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"The emergence of selection rules and their encounter with group theory, 1913-1927"

Abstract:
In today’s quantum mechanics and quantum field theory, the observable signature of a symmetry is often sought in the form of a selection rule: a missing radiation frequency, a particle that does not decay in another one, a scattering process which fails to take place. The connection between selection rules and symmetries is effected thanks to the mathematical discipline of group theory. In the present paper, I will offer an overview of how the productive synergy between selection rules and group theory came to be. The first half of the work will be devoted to the emergence of the idea of spectroscopic selection rules in the context of the old quantum theory, showing how this notion was linked with an interpretive scheme of theoretical nature which, once combined with group theory, would bear many fruits. In the second part of the paper, I will focus on the actual encounter between selection rules and group theory, and on the person largely responsible for it: Eugene Wigner. I will attempt to reconstruct the path which led Wigner, of all people, to be the agent effecting this connection..

Keywords: selection rules; group theory; Eugene Wigner; symmetry; old quantum theory

1. Introduction: selection rules and group theory in today's physics

In today's quantum mechanics and quantum field theory, "selection rules" indicate which transitions between the states of a given quantum system may or may not occur as an effect of a specific perturbation.[1] In atomic and molecular spectroscopy, selection rules determine which electromagnetic radiation frequencies may be emitted or absorbed by a system as it passes from one energy state to another (Herzberg, 1937, pp. 152-161). In quantum field theory, processes of decay or scattering of elementary particles are conceived as transitions of the quantum field between "particle states" , and selection rules express which transitions may occur as a result of strong or electro-weak interactions (Martin et al., 1992, pp. 211-215).

The existence and the specific patterns of selection rules are usually explained in terms of

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[1] I wish to thank the anonymous referees for their suggestions on how to improve the present paper.

symmetries: when the unperturbed system and the perturbation are both invariant with respect to a given transformation, no transition breaking this invariance may occur (Heine, 1960, pp. 1-12, Martin et al., 1992, pp. 81-131). For example, if an invariance with respect to a mirror transformation is present, no transition can connect states that are mirror images of each other. Symmetry arguments of this kind can also be formulated in terms of conservation laws. In the previous example, one can say that states which are mirror images of each other have opposite parity and that, when mirror symmetry holds, parity has to be conserved.

The connection with symmetries allows to formulate exact predictions for selection rules even in those cases where few details are known about the dynamics of a system. In such cases, results can be obtained with the help of group theory, a branch of mathematics dealing - among other things - with closed sets of transformations (e.g. all rotations, all mirror inversions) and the way in which a given set of objects is changed by them (Heine, 1960). For example, group theory allows to classify the energy states of complex molecules and to derive the relevant selection rules for emission and absorption of radiation (Bunker et al., 1998, pp. 414-473). In quantum field theory, group theory is an important - and sometimes the only - tool for determining the characteristic of particles by studying their decay products (Cheng et al., 1984, pp. 86-124). In principle, the same results could be obtained also by direct computations on a case-by-case basis, but in reality it is hard to imagine how some situations might be mastered without the apparatus of group theory.

In this paper, I will offer an overview of how the productive synergy between selection rules and group theory came to be. The first half of the work will be devoted to the emergence of the notion of spectroscopic selection rules in the context of the old quantum theory. The discussion aims at showing how the notion of selection rules, far from being a purely empirical, descriptive tool, was heavily laden with an interpretive scheme of theoretical nature which, once combined with group theory, would bear many fruits. In the second part of the paper, I will focus on the actual moment in which the encounter between selection rules and group theory took place, and on the person largely responsible for it: Eugene Wigner. Wigner's early work in group theory and quantum mechanics has already been dealt with more than once in secondary literature (Chayut, 2001, Mehra et al. 2000, pp. 472-499, Scholz, 2006). Thus, it is well known that Wigner, when he wrote his first group theory papers in 1926-1927, had a grasp of that discipline much smaller than mathematicians like Hermann Weyl or John von Neumann. In fact, in 1926 Weyl was already reflecting on how to employ group theory to better understand the new quantum mechanics (Scholz, 2006, pp. 461-469). However, it was Wigner who came to the idea of using it for explaining spectroscopic selection rules, while Weyl's reflections took a different - albeit equally productive -

direction. In my analysis, I will attempt to reconstruct the path which led Wigner, of all people, to be the agent effecting the connection between selection rules and group theory.

