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Mutually Supporting Evidence in Atomic Spectra

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1 Introduction

Gases and vaporized metals, when heated or energized by electric discharges, emit light or electromagnetic radiation in the invisible parts of the spectrum. In the nineteenth century, spectroscopists began detailed measurements of the frequencies emitted by various substances. The most striking result was that, commonly, the emitted spectra did not consist of a continuous range of frequencies, but only specific frequencies organized regularly in series. Identifying which frequencies were emitted by each substance under which circumstances proved a challenge that occupied the spectroscopists for decades. Their efforts required many ingenious approaches. What resulted was a complicated network of relations of evidential support that is the subject of this chapter. In it we will see mutual relations of support, crossing over each other, and at two levels.

We will look only at the simplest of the emission spectra, that of hydrogen, for that is already sufficient to display this multiplicity of relations of mutual support. We shall take as the simplest item of evidence the proposition that excited hydrogen produces electromagnetic radiation at such and such frequency or wavelength. One such item asserts the fact that a prominent line in the hydrogen spectrum, the first “ H_{α} ” line of the Balmer series, is at wavelength 656.2 Angstroms. Once a spectroscopist has identified some lines in the spectrum of a substance, it proved possible to identify others by means of device introduced in 1908 by

Walther Ritz. It is his “combination principle.” It asserted that adding or subtracting the frequencies of certain¹ known lines in a spectrum will yield more lines.

If there are two lines with the frequencies² ν_{12} and ν_{23} of the right type, then there is a third line at the frequency $\nu_{13} = \nu_{12} + \nu_{23}$. These additions are easily inverted. If we have lines at the frequencies ν_{12} and ν_{13} , then there is a third line at the frequency $\nu_{23} = \nu_{13} - \nu_{12}$. And, if we have lines at the frequencies ν_{23} and ν_{13} , then there a third line at the frequency $\nu_{12} = \nu_{13} - \nu_{23}$. Each of these applications of the Ritz combination principle expresses a relation of support.

There are three and they cross over one another in relations of mutual support:

Lines at ν_{12} and ν_{23} support a line at ν_{13} .

Lines at ν_{12} and ν_{13} support a line at ν_{23} .

Lines at ν_{23} and ν_{13} support a line at ν_{12} .

There are more than just a few of these sets of mutually supporting items of evidence. Since the emission spectrum of hydrogen contains infinitely many lines, there are infinitely many of them.

Sections 2 and 3 recall the discovery of the various series of lines of the hydrogen spectrum and their systematization by Ritz through his combination principle. Section 4 explores how the principle allows a dense network of relations of mutual support among the lines. If the Ritz combination principle is taken as premise, these relations of support are expressed by deductive inferences. They combine to produce a totality in which the observed lines of the hydrogen spectrum provide inductive support for the series of infinitely many lines.

Section 5 asks a further evidential question: What supports the Ritz combination principle? Is it merely to be supported as a generalization over observed lines in the spectrum? What fact warrants it? The decisive theoretical development came in 1913 when Niels Bohr proposed an atomic mechanism capable of producing precisely the spectra observed. It became one of the foundations upon which modern quantum theory was built. Bohr’s theory, to be outlined in Section 6, proposed that the lines arise when an excited electron drops or jumps down

¹ This word “certain,” meaning “some carefully chosen,” indicates an important restriction. The principle does not work for all pair of lines.

² The two indices arise from the simple two parameter formulae (1) – (6) below, found empirically to systematize the frequencies of the lines present.

from a higher to a lower energy state. Each jump leads to emission of radiant energy with a frequency proportional to the energy emitted. This mechanism provided a direct explanation of the Ritz combination principle. The two frequencies ν_{12} and ν_{23} corresponded to two emissions in a two-step jump. If the jump is taken in a single step, the frequency $\nu_{13} = \nu_{12} + \nu_{23}$ results directly from the requirement that the two-step jump or the single step jump liberate the same quantity of energy.

The Ritz combination principle provides another instance of the crossing over of relations of support, but now at a more elevated level of the theory. On the one hand, as described in Section 7, the combination principle, taken as a datum from observational spectroscopy provides evidential support for the Bohr theory; and it was reported as such. Using a few notions from his theory, the principle translates directly in the emission mechanism Bohr proposed. However, on the other hand, as reported in Section 8, the converse relation of support also holds. Once quantum theory is established it entails the Ritz combination principle. The converse relation of support is important, for what quantum theory eventually provides is a corrected version of the principle. For some of the lines the original Ritz principle predicts are “forbidden,” that is they correspond to electron jumps precluded by quantum theory. What results is an embellished Ritz combination principle, supplemented by so-called “selection rules” that indicate which lines are forbidden.

