U.P.B. Sci. Bull., Series A, Vol. 85, Iss. 4, 2023 ISSN 1223-7027

FAST THEOREMS TO IDENTIFY THE MULTIPLET PEAKS AND THE LINK TO THE FACTOR EQUIVALENT TO RYDBERG'S CONSTANT FOR H-I

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In the quantum frame and dipole approximation for the Hydrogen atom, the paper provides a spectral model (QS-Model) based on the concept of the multiplet-peaks and also on the theorems of multiplets (BMT). These theorems show the transitions and their associated peaks in their multiplets. On the other hand, in this model, starting from the expression of energy levels of atomic structure in Dirac's theory, the wavelengths of multiplet-peaks in fine structure-approximation (fs-apx) are calculated. Based on the available NIST-data for the first five spectral series, the QS-Model is validated. This validation contains an observed-computed (O-C) type-analysis during which the improving-problem of the data for Balmer to Pfund series is examined. We give an analytical method and calculate the proportionality factor equivalent to the Rydberg constant in this model.

Keywords: H-I spectra, fine structure approximation, multiplets, Rydberg constant, NIST.

85A99, 81V45, 78A40, 81-11.

1. **Introduction**

The precise spectroscopic data observed in the hydrogen spectra improves our knowledge about the events in the microworld. Kramida's papers [1, 2] discuss the alpha line of the Balmer series, analyzing its spectral composition and specifying the transitions in fine structure- as well as in hyperfine structure-approximations (fs-, hfs-apx) within the Dirac theory [3] and also in Quantum electrodynamics theory [4].

In this work, in quantum frame of Hydrogen atom, we propose to start from Kramida's analysis and provide a spectral model (QS-Model) to identify the relevant lines for a multiplet in fs apx. by specifying the quantum states

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[5] which are involved in the transitions who generate them. Moreover, the wavelength of these lines are calculated in QS-Model.

Thus, we produce QS-Model and obtain its validation based on available data for the first five spectral series from NIST-database [1].

There is one additional result of our model: the analysis of calculated wavelengths provided by our model in relation to the data available from NIST-database. A special case occurs in Balmer and Paschen series, for which we proposed an analytical way which belongs to the type of the inverse problem- from the effect to the cause- to investigate the Rydberg constant which is one of the most important constants in physics. Its dermination is the keystone of accuracy of mesurements in order to understand the particle and laser physics and to obtain a better idea of phenomena at the subatomic scale [6].

The structure of the paper is as follows:

In section S2 we present a selection data from NIST-database for H-I and in section S3 we provide a description of QS-Model.

In section S4 we validate the QS-Model and investigate the improving-problem of the data for Balmer to Pfund series.

We conclude underlining the utility of BMT(the theorems of multiplets) in QS-Model to obtain a fast and efficient spectral method/procedure to identify the lines in fs-apx and also to study the behaviour of similar Rydberg constant factor for H-I spectrum.

2. Selecting of Multiplets-data for H-I

In the quantum theory, the quantum states of the H-atom is described by three quantum numbers: n- the principal quantum number, ℓ- the orbital quantum number, j-the total angular quantum number in fs-apx. Thus, a quantum-state is characterised by the triplet (n, ℓ, j). The transitions between different quantum states generate spectral lines described by their wavenumber and intensity. In the following, the wavelength is expressed in $\mathring{A}$, the intensity in *a.u.* as it is provided by NIST spectral database for H-I spectra.

Based on the available NIST-data for the first five series, we observe that a multiplet of the series Sn contains n representative spectral lines in fs-apx and call them the multiplet-peaks. A *multiplet* $(Sn)k$ is a set of spectral lines generated by transitions between the fs-components of levels (n, ℓ) and (n', ℓ'), k being $n' - n$. For example, using data from NIST, figure 1 illustrates $(S1)1$-the first multiplet of Lyman series, $(S3)k = 2..3$ -the 2nd and respectively 3rd multiplets of Paschen series, and $(S4)2$-the second multiplet of Brackett series [7].