2. Bohr's frequency condition (1913)

The generalized notion of "selection rules" ("Auswahlregeln") as we know it today was already common in 1926-1927, as shown for example in Friedrich Hund's manual of spectroscopy (Hund, 1927, pp. 17-19, p. 27, p. 60). An exhaustive treatment of the emergence of this notion would require sifting through and discussing a much broader range of sources than is possible in the context of the present paper, and my analysis shall be limited to published papers of the main contributors to the historical development. Nonetheless, I believe that even such a rough sketch of the subject is worth offering since, until now, historical discussion of the old quantum theory has mainly focused on the development of atomic structure, and on the interpretation of specific spectroscopic evidence, such as X-ray spectra or the Zeeman effect (Forman, 1968, 1970, Heilbron, 1964, 1967). With the partial exception of Forman 's (1970) study of Alfred Landé's work on Zeeman spectra, no one has addressed the question of when historical actors started regarding spectroscopic data as providing experimental evidence in the form of "missing" lines. The starting point of my discussion will be Niels Bohr's trilogy of 1913. Even though in this work no notion of selection rules appeared, it contained the two key elements of the scheme discussed in the introduction: quantum states and transitions between them. I will discuss Bohr's paper with particular attention to his attempt at interpreting the empirical formulas for atomic spectra which were known in his time.

Bohr (1913) put forward the innovative notion that atoms could exist in special "stationary states" of given energy in which they did not radiate, even though the laws of classical electrodynamics would have required them to do so.[2] Radiation only occurred in conjunction with a transition of the atom from one energy level (W_1) to another (W_2). As suggested by the discrete structure of atomic spectra, only a discrete set of energy values were possible. Bohr combined classical mechanics with a quantization condition involving Planck's quantum of action h, and proposed an expression for the energy levels of the hydrogen atom which depended on an integer "quantum number" τ:

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[2] Beside primary sources, as a basis for my overview on the development of the old quantum theory, I have used Heilbron, 1964, Hund, 1984, pp. 68-72, Jammer, 1966, pp. 63-156, Mehra et al., 1982, pp. 155-257.

$W_\tau = (2\pi^2 me^4)/(h^2\tau^2)$ (Bohr, 1913a, p.8),[3]

where m and e were the mass and charge of the electron. To determine the radiation frequency v associated to a transition from energy W_{τ_1} to energy W_{τ_2}, Bohr introduced a further hypothesis, which was later referred to as "Bohr's frequency condition":

$W_{\tau_2} - W_{\tau_1} = h\nu$ (Bohr, 1913a, p. 8).

Using this condition together with his expression of the energy levels of the hydrogen atom, Bohr could recover the empirical formula describing the spectrum of that element:

$\nu = (2\pi^2 me^4)/h^3\ (1/(\tau_2)^2 - 1/(\tau_1)^2)$ (Bohr, 1913a, pp. 8-9).

Bohr's model also accounted for the general structure of atomic spectra as expressed by Ritz's "combination principle" (Hund, 1927, pp. 1-5, Hund, 1984, pp. 62-64). According to this principle, which had been developed by Walther Ritz on the basis of formulas by Johannes Robert Rydberg, the radiation frequencies characteristic of each element could be expressed as the difference between two "terms", each of which depended on an integer τ_i:

$\nu = F_r(\tau_1) - F_s(\tau_2)$ (Bohr, 1913a, p.11).