2. The Discovery of Regularities in Emission Spectra

The emission spectrum of hydrogen contains lines at many frequencies. They are called “lines” since the early methods of spectroscopy capture the different frequencies present in the light as lines on a photographic plate. The frequency or wavelength of the light is recovered from distance measurements on the plate. An example from Fowler (1922, p. 8) is shown in Figure 1.

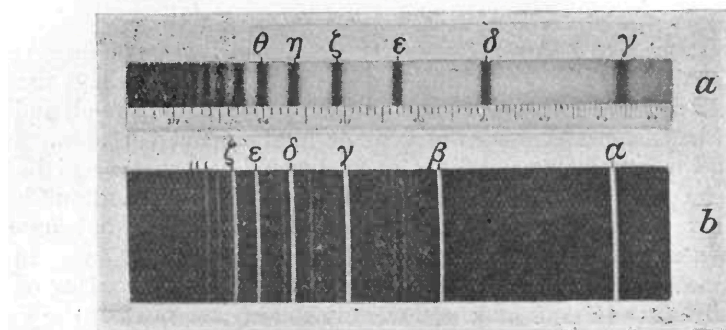


FIG. 1.—THE SPECTRUM OF HYDROGEN : (a) IN SIRIUS, (b) IN VACUUM TUBE.

Figure 1. A spectrograph of the spectrum of hydrogen

The first formula to embrace some of these lines with enduring success was posited by Balmer (1885) for strong lines in the visible spectrum. In modernized form his formula for the frequencies of lines in the “Balmer series” was

$$\nu(2, m) = R(1/2^2 - 1/m^2) \quad (\text{“Balmer”}) \quad (2)$$

The different values of $m = 3, 4, 5, \dots$ gave specific lines in the spectrum shown in Figure 1.

$$H_\alpha: \nu(2, 3) = R(1/2^2 - 1/3^2)$$

$$H_\beta: \nu(2, 4) = R(1/2^2 - 1/4^2)$$

$$H_\gamma: \nu(2, 5) = R(1/2^2 - 1/5^2)$$

$$H_\delta: \nu(2, 6) = R(1/2^2 - 1/6^2)$$

...

In the following decades, similar formulae were found for other lines in the hydrogen spectrum

$$\nu(1, m) = R(1/1^2 - 1/m^2) \quad m = 2, 3, 4, \dots \quad (\text{“Lyman”}) \quad (1)$$

$$\nu(3, m) = R(1/3^2 - 1/m^2) \quad m = 4, 5, 6, \dots \quad (\text{“Paschen”}) \quad (3)$$

$$\nu(4, m) = R(1/4^2 - 1/m^2) \quad m = 5, 6, 7, \dots \quad (\text{“Brackett”}) \quad (4)$$

$$\nu(5, m) = R(1/5^2 - 1/m^2) \quad m = 6, 7, 8, \dots \quad (\text{“Pfund”}) \quad (5)$$

Each series is named after the spectroscopist responsible for its identification.

This quick recitation of the various formulae masks the magnitude of the problems faced by the spectroscopists. Decades separated the recovery of these series. While Balmer’s formula was reported in 1885, the terms of the Paschen series began to be verified around 1908, as announced by Ritz (1908). Lyman (1914) reported his ultraviolet spectrum in a letter to *Nature*

of 1914. Brackett (1922) reported more lines in the Paschen spectrum and the first two members of newly discovered Brackett series.

There were multiple problems to be overcome. The first four lines of the Balmer spectrum, H_{α} to H_{δ} , are easiest to find since they are in the visible spectrum. The Lyman series lies in the ultraviolet and the remaining series are in the infrared. These different ranges require different instrumentation to separate the frequencies and register them. Controlled conditions, such as low pressures, are needed to manifest sharp lines. Then some of the lines reported have celestial origins in spectrographs taken of stars. Since we have no independent samples of the matter of the stars, how do we know just which excited matter produced them? How are they to be matched up with spectra produced by excited matter on earth? The spectrograph in Figure 1 shows such a case. The upper set of lines arises in light from the star Sirius. The lower set comes from light emitted by excited hydrogen in a terrestrial laboratory. Fowler (1922, p. 7) suggests that the celestial lines may be identified as an extension of those in a spectrum found terrestrially if they fall near enough on a definite curve. Figure 2 shows such a curve from Fowler (1922, p.14). The vertical axis plots the m of (1), (2) and (3); and the horizontal axis plots frequency:

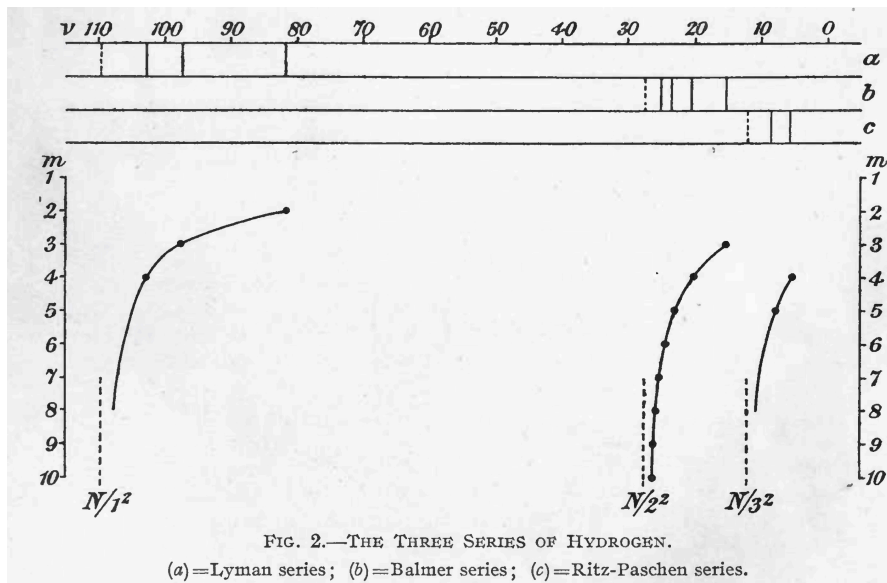


Figure 2. Frequencies of series form definite curves

A trace of these different sources appears in Bohr's (1913) celebrated paper on his theory of atom. He notes (p. 9) that then only nine lines of the Balmer series had been observed terrestrially in vacuum tubes, whereas 33 had been observed in celestial spectra.

Finally, even when definite series are identified in some spectrum, it is not always clear that all the series derive from the same substance. Sommerfeld (1923, pp. 207-208) reports two series that were originally attributed to hydrogen because of the similarity to the Balmer formula (2) for hydrogen. They are

$$\nu = R(1/1.5^2 - 1/m^2) \quad m = 2, 3, 4, \dots \quad (\text{"Principal series"})$$

$$\nu = R(1/2^2 - 1/(m+0.5)^2) \quad m = 2, 3, 4, \dots \quad (\text{"Second subsidiary series of hydrogen"})$$

One outcome of Bohr's 1913 atomic theory was that these series would result from an atom with a nuclear charge twice that of hydrogen, so that the constant "R" in these formulae is four times greater than that for hydrogen. That is, they derive from helium and not hydrogen. This conversion is easily accomplished by multiplying the above formulae by 4/4. We now have:

$$\nu = (4R) (1/3^2 - 1/m^2) \quad m = 4, 5, 6, \dots \quad (\text{"Principal series"})$$

$$\nu = (4R) (1/4^2 - 1/m^2) \quad m = 5, 6, 7, \dots \quad (\text{"Second subsidiary series of hydrogen [?]"})$$

The attribution of the spectra to helium was already made immediately by Bohr (1913a) in a letter to *Nature*.

3. The Ritz Combination Principle

Given the variety and difficulty of the problems facing the spectroscopists in locating and grouping spectral lines, any assistance in the heuristics would be useful. Such was offered by Ritz (1908). Rydberg had noted that formulae for spectral lines could be simplified if they were written in terms of wave number, which is the inverse of wavelength.³ Then the formulae could be expressed as a difference of two terms, as is done in (1) to (5) above. This fact enabled Ritz

³ The spectroscopists preferred to report wavelengths since they were more directly measurable than frequency. To convert wavelengths to frequencies required multiplication by the speed of light: frequency = (speed of light) / wavelength. Using inverse wavelength as a surrogate for frequency avoids systematic errors introduced by errors in the value of the speed of light employed.

(1908) to propose what he called his “principle of combination” (*Kombinationsprinzip*) (p. 523). Its value, as Ritz noted in the first sentence of his paper,⁴ is that one could use known spectral series to discover new ones. He applied it to a range of spectra, including those of hydrogen, helium and the alkali and alkaline earth metals.

