## HISTORY

## Niels Bohr (1885–1962): On the Wing of a Butterfly, Johann J. Balmer (1825–1898)

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In celebration of the 100th anniversary of the first modern atomic model proposed by *Niels Bohr* in 1913. Dedicated to my former mentors of chemistry: *Stanley Ziegler, Sidney Bluestone, David Zellmer, Robert Kallo,* and *Stephen Rodemeyer.* 

By the year 1913, a number of revolutionary events had begun to transform the landscape of physics. In 1900, *Max Planck* (1858–1947) had proposed that energy radiated in quanta or packets. The announcement of the photoelectric effect in 1905 by an unassuming Swiss patent worker by the name of *Albert Einstein* (1879–1955) clearly implicated that light energy, or the photon, later coined by *Gilbert N. Lewis* (1875–1946) in 1926, was also quantized and showed unprecedented particle-like properties. More startling was the discovery by *Ernest Rutherford* (1871–1937) who demonstrated that the atom consisted of a hard positive center surrounded by electrons. *Niels Bohr* (1885–1962), then a young postgraduate, was deeply involved in understanding the structure of the atom. He needed physical or experimental evidence to substantiate his intuitive ideas. Ironically, that evidence had already been published in the year of his birth by *Johann J. Balmer* (1825–1898), a Swiss mathematics teacher at a secondary school for girls.

Introduction - Early Models of the Atom. - Bohr's early formulation of his model of the atom was based on *Rutherford*'s nucleus model (*Fig. 1, a*) in which the negative electrons were attracted and held in a circular-like orbit around the positive nucleus center. *Rutherford*'s team demonstrated this by shooting  $\alpha$ -particle bullets at the atom. Their amazement piqued when the bullet trajectories were sometimes deflected by the atom implying the mass was mainly concentrated in the center. The idea of a miniature solar system as an atomic model had a certain romantic if not unifying appeal for Nature's grand design, since the laws of gravity described by the legendary Sir Isaac Newton (1642–1727) had already withstood the test of time. Although the planetary orbits could be observed and measured, the orbits of the electrons were neither seen nor measured. Bohr's atomic model was published in the Philosophical Magazine between July and November 1913 as a 'Trilogy' entitled, 'On the Constitution of Atoms and Molecules' [1]. However, it and similar planetary-based models defied Maxwell's laws or classical physics in which a revolving charged particle must radiate energy and consequently collapse into the nucleus. Clearly, in the atom this did not occur! Bohr daringly invoked *Planck's* constant, the 'new quantum physics'1) meaning the electron

<sup>&</sup>lt;sup>1</sup>) This early expression was later revised to 'the old quantum physics', with the application of matrix mechanics in 'the new quantum physics' era initiated by Werner Heisenberg (1901–1976) and Max Born (1882–1970) in 1925.

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was not allowed to radiate energy except in discrete quanta when it changed states. Hence, *Bohr*'s electrons were in effect confined to a stationary state or orbit about a central nucleus. On the other hand, *Thomson*'s plum-pudding atomic model had the positive charge distributed throughout the atomic pudding with the plum-like electrons or '*corpuscles*' organized in dynamic circular regions within the atom (*Fig. 1,b*).



Fig. 1. a) Rutherford's planetary-based nucleus model. b) Thomson's plum-pudding model.

Clearly, *Thomson*'s model was not supported by *Rutherford*'s experimental results. Additionally, *Thomson*'s outer circle of electrons supposedly shielded the inner circle of electrons from losing energy and falling into the positive-charged nucleus. However, this explanation paled as an apparent contradiction for the simple one-electron hydrogen atom and was never fully addressed. In contrast, *Bohr* had speculated in the second part of his *Trilogy* that electron occupation of orbits furthest from the nucleus influenced the atom's bonding properties. *Bohr* urgently needed physical evidence to raise his theoretical model of the atom above the many other atomic models.

Niels Bohr's Biography. – In 1911, Niels Bohr (Fig. 2) had just completed a doctorof-philosophy degree in physics at Copenhagen under Christian Christiansen (1843–



Fig. 2. Niels Bohr (1885–1962). Photograph from http://en.wikipedia.org/wiki/Niels\_Bohr.

