	12.00		1	0.149	0.707
	2	**0.10700**	10.5	**9**		2	0.149	0
4	0	0.06440	24	24.60	3	**0**	**0.557**	**1**
	1	0.06444	23	23.60		1	0.198	0.860
	2	0.06490	21	21.21		2	0.154	0.580
	3	**0.06970**	18	**16**		3	0.174	0

TABLE 1. The values of $DML_{n\ell}$ (left panel) and $Del_{\ell m}$ (right panel).

distribution $DML_{2\ell}$ reaches its maximum value for $\ell = 1$. Average radii $\langle r\rangle_{2\ell}$ corresponding to the shell $n = 2$ respect the following order relation: $5a_0 = \langle r\rangle_{2p} < \langle r\rangle_{2s} = 6a_0$. Also, the electron density in the angular factor Del_{1m} reaches its maximum value for $m = 0$. So, the quantum state $(2, 1, 0)$ is a significant state. Then, for $n = 3$, the radial distribution $DML_{3\ell}$ reaches its maximum value for $\ell = 2$. Average radii $\langle r\rangle_{3\ell}$ give the sub-shells order relation: $10.5a_0 = \langle r\rangle_{3d} < \langle r\rangle_{3p} < \langle r\rangle_{3s} = 13.5a_0$. The electron density Del_{2m} reaches its maximum value for $m = 0$. So, for shell $n = 3$, the probability function reaches its maximum on sub-shell $\ell = 2$ exactly on an its orbital with $m = 0$. Thus, we obtain that state $(3, 2, 0)$ is also a significant state. For $n = 3$, the radial distribution $DML_{4\ell}$ reaches its maximum value for $\ell = 3$. For average radii $\langle r\rangle_{4\ell}$ the sub-shells order relation is: $18a_0 = \langle r\rangle_{4f} < \langle r\rangle_{4d} < \langle r\rangle_{4p} < \langle r\rangle_{4s} = 24a_0$. The electron density Del_{3m} reaches also its maximum value for $m = 0$. As in the above cases, we obtain the state $(4, 3, 0)$ as a significant state, too.

Proposition 1.2: For a fixed n, the radial distribution $DML_{n\ell}$ reaches its maximum for a certain ML-radius on ML-sub-shell $(n, n-1)$ which we call the special quantum state. Moreover, the electron density $Del_{n-1\,m}$ reaches its maximum on ML-orbital $(n, n-1, 0)$ which we call the significant quantum state. So, for the shell n there are two types of maximum localization quantum states (MLqs), namely a ML-sub-shell corresponding to its ML-radius, respectively a ML-orbital for $m = 0$ (inside of ML-sub-shell).

3.2. QM: Maximum relative intensity lines of fine structure multiplets

The spectral lines of hydrogen (H I) measured by spectroscopic methods are obtained as the radiation emission to the transition from one quantum state to another. According to NIST database [8] which includes the *fs* lines, the relative intensities of multiplets are given in tables 2, 3, and 4. We

Range (Å)	HI series line-α	Wavelength (Å)	Intensity (a.u.)
1200 - 1230	αLy	**1215.66823**	**7.003e+08**
		1215.67364	3.502e+08
6550 - 6565	αBa	6562.70970	4.756e+07
		6562.72483	1.982e+07
		6562.75181	9.290e+05
		6562.77153	9.909e+06
		6562.85177	**8.561e+07**
		6562.86734	9.512e+06
		6562.90944	1.858e+06
18700 - 18800	αPa	18750.68381	4.767e+06
		18750.72050	2.491e+06
		18750.82881	2.486e+05
		18750.88135	1.246e+06
		18751.01086	1.569e+07
		18751.01149	8.580e+06
		18751.06422	2.825e+04
		18751.06508	9.533e+05
		18751.11120	**2.241e+07**
		18751.13794	1.121e+06
		18751.19130	2.542e+05
		18751.21008	4.974e+05
		18751.22507	1.413e+05

TABLE 2. The relative intensity lines of αLyman multiplet (measured in vacuum) and also αBalmer and αPaschen multiplets (measured in air) for H I.

present in table 5 Ritz -λ values in air [8], for transitions $n \to n+1$ with $n = 1, 2, .., 5$ and between their special states or ML-sub-shells.

Proposition 2.1: Comparing the wavelength values from tables 2, 3, and 4 with the ones from table 5, we observe that transitions between special quantum states or ML-sub-shells (see tab. 5) give the maximum relative intensity lines (bolded values in tables 2, 3, and 4) of their multiplets. These multiplets correspond of αLy, αBa, .., αPf series transitions in *fs* approximation.