In a first approximation, all functions F had the same form, but differed in the values of some constants appearing in them. By keeping the index τ_1 of the first function fixed and letting τ_2 run through its possible values, one could obtain with good approximation the frequencies corresponding to various observed spectroscopic series. The main series were usually referred to as “sharp”, “principal”, “diffuse” and “fundamental” ones, and the corresponding functions were therefore traditionally labeled with the letters *s, p, d, f* ($F_s(\tau), F_p(\tau), \ldots$) . These labels would later on come to represent different values of atomic angular momentum, but, at this stage, there was no suggestion of such a connection. Bohr's new result consisted in the fact that his model could explain the combination principle by interpreting each function F as representing the energy of a stationary state characterized by a quantum number τ. Within the limits of contemporary spectroscopy, all values of τ seemed to generate a spectral term, so no question of "missing lines" arose. This would only happen when additional quantum numbers were introduced.

3. Sommerfeld's quantum inequalities (1915-1916)

The most successful extension of Bohr's atomic theory was due to Arnold Sommerfeld. Sommerfeld presented his results in 1915 at the *Bayerische Akademie der Wissenschaften,* but I will refer to

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[3] Unless otherwise stated, formulas are quoted in the exact form in which they appear in the original sources.

them in the more elaborate form in which they were published in 1916 (Sommerfeld, 1916a). In Sommerfeld's theory, the stationary states of the hydrogen atom were defined not by one, but by three quantum conditions, each giving rise to a quantum number. In absence of external fields, only two of these quantum numbers were relevant for determining the energy value: the "azimuthal quantum number" n, corresponding to the angular motion of the electron along its (circular or elliptical) orbit, and the "radial quantum number" n', corresponding to variations of the distance between the electron and the nucleus (Sommerfeld, 1916a, pp. 5-20, 28-33).

The azimuthal quantum number is of particular interest for our discussion, because it will come to be regarded as the quantum equivalent of classical angular momentum. By assuming the validity of Bohr's frequency condition, Sommerfeld showed that the two quantum numbers n and n' could be used to explain both the fine structure of hydrogen lines and the complex structure of the spectra as described by the Rydberg-Ritz formula (Sommerfeld, 1916a, pp. 68-80). However, if all possible combinations of the two new quantum numbers were taken into account, one would have obtained many more spectral lines than were actually observed. Without explicitly mentioning this problem, Sommerfeld proposed additional quantum conditions for n and n' which could help solve it: he postulated that a quantum transition $(m, m') \rightarrow (n, n')$ could only occur if both quantum numbers did not increase, and expressed this condition in two "quantum inequalities" ("Quantenungleichungen"):

$m \geq n$ and $m' \geq n'$ (Sommerfeld, 1916a, pp. 23-24).

Sommerfeld's inequalities cannot be regarded as empirical selection rules, since they had rather a theoretical justification than an experimental one. In fact, Sommerfeld immediately anticipated that comparison with spectroscopic data would show that the second inequality was valid without exception ("ausnahmslos"), while the first one was only "roughly correct" ("im groben richtig") (Sommerfeld, 1916a, p. 24). Thus, the quantum inequalities were assumed relevant despite their lack of general empirical validity: they were part of a complex theory, albeit a still sketchy one, and not just rules describing the structure of spectral lines. After the comparison with experiment, Sommerfeld concluded:

> The origin of Rydberg's complete line system remains obscure for us, as well as the spectra of all non-hydrogen-like elements; however, it is in all probability based on some kind of quantum inequality.[4]

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[4] "Der Ursprung der Rydbergschen vollständigen Liniensysteme ist uns zwar, wie die Spektren der wasserstoffunähnlichen Elemente überhaupt, dunkel; er beruht aber höchswahrscheinlich auf einer Art Quantenungleichung" (Sommerfeld, 1916a, p. 80).