1917). His father, *Christian Bohr* (1855–1911), tenured professor at Copenhagen University, had been nominated three times for the *Nobel* Prize for physiology and medicine [2]. In 1911, however, *Bohr* had spent a disappointing stay at the Cambridge laboratory where the great physicist *Joseph J. Thomson* (1856–1940) had taken little interest in his ideas. Neither did it help that *Bohr* was openly critical of *Thomson*'s atomic model. With *Thomson*'s permission, *Bohr* transferred to Manchester to study in *Rutherford*'s group. *Bohr*'s struggle to understand the inner architecture of the atom was like swimming against the current. Many scientists in this period of time, indeed famous ones like 1909 chemistry *Nobel laureate*, *Wilhelm Ostwald* (1853–1932) and Austrian physicist *Ernst Mach* (1838–1916), believed that the idea of atoms was nothing more than a heuristic construct to convey physical ideas about everyday reality. In their minds, atoms did not really exist! More disheartening in *Bohr*'s time, '*atomic theory was not only a* small *field of physics, it was not highly regarded in the physics community*' [3].

Johann J. Balmer's Biography. – Johann Jakob Balmer (1825–1898; Fig. 3), the eldest son of six siblings was born in Lausen in the Swiss half-canton, Baselland. His father, also named Johann Jakob, was the mayor of Lausen and chief justice in nearby Liestal. His mother, *Elisabeth Rolle*, was a dedicated seamstress who married and cared for their five sons and one daughter. Johann had inherited the clarity of his father and the artistic sensitivity of his mother. Young Johann attended elementary school in Lausen and later carried out his matriculation with the supervision of Professor *Ectert* in the mathematics department, and later applied his early mathematical experiences to the study ancient architecture.



Fig. 3. Johann J. Balmer (1825–1898). Photograph courtesy of the Universitätsbibliothek Basel.

In his early twenties, *Balmer* attended lectures at Karlsruhe and Berlin where he heard lectures from the philosopher *Friedrich Schelling* (1775–1854) and the educator

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Fig. 4. Balmer's *doctoral study of the geometry of the cycloid*. Courtesy of the Universitätsbibliothek Basel.

Adolph Diesterweg (1790–1866). Upon his return to Basel, Balmer completed his Ph.D. in 1849 with a schematic geometric study of the cycloids (Fig. 4). The cycloid was the name coined by the artist and mathematician Galileo Galilei (1564–1642) which described the curve traced by a point on the circumference of a rolling circle or wheel. Ironically, the cycloid was found to be the mathematical solution to many seemingly disparate problems [4]. Among them, a fundamental constant, the Rydberg constant ( $R_{\rm H}$ ), crossed Balmer's footsteps later in his chance study of a problem in spectroscopy. In a real sense, Balmer's dissertation concerning cycloids became a combination of mathematical and artistic expression in one [5].

In 1850, young *Balmer* married *Christine Pauline Rinck*, a minister's daughter from Grenzach, Germany. Of their three sons and three daughters, the youngest son, *Wilhelm* (1865–1922) became a reputed artist, and *Lydia* (1855–1938) married *Ludwig Knapp* (1851–1905), whose mother *Katharina Elise Liebig* (1820–1890) from Darmstadt was sister to *Justus von Liebig* (1803–1873), the world-famous chemistry

mentor in Giessen [6]. The *Balmer-Rinck* family lived out their years near the later site of the fine-chemicals company (1896) *Hoffmann-La Roche*. Through the years, family members including *Balmer* were interned to their final resting place in a family grave at *Spalen* cemetery, site of today's Universitätsbibliothek Basel near the Botanical Gardens. The cemetery remains were eventually relocated to nearby *Wolf-Gottesacker* cemetery in Basel (*Fig. 5*).



Fig. 5. *The* Balmer *family grave at Wolf-Gottesacker cemetery.* Photograph by *G. W. Craig.* 

After completion of his doctorate, *Balmer* found immediate work to teach mathematics and writing at a school for girls. Since his teaching duties were only parttime, it allowed him to develop his artistic interests in the architecture of ancient cultures.

