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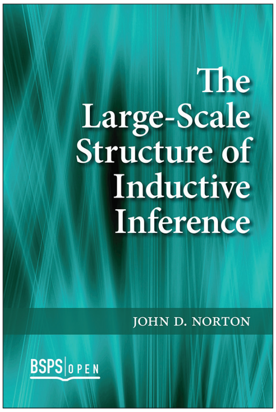

THE LARGE-SCALE STRUCTURE OF INDUCTIVE INFERENCE

John D. Norton

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Mutually Supporting Evidence in Atomic Spectra

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 to be a challenge that occupied 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 itis already sufficient to display this multiplicity of relations of mutual support. We will 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 is possible to identify others by means of a device introduced in 1908 by Walther Ritz, his "combination principle."

It asserted that adding or subtracting the frequencies of certain[1] known lines in a spectrum will yield more lines.

If there are two lines with the frequencies[2] 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 is 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.

In Sections 2 and 3, I recall the discovery of the various series of lines of the hydrogen spectrum and their systematization by Ritz through his combination principle. In Section 4, I explore how the principle allows a dense network of relations of mutual support among the lines. If the Ritz combination principle is taken as a premise, then 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.

In Section 5, I ask a further evidential question. What supports the Ritz combination principle? Is it merely to be supported as a generalization about observed lines in the spectrum? Which 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

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[1] The word *certain*, meaning "some carefully chosen," indicates an important restriction. The principle does not work for all pairs 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.

excited electron drops or jumps down from a higher to a lower energy state. Each jump leads to an 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, then the frequency $\nu_{13} = \nu_{12} + \nu_{23}$ comes 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 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 that Bohr proposed. 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. Some of the lines that 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 “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 captured the different frequencies present in the light as lines on a photographic plate. The frequency or wavelength of the light was recovered from distance measurements on the plate. An example from Fowler (1922, 8) is shown in Figure 9.1.

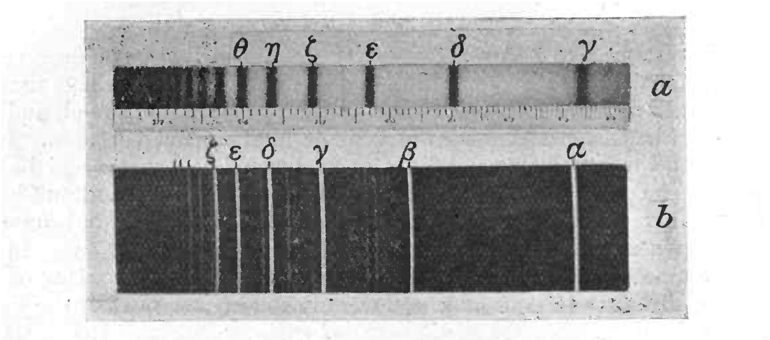

Figure 9.1. A spectrograph of the spectrum of hydrogen

The first formula to embrace some of these lines with enduring success was posited by Balmer ([1885] 1967) for strong lines in the visible spectrum. In modernized form, his formula for the frequencies of lines in the "Balmer series" was

$$\nu(2, m) = R(1/2^2 - 1/m^2) \qquad \text{("Balmer")} \qquad (2)$$

where R is a constant. The different values of $m = 3, 4, 5, \ldots$ gave specific lines in the spectrum shown in Figure 9.1.

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

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

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

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

$$\ldots$$

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

$$\nu(1, m) = R(1/1^2 - 1/m^2) \qquad m = 2, 3, 4, \ldots \qquad \text{("Lyman")} \qquad (1)$$

$$\nu(3, m) = R(1/3^2 - 1/m^2) \qquad m = 4, 5, 6, \ldots \qquad \text{("Paschen")} \qquad (3)$$

$$\nu(4, m) = R(1/4^2 - 1/m^2) \qquad m = 5, 6, 7, \ldots \qquad \text{("Brackett")} \qquad (4)$$

$$\nu(5, m) = R(1/5^2 - 1/m^2) \qquad m = 6, 7, 8, \ldots \qquad \text{("Pfund")} \qquad (5)$$

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. Although 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* that year. Brackett (1922) reported more lines in the Paschen spectrum and the first two members of the newly discovered Brackett series. Pfund (1924) reported the first line of the Pfund 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 spectrum, and the remaining series are in the infrared spectrum. 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 9.1 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, 7) suggests that the celestial lines can be identified as an extension of those in a spectrum found terrestrially if they fall near enough on a definite curve. Figure 9.2 shows such a curve from Fowler (14). The vertical axis plots the *m* of (1), (2), and (3), and the horizontal axis plots frequency.