Here, the quantum inequalities seemed to have the same status as the quantization conditions. One reason why, in 1916, Sommerfeld saw no need for interpreting all spectra in terms of energy levels and selection rules, was that, as noted by Heilbron (1967, p. 469), he still had doubts about the general validity of Bohr's frequency condition.

> I believe that this use of quantum theory, Bohr's frequency condition, despite its extraordinary effectiveness with respect to the combination principle of spectral lines, is indeed still preliminary.[5]

According to Sommerfeld, the frequency condition failed in the case of the Stark effect (radiation in electric fields) and especially for X-ray spectra, making the combination principle inapplicable (Heilbron, 1967, pp. 468-470, Sommerfeld, 1916a, p. 14, p. 33, 1916b, p. 161). Similar doubts were expressed at this time also by Peter Debye (Debye, 1916). Debye applied the new quantum theory to the Zeeman effect (radiation in magnetic field) using three quantum numbers, and managed to explain the normal Zeeman effect by imposing *ad hoc* conditions on a quantum number. However, he did not think of "selection rules", but instead concluded:

> It seems that, here, real progress can only be obtained by finding a detailed substitute for Bohr's second principle $h\nu$ = energy difference. This is anyway already the main unsolved problem in this field.[6]

Sommerfeld's quantum inequalities were not selection rules, but represented a first step in the emergence of that notion. Paul Sophus Epstein applied Sommerfeld's approach to the theory of the Stark effect (Epstein, 1916). He, too, introduced three quantum numbers - albeit different from Sommerfeld's - and imposed for a transition $m_i \rightarrow n_i$ the quantum inequalities:

$$n_1 \leq m_1,\ n_2 \leq m_2,\ n_3 \leq m_3\,,$$

which he described as providing a "selection principle" ("Auswahlprinzip") (Epstein, 1916, p. 148, p. 150). This is the earliest occurrence of the term "selection" ("Auswahl") that I have run across in spectroscopic context and, as we shall see, the expression "selection rules" can indeed be traced back to it. However, the word " principle" underscores the theoretical character of the notion.

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[5] "Ich glaube, daß diese Verwendung der Quantentheorie, die Bohrsche Frequenzbedingung, trotz ihrer außerordentlichen Leistungsfähigkeit in Hinsicht auf das Kombinationsprinzip der Spektrallinien, doch nur provisorisch ist" (Sommerfeld, 1916a, p. 14).

[6] "Es scheint, daß ein wesentlicher Fortschritt hier nur zu erreichen ist, indem man für den zweiten Bohrschen Ansatz $h\nu$ = Energiedifferenz eine detaillierten Ersatz substituiert, was ja sowieso auf diesem Gebiete als vorderhand ungelöste Aufgabe an der Spitze steht" (Debye, 1916, p. 511).

Later in 1916, Sommerfeld successfully associated a value of the azimuthal quantum number to each of the functions F_i appearing in the Rydberg-Ritz combination formula

$\nu = F_r(\tau_1) - F_s(\tau_2)$.

In this way, the labels traditionally indicating the various spectral series (*s, p, d, f*) came to be associated with the values of the azimuthal quantum number and, later on, with those of (orbital) angular momentum (Sommerfeld, 1916c, pp. 152-166). Sommerfeld's main focus in this work was the theoretical derivation of the structure of the spectral terms (i.e. the functions F) and, as far as possible, of the numerical values of the various constants appearing in them. Spectroscopic evidence also showed that not all functions combined with all others, and one might have expressed this fact by saying that the azimuthal quantum numbers assigned by Sommerfeld could only change by one unit. Yet, in this paper, Sommerfeld did not even mention “missing lines”, let alone formalize them in terms of selection rules.

In conclusion, we can say that, in 1916, Bohr's interpretation of spectral lines was accepted for those cases in which it fitted experimental evidence, but was not generally regarded as a valid scheme for interpreting all observed spectra. In an analogous way, there was no cogent reason to believe that, given any two stationary states, a spectral line corresponding to the transition between them was to be expected, and should be declared "missing" if it failed to appear. Moreover, the empirical formulas through which theorists dealt with spectroscopic evidence could not necessarily be seen as saying something about lines that were not observed. It was only later on that the non-combination of spectroscopic terms attracted the attention of theorists as a possible testing ground for theoretically-based "selection principles".