By the age of forty, these broad interests led to *Balmer*'s habilitation (qualification to teach at the university level) with a dual scientific and philosophical investigation curiously entitled, '*The Prophet Ezechiel's Vision of the Temple*'. His account of this biblical monument disclosed the numerical and mathematical relationships found in the temple's chambers, columns, steps, and architectural dimensions [7]. He continued teaching at the girls' school but simultaneously prepared his often diverse lectures at the Universität Basel. His lecture themes varied from *i*) portrayal and construction of higher geometric forms, *ii*) the stereo-perspective of crystals, and *iii*) one of his favorite subjects, the architecture of ancient buildings in Jerusalem. He taught this last theme with special care to aspiring theology students in the role of a kind of *Schattenlehrer* or teacher of the occult [8]. Munich Professor of Physics *Ludwig Hartmann* noted, '*Balmer was deeply religious or one might say a mystic*' [8]<sup>2</sup>). For *Balmer*, he was convinced that a prescribed heavenly harmony remained to be discovered between art and the laws of *Nature* [8].

<sup>2) &#</sup>x27;Balmer war ein tiefes, religiöses, ja darf vielleicht sagen mystisches Empfinden im Fühlen zu eigen'.

However, it was due to *Balmer*'s attraction to mathematical puzzles that brought him in discussion with a fellow colleague, Professor of Physics, *Eduard Hagenbach-Bischoff* (1833–1910) at the Universität Basel [9]. *Hagenbach* convinced *Balmer*, then a *Dozent* (lecturer) at the Universität Basel, to find a mathematical relationship for the four hydrogen spectral lines reported earlier by *Anders J. Ångström* (1814–1874) [10]. Although *Hagenbach* was eventually appointed Universität chancellor, his son and successor in physics, *August Hagenbach* (1871–1955), assumed the reins in the usage of spectroscopy for the characterization of molecules [11].

History of Spectroscopy. - Although early developments appeared also in the United States [12], spectral analysis, as it was referred to then, was a technique described in Germany by the well-known chemist Robert Bunsen (1811-1899; Fig. 6) and physicist, Gustav Robert Kirchhoff (1824-1887; Fig. 7). Their collaborative invention consisted of a spectroscope or prism to diffract the light given off by an element as it was heated in a flame using Bunsen's famous laboratory burner that produced less soot. Analysis of the light emission from each element revealed a characteristic pattern or 'fingerprint' of spectral lines. Often characteristic for each element was its spectacularly colored flame. This analytical technique proved fruitful in the discovery of many new elements, such as rubidium (Latin meaning red) and cesium (Latin meaning sky blue) [13]. In fact, rubidium was identified in 1862 by Bunsen's young assistant, Julius Piccard (1840-1933), who later became professor at the Universität Basel [14]. His twin sons, chemist Jean Felix Piccard (1884-1963) and physicist Auguste Piccard (1884-1962), both established notable careers. The Piccard dynasty continued into the 20th century with grandson Jacques Ernest-Jean Piccard (1922-2008) who was the first to explore the Challenger Deep (in the Marianas Trench) in the bathosphere 'Trieste' in 1960, and the more recent 1999 non-stop circumnavigation of the world in a hot-air balloon was accomplished by Julius' greatgrandson Bertrand Piccard (b. 1959) [15].



Fig. 6. Robert Bunsen (1811–1899). Photograph courtesy of the Chemical Heritage Foundation Collections.



Fig. 7. Gustav Robert Kirchhoff (1824–1887). Photograph from http://en.wikipedia.org/wiki/ Gustav\_Kirchhoff.

However, let's return to the spectral lines of atomic hydrogen measured by *Ångström* in 1853 (*Fig. 8*). Well into his sixty-years of age, *Balmer* successfully derived an equation and reported his results in *Naturforschende Gesellschaft* in Basel [16].



Fig. 8. The four spectral emission lines of hydrogen in the series known to Balmer are shown in black. Balmer's predicted fifth line which was later verified by Ångström is shown in dark violet.