A good statement of the principle is provided by Ritz himself in a note found posthumously in his papers and published as an appendix to Ritz (1908) in his *Gesammelte Werke* (*Collected Works*) (1911, p. 162). Sommerfeld (1923, p.205) quotes Ritz as giving this formulation:⁵

By additive or subtractive combination, whether of the series formulae themselves, or of the constants that occur in them, formulae are formed that allow us calculate certain newly discovered lines from those known earlier.

The principle is incomplete since it does not specify which additions and subtractions are those that yield new lines. The necessary supplement is provided in each application by a formula that represents the line frequency as a difference of two terms. Its application to hydrogen proceeded from assuming that the series of hydrogen conform to a general formula

$$\nu(n, m) = R(1/n^2 - 1/m^2) \quad n = 1, 2, 3, \dots \quad m = 2, 3, 4, \dots \quad (6)$$

where we always have $m > n$. It follows that a new line in the spectrum can be identified by taking the difference in the frequencies of two known lines, as long the expression (6) for each shares a common term. For example, the lines H_α and H_β can be subtracted in this way since they share a $1/2^2$ term that is eliminated by the subtraction:

⁴ “In the following, it will be shown that, from known spectral series of an element, one can derive new series without introducing any new constants. Through this especially, almost all the series and lines recently discovered in the alkalis by Lenard, Konen and Hagenbach, Saunders, Moll, Bergman etc. come to be represented exactly.” (p. 523)

⁵ Sommerfeld’s report is abridged. In place of “...certain newly discovered lines from those known earlier,” Ritz’s text specifies lines of alkalis discovered then recently by Lenard and others, as well as new elements, in particular helium.

$$H_{\beta}: \nu(2, 4) = R(1/2^2 - 1/4^2)$$

$$H_{\alpha}: \nu(2, 3) = R(1/2^2 - 1/3^2)$$

__subtract____

$$\nu(3, 4) = R(1/3^2 - 1/4^2)$$

What results is the first line $\nu(3, 4)$ of the Paschen series (3), which was not an established series in 1908. It led to an immediate affirmation of the correctness of Ritz's proposal. In his paper, Ritz (1908, p. 522) reported with obvious satisfaction that Paschen had informed him by letter ("Nach einer brieflichen Mitteilung") that he had observed just this line in the infrared.

4. Mutually Supporting Evidence

For Ritz, the combination principle was valuable as a means of discovering new lines. At the same time, it was the warrant for an inference from the existence of some lines to others. The evidence of the lines H_{α} and H_{β} of the Balmer series supports the line $\nu(3, 4)$ of the Paschen series. This subtraction can be reversed into an addition that supplies a different relation of support:

$$H_{\alpha}:- \nu(2, 3) = R(1/2^2 - 1/3^2)$$

$$\nu(3, 4) = R(1/3^2 - 1/4^2)$$

__add____

$$H_{\beta}: \nu(2, 4) = R(1/2^2 - 1/4^2)$$

That is, the frequencies of the H_{α} line and the $\nu(3, 4)$ line can be added to recover the H_{β} line. In this addition the common $1/3^2$ terms cancel. That is, the H_{α} line and the $\nu(3, 4)$ line support the H_{β} line.

These two relations show the crossing over of relations of support. In the first, the H_{β} provides support for the $\nu(3, 4)$ line. In the second, the $\nu(3, 4)$ line provides support for the H_{β} line. Since the full range of series covered by relations (6) has infinitely many lines, there will be infinitely many of these relations of support, crossing over in many ways.

These relations of support can be captured in infinite sets of relations of support. For example, the Ritz combination principle can be applied to the infinitely many lines of the Balmer

series (2) to support the Paschen (3), Bracket (4) and Pfund (5) series. For the first, lines in the Balmer series can be subtracted to cover the entire Paschen series:

$$\begin{aligned} \nu(2, m) &= R(1/2^2 - 1/m^2) \quad (m > 4) \text{ Balmer} \\ H_\alpha: \nu(2, 3) &= R(1/2^2 - 1/3^2) \\ \text{--- subtract ---} & \\ \nu(3, m) &= R(1/3^2 - 1/m^2) \quad (m > 4) \text{ Paschen} \end{aligned}$$

Additional lines are needed as supplementary evidence if series in the sequence of (1), (2), (3), (4) and (5) are to support those earlier in the sequence. For example, we take as an extra datum $\nu(1, 2)$, the first line of the Lyman series (1), then the entire Lyman series is recovered by addition from the Balmer series:

$$\begin{aligned} \nu(1, 2) &= R(1/1^2 - 1/2^2) \\ \nu(2, m) &= R(1/2^2 - 1/m^2) \quad (m > 2) \text{ Balmer} \\ \text{--- add ---} & \\ \nu(1, m) &= R(1/1^2 - 1/m^2) \quad (m > 1) \text{ Lyman} \end{aligned}$$