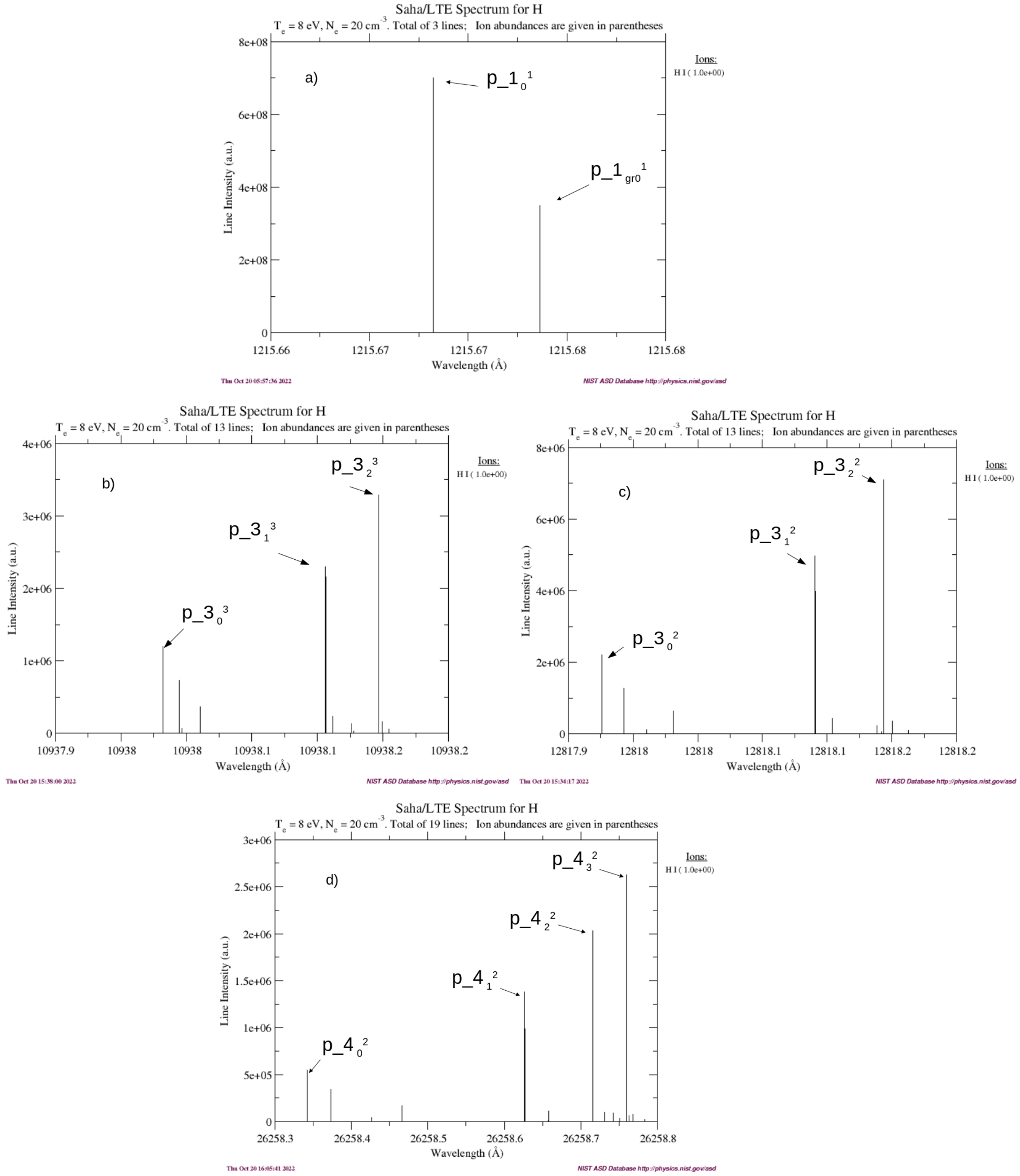

FIGURE 1. Spectral lines representation as it is provided by NIST for: a - Ly_1 the 1st line of Lyman series, b-c - $Pa_{\mathbf{2\text{-}3}}$ the 2nd-3rd spectral lines of Paschen series, d - $Br_{\mathbf{2}}$ the 2nd line of Brackett series, $https : //physics.nist.gov/PhysRefData/ASD/lines_form.html$