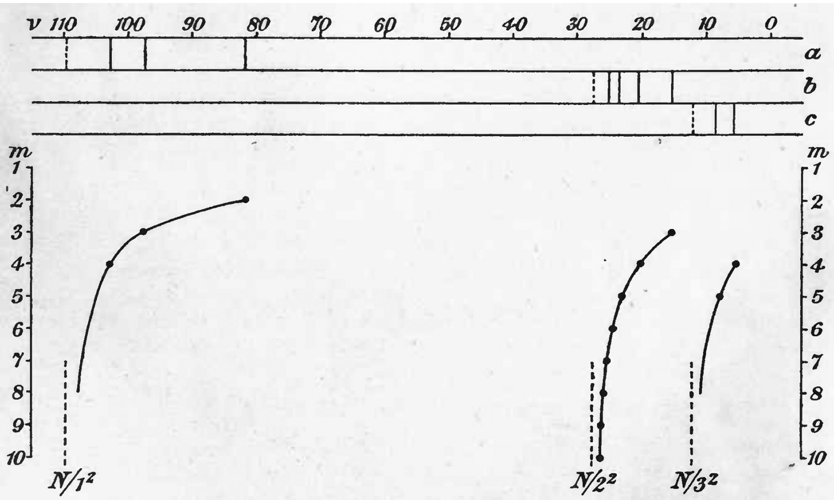

FIG. 2.—THE THREE SERIES OF HYDROGEN.
(*a*) = Lyman series; (*b*) = Balmer series; (*c*) = Ritz-Paschen series.

Figure 9.2. Frequencies of series form definite curves

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

Finally, even when definite series are identified in some spectrum, it is not always clear that all of the series derive from the same substance. Sommerfeld (1923, 207–08) reports two series originally attributed to hydrogen because of the similarity to the Balmer formula (2) for hydrogen. They are

$\nu = R(1/1.5^2 - 1/m^2)$ m = 2, 3, 4, . . . ("Principal series")

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

One outcome of Bohr's atomic theory of 1913 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

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

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

The attribution of the spectra to helium was already made immediately by Bohr (1913b) 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 (1890, 331) had noted that formulae for spectral lines could be simplified if they were written in terms of wave number, the inverse of wavelength.[3] Then the formulae could be expressed as a difference of two terms, as done in (1) to (5) above. This fact enabled Ritz (1908, 523) to propose what he called his “principle of combination” (*Kombinationsprinzip*). 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, 162). Sommerfeld (1923, 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,

---

[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.

[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” (Ritz, 1908, 523).

[5] Sommerfeld’s (1923) report is abridged. In place of “certain newly discovered lines from those known earlier,” Ritz’s (1908, 523) text specifies lines of alkalis then recently discovered by Lenard and others, as well as new elements, in particular helium.

> formulae are formed that allow us to 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 assumed that the series of hydrogen conforms to a general formula

$$\nu(n, m) = R(1/n^2 - 1/m^2) \qquad n = 1, 2, 3, \ldots \quad m = 2, 3, 4, \ldots \tag{6}$$

in which 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 as the expression (6) for each shares a common term. For example, the lines Hα and Hβ can be subtracted in this way since they share a $1/2^2$ term eliminated by the subtraction:

Hβ: $\nu(2, 4) = R(1/2^2 - 1/4^2)$

Hα: $\nu(2, 3) = R(1/2^2 - 1/3^2)$

__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), not an established series in 1908. It led to an immediate affirmation of the correctness of Ritz's proposal. In his paper, Ritz (1908, 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 spectrum.

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____________________

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

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 can be captured in infinite sets. 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:

$$\nu(2, m) = R(1/2^2 - 1/m^2) \quad (m > 4) \text{ Balmer}$$

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

__subtract________________________________

$$\nu(3, m) = R(1/3^2 - 1/m^2) \quad (\mathrm{m} > 4) \text{ Paschen}$$

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), and then the entire Lyman series is recovered by addition from the Balmer series:

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

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

__add____________________________________

$$\nu(1, m) = R(1/1^2 - 1/m^2) \quad (\mathrm{m} > 1) \text{ Lyman}$$

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

$\nu(3, m) = R(1/3^2 - 1/m^2) \quad (m > 3)$ Paschen

H_α: $\nu(2, 3) = R(1/2^2 - 1/3^2)$

__add______________________________

$\nu(2, m) = R(1/2^2 - 1/m^2) \quad (m > 3)$ Balmer

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

Ritz combination principle
Balmer series
____deduce____________
Paschen series

Ritz combination principle
H_α line
Paschen series
____deduce____________
Balmer series

Similar computations realize many more like-structured relations of mutual support that cross over each other, including

the Paschen series supports the Bracket and Pfund series;

the Bracket and Pfund series support the Paschen series;

the Bracket series supports the Pfund series;

the Pfund series supports the Bracket series;

et cetera.

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. Those 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, we take considerable inductive risk 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, as we shall see below, the Ritz combination principle itself needed to be modified by selection rules that prohibit certain lines when we move beyond the hydrogen spectrum.

Although combining deductive relations to yield inductive support overall might appear at first to be 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 that 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. In Chapter 2, "Large-Scale Structure: Four Claims," I reflected on other examples of deductive relations of support combining to provide overall inductive support.

The massively entangled network of relations of mutual support goes well beyond the heuristic guidance of Ritz's original purpose. For that narrower purpose, the most useful are the inferences from readily available lines to those not yet discovered. My 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 previous section all employ the Ritz combination principle as a premise. None of the inferences in that section provides support directly for the Ritz combination principle. Rather, they all merely use it. With the qualification 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 has been unclear what that fact is.

