International Journal of Applied Physics
http://www.iaras.org/iaras/journals/ijap

Research of Atomic and Molecular Terms

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Abstract: - This report is about creation of information models of light quantization and absorption by an atom and/or a molecule in a language alternative to the one-electron approach. For this purpose the analysis of trigonometrical functions has been done which has revealed quantum numbers which have been applied to differentiating interpretation of the concepts "quantum"/"photon" and getting earlier unknown dependences for the terms of neutral atoms and diatomic homonuclear molecules. It has enabled to enter actual multielectronic classification of atoms and molecules. The idea of relative additivity of nuclear terms during formation of diatomic molecules has shown efficiency of the models obtained in such a way for multielectronic classification and systematization of optical functions and electronic structure of external shells of molecules.

Key-Words: - information models of radiation/absorption, alternative to the one-electron approach, signal of atomic and molecular terms.

1 Introduction

Quite often researchers [1] are surprised by the fact that *the quantum theory developed for systems of nuclear sizes works well also for scales much smaller and considerably bigger. There is a feeling that all properties of matter are quantum-mechanical,* – scientists conclude and ask the question: *What can we learn about the quantum optics, using the concept of information?* In particular, this paper is devoted to this question too.

At the same time, other scientists remind that the quantum mechanics for its history has faced larger number of crises, contradictions, interpretations and recessions of interest than any other science. Albert Einstein could not reconcile with its consequences [2] till the end of his life. So, for example, it is considered that quantized energy of optical radiation in the form of “photon” has no reliable justification in the theoretical physics [3, p. 1189, 1213]. Probably therefore today, appeals sound even more often: *Time to begin anew, to throw out the existing axioms of quantum mechanics and to return to the fundamental physical principles has come. And where to find them? – in the quantum theory of information* – Christopher Fuchs, a quantum physicist from the Bell Laboratories claims (quote of [4, p.379]).

Information appears only about data. But data in quantum mechanics are ambiguous (the principle of uncertainty) and are inconsistent (one-electron approach for multielectronic systems) quite often that can be proved only by mathematical methods, for example, during quantization of the field [3, p.1189]. Therefore it is necessary to look for other ways of information search. The essence of information modeling is identification of characteristic parameters and attributes of difficult phenomena with elimination of insignificant ones to create basic prerequisites for development of a relevant theory. So, for example, study of spectral characteristics of stationary conditions of nuclear and/or molecular systems and characteristics of transitions between energy levels is reduced to the Ritz principle for the main series (the Lyman system in absorption) where only transitions from the main $E_1 = 0$ level to higher E_n are considered so that the energy difference between states is determined by size of the spectral term T_n proportional to transition frequency ν

$$\Delta E = E_n - E_0 = E_n = T_n = ch/\Delta\lambda, \qquad (1)$$

where h is the Planck constant, c is the light velocity, λ is wavelength. Due to this model, the ratios determining the arrangement of spectral lines in various series can be obtained from the combinational principle of Ritz according to the Grotrian diagrams, which theorists apparently consider excessively unambiguous and consistent [5].

The current state of the theory of nuclear spectra allows rather strict consideration only in the case of one-electron atoms, i.e. for atom of hydrogen and hydrogen-like ions He$^+$, Li2+, Be3$^+$, etc. If physically electrons compose a uniform system in a polyatomic atom and/or molecule whether then it would be admissible to select separate electrons about which the concept in an atom/molecule was based on the one-electron approach? [6, p. 197, 721-732; 8, p. 29-36]. In this regard there is a question: whether there is an alternative to the one-electron description of multielectronic atoms and/or molecules?

Perhaps, it makes sense to analyze tangential functions for research of characteristics of a substance at absorption of radiation? The appeal to this type of the trigonometric functions (TF) has been caused by the fact that the system of harmonious octaves [7, p.109] correlates with the optics of radiation sources on characteristic features of their trigonometric functions [8].