From figure 1-a, we see the spectral group noted by $gr0^1$ of $(S1)1$-multiplet. This group is made of two peaks indicated on figure by labels $p_{1_{0^1}}$ and $p_{1_{gr0^1}}$, respectively. Generalizing this notation we define: a *spectral group-ℓ^k in multiplet* $(Sn)k$ as the group of spectral lines with a conserved value for $j = \ell + 1/2$. Then, in multiplet $(Sn)k$ we define the *representative peak* of group-ℓ^k as line of maximum relative intensity from that group. A *multiplet-peak* $p_{n_{\ell k}}$ is the *ℓ-th* representative spectral line of the multiplet $(Sn)k$ in fs-apx.

We observe in figure 1 that $(S1)1$-multiplet represents an exception because it contains two peaks and only one of them is a representative peak according to our definition , e.g. $p_{1_{0^1}}$, while the second peak $p_{1_{gr0^1}}$ needs a special treatment in our peaks-clasification. So, for the Lyman series a special analysis of the peaks-type $p_{1_{gr0^k}}$ for an order k of the multiplet $(S\mathbf{1})k$ is necessary.

We identify the following multiplets in fs-apx from NIST-database [8] : $(S1)k = 1..5$ [9, 10], $(S2)k = 1..5$ [11, 12, 13], $(S3)k = 1..3$ [14], $(S4)k = 1..2$ [15], and $(S5)1$ [16].

The measured-wavelengths of these multiplets taken from NIST are tabulated in column 5 of tables 1& 2. This data is used in the analysis to validate the QS-Model.

3. Quantum Spectral-Model

In the dipole-approximation for the Hydrogen at the quantum atomic scale in fine structure with respect of the spectral rules, we provide a quantum-spectral model (QS-Model). This model contains theorems and formulae for a fast identification of spectral line in fs-apx for H-I spectra.

3.1. The expression of energy in fine structure-approximation

Starting from the energy of the quantum states of H atomic structure, and taking into account the Dirac approximation which includes relativistic effects, the Dirac energy for hydrogen has the expression:[3]

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

where $n = 1, 2, ..$ is the principal quantum number, $j = 1/2, 3/2, .., n - 1/2$ is the total angular momentum quantum number , and α is the fine-structure constant [17].

For a more easy approach to identify the fs-components of spectral lines, we propose the ℓ-version for energy in Dirac's theory.

Proposition 1:

So, according to Dirac's theory in fs-apx, for a state $(n, \ell, j = \ell + 1/2)$ with $\ell = 0..(n - 1)$, the expresion of energy state can be written:

$$E_{n\ell} = E_n \left[1 + \frac{\alpha^2}{4 \cdot n^2} \cdot \left(4 \cdot \frac{n}{\ell + 1} - 3 \right) \right] = E^{+}_{(n,\ell)}, \tag{2}$$

where

$$E_n = \frac{E1}{n^2}, E1 = -13,6eV[17], \tag{3}$$

and the notation $E^{+}_{(n,\ell)}$ for E_{nj} with $j = \ell + 1/2$.

Proposition 2:

For the case $j = \ell - 1/2$, the expresion of energy state is:

$$E^{-}_{(n,\ell)} = E_n \left[1 + \frac{\alpha^2}{4 \cdot n^2} \cdot \left(4 \cdot \frac{n}{\ell} - 3 \right) \right] = E^{+}_{(n,\ell-1)}, 0 < \ell \leq (n-1). \tag{4}$$

Proposition 3:

Thus, the energy state $(n, \ell, j = \ell - 1/2)$ is equal in numerical value with the one $(n, \ell - 1, j = \ell + 1/2)$.

Proposition 4:

Moreover, for the peaks in fs-apx computed exclusively using the expresion $E^{+}_{(n,\ell-1)}$ or $E^{-}_{(n,\ell)}$, we found that:

$$p^{-}_{n_{\ell k}} = p^{+}_{n_{(\ell-1)^k}}, 1 \leq \ell \leq (n-1), \tag{5}$$

where $p^{+}_{n_{(\ell-1)^k}}$ and $p^{-}_{n_{\ell k}}$ are the peaks corresponding to "+" case, respectively to "-".