In his formula (*Eqn. 1*; for the H-atom)<sup>3</sup>), *Balmer* found a unique relationship in which the inverse of the wavelength  $(1/\lambda)$  of each line was proportional to a constant ( $K_{\rm B}$ ) multiplied by the difference of the inverse squares of small integers (*n*); note  $K_{\rm B} = 4/B$  [16].

$$\tilde{\nu} = \frac{1}{\lambda} = K_{\rm B} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \tag{1}$$

where  $K_{\rm B} = 4/B = 1.097 \times 10^7 \,{\rm m}^{-1}$ ,  $n_2 = 2$ , and  $n_1 > 2$  (*i.e.*, 3, 4, 5, ...).

$$\lambda = 3645.6 \ (n^2/(n^2 - 2^2)) \text{ Å}$$
<sup>(2)</sup>

<sup>3)</sup> The general *Balmer* formula

expressed explicitly the wavelength ( $\lambda$ ) directly proportional to a fundamental wavelength, 3645.6 Å (1 Å = 10<sup>-10</sup> m), known as the *Balmer* constant (*B*) multiplied by an expression containing the squares of small integers, n = 3, 4, 5, etc. [16].

As we will see, the significance of the integer values  $(n_1 \text{ and } n_2)$  was only fully recognized 28 years later by *Bohr*. The values of the measured and calculated wavelength using *Balmer*'s formula for the line spectra were convincingly close [16] (Table)! He was also able to predict a fifth spectral line which was unknown to *Balmer* at the time. *Hagenbach* later informed *Balmer* that the predicted line had been verified by Ångström [16][17] (*Table, Entry* v)!

Table. Wavelength Comparison of Each Spectral Line. Data taken from the original reference [16].

Entry	$n_2$	$n_1$	$\lambda$ (calc.) [10 <sup>-7</sup> mm]	$\lambda$ (obs.) [10 <sup>-7</sup> mm]	$\Delta\lambda \ [10^{-7} \text{ mm}]$
i	2	3	6562.08	6562.10	+0.02
ii	2	4	4860.8	4860.74	-0.06
iii	2	5	4340	4340.1	+0.1
iv	2	6	4101.3	4101.2	-0.1
v	2	7	3968.1	3969.65	+1.55

Other spectral series were later discovered in the ultraviolet (1906; Lyman series,  $n_2 = 1$ ) and in the infrared regions (1908; Paschen series,  $n_2 = 3$ ; 1922; Brackett series,  $n_2 = 4$ ). Although the physical origin of the visible spectral lines still remained a mystery, their position and relationship to the H-atom were now mathematically distinguishable through Balmer's formula. Similar mathematical descriptions of observed spectral-line patterns quickly followed by notable spectroscopists. In 1889, the Swede Johannes R. Rydberg (1854–1919) showed that the Balmer series ( $n_2=2$ ) in the visible region was indeed a subgroup that belonged to the other spectral series. In Rydberg's mathematical description, the line spectra of elements were combined by using a more generalized equation, the so-called Rydberg formula (Eqn. 3).

Wavenumber	$ ilde{ u}=R_{ m H}igg(rac{1}{n_2^2}-rac{1}{n_1^2}igg)$	(3)
Rydberg constant	$R_{\rm H} = K_{\rm B} = 1.096779 \times 10^7 \ {\rm m}^{-1}$	
Values for <i>n</i>	$n_2 = 2$ and $n_1 > 2$ , <i>i.e.</i> , 3, 4, 5,	

Instead of wavelength, *Rydberg*'s formula expressed the wave number ( $\tilde{\nu}$ ) of each spectral line which was proportional to the *Rydberg* constant ( $R_{\rm H} = 1.09760 \times 10^7 \,\mathrm{m^{-1}}$ , subscript H for the H-atom) multiplied by the difference of the inverse squares of integers (*i.e.*,  $1/n_2^2 - 1/n_1^2$  where n = 1, 2, 3, 4, 5 and  $n_1 > n_2$ ). Although the physical significance of this constant was still unknown, we see now the relationship of the *Rydberg* and *Balmer* constants in *Eqns. 3* and *I*, respectively, since they both accompany the same *n*-integer expression. Since  $R_{\rm H} = K_{\rm B}$ , therefore,  $R_{\rm H} = (4/B)$ . In retrospect, the spectral lines did not show the expected acoustic harmonic or overtone analogy well-known for musical notes.