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[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 (1915, 1923, 474).

We might be tempted to say that, when a general formula this simple fits all of the cases at hand, we have a license to infer to it. I developed the familiar difficulty at length in Chapter 6 of *The Material Theory of Induction* (Norton 2021). 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 be as successful as it is only if it is part of a larger regularity whose precise character is not currently known to us. Something like this is 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 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 idea 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.

We can 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, according to II, is

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

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

$$\Omega(n) = R/n^2 \qquad n = 1, 2, 3, \ldots \tag{8}$$

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 9.3. 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 orbit, 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.

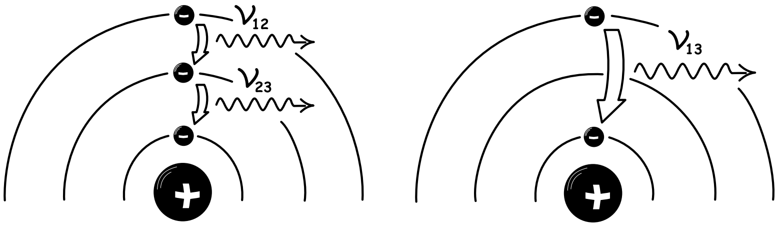

Figure 9.3. Physical basis of the Ritz combination principle

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 $R = 2\pi^2 me^4/h^3$, where m is 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, Bohr reported, was 3.1 x 10^{15}. It matches closely enough to the value that he reported from spectral observations, 3.290 x 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 elaborate versions of his theory, the "old quantum theory," this result was the simplest case of the quantization of action. In the "new quantum theory" that emerged in the mid-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-quoted remark, reported by Bohr's assistant and confidant, Léon Rosenfeld, Bohr remarked that, "as soon as I saw Balmer's formula, the whole thing was immediately clear to me" (quoted in Duncan and Janssen 2019, 14).

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[7] For an early authoritative textbook account, see Sommerfeld (1923, 211–18). Norton (2000) develops these details with special focus on the evidential relations.

The evidential support that the Ritz principle gave to Bohr's emerging theory was widely recognized. Max Born (1935, 85) was forthright about it: "A direct confirmation of this [Bohr's 1913a] theory can be seen in the following fact. . . ." He proceeded to explain in detail and with a figure similar to Figure 9.3 how Ritz's combination principle (identified by this name) is a consequence of the cascade of emissions described in the preceding section.

Sommerfeld (1923), in his early, authoritative volume on the old quantum theory, was similarly forthright. He introduced the Ritz combination principle by name, along with the quotation given above, and then explained its application in detail. He then characterized its significance:

> 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 . . . [equation (7) above], which likewise taught us to regard the frequency of a spectral emission as the difference between two energy-levels. (205–06; Sommerfeld's emphasis)

If we approach the support relations materially, then we can be more precise in just what Ritz's combination principle provides to Bohr's theory. Bohr's posit II above associates spectral lines with electron jumps between stable orbits of different energy. Using the posit as a 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 that this 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 of these 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,[8] $\Omega(n) = R/n^2$.

If we follow Sommerfeld (1923) 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 of the inductive risk is taken in accepting posit II provisionally as a hypothesis.

8. Quantum Theory Confirms the Ritz Combination Principle

In the early years of quantum theory, it was natural to focus on the support that the Ritz combination principle provided for the developing theory. 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 quantum theory developed, became more established, and evolved into the later "new quantum theory," this orientation reversed. A 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 quantum theory, for that support derived from a definite physical ontology and replaced what I called "numerology" above.

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.[9] 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 ones are allowed was governed by "selection rules." The jumps allowed in Bohr's

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[8] 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.

[9] Another example of this type of correction is seen in the previous chapter on Newton and the inverse square law of gravity. Kepler's elliptical orbits of the planets support 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.

original theory were constrained only by energy conservation. Such jumps must also conform to the conservation of angular momentum. The emitting electron must lose just the angular momentum carried off by the emitted radiation.[10] 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 give us direct evidence of only a finite subset of the infinity of lines possible. That finite evidence can support Ritz's combination principle among the lines observed. When we move past hydrogen spectra, this finite evidence can indicate when the principle fails. If, however, we derive the principle from a fully developed quantum theory, then 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 theory of 1913. Sommerfeld (1923) introduced the "azimuthal quantum number" among other numbers. His authoritative treatment of the old quantum theory included an extensive account of a selection rule for atomic spectra. He states it as follows:

> **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*. (266; Sommerfeld's emphasis)

This selection rule was carried over[11] and vindicated by the wave mechanics of the new quantum theory. It was rapidly absorbed into textbook expositions, such as Pauling and Bright (1935, Section 40f).

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

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[10] In the full quantum electrodynamic 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 $h/2\pi$.

[11] 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, 183).

> 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 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. (307–08)

9. Conclusion

The investigation of atomic spectra and their relation to quantum theory illustrates the nonhierarchical structure of relations of evidential support. There is a massively entangled set of 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 nonhierarchical relations of support, for initially the principle provided important evidential support for the newly emerging quantum theory. As that 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 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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