The Eqs (4)-(5) give us the chance to work only with the terms of ℓ-version for energy state $E_{(n,\ell)}$ of Eq. (2) and without losing the generality of the problem.

3.2. The theorems of multiplet-peaks

In order to easily identify the representative- and special-group- peaks in fs-apx , we propose the following two theorems called shortly BMT.

The first theorem solves the general case for representative peaks $p_{n_{\ell k}}$ for $(Sn)k$-multiplets.

Theorem 1:

For a specific $n \geq 1$,to identify the lambda-peaks $p_{n_{\ell k}}$, the transitions are:

$$(n, \ell, \ell + 1/2) \rightarrow (n + k, \ell + 1, \ell + 3/2), \forall k \geq 1. \tag{6}$$

The transitions for lambda-peaks $p_{n_{\ell k}}$ respect the selection spectral rules $D\ell = Dj = +1$ [3].

Corollary 1:

Based on BMT and considering the case of $D\ell = +1$, for $(Sn)k$-multiplets we compute the BMT-wavelengths of peaks-ℓ^k, $\ell = 0..(n-1)$, $k \geq 1$, as follow:

$$\lambda^{BMT}_{peak_{n_{\ell k}}} = \lambda^{Ry}_{n \to n+k} \cdot \frac{1}{\left\{1 + \frac{\alpha^2}{4} \cdot \frac{1}{k \cdot (2n+k)} \cdot \left[\frac{(n+k)^2}{n^2} \cdot \left(4 \cdot \frac{n}{\ell+1} - 3\right) - \frac{n^2}{(n+k)^2} \cdot \left(4 \cdot \frac{n+k}{\ell+2} - 3\right)\right]\right\}}, \tag{7}$$

where

$$\lambda^{Ry}_{n \to n+k} = \frac{(n \cdot (n+k))^2}{k \cdot (2n+k)} \cdot \frac{1}{R_H}, R_H = 1,096775 \cdot 10^7 \cdot m^{-1}[17]. \tag{8}$$

The second theorem resolves the *exceptional* case for the special peaks $p_{1_{gr0^k}}$ of $(S1)k$ -multiplets.

Theorem 2:

To identify the lambda-peaks $p_{1_{gr0^k}}$, the transitions are:

$$(1, 0, 1/2) \to (1+k, 0, 1/2), \forall k \geq 1. \tag{9}$$

The transitions for lambda-peaks $p_{1_{gr0^k}}$ respect the selection spectral rules $D\ell = Dj = 0$ [3].

Corollary 2:

Considering the case of $D\ell = 0$, in $(S1)k$-multiplets we compute the BMT-wavelengths of peaks-$p_{1_{gr0^k}}$ for $k \geq 1$ as follows:

$$\lambda^{BMT}_{peak1_{gr0^k}} = \lambda^{Ry}_{1 \to 1+k} \cdot \frac{1}{\left\{1 + \frac{\alpha^2}{4} \cdot \frac{1}{k \cdot (2+k)} \cdot \left[(1+k)^2 - \frac{1}{(1+k)^2} \cdot (2k-1)\right]\right\}}. \tag{10}$$

Based on theorems 1& 2 (BMT), the wavelength values are calculated as in Corollaries 1& 2, respectively, and their numerical values via Eqs. (7)-(8),(10) are presented in column 4 of tables 1& 2, respectively.

4. Data analysis

In tables 1& 2 we present the results of application of QS-Model-analysis over all available multiplets of Lyman..Pfund series or $S1-5$. We indicate by bold the MLpeaks which are the last and highest peaks of their multiplets [5].

We use the following notations: $\lambda^{NIST}_{peak_{n_{\ell k}}}$ as observed wavelength via NIST-selected-data and $\lambda^{BMT}_{peak_{n_{\ell k}}}$ as computed-wavelength via QS-Model. Therefore, using the available data from NIST-database and also the BMT-lambda-values calculated via QS-Model, we can make an analysis of "O-C"problem [18] in order to validate our model over these existing data-multiplets in fs-apx.