If we take as an extra datum the H_α line of the Balmer series, then the Paschen series supports the Balmer series.

$$\begin{aligned} \nu(3, m) &= R(1/3^2 - 1/m^2) \quad (m > 3) \text{ Paschen} \\ H_\alpha: \nu(2, 3) &= R(1/2^2 - 1/3^2) \\ \text{--- add ---} & \\ \nu(2, m) &= R(1/2^2 - 1/m^2) \quad (m > 3) \text{ Balmer} \end{aligned}$$

Two of these relations of support cross over one another and can be represented more compactly as

Ritz combination principle	Ritz combination principle
Balmer series	H_α line
--- deduce ---	Paschen series
Paschen Series	--- deduce ---
	Balmer Series

Similar computations realize many more like-structured, crossing-over relations of mutual support, including:

the Paschen series supports the Bracket and Pfund series;

the Bracket and Pfund series supports the Paschen series;
the Bracket series supports the Pfund series;
the Pfund series supports the Bracket series;
etc.

It is noteworthy that all of the individual relations of support just described are implemented by deductive inferences. We can infer deductively from some subset of lines, via the Ritz combination principle, to the larger portions and even the entire set in (6). Nonetheless, accepting the entirety of the series does involve inductive risks. The inductive risks enter in accepting the premises that figure in the individual deductions. We take a small inductive risk in accepting the correctness of the report of the existence of each line. Most notably, considerable inductive risk is taken in accepting the combination principle, since it has infinite scope. That the risk is considerable is seen most easily from the fact that later investigations introduced a small “fine structure” splitting of the lines in the series described above.⁶ More significantly, we shall see below that the Ritz combination principle itself needed to be modified by selection rules that prohibit certain lines when we move beyond the hydrogen spectrum.

While combining deductive relations to yield inductive support overall may at first appear paradoxical, it is not so. All that has happened is that the inductive risks taken in accepting the premises of the deductions are the only inductive risks we need to take. Once they are taken, we can proceed with maximally secure deductive arguments. This type of support is inductively more secure than combining inductive relations of support in a similar way. No further inductive risk is taken in accepting these component deductive inferences, whereas further inductive risk would be taken if they were replaced by inductive inferences. Chapter 2, “Large-Scale Structure of Inductive Support,” reflected on other examples of deductive relations of support combining to provide overall inductive support.

The massively entangled network of relations of mutual support go well beyond the heuristic guidance of Ritz’s original purpose. For that narrower purpose, the most useful are the

⁶ The splitting, reported by Sommerfeld in 1916, resulted from relativistic corrections to Bohr’s atomic theory. Sommerfeld found that differences in the eccentricities of the elliptical electron orbits of the theory led to slight differences in their energies. See Sommerfeld (1915; 1923, p. 474).

inferences from readily available lines to those not yet discovered. Our concern here, however, is not so narrow. It is to discern the full structure of the relations of inductive support.

5. Supporting the Ritz Combination Principle

The inferences reported in the last section all employ the Ritz combination principle as a premise. None of the inferences in the last section provide support directly for the Ritz combination principle. Rather they all merely use it. For, with the qualification to be noted below, the principle is a standard part of atomic spectroscopy.

What evidence supports the Ritz combination principle? One might be tempted to answer that we have many instances of the general formula (6) and no counterexamples. So we can inductively infer to (6) and from it deduce the Ritz combination principle for the hydrogen spectrum. The trouble is that a generalization—any generalization—requires a warranting fact. So far, it is unclear what that fact is.

We might be tempted to say that, when a general formula this simple fits all the cases at hand, we have a license to infer to it. The familiar difficulty was developed at length in Chapter 6 of *The Material Theory of Induction*. We lack both a notion of simplicity precise enough to warrant these inferences; and we lack a factual basis for the inductive powers of such a notion.

As an intermediate attempt to warrant the generalization, we might suggest that a formula as simple as (6) can only be as successful as it is if it is part of a larger regularity whose precise character is not presently known to us. Something like this quite plausible. However, it rests on the supposition of further facts not so far produced. That, at least, was the situation in 1908 when Ritz proposed his principle. In 1913, circumstances would change. Then Bohr proposed his novel theory of the atom. That theory used Ritz's principle and the formula (6) as evidential support. Soon, the relation of support would become mutual when the quantum theory that emerged from Bohr's theory provided support for a modified version of Ritz's principle.