Taking into account these problems, targets of this work are tangential sampling of a light continuum to define dependence of nuclear terms T_n of the main series on the photon value E_γ of natural light and, in turn, determination of the electronic terms of molecules T_e from terms T_n forming a molecule of effective atoms. The ultimate purpose is the study of spectroscopic regularities in the information models (**IM**) of quantization (**IMQ**), absorption of light by atom (IM of atomic absorption – **IMNA**) and relative additivity of atomic terms (**IMAT**) during formation of molecules by them.

2 Theoretical background

We use combination of the Cartesian coordinate system and the polar one with the required functions in radians for achievement of the purpose. Linear sampling of a light continuum can be done with the straight line equation in the Cartesian coordinates $y = kx + b$, where $k = \mathrm{tg}\,\varphi$ is the slope of straight line with angle φ from the *Ox* axis, b is the segment cut by a straight line on the *Oy* axis. At the sampling step determined by the slit width $\Delta\lambda$, compliance is obtained between the wavelength λ and the relevant serial number Z_λ in the continuum "spectrum". For example, at the sampling step 1 nm, by starting the continuum from the wavelength 1 nm, we have

$$Z_\lambda = \lambda/\Delta\lambda = \lambda, \qquad (2)$$

from which $k = 1$, $b = 0$ that gives $\mathrm{tg}\,\varphi = ¼\pi$ value with formal $[Z(\lambda)] \equiv [\lambda]$ dimension of length *[nm]*.

It follows from the ratio (2) that it is possible to establish dependence $Z_i(\lambda_i)$ for arbitrarily set wavelength in the continuum at some "slit width" $\Delta\lambda$ with the meter to nanometer scale coefficient $N = 10^9$

$$Z_\lambda = N\,[\lambda/\Delta\lambda + (1 - 1/\Delta\lambda)],$$

where $\lambda/\Delta\lambda$ is the resolving power at the difference of wavelengths $\Delta\lambda$, which are "separated by hardware function" yet. In turn, the interrelation of $E(\lambda)$ and $\mathrm{tg}\,\varphi$ has been obtained at coordination of sufficient resolving power $\lambda/\Delta\lambda \approx 10^6$ with the relevant area of spectrum [3, p.31]

$$Z_\lambda = \lambda_i/(\lambda_k - \lambda_i) = E_k/(E_i, - E_k). \qquad (3)$$

It follows from the formulas (1) and (3) that

$$Z_\lambda = ch/E_i\,(\lambda_k - \lambda_i). \qquad (4)$$

On the other hand, if the continuum of natural light is presented through change of energy (1) as a function of wavelength variation $\Delta\lambda$ and the relation of tangent square of this energy to this variation $\mathrm{tg}^2 E/\Delta E(\Delta\lambda)$, then we get the tangential functions of discrete decomposition of light to characteristic components

$$ch = \lambda_\varphi \frac{Z_\varphi \varphi}{q}, \qquad (5)$$

where q is the integer slope of transformation of energy of a photon $E = Z_\varphi/q$ to the energy of an electron $E = eU$ at equilibrium interaction of light with substance. This dependence has already demanded sampling of light stream in polar coordinates with radians (the length of an arch l is equal to the radius-vector *r(p)* with the polar angle *φ).*

Transition to the Cartesian coordinates has been done for correlation with the linear sampling

$$\frac{l}{r} = \frac{y}{x} = \frac{p\sin\varphi}{p\cos\varphi} = \tan\varphi = 1 = ¼\pi,$$

which presupposes division of the steps of sampling by $¼\pi$ in each octave (volume *2π)* per relevant serial numbers of Z_φ (φ) under the condition:

$$\Delta\varphi = \Delta E/\Delta Z_\varphi = ¼\pi.$$

It follows from the ratio (5) that the value Z_φ for a discrete spectrum $\tan 2E/\Delta E(\Delta\lambda)$, at the same resolution $\lambda/\Delta\lambda$ as for Z_λ is equal to

$$Z_\varphi = chq/\lambda_\varphi\,\varphi. \qquad (6)$$

If the dimension *of* Z_φ is electron-volt per radian *[eV/rad]*, unlike the dimension of length Z_λ *[nm]* then it is possible to connect their λ by a uniform algorithm of sampling with serial numbers Z_λ и Z_φ in a linear continuum and/or a discrete spectrum.