The description of tables 1& 2 is thus: in column 1, we consider the available multiplets from NIST-database; in column 2, we enumerate the peaks belonging to multiplets which are specified in col.1; in column 3, we compute Rydberg's wavelengths for peaks of col.2 via formula specified in the Eq. (8);in column 4, we calculate the wavelength values for peaks of col.2 via BMT-theorems and formulas (6)-(10) respectively; in column 5, we present the NIST-measured-wavelength values for peaks of col.2; in column 6, we calculate the O-C values computed by differences between col. 5 and col. 4 which represent the difference between the measured value given by NIST and the value calculated by QS-Model.

So, in table 1, we prezent the multiplets $(Sn)k = 1 - 5$ of the spectral series $S1 - 2$.

TABLE 1. Wavelength values for $(Sn)k = 1-5$- multiplets from $S1 - 2$-series

$(Sn)k$	$n_{\ell k}$	$\lambda^{Ry}_{n\to n+k}[\mathring{A}]$	$\lambda^{BMT}_{peak_{n_{\ell k}}}[\mathring{A}]$	$\lambda^{NIST}_{peak_{n_{\ell k}}}[\mathring{A}]$	$O-C=\Delta\lambda^{NIST-BMT}_{peak_{n_{\ell k}}}[\mathring{A}]$
$(S1)1$	1_{0^1}	1215.685	**1215.6651**	1215.668	+0.00**3**
	1_{gr0^1}		1215.6705	1215.674	+0.003
$(S1)2$	1_{0^2}	1025.7345	**1025.7197**	1025.722	+0.002
	1_{gr0^2}		1025.7209	1025.723	+0.002
$(S1)3$	1_{0^3}	972,55	**972.5348**	972.5366	+0.002
	1_{gr0^3}		972.5352	972.5337	+0.002
$(S1)4$	1_{0^4}	949,75	**949.7412**	949.7430	+0.002
	1_{gr0^4}		949.7414	949.7430	+0.002
$(S1)5$	1_{0^5}	937,81	**937.8017**	937.8030	+0.00**1**
	1_{gr0^5}		937.8018	937.8040	+0.002
$(S2)1$	2_{0^1}	6564.70	6564.528	6562.73	-1.8
	2_{1^1}		**6564.669**	6562.85	-1.**8**
$(S2)2$	2_{0^2}	4862.7415	4862.6403	4861.28	-1.3
	2_{1^2}		**4862.7231**	4861.36	-1.3
$(S2)3$	2_{0^3}	4341,73	4341.6505	4340.43	-1.2
	2_{1^3}		**4341.7179**	4340.49	-1.2
$(S2)4$	2_{0^4}	4102,94	4102.863	4101.70	-1.2
	2_{1^4}		**4102.9237**	4101.76	-1.1
$(S2)5$	2_{0^5}	3971,24	3971.168	3970.04	-1.2
	2_{1^5}		**3971.2251**	3970.10	-1.**1**

From table 1 we remark that O-C values for series $S1$ are approximatively $10^{-3}\mathring{A}$ which means that calculated values for the wavelengths of the peaks are in good agreement with the measured values given by NIST-database. Also, all the values of O-C are positive. The O-C values are of order unity and all negative for series $S2$. For both series, the O-C values are inversely correlated to the rise of k order of each series and improved.

TABLE 2. The wavelength-values of available multiplets for the spectral series $S3-5$