6. Bohr's Theory of the Atom

Bohr's celebrated theory of the atom was based on Rutherford's nuclear account of the atom. According to it, a hydrogen atom consists of a very massive, positively charged nucleus with a light, negatively charged electron orbiting it. To this Bohr added two ideas. Classical

electrodynamics requires that this orbiting electron must radiate its energy electromagnetically and thus be pulled rapidly into the nucleus. Bohr simply posited otherwise:

I. There are stable orbits for the electron.

The energies of these orbits were to be computed by standard electrostatics. Bohr further supposed that electrons could jump between these stable orbits. Another posit connects these jumps to emission spectra.

II. When an electron drops down from a more energetic stable orbit to a less energetic one, closer to the nucleus, the energy E it loses reappears as electromagnetic radiation with a frequency ν , according to $E = h\nu$, where h is Planck's constant.

Denote the (negative) energies of two stable orbits as W_1 and W_2 , with $W_1 > W_2$. When an electron drops from the first to the second orbit, it emits electromagnetic radiation of frequency ν_{12} whose value is, according to II:

$$\nu_{12} = (W_1 - W_2)/h \quad (7)$$

Comparison with the general spectral formula (6) then allows us to identify the (negative) energies of the stable orbits

$$\Omega(n) = R/n^2 \quad n = 1, 2, 3, \dots \quad (8)$$

The striking outcome here is that, from the spectral formula (6), we infer that the energies of the stable orbits do not form a continuous set. Rather they form a discrete set whose members are indexed by n . Bohr's posits I. and II. do not presume discreteness. It is inferred from the evidence of the spectra.

The Bohr theory clarified Ritz's combination principle. In its original form, the principle was the recognition of a bare numerical regularity. It was a kind of scientifically useful numerology. Bohr's theory gave it a physical basis. Consider the case shown in Figure 3. An electron in an excited hydrogen atom drops to a lower energy orbit, emitting radiation of frequency ν_{12} with energy $E_{12} = h\nu_{12}$. In a second jump, it drops to a still lower energy orbit, emitting radiation of frequency ν_{23} with energy $E_{23} = h\nu_{23}$. Had the electron jumped directly from the first orbit to the final, it would have emitted radiation of frequency ν_{13} with energy $E_{13} = h\nu_{13}$.

We have two cases, one with two successive jumps and the other with a single jump. They are between the same initial and final orbits. Thus the energy radiated in each must be the same:

$$E_{13} = E_{12} + E_{23}$$

Applying $E = h\nu$ to each of these three energies, we recover

$$\nu_{13} = \nu_{12} + \nu_{23}$$

This last sum is the Ritz combination principle applied to the hydrogen spectrum. Its physical foundation is now displayed.

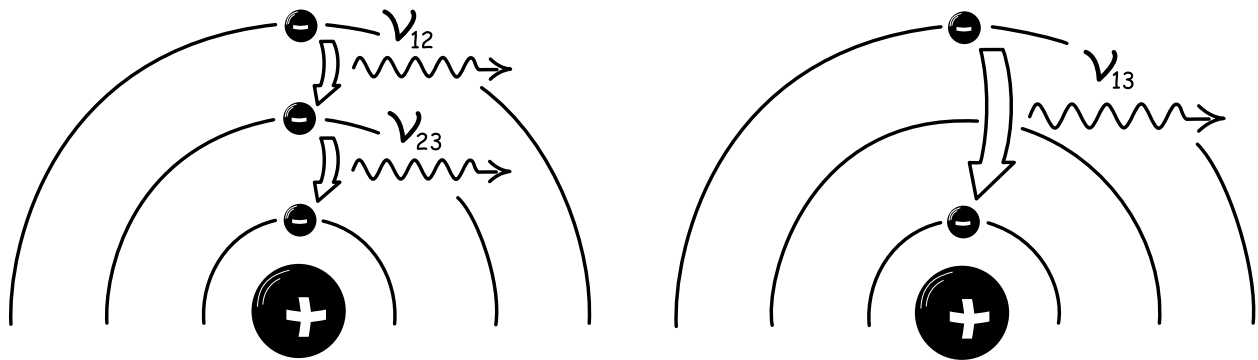


Figure 3. Physical Basis of the Ritz Combination Principle

There is much more in Bohr's theory and these details have been elaborated frequently elsewhere.⁷ Using further conditions, Bohr concluded that the constant R in (6) and (8) is given by $R = 2\pi^2me^4 / h^3$, for m the mass of an electron and e its charge. The value of R , computed from this formula using the best-known values of m , e and h , was, Bohr reported, 3.1×10^{15} . It matches closely enough to the value Bohr reported from spectral observations, 3.290×10^{15} .