The discrete signal of both ones can be considered as a result of multiplication of functions (4) and (6):

$$Z_\lambda Z_\varphi = \frac{c^2 h^2 q}{E_\lambda \lambda_\varphi \Delta\lambda_\varphi}, \qquad (7)$$

that yields an alternative result depending on size of q: $q = 0$ in the continuum $Z(\lambda)$ of the light stream, according to which $Z_\lambda Z_\varphi = 0$ whereas the value $Z_\lambda Z_\varphi = 1578{,}63$ *nm·eV/rad* in the discrete spectrum of $Z(\varphi)$ at $q = 1 \div 8$ that is shown in fig. 1 with vertical lines with the numbers on top of the relevant Z_φ and $Z_\lambda Z_\varphi$ for the 1 octave.

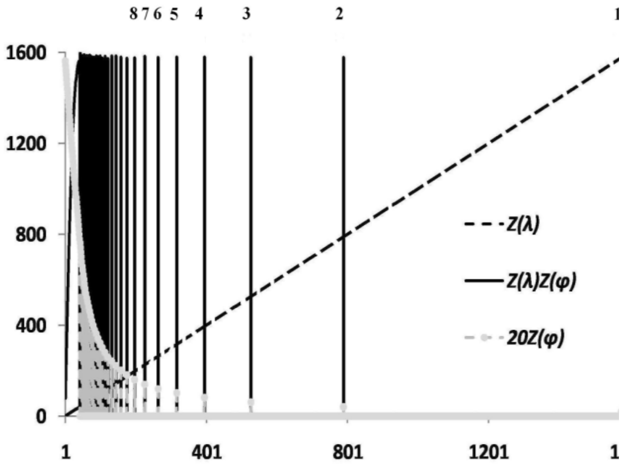

Fig. 1. Sampling of the light continuum in the IMQ. The abscissa is the wavelength in nm; the ordinate $Z(\lambda)$ nm, $Z(\varphi)$ eV/rad and $Z_\lambda Z_\varphi$ nm·eV/rad.

The ratio between $Z_\varphi = 4ch/\pi\lambda_\varphi$ and $Z_\lambda = ch/E_i\Delta\lambda_{ik}$ while matching of the scales of λ_{ik} and λ_φ on the abscissa is presented in fig. 1 from where it follows that $Z(\lambda)$ linearly grows with wavelength increase according to equation (4) whereas $Z(\varphi)$ decreases according to (6). $\lambda_\varphi Z_\varphi$has appeared identical for the relevant $Z_\lambda Z_\varphi$ and equal to 1578.63 nm·eV/rad that corresponds to the value $4ch/\pi$.

At the same time in the area of the hard x-ray and gamma radiations (λ <40 nm, from $Z_\varphi = 42$), the quantization gains another character, which is not connected with IMQ sampling on Z_φ. Perhaps it is caused by reduction of the resolving power $\lambda/\Delta\lambda = 10^5$ in this area [7, page 31] with the given "slit width" of 1 nm.

3 Division of a photon and a quantum

Experience of creation of information models has shown that information as a product and/or result, turns into data immediately. What's the matter? How it is possible and whether it is possible to divide data and information, and, in particular, a quantum and a photon?

The natural light presented through change of energy according to (1) as a function of change of wavelength $\Delta\lambda$, the relation of squared tangent of this value of energy to these changes $\tan^2 E/\Delta E(\Delta\lambda)$ give directly the tangential functions (**TF**) of decomposition to the characteristic components presented in fig. 1.