$(Sn)k$	n_{ℓ^k}	$\lambda^{Ry}_{n\to n+k}[\mathring{A}]$	$\lambda^{BMT}_{peak_{n_{\ell k}}}[\mathring{A}]$	$\lambda^{NIST}_{peak_{n_{\ell k}}}[\mathring{A}]$	$O-C=\Delta\lambda^{NIST-BMT}_{peak_{n_{\ell k}}}[\mathring{A}]$
$(S3)1$	3_{0^1}	18756.28	18755.818	18750.83	-5.0
	3_{1^1}		18756.145	18751.011	-5.1
	3_{2^1}		**18756.245**	18751.11	-5.1
$(S3)2$	3_{0^2}	12821.6817	12821.4898	12817.92576	-3.6
	3_{1^2}		12821.6219	12818.09075	-3.5
	3_{2^2}		**12821.6642**	12818.14378	-3.5
$(S3)3$	3_{0^3}	10941.1684	10940.9863	10937.98199	-3.0
	3_{1^3}		10941.1101	10938.106	-3.0
	3_{2^3}		**10941.1509**	10938.1466	-3.0
$(S4)1$	4_{0^1}	40522.846	40521.897	40521.87	-0.03
	4_{1^1}		40522.52	40522.49	-0.03
	4_{2^1}		40522.704	40522.67	-0.03
	4_{3^1}		**40522.79**	40522.76	-0.03
$(S4)2$	4_{0^2}	26258.804	26258.3627	26258.3426	-0.02
	4_{1^2}		26258.6463	26258.6264	-0.02
	4_{2^2}		26258.7357	26258.7159	-0.02
	4_{3^2}		**26258.7789**	26258.759	-0.02
$(S5)1$	5_{0^1}	74598.876	74597.23	74597.17	-0.06
	5_{1^1}		74598.28	74598.22	-0.06
	5_{2^1}		74598.59	74598.53	-0.06
	5_{3^1}		74598.73	74598.67	-0.06
	5_{4^1}		**74598.81**	74598.75	-0.06

The same analysis is made for the already measured multiplets for series $S3-5$ and the results are presented in table 2.

The data from table 2 shows us that the O-C values for series $S3$ are also of order unity as series $S2$, but the values are greater.

For series $S4-5$ the O-C values are of order of $10^{-2}\mathring{A}$ and can be considered acceptable. In adding, for all series $S3-5$ the O-C values are negative and improves with the rise of k order of the series.

4.1. Validating of Quantum Spectral-Model

As we can see in table 1, the exception about O-C values sign occurs for multiplets $(S1)k = 1-5$ where we have $\lambda^{BMT}_{peak_{1_{\ell k}}} < \lambda^{NIST}_{peak_{1_{\ell k}}} < \lambda^{Ry}_{(S1)k}$. From tables 1& 2, we obtain for $(Sn)k$ with $n = 2..5$ the following lines order :

$\lambda^{NIST}_{peak_{n_{\ell k}}} < \lambda^{BMT}_{peak_{n_{\ell k}}} < \lambda^{Ry}_{(Sn)k}$. These aspects explain the O-C sign found in analysis of the first five series.

In addition, from tables 1& 2, we notice that for a certain series Sn the absolute "O-C" values for the multiplets $(Sn)k$ form a decreasing string, hence the "O-C" values become improved as k increases, while the "O-C" value string retains its sign.

In accordance to tables 1& 2, the "O-C"-differences present acceptable values for the series $S1$ and $S4-5$ of H-I. However, for the spectral series $S2-3$, the O-C values are of order unity. To investigate this aspect and solve it, we introduce and develop an analysis on *the proportional factor and equivalent to Rydberg's constant.*

Then, in table 2, the O-C values for series $S5$ are double in absolute value than the ones of $S4$. This may herald an expected increase of this proportional factor for the Humphreys series.

4.2. The equivalent Rydberg's constant factor

Further we begin by considering an equivalent entity to Rydbergs constant and obtain the corrections for theoretical wavelengths from Eq.(7-8),(10). For that we propose to use the mathematical method called Lagrange's method of variation of the Constants. Its virtue is that it is infallible as a general method to solve inhomogeneous linear ordinary differential equations as well as the classical method in the improving of orbital elements [19].

So, as an interesting effect of our O-C analysis in QS-Model, we observe that the O-C values for $S2-3$ [20, 11, 12] are of order unity. In order to investigate this aspect of the H-I spectra for these series, we introduce the ratio factor between the wavenumber and energy-states difference. Thus, we determine an equivalent to the Rydberg constant denoted $R(n)$. Then, we propose to estabilish the accuracy-degree of the O-C values for series $S2-3$ comparable with that of series $S4-5$, i.e., about $10^{-2}\mathring{A}$.