Bohr also showed that the stable orbits of (8) coincided with the orbital angular momentum of the electron taking on integer values in units of $h/2\pi$. This formulation of the discreteness of the stable states of (8) became increasingly important as Bohr's theory evolved. In more elaborated versions of his theory, the so-called "old quantum theory," this result was the simplest case of the quantization of action. In the "new quantum theory" that emerged in the mid

⁷ For an early authoritative textbook account, see Sommerfeld (1923, pp. 211-218). Norton (2000) develops these details with special focus on the evidential relations.

1920s, this result coincided with the fact that stable electron orbitals are eigenstates of the angular momentum operator.

7. The Ritz Combination Principle Supports Quantum Theory

The first half of the mutual relations of support is that the newly emerging quantum theory was supported by the Ritz combination principle. This support has been evident from the start. In a much quoted⁸ remark, reported by Bohr's assistant and confidant, Leon Rosenfeld, Bohr remarked that "as soon as I saw Balmer's formula, the whole thing was immediately clear to me."

The evidential support the Ritz principle gave to Bohr's emerging theory was widely recognized. Max Born (1935, p. 85) is forthright about it: "A direct confirmation of this [Bohr's 1913] theory can be seen in the following fact..." He proceeded to explain in detail and with a figure similar to Figure 3 above how Ritz's combination principle (identified by this name) is a consequence of the cascade of emissions described in the preceding section.

Sommerfeld, in his early, authoritative volume on the old quantum theory, is similarly forthright. He introduced the Ritz combination principle by name, along with the quote given above; and then explained its application in detail (1923, pp. 205-206). He then characterized its significance (emphasis in original):

The principle of combination has maintained itself in the whole region of spectroscopy from infra-red to X-ray spectra as an *exact physical law* with the degree of accuracy that characterises spectroscopic measurement. It constitutes the foundation on which Bohr's theory of spectra rests, and is, in essence, identical with Bohr's law (cf. Chap. I, § 6, eqn. (6)) [eqn (7) above], which likewise taught us to regard the frequency of a spectral emission as the difference between two energy-levels.

If we approach the support relations materially, we can be more precise in just what Ritz's combination principle provides Bohr's theory. Bohr's 1913 posit II above associates spectral lines with electron jumps between stable orbits of different energy. Using the posit as a

⁸ As quoted in Duncan and Janssen (2019, p. 14).

warranting fact, we infer *from* each spectral line *to* the existence of an electron jump in the hydrogen atom between stable energy states.

The Ritz combination principle adds something very important to this last inference. All this last inference gives us is the energy *differences* between the energies of the stable orbits. Posit II does not specify how these stable energy states are related. It might just be that each line derives from its own unique set of energy states and that no other line derives from electron jumps to or from them. The principle assures us that it is possible to find a single set of energies of stable orbits such that all these stable orbits are accessible to the electron in a hydrogen atom. More precisely it follows from the spectral formula (6) that such a set of energies is given by the relation (8) of the Bohr theory,⁹ $\Omega(n) = R/n^2$.

If we follow Sommerfeld and take the Ritz combination principle as holding universally for all spectral lines, including those not observed, then the relation of support is deductive. All the inductive risk is taken in accepting posit II provisionally as an hypothesis.

8. Quantum Theory confirms the Ritz Combination Principle

In the early years of quantum theory, it was natural to focus on the support the Ritz combination principle provided for the developing quantum theory. For the principle itself was rightly judged to be more securely supported by spectroscopic evidence. The developing quantum theory was speculative and even required physicists to overlook a glaring contradiction with classical electrodynamics. As the quantum theory was developed, became more established and evolved into the later “new quantum theory,” this orientation reversed. A now more secure quantum theory provided support for the Ritz combination principle directly. The principle is a deductive consequence of the account given by quantum theory of the origin of the spectra. It also became more congenial to see support for the Ritz combination principle in the quantum theory, for that support derived from a definite physical ontology and replaced what I called “numerology” above.

⁹ The formula is determined only up to an additive constant that plays no role in energies and frequencies of the radiation emitted. The inference is only to the possibility of the single set of energies described. It does not preclude a more complicated set that simulates the behavior of the simpler set, even though in practice this complication would be dismissed as contrived.