It is indicative that all points of this octave ($\varphi_1 = 0{,}78539$, $\varphi_2 = 1{,}57080$, $\varphi_3 = 2{,}35619$ etc) within 5 and above digits coincide with the known scale of energy in electron-volt ($E_1 = 0{,}78539$ eV, $E_2 = 1{,}57080$, $E_3 = 2{,}35619$ etc). From here according to the formula (1), wavelengths λ and the numbers q and Z corresponding to serial numbers of indexes of φ and E have been obtained.

Verification of the obtained octave: the charge and/or a term of an atom/molecule has to be multiple to an elementary charge and/or a term. And it has already indicated possible ratio of the TF parameters with ratio of angles of radiation impact on substance as it is presented in the table 1.

Adequacy of the values of the first octave obtained in such way has also confirmed by compliance of the energy $E_1 = 0{,}78539$ eV in the point of intersection of curves $\sin^2 E/\Delta E(\Delta\lambda)$ and $\cos^2 E/\Delta E(\Delta\lambda)$ i.e. the characteristic value $\tan^2 E/\Delta E(\Delta\lambda)$ at $\lambda = 1578{,}63$ nm. And it, in its turn, has confirmed the famous provision on minimization of quantum effects upon transition of radiation from the visible range to IR under normal conditions of experiment (in particular, for weak fields).

At the assumption that a photon is a source radiation with energy $h\nu$ and the unit eV, and a quantum is its "angle" of incidence on the projection/atom in radians, the equation (5) has naturally included both quantity Z and quality q of photons relevant to the corresponding parameters of electrons as self-coordinated codes of information processing. Since 1 eV = 1 eV/rad in the Ist octave and it equals to relevant values per (5) in the subsequent ones then from positions of the theory of dimensions, the elementary principles of radiation quantization $Z = qE/\varphi$ with relevant creation of IMQ as functions IMQ(TF) and IMAA(TF) have been obtained.

Strictly speaking from the informatics positions, a photon and a quantum have been separated in the physical sense not only quantitatively but qualitatively too. Because if we consider h in the formula $E = h\nu$ as a proportionality factor between continuums of energy and frequency only, then what is the physical sense of their quantization?

Whether it is in sampling $\hbar = h/2\pi$ only or there could be some natural ways of identification of the discreteness in the continuums of energy and frequency? Since energy values of a photon are expressed by the ratio between q, Z, φ then at the "initial" energy of IMQ $E_1 = 0{,}78539$ eV corresponding to the angle $\varphi = ¼\pi$ from the formula (5), the following ratio has been obtained

$$E_1 = {}^1/_4\pi\, {}^Z/_q.$$

Taking into account that for the first member of an octave $q = \varphi_i/\varphi_1 = 1$,

$$E = {}^1/_4\pi\, Z.$$

From here it follows that, on the one hand, the value Z is an expression of energy per radian and, on the other one, is an original quantum number, which consistently increases by unit at the quantization step *¼π*.

In other words, if earlier the quantization was done with the step *2π*

$$\hbar = h/2\pi = E/2\pi\, \nu,$$

then in IMQ, the quantization value

$$\hbar\, \nu = ⅛ Z, \qquad (8)$$

firstly, gives the integer values Z of photons number by the equality (6), which are absent in (1), secondly, is the dependence on quantum numbers mediated by (2)-(9). And what is the most essential, *Z* follows naturally from the light nature because both the first and all other nodal points of TF are connected with each other by the uniform information denotation $\Delta E(\Delta\lambda)$.