4. Selection principles, conservation laws and symmetry arguments in the work of Bohr and Rubinowicz (1918)

Between 1916 and 1918, physicist worked both on expanding the Bohr-Sommerfeld model and on improving experiments on spectral frequencies, intensities and polarizations. Despite the efforts of the theoreticians, no viable alternative was found to Bohr's frequency condition. In 1917, Sommerfeld seemed to have set aside his doubts about its validity, and instead focused on the theoretical determination of radiation intensities (Sommerfeld, 1917). In this context, he explicitly addressed the question of the possible theoretical significance of "missing lines" ("ausfallende Linien", Sommerfeld, 1917, pp. 95-100, pp. 106-109). However, he did not describe the missing lines in terms of selection rules, but rather developed further his theory of quantum inequalities, and followed Epstein in calling them a "selection principle" (Sommerfeld, 1917, p. 109).

In 1918, two authors proposed, independently from each other, two theoretical mechanisms capable of accounting for (some) missing lines: Niels Bohr and Wojciech (Adalbert) Rubinowicz, a Polish physicist who had been working in Munich as an assistant to Sommerfeld in the years 1917-1918 (Bohr, 1918a, 1918b , Rubinowicz, 1918a, 1918b). I will expound Rubinowicz's work first, as it is particularly relevant for our story.

The starting point of Rubinowicz' papers on "Bohr's frequency conditions and the conservation of angular momentum" ("Bohrsche Frequenzbedingungen und Erhaltung des Impulsmoments"), part I and II, were the two key assumptions of the Bohr-Sommerfeld model: the existence of a discrete set of stationary states and Bohr's frequency conditions (Rubinowicz, 1918a, p. 441). From these premises, Rubinowicz derived a theoretical "selection principle" ("Auswahlprinzip") which he characterized as a "more exact version" ("exaktere Fassung") of Sommerfeld's quantum inequalities (Rubinowicz, 1918a, p. 441, 1918b, p. 466, p. 473). The new ingredient that allowed him to obtain this result was the assumption that the law of conservation of angular momentum would be valid for the system "Atom + the electromagnetic field emitted by an electron transition" (“Atom + das beim Elektronenübergange ausgestrahlte elektromagnetische Feld” Rubinowicz, 1918a, p. 441). This conservation law was valid in classical electrodynamics and Rubinowicz hoped that it would lead to positive results also in the quantum case. In his reflections, he took it as a "fact" ("Tatsache") that Sommerfeld's azimuthal quantum number n, when multiplied by the constant $h/2\pi$, represented the physical quantity "angular momentum" of an atom (Rubinowicz, 1918a, p. 441). This was a premise which not everyone at that time would have been ready to share, even though it was quite common to speak of the quantization of angular momentum in units $h/2\pi$, an analogy which Bohr himself had suggested as an interpretation "by help of symbols taken from ordinary mechanics" (Bohr, 1913a, p. 15,). Rubinowicz did not state explicitly why angular momentum would be conserved and, since he had no mathematical model for the atom-radiation interaction, his assumption was necessarily based only on a qualitative physical reasoning. This, in turn, could only find an implicit justification in the spherical symmetry of the system which, in the classical case, would have led to angular momentum conservation.[7] However, Rubinowicz did not address this question, but simply assumed angular momentum conservation.