**The Missing Link.** – Let's leap ahead 28 years. *Bohr* was involved in a stimulating discussion concerning the impact of his planetary version of the atom. At the time, *Hans Marius Hansen* (1886–1956), then a young Danish assistant professor of physics,

had carried out spectroscopic experiments in Göttingen. He had queried Bohr about his atomic model and its ramifications about emission spectroscopy. Hansen insisted that Bohr checked Balmer's formula. Bohr had not been fully aware of the formula but he exclaimed, 'as soon as I saw Balmer's formula, the whole thing was immediately clear to me' [18]. The physical significance was clear not only for the spectral lines but for Bohr's own theory. Bohr recognized the n-integer expression in the formula as representing the difference of two energy states (initial  $n_i$  and final  $n_f$ ) for the single electron in H-atom. The existence of more than one spectral line for hydrogen implied to Bohr that the single electron may exist in even higher excited states. Thus, the spectral lines represented the energy quanta released, i.e., Einstein's photon emission when the electron *dropped* from a higher energy level,  $n_i$  to a lower one,  $n_f$  (*Fig.* 9). In reverse direction, this transition was observed as an energy absorption and appeared as a black or colorless column in the light spectrum. Bohr's prediction of two additional hydrogen emission lines using *Balmer*'s formula was verified by their discovery in 1906 by Theodore Lyman (1874-1954). Previously, Planck and Einstein had unquestionably assumed that the wavelength of the spectral lines corresponded merely to the frequency or energy of the electron as it orbited the nucleus!

*Bohr*'s conviction was that the stationary energy states of the electron were derived from classical mechanics, *i.e.*, the angular momentum of the electron in its orbit ( $r \times$ 



Fig. 9. The structure of the Bohr hydrogen atom

mv) about the nucleus was an integer multiple (n) of *Planck*'s quantum of action  $(h/(2\pi)^4)$ . Moreover, the electron's energy (E) was found by *Planck*'s radiation law E = nhv.

However, *Bohr* realized that the electron transitions between energy states were not satisfactorily described by classical mechanics but required a new mathematics, the then emerging quantum mechanics. *Bohr* was encouraged by the subtle clue in *Balmer*'s formula that the spectral line originated from the energy difference between two energy states. Therefore, based on these empirical assumptions and using classical mechanics, he derived the *Bohr* equation (*Eqn. 4*) for the energy with a similar format to *Balmer*'s formula but now showing the *Rydberg* constant expressed in terms of physical constants known for the atom [19].

$$Bohr's \text{ derivation of energy:} \quad E = -2 \pi^2 m Z^2 \frac{e^4}{h^2} \left(\frac{1}{n^2}\right)$$
Energy difference for H : 
$$\Delta E = 2\pi^2 m \frac{e^4}{h^2} \left(\frac{1}{n^2_2} - \frac{1}{n^2_1}\right) \qquad (4)$$

$$Planck's \text{ energy:} \qquad E = h\nu = \frac{hc}{\lambda}$$

$$\frac{\Delta E}{hc} = \frac{1}{\lambda}$$

$$\frac{1}{\lambda} = R_{\rm H} \left(\frac{1}{n^2_2} - \frac{1}{n^2_1}\right) \qquad (3)$$

$$Rydberg \text{ constant :} \qquad R_{\rm H} = 2\pi^2 m \frac{e^4}{h^3 c}$$

*Bohr* was completely elated because his calculations of the atomic dimensions and spectral data were impressively accurate when compared to the experimentally measured dimensions for the H-atom. In addition, the mysterious *Pickering–Fowler* spectral lines were now explainable as electron transitions arising from the charged He nucleus which was twice as heavy but isoelectronic with the H-atom. The He had been an undetected contaminant in earlier H-atom experiments [20]! How and when the electron makes the energy transition, known as the *quantum leap*, still remains a mystery. Ironically today, the lay definition of a quantum is misconstrued to mean a *'giant or huge'*, although in physical terms it corresponds often to a miniscule change in energy states.

Bohr remarked several years later in a 1962 interview, that as he saw Balmer's formula: 'One thought [that] spectra are marvelous, but it is not possible to make progress there. Just as if you have the wing of a butterfly, then certainly it is very regular with the colors and so on, but nobody thought one could get the basis of biology from the coloring of the wing of a butterfly. So that was the way to look at it [21].'