In its turn, the value q by the formula (5) shows qualitative differences of photons in each octave, according to the angle *φ*

$$\varphi = ¼\pi\, q.$$

Formulas (6) and (8) where the angle value has been replaced with frequency *ν* and quantum energy (number of photons per radian Z) have attracted attention that at their substitution to the Planck formula have given direct confirmation of the previous conclusion on equality (6)

$$E = h\nu = \varphi_1\, Z. \qquad (9)$$

From these positions, the dimensional compliances of energy and radiation incidence angle (1 eV = 1 rad) have appeared explainable since not absolute values of energy but relative, i.e. their changes relative to changes of angle/projection and/or wavelength have been used in all formulas of TF. Because earlier we have presented experimental data [9], according to which the criterion of manifestation of radiation maxima/minima in octaves is change of energy of radiation *ΔE* in IMQ and/or its absorption by atom in IMAA with values, which, on the one hand, are multiple of *Δπ*, and, on the other, of *Δλ*.

Linear dependence of the product $\lambda_{ik}(n)E_\varphi(n)$ on Z (Fig. 2) has been noted in absorption, which has allowed to extrapolate values of nuclear terms up to potentials of ionization of neutral atoms that, on the one hand, is almost unattainable within quantum mechanical calculations and, on the other one, has allowed to supplement and/or correct the known databases on nuclear spectroscopy [9].

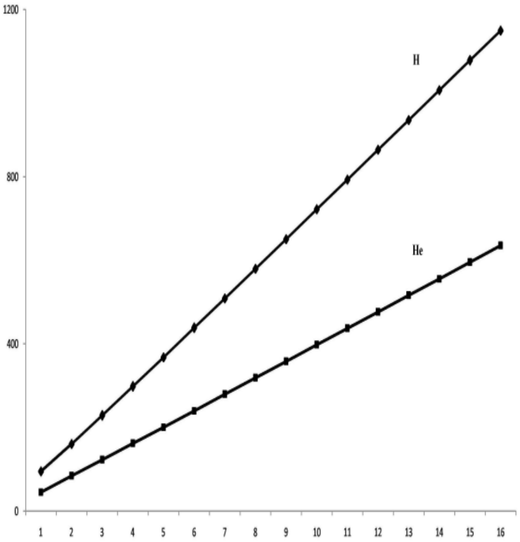

Fig. 2. Regressions of the atomic terms of hydrogen and helium depending on sampling of the light field. The abscissa is Z, the ordinate is $\lambda_{ik}(n)\ E_\varphi(n)$*, nm·eV*

4 Terms of molecules

Since angles, terms and dependences of radiation parameters on quantum numbers *n* and *l* have been defined by means of quantum numbers *E*, *q*, *φ*, *Z*, then for verification of assumptions about the principles of IM construction in molecular spectroscopy, the information model of additivity of terms (IMAT) has been used, according to which the electronic term T_e^{ab} of the molecule *ab* correlates with the relative sum of terms T_n of atoms *a* and *b* at their minimum distinction in size:

$$T_e^{ab} = K_i \sum\nolimits_{a,b} T_{n,l}^{a,b} \left|\Delta T_{n,l}^{a,b}\right. \to \min \qquad (10)$$
$$(\Delta n = 0;\ 1;\ \Delta l = 0;\ 1),$$

where K_i is the coefficient of IMAT correlation; Δn and Δl are distinction of conditions of the atoms forming a molecule on the main *n* and orbital *l* quantum numbers.