Using classical electromagnetism, Rubinowicz computed the angular momentum of a spherical wave and showed that, when renormalized by $h/2\pi$, it had an absolute value equal or less than one. (Rubinowicz, 1918a, pp. 443-444). This led to a selection principle for the azimuthal quantum number: $\Delta n = 0, \pm 1$ (Rubinowicz, 1918a, pp. 444-445). In testing his result against

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[7] The relationship between symmetries and conservation laws was proven in its most general form by Emmy Noether only in 1918, but was already known since the previous century for specific cases like angular momentum (Kastrup, 1987).

experimental evidence, Rubinowicz did not cite Sommerfeld's (1916c) paper connecting the spectroscopic terms of the Rydberg-Ritz formula to different values of the azimuthal quantum number, but rather followed the reasoning of Sommerfeld (1917), concluding that his own selection principle fared at least as well as Sommerfeld's quantum inequalities, and that it could also explain some features of Zeeman and Stark spectra (Rubinowicz, 1918b, pp. 472-473). Like quantization conditions and quantum inequalities, Rubinowicz's selection principle was primarily a theoretical notion.

Let us now go on to Bohr's paper, in which he once again employed his idea of a correspondence between classical and quantum theory. He wrote:

> In a stationary state of a periodic system, the displacement of the particles in any given direction may always be expressed as a Fourier series of harmonic vibrations:
>
> $\xi = \Sigma\, C_\tau \cos 2\pi\, (\tau\omega t + c_\tau)$ (Bohr, 1918a, p. 15)

Here, ξ was the displacement, t the time, ω the frequency of the classical oscillator (not the radiation frequency ν) and τ an integer number. In classical electrodynamics, this situation would have led to the emission of radiation in all the harmonics $\tau\omega$, with the intensity of each depending on its coefficient C_τ (Bohr, 1918a, p. 15). For example, a harmonic oscillator only presented, and therefore radiated, the term with $\tau=1$. In a quantum system, so Bohr's theory, the intensity of the radiation emitted in a transition with a change of quantum number $\Delta n = \tau$ was proportional to the coefficient C_τ of the τ-th Fourier component of the expansion. Since the angular motion of an electron along its orbit was equivalent to that of a harmonic oscillator, the classical expansion of the displacement with respect to the relevant angular coordinate only had the $m=1$ term, and the azimuthal quantum number could therefore only change by $\Delta n = \pm 1$ (Bohr, 1918a, p. 16, pp. 67-68).[8]

Bohr compared this result with the fine structure of hydrogen-like spectra, but did not mention Sommerfeld's interpretation of the Rydberg-Ritz combination formula in terms of the azimuthal quantum number (Bohr, 1918b, p. 67). It was only in the third part of his study, published in 1922, that he discussed Sommerfeld's classification, and noted the fact that, thanks to it, his own result was shown to be in perfect agreement with experiment (Bohr, 1922, pp. 103-104). This seems to suggest that, in deriving his theory, Bohr had no specific experimental evidence in mind which should be explained.

It was left to Sommerfeld, in the first edition of *Atombau und Spektrallinien* (1919), to

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[8] The two motions were shown to be equivalent by using the adiabatic hypothesis, or "mechanical transformability", as Bohr preferred to call it"(Bohr, 1918a, p. 8).

connect Bohr and Rubinowicz's results to his own interpretation of spectral terms as linked to azimuthal quantum numbers. Sommerfeld showed a very clear preference for the theory of his former assistant Rubinowicz, which he discussed at length (Sommerfeld, 1919, pp. 390-411). Rubinowicz's "selection principle" was for Sommerfeld a means to bridge the gap between classical and quantum physics: Bohr's frequency condition expressed the conservation of energy in a radiation process and thus, "with the same right, we shall now require the conservation of momentum and angular momentum" ("mit demselben Recht werden wir jetzt die Erhaltung des Impulses und des Impulsmomentes fordern", Sommerfeld, 1919, p. 381). Sommerfeld expounded Rubinowicz's theory and, at the end of his discussion, briefly mentioned Bohr's result (Sommerfeld, 1919, pp. 401-403). He admitted that Bohr's condition $\Delta n = \pm 1$ fitted much better the Rydberg-Ritz formula than Rubinowicz's, but made clear the epistemological gap he perceived between a theoretically significant selection principle like Rubinowicz's, on the one side, and Bohr's empirically successful condition, on the other. The latter, he described as a "magic wand" ("Zauberstab") to make quantum theory useful in practice (Sommerfeld, 1919, pp. 406-411, quote from p. 402).