What further strengthens the inverted relation of support is that the development of quantum theory showed that the full Ritz combination principle, when applied to spectra beyond those of hydrogen, needed corrections.¹⁰ For it turned out that not all of the lines predicted by the principle occurred. Some transitions turned out to be “forbidden” and the determination of which are allowed was governed by “selection rules.” The jumps allowed in Bohr’s original theory were constrained only by energy conservation. Such jumps must also conform with the conservation of angular momentum. The emitting electron must lose just the angular momentum that is carried off by the emitted radiation.¹¹ In the case of the simple hydrogen spectrum, the additional condition does not further limit the spectra beyond the limitations of energy conservation. However, that is only a special case. Spectra of other elements do have forbidden lines.

Through these considerations, the reverse direction of support, from quantum theory to Ritz’s combination principle, becomes more secure. The observation of spectra can only give us direct evidence of a finite subset of the infinity of lines possible. That finite evidence can support Ritz’s correspondence principle among the lines observed. When we move past hydrogen spectra, This finite evidence can give indications of when the principle fails. If, however, we derive the principle from a fully developed quantum theory, we recover the principle in its most general form as it applies to the infinity of lines in some spectrum. We also recover a way of determining when certain lines are forbidden and a principled physical account of why they are forbidden.

This inversion had already occurred under the old quantum theory. As the theory developed, new quantum numbers were added, beyond the single quantum number “ n ” of Bohr’s 1913 theory. Sommerfeld introduced the “azimuthal quantum number,” among other numbers.

¹⁰ Another example of this type of correction is seen in the chapter on Newton and the inverse square law of gravity. Kepler’s elliptical orbits of the planets supports the inverse square law. Yet that law, when developed systematically by Newton, leads to corrections to the elliptical orbits due to perturbations from other celestial bodies.

¹¹ In the full quantum electrodynamical analysis, an emitted photon carries off $h/2\pi$ of angular momentum. It follows that the emitting electron can only jump to a state whose angular momentum differs from its starting state by $h/2\pi$.

His authoritative treatment of the old quantum theory included an extensive account of a selection rule for atomic spectra. He states it as (1923, p. 266, Sommerfeld's emphasis):

The principle of selection states: *the azimuthal quantum number can at the most alter by one unit at a time in changes of configuration of the atom.*

This selection rule was carried over¹² and vindicated by the wave mechanics of the new quantum theory. It was rapidly absorbed into textbook expositions, such as Pauling (1935, §40f.)

In his article for *Review of Modern Physics*, Gibbs (1932, p. 307) reflects on the need to qualify the Ritz combination principle:

The later development of the quantum theory has shown that for certain types of radiation some of the Ritz combination lines are “forbidden” or perhaps better are extremely improbable under ordinary circumstances. The degree of probability for these “forbidden” lines varies widely for different combinations and accordingly under certain conditions of pressure, electric field, and mode of excitation some of the more probable of these improbable or “forbidden” lines are observed.

After reporting the discovery of the Brackett and Pfund series, Gibbs (pp. 307-308) recorded what amounts to the inversion of the relations of support:

These series, both of which lie well out in the infrared, were discovered sometime after the theoretical basis for the combination principle had been completely changed and elaborated by the introduction of the quantum theory. Indeed the theoretical arguments advanced by Ritz in proposing this principle were quite unsound even in terms of the older classical theory. It is an excellent example of how a fundamentally correct idea is envisioned through false reasoning, to be later explained on an entirely new basis, the theoretical development of which was encouraged and assisted to some extent by the very idea itself.

9. Conclusion

The investigation of atomic spectra and their relation to quantum theory illustrates the non-hierarchical structure of relations of evidential support. There is a massively entangled set of

¹² Sommerfeld's “at most one unit” is replaced by exactly one unit for the quantum numbers l and m in the case of hydrogen. See Slater (1960, p. 183).

relations of support among the infinitely many propositions that assert the existence of specific spectral lines. The fact that warrants these relations of support is the Ritz combination principle. It too enters into non-hierarchical relations of support. For, initially, the principle provides important evidential support for the newly emerging quantum theory. As that quantum theory developed and became better established, this relation of support was inverted. The quantum theory was seen as providing evidential support for the Ritz combination principle. This inversion is appropriate since the quantum theory indicated that the Ritz combination principle had to be supplemented or corrected to accommodate “forbidden lines.” The quantum theory could provide both a systematic means of identifying these forbidden lines and a physical basis for forbidding them.

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