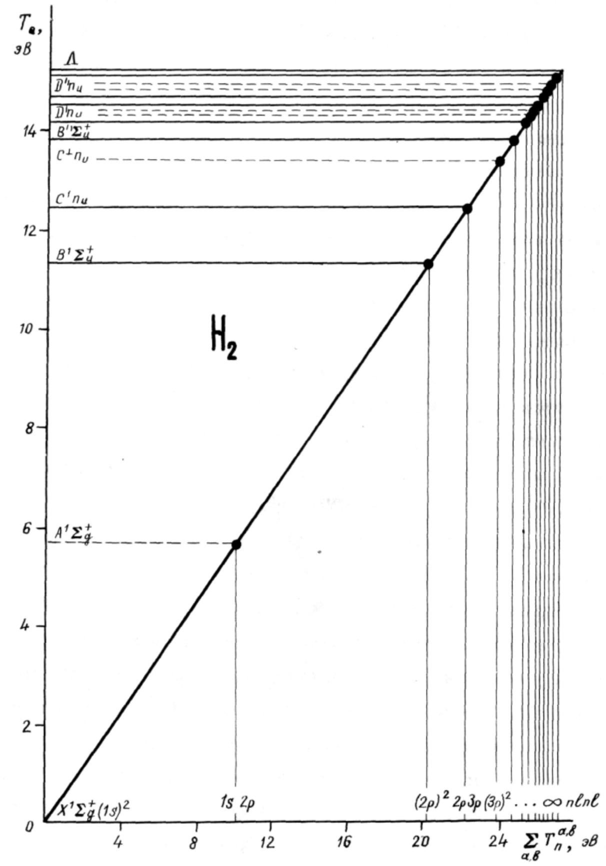

Fig. 3. Formation of H_2 terms by the sums of terms of H. The abscissa is the sums of nuclear terms, the ordinate is the H_2 terms.

The electronic spectrum of absorption of H_2 as a spectrum of the simplest molecule, has enabled to make the conclusions about distribution of electronic density in a molecule. According to the one-electron approach, T_e H_2 is interpreted by transitions of one of two electrons when fixing the second one in the main state. A question: how this approach can explain the fact that one of two "equal" electrons passes into the excited state whereas another one don't? Therefore the *Ki* coefficient, which is taken out before the sum sign in the formula (10), indicates that the equal part of the electronic density of both atoms participates in the electronic transition.

The analytical dependence of IMAT shown in fig. 3 visually and precisely (dispersion $\sigma = 0{,}0025$ for all states up to the potential of ionization of H_2) describes the electronic terms of molecules through quantum numbers and terms of the atoms forming a molecule [10]. The achieved accuracy in many respects exceeds the accuracy of calculations reached in model assumptions of quantum chemistry about one-electron excitement of the two-electronic H_2 system. Reliability of IMAT at interpretation of a molecular spectrum of caesium, is shown in fig. 4.

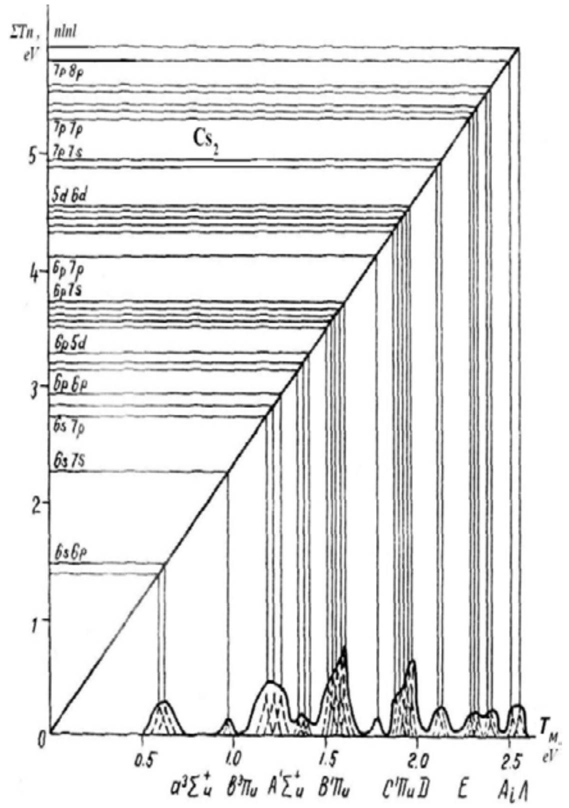

Fig. 4. Compliance of IMAT to the range of Cs_2. The abscissa is the spectrum and the electronic terms; the ordinate is the sums of nuclear terms.