Theorem 3:

In QS-Model, in order to obtained the corrections of calculated wavelengths $\lambda^{BMT}_{peak_{n_{ML^1}}}$ referring of $10^{-2}\mathring{A}$ accuracy, the constant factor in n to be used is:

$$R(\mathbf{n}) = \frac{(n\cdot(n+1))^2}{(2n+1)\cdot(\lambda^{NIST}_{peak_{n_{ML^1}}} + 10^{-2})} \cdot \frac{1}{\left\{1 + \frac{\alpha^2}{4}\cdot\frac{[(n+1)^2+n^2]}{(n\cdot(n+1))^2}\right\}}, n > 1. \tag{11}$$

Table 3. Modeling of the similar factor to the Rydberg constant for series $S2-5$ in $10^{-2} accuracy$

$(Sn)1$	$\Delta\lambda_{peak_{n^1_{ML}}} = \lambda^{NIST}_{peak_{n^1_{ML}}} - \lambda^{BMT}_{peak_{n_{\ell k}}}$ [Å]	$\lambda^{NIST}_{peak_{n^1_{ML}}}$ [Å]	$R(\mathbf{n})[10^7 m^{-1}]$
$(S\mathbf{2})1$	$-2\cdot 10^{+0}$	656**2.85**	1,09**7077**397
$(S\mathbf{3})1$	$-5\cdot 10^{+0}$	1875**1.11**	1,09**7074**788
$(S4)1$	$-2\cdot 10^{-2}$	40522.76	1,096775*56*
$(S5)1$	$-6\cdot 10^{-2}$	74598.75	1,096775*71*

In the first column of table 3, we synthesize the precision degree of O-C values for the series $S2-5$ (see in tables 1& 2). We recall in middle column of the same table the lambda MLpeaks of multiplets for the same series. Finally, in the last column of table 3, we give the numerical results of Eq.(11). These represent the values of the factor equivalent to the Rydberg constant for $n = 2..5$. The $R(n)$-values help us to compute in our model the corrected values for $\lambda^{BMT}_{peak_{n_{ML}1}}$ relative to a specified series Sn with $n = 2..3$ for an accuracy of $10^{-2}\mathring{A}$.

In last column of table 3, one observes for Brackett and Pfund series that the factor R(n) is close to the one of Lyman series value $R_H = 1,09\mathbf{6775}\cdot 10^7\cdot m^{-1}$ [17]. In the same column, one observes that the corresponding values for this factor R(n) for series $S2-3$ are just slightly larger than $1,096775\cdot 10^7\cdot m^{-1}$. Now, we can conclude that our procedure ensures an accuracy near $10^{-2}\mathring{A}$ over Balmer and Paschen series in H-spectrum for lambda calculated in QS-Model by using the factor R(n) values from tab3 in Eq. (8).

Conclusions

We have built QS-Model, specifying the states between which the transitions that generate spectral lines in fs-approx of the multiplet-peaks occur. We validated the BMT for the representative peaks (Theorem 1) on available NIST data, more precisely for the first five series $S1-5$. We validated BMT on the Lyman series exception (Theorem 2) from the available NIST data for this series, i.e. the first five multiplets $(S1)k = 1-5$. In addition, QS-Model has the advantage that BMT makes it faster and simpler (via Theorem 2) than the Dipole approximation model in Dirac theory to identify multiplet-peaks in fs-apx (Corollaries 1-2).

Further, from O-C type analysis, we obtain for the series $S1$ and $S4-5$ acceptable values. The exception occurs for series $S2-3$, and we solved it by an analytical approach introducing the proportional factor similar to the Rydberg constant in Balmer and Paschen series for which we have not yet a physical explanation. We have calculated the corresponding values of propotional factor R(n) (Theorem 3) to improve the O-C values on series $S2-3$ and, thus, to ensure an accuracy order for series $S2-3$ comparable to the one of series $S4-5$.

Finally, by providing of QS-Model, we gived a method to distinguish among NIST data between the lines in *fs*- and *hfs*-approximations, respectively, this aspect being discussed in Kramida's papers.

Acknowledgments

This article is in memory of Professor Dr. Constantin Udrişte from "Polytehnica" University of Bucharest. The authors would like to acknowledge the help received from physicist Agneta A. Mocanu from The Faculty of Physics, Bucharest University, and dr. Erika Varga-Verebelyi from Konkoly Observatory, Budapest.

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