To support our discovery, we can see Kramida's considerations about the observed H spectrum of αBalmer transition. In accord with Kramida's research (see [9] p. 5), we observe that the transition between the states $2P_{3/2}$ and $3D_{5/2}$ (in other words between the ML-sub-shells $(2,1)$ and $(3,2)$) provides the spectral line of maximum relative intensity in the associated multiplet. This is further confirmation of our above results.

Finally, we can generalize all of these thus:

Range (Å)	HI series line-α	Wavelength (Å)	Intensity (a.u.)
40500 - 40530	αBr	40521.86640	9.686e+05
		40521.93760	5.767e+05
		40522.21210	8.411e+04
		40522.32220	2.884e+05
		40522.48747	2.830e+06
		40522.48920	1.744e+06
		40522.61740	1.937e+05
		40522.67380	6.418e+06
		40522.67420	4.044e+06
		40522.73768	2.022e+05
		40522.73840	2.821e+03
		40522.76012	**8.320e+06**
		40522.79858	2.377e+05
		40522.86320	5.641e+04
		40522.86490	1.327e+05
		40522.86650	3.949e+04
		40522.96310	1.682e+05
		40522.99920	7.373e+04

TABLE 3. The relative intensity lines of αBrackett multiplet (measured in air) for H I.

Proposition 2.2: For the transition $n \to n+1$, the maximum relative intensity line of corresponded *fs* multiplet is given exactly by the transition between corresponded ML-sub-shells, namely the transition $(n, n-1) \to (n+1, n)$.

Range (Å)	HI series line-α	Wavelength (Å)	Intensity (a.u.)
70090 - 78109	αPf	74597.17250	2.870e+05
		74597.29760	1.862e+05
		74597.85200	3.425e+04
		74598.05170	9.308e+04
		74598.21910	7.758e+05
		74598.22440	5.166e+05
		74598.46910	7.351e+03
		74598.47570	5.740e+04
		74598.52770	1.108e+06
		74598.53009	1.634e+06
		74598.65340	5.542e+04
		74598.65542	2.139e+03
		74598.67000	2.118e+06
		74598.67160	3.081e+06
		74598.74500	6.051e+04
		74598.74663	4.841e+02
		74598.75164	**3.781e+06**
		74598.80192	7.002e+04
		74598.87100	4.278e+04
		74598.87232	1.307e+04
		74598.87695	1.694e+04
		74598.90340	6.616e+04
		74598.90674	2.995e+04
		74599.15530	6.850e+04
		74599.22330	3.676e+04

TABLE 4. The relative intensity lines of αPfund multiplet (measured in vacuum) for H I.

n $\to n+1$	Wavelength (Å)	Lower level: Conf., Term, J	Upper level: Conf., Term, J
$1 \to 2$	**1 215.66823**	1s ^2S 1/2	2p $^2P^0$ 3/2
$2 \to 3$	**6 562.85177**	2p $^2P^0$ 3/2	3d ^2D 5/2
$3 \to 4$	**18 751.11120**	3d ^2D 5/2	4f $^2F^0$ 7/2
$4 \to 5$	**40 522.76012**	4f $^2F^0$ 7/2	5g ^2G 9/2
$5 \to 6$	**74 598.75164**	5g ^2G 9/2	6h $^2H^0$ 11/2

TABLE 5. The wavelength values for transitions between special quantum states $(n, n-1)$, $n = 1, .., 6$ for H I.

4. **Conclusions**

In our approach, we used a quantum model whereby we identified both the special quantum states $(n, n-1)$ or ML-sub-shells which show a maximum value for the radial distribution as well as the significant quantum states $(n, n-1, 0)$ or ML-orbitals which show also a maximum value for the electron density (table 1, Prop. 1.1 & 1.2). Furthermore, the transition between ML-sub-shells explains the occurrence of maximum relative intensity line of fine structure multiplet. We confirmed this key result of QM by using NIST database for the first five H-spectral series (Prop. 2.1 & 2.2).

Also, for the first four H levels, we obtained numeric values of radial distribution, electron density, ML-radii and also the ordered sequences of the sub-shells average radii showing that, such as for $n = 4$:

$18a_0 = \langle r\rangle_{4f} < \langle r\rangle_{4d} < \langle r\rangle_{4p} < \langle r\rangle_{4s} = 24a_0$.

Consequently, we consider that the transitions $1S_{1/2} \to 2P_{3/2}$, $2P_{3/2} \to 3D_{5/2}$, .., $5G_{9/2} \to 6H_{11/2}$, are the main contributors to αLy, αBa, .., αPfund lines in the H-absorption spectra, respectively.

Note that these orbitals are suitable for studying alkali metals and ionic species X^+, namely the hydrogen-like atoms.

We will continue this subject in a future paper.

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