The diagram of dependence of *Ki* for the IIa-VIIa elements of the periodic table groups has been done with the condition that each line *Ki* is put consecutively, starting from the low-lying $T_e^{ab}(T_n^a+T_n^b{}_{n+1})$ so that the same sum of *Tp* can't represent other overlying term of a molecule. The next straight lines *Ki* represent higher terms of atoms up to ionization potential as it follows from fig. 5 for the molecules C_2 and O_2. The concept "molecule intemer" has been entered, which distinguishes a bond with definite P_{ab}, for accurate characterization of chemical compounds with different orders of the P_{ab} bond. From here the conventional designation of the diatomic molecule Э_2 is represented as ${}_{Pab}\text{Э}_2$, where the left lower P_{ab} index is the ratio of the bond between atoms *a* and *b* in the molecule *ab*. So, for example, the oxygen molecule with double bond is designated ${}_2O_2$; with threefold ${}_3O_2$, etc.

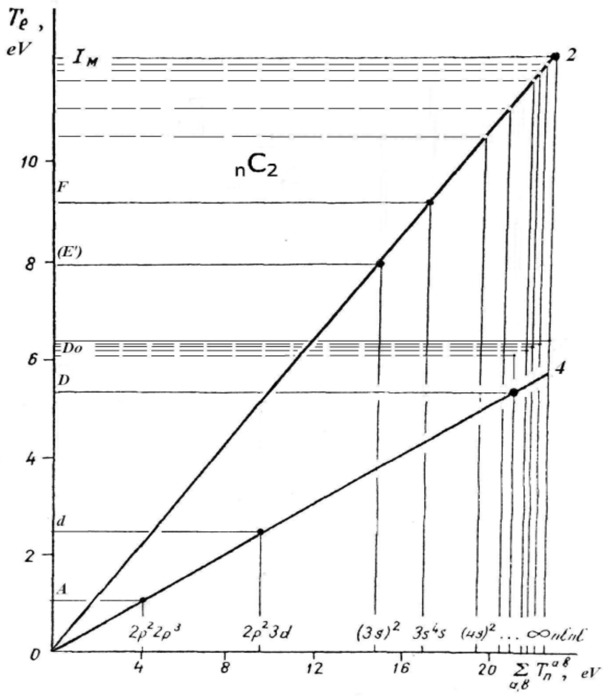

Fig. 5. *The molecular terms vs. the sums of nuclear terms at the intemer of C_2 . The abscissa is designations and the sums of nuclear terms in eV, the ordinate is electronic terms of a molecule, in eV. On the right, the relevant values of valent electrons (stoichiometric values) are shown.*

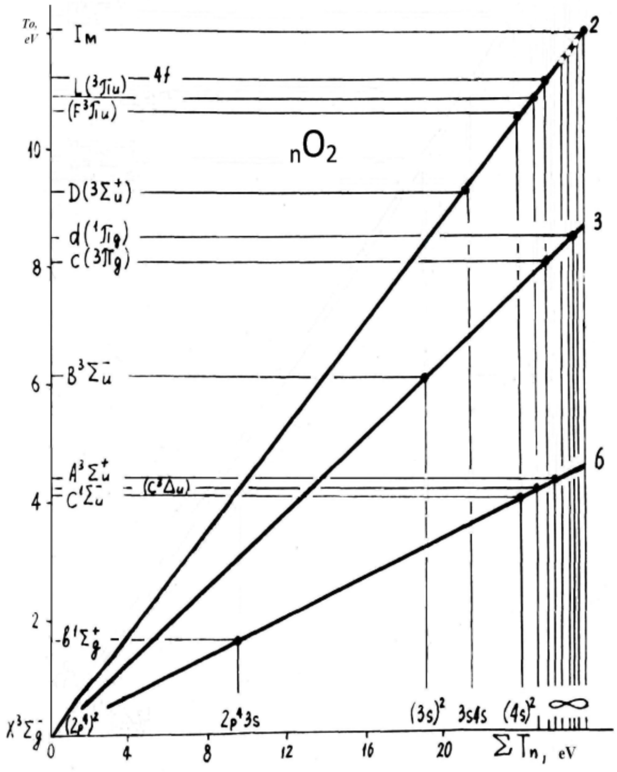

Fig. 6. The molecular terms vs. the sums of nuclear terms at the intemer of O_2. Legend see Fig5.