5. From selection principles to selection rules (1918-1924)

As shown in the previous pages, the aim of theoretical physicists like Bohr, Rubinowicz and Sommerfeld in formulating their selection principles had not been primarily to explain spectral structures, but rather to refine their own theories in such a way, as to better understand the inner structure of the atom. It was as a continuation of this program with other means, that those same theoretical physicists eventually came to endorse what Forman (1970) called an *a posteriori* approach: trying to formulate the empirical evidence of the spectra in the theoretical terms of "quantum numbers" and "selection principles", and then using the resulting pattern as a starting point for new theoretical analyses (Forman, 1970, p. 186). In doing so, they combined their own theoretical agendas with an approach that spectroscopists had been successfully applying since the previous century: attempting to combine the frequencies of different spectral lines of the same system with the aim of uncovering regular patterns.

Combining spectral lines to obtain other spectral lines may sound very similar to combining spectral lines into energy levels, but in the early 1920's it was not so. In his study of Landé's path to the interpretation of the anomalous Zeeman effect, Forman (1970) has given a masterful analysis of how difficult it was for the historical actors, Landé in particular, to approach the interpretation of spectra in what we today regard as the most obvious way: decomposing each spectral line into the difference of energies specified by certain quantum numbers. According to Forman, it was Sommerfeld who took the decisive step of abandoning *a priori* attempts at predicting spectra primarily on the basis of theoretical considerations, and opting instead for the *a posteriori* approach of letting empirical evidence guide both the assignment of quantum numbers and the determination of the corresponding selection principles (Forman, 1970, pp. 186-187). In his study of the Zeeman effect, Sommerfeld wrote:

> A general remark which does not say anything new to spectroscopists must be kept in mind in the following pages: the aim of spectroscopy is not so much the knowledge of lines (energy differences), but rather the knowledge of terms (the energy level themselves), in which the frequencies of the lines can be decomposed according to the combination principle.[9]

Thus, the "combination principle" which Ritz had formulated for spectral lines had now come to refer to energy levels. Sommerfeld also claimed that the notion that the combination principle could apply to Zeeman spectra had only been explicitly formulated a few months earlier (Forman, 1970, p. 186, Sommerfeld, 1920, pp. 240-241). Moreover, he assumed that the combinations were subject to "some sort of selection principle" ("eine Art Auswahlprinzip") like Rubinowicz's, which acted on a new, "hidden" ("verborgen") quantum number (Sommerfeld, 1920, pp. 230-231). However, Sommerfeld did not try to extract from experimental evidence the features of this new selection principle, and instead simply extended Rubinowicz's principle to the hidden quantum number (Forman, 1970, pp. 190-194, Sommerfeld, 1920, p. 231). Thus, despite the good premises, no new, empirically-based selection rules made their appearance in this paper.

With time, the exchange between atomic theory and spectroscopy became increasingly close. In a lecture held in Berlin in 1920, Bohr represented the theoretical energy levels of sodium in a diagram, and connected with lines those levels between which transitions could occur (Bohr, 1920). He then used his theory to explain why some transitions were forbidden. Later in the same year, Walter Grotrian used Bohr's diagrammatic method to represent new spectroscopic data on the element neon: using the Rydberg-Ritz formula, he interpreted each line as the difference of two energy levels, plotted the levels as Bohr had done, and noted the regularities in the way in which they did or did not combine with each other into spectral lines (Grotrian, 1920).