<sup>&</sup>lt;sup>4</sup>) The symbol *m* is the mass of the electron, v is the velocity of the electron, v denotes the frequency or the energy of the electron, *e* is the energy of the emitted photon, *Z* is the atomic number (for H = 1), and *r* is the radius of its orbit about the nucleus.

In fact, it was a monumental surprise that the color of the wing, in a sense, did lead to the identification of the biology of the butterfly! The origin of the spectral lines of the natural elements was not only explainable, but it impressively predicted new spectral lines which were indeed discovered. A comparison with the light spectra of stars in other galaxies was another exciting revelation of its potential application for star exploration from earth! It marked the birth of a new science later christened, astrophysics [22].

However, ensuing investigations of the *Bohr* atom model revealed that it was accurate only for one-electron atomic systems and required an extensive refinement of *Bohr*'s basic ideas to fit the more complex atomic systems. More importantly, however, *Bohr*'s model established the application of quantum numbers and its systematic ordering of the elements in the periodic table. Also, *Bohr*'s concepts further established that the atomic configurations of the outer valence orbitals formed the basis for understanding the chemical bonding properties which all chemistry, physics, and biology students learn today!

**Conclusions.** – In the history of humanity, the fascination and curiosity with Nature's beauty has unarguably motivated countless scientific discoveries. *Balmer*'s own interests in art and biblical architecture were no different. As he investigated the spectral lines of hydrogen, *Balmer* may have imagined them as the marble pillars of an ancient temple. It was *Balmer*'s fascination with Nature's mathematical design and its influence in ancient architecture that ironically provided *Bohr* with the missing clue to understand and confirm the architecture of the atom.

Balmer's equation was ranked 12th by popular vote in a conducted survey of 'the greatest equations ever' by readers of Physics World in 2010. Survey author and analyst, Robert Crease, remarked, 'a great equation does more than set out a fundamental property of the universe, delivering information like a signpost, but works hard to wrest something from Nature' [23]. Indeed, Bohr was an able athletic adversary in sports as a youth! Inspired by Balmer's formula, Bohr made a visionary interpretation of the inner structure of the atom which neatly transformed the chaotic spectroscopic data, collected since the time of Bunsen and Kirchhoff into a genuinely useful system. Although, Bohr's atomic model was accurate only for one-electron systems, his brilliant insight opened a new era of quantum order for the periodic table by the use of quantum numbers and the development of the new quantum mechanics. Einstein fondly referred to Bohr's atom as the 'musicality in the sphere of thought' [24]. In 1963, Denmark issued a postage stamp dedicated to Bohr for his historical breakthrough in science (Fig. 10).



Fig. 10. Celebration of the Bohr atom in a Danish postage stamp. Personal collection, G. W. Craig.

As *Newton* before them, *Bunsen* and *Kirchhoff* were also captivated by the power of the prism to diffract light. They developed their early spectroscope based on this fascination to analyze the light from burning the natural elements to the light from *'burning'* stars. It established astrophysics to extend our perception of the universe on a cosmological level! In yet a broader sense, their fascination led to our modern spectroscopic instruments such as IR, UV, NMR, ESR, and microwave spectroscopy which have become powerful tools for understanding atomic and molecular architecture. The eminent synthetic chemist *Robert B. Woodward* (1917–1979) promoted such instrumental analyses with chemical reactivity studies to reveal new structure–reactivity properties of many complex natural products, well before the advent of X-ray crystallography became practical [25].

As often quoted from *Newton*'s reference to his own experience in scientific discovery: '*if I have seen further, it is by standing on the shoulders of giants*' [26]. Johann Jakob Balmer was not a giant in scientific stature, but he was well-educated in mathematics, ancient architecture and religion. Balmer's remarkable attraction to puzzles provided the missing link, the Rosetta Stone that decoded the language of light spectra into the language of atomic structure. One may imagine Bohr, the visionary physicist, rising to tiptoe only slightly but not on Balmer's modest shoulders but on his own metaphor, 'the wing of the butterfly' of spectroscopy which inspired so much foresight into the next galaxy! Alas, Balmer was also honored by the christening of a street in Basel (Fig. 11) and the prestigous Balmer Prize, awarded to a teacher working at the high school level in Switzerland for innovation in chemistry teaching.



Fig. 11. J. J. Balmer-Strasse in Basel, Switzerland. Photograph by G. W. Craig.

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