From here existence of certain intemers, i.e. an order (ratio) of a chemical bond of $P_{ab}=s/2$ between atoms *a* and *b* in the molecule *ab* is estimated by value K_i:

$$P_{ab} = s_e /2= 1/2K_i.$$

In other words, the existence of a certain intemer of a molecule depending on its excitement energy is determined with the $T_e(T_n)$ and the K_i values, which found proximity to the characteristic value $1/s_e$.

5 Conclusion

Schematic coordination of certain attributes of nuclear and molecular terms according to the Russell-Saunders Coupling Scheme (LS bond) with parameters of the created IM is shown in table 2.

Correlations between IM values and LS scheme for one-electron atom have enabled to compare earlier known and the achieved ratios. From here it has followed that we have got a multielectronic alternative to the one-electron approach that has corresponded to achievement of this work purpose.

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Table 1. Correlation of the first octaves with quantum numbers TF *⁾

q, φ \n		1			2			3		
q	φ, rad	Z	λ, nm	E, eV	Z	λ, nm	E, eV	Z	λ, nm	E, eV
1	0,78540	1	1578,63	0,79	9	175,40	7,07	17	92,86	13,35
2	1,57080	2	789,31	1,57	10	157,86	7,85	18	87,70	14,14
3	2,35619	3	526,21	2,36	11	143,51	8,64	19	83,09	14,92
4	3,14159	4	394,65	3,14	12	131,55	9,42	20	78,93	15,71
5	3,92699	5	315,73	3,93	13	121,43	10,21	21	75,17	16,49
6	4,71239	6	263,10	4,71	14	112,76	11,00	22	71,76	17,28
7	5,49778	7	225,52	5,50	15	105,24	11,78	23	68,63	18,07
8	6,28318	8	197,33	6,28	16	98,67	12,57	24	65,78	18,85

*⁾ Note to table 1: comparative semantics of numbers n, q, φ, Z is given in table 2.

Table 2. Modeling of correlation between the LS scheme and IM parameters

	LS	IMQ	The periodic table	IMAA	IMAT
n	The main quantum number of $n=1$, 2, 3,…, ∞	Octave No. $n = Z_{2\pi} / q_{2\pi}$	Period No. (number of shells) 1(K), 2(L) …	No. of nuclear term $n = Z_n + 1$	Minimum distinction of terms on Δn = 0; 1
l	Orbital quantum number l = 0,1,2, 3, …	No. (.) of TF for all area $l=n-1= Z_n$	No. of group (number of valent electrons)	Characteristic of valent electrons	Minimum distinction of terms on Δl =0; 1
Z	Element No. (total number of electrons)	Number of photons per radian $Z_\gamma = q \cdot E / \varphi$	Element No. (total number of electrons)	Number of terms Quantity of electrons $Z_e = E_\varphi / \varphi_1$	Electronic density $s_e = 1/ K_i$
q	L, S, J quantum numbers of atom 0(S), 1(P), …	No. (.) of TF in an octave Quality of photons $q = 4\varphi \cdot/\pi$	No. (.) in every period $q = \varphi n/\varphi 1$	Value of a term in atom Quality of electrons $q=\lambda n \cdot \varphi \cdot Z/ch$	nlnl – quantum numbers of a molecule (by Ridberg's conditions)
φ	$\hbar = h/2\pi$ (360o)	$\varphi_1 = \varphi/q$ (45o)	$\varphi_1 = \pi/4$ (45o)	$h= \pi \cdot \lambda_n \cdot Z/ 4c$ (45o)	$\varphi_m = arctg\ K_i$
E	$E = h\nu$	$E = Z \cdot \varphi/q$	$E_\varphi = \varphi_1 \cdot Z$	$E_n = ch / \lambda_n$	$E_m = K_i \sum E_n$