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[9] "Eine allgemeine Bemerkung, welche dem spektroskopischen Fachmanne nichts Neues sagt, ist für alles folgende im Auge zu behalten: Das Ziel der Spektroskopie ist nicht so sehr die Kenntniss der Linien (Energiedifferenzen), sondern die Kenntnis der Terme (der Energiestufen selbst), in die sich die Schwingungszahlen der Linien nach dem Kombinationsprinzip zerlegen lassen" (Sommerfeld, 1920, p. 222).

This approach would eventually lead to Landé's interpretation of the anomalous Zeeman spectra. However, Forman (1970) has shown how difficult it was for Landé, when trying to implement Sommerfeld's *a posteriori* approach, to refrain from combining spectral lines into spectral lines, and to focus only on (hypothetical) energy levels (Forman, 1970, pp. 195-207, pp. 221-231). The result of his efforts was an energy scheme involving three quantum numbers, which he referred to as azimuthal quantum number *n* (later: *l),* inner quantum number *k* (later: *j*) and magnetic quantum number *m* (Landé, 1921, p. 241). For each quantum number, he derived "selection rules" ("Auswahlregeln", Landé, 1921, pp. 323-324) which, depending on the circumstances, corresponded to the "selection principle" of Rubinowicz or Bohr (Landé, 1921, pp. 231-232). Thus, in his 1921 paper, Landé used not only the term "selection rules", but also a notion which largely corresponded to the one whose emergence we are investigating, even though Landé still underscored the connection of his selection "rules" to the theoretical selection "principles" of Rubinowicz and Bohr.

From the dialogue between theory and experiment, a powerful heuristic tool had emerged and, from then onward, it would be extensively used to make sense of old and new spectroscopic material in optical and X-ray range, both in absence and in presence of external fields (Hund, 1927, p. 17, pp. 26-27, p. 60, Hund, 1984, pp. 97-101, pp. 114-124)). In this process, selection principles eventually came to be regarded as one of the many empirical "rules" and formulas which spectroscopists had been developing since the late nineteenth century.

6. Selection rules in the new quantum mechanics (1925-1926)

In 1925, the new quantum mechanics began to emerge and, by 1926, some - but not all - selection rules had found a justification in the new formalism. In the present paper, it is not possible for me to discuss these developments in detail and I will limit myself to stating those results which are relevant for our story.

In the matrix mechanics of Werner Heisenberg, Max Born and Pascual Jordan, observable quantities like position *q* and momentum *p* were associated with infinite-dimensional matrices whose rows and columns were labeled by the quantum numbers of the stationary states of the system (Born et al., 1925, Born et al., 1926, Heisenberg, 1925). If *q* was a cartesian coordinate of the electron in an atom, then the square modulus of the matrix elements $q(n, n')$ was regarded as representing the probability of the radiative transition $n \rightarrow n'$ (Born et al., 1925, pp. 866-867, Born et al., 1926, pp. 578-579, Heisenberg, 1925, p. 886). The three authors derived the operator associated with angular momentum, showing that it was quantized to integer or half-integer multiples *j* of $h/2\pi$ and that, in radiation processes, it obeyed the "selection principle" ("Auswahlprinzip") $\Delta j = 0, \pm 1$ (Born et al., 1926, pp. 595-605, quote from p. 600 and p. 602). With the advent of Erwin Schrödinger's quantum mechanics in 1926, the stationary states of atoms and molecules came to be associated with a wave function $\psi(x)$ solving Schrödinger's equation (Jammer, 1966, pp. 255-280). Using perturbation theory, Schrödinger showed how the formula for radiation intensities of matrix mechanics could be understood in wave mechanics as based on the electric dipole of the atom (Schrödinger, 1926, pp. 755-756).

Selection rules had found a place in the new quantum mechanics, but did not seem to be receiving much attention from theoretical physicists. In 1925, Heisenberg, Born and Jordan had showed that matrix mechanics provided a quantum equivalent of the classical conservation of angular momentum, but they had not attempted to connect the relevant selection rules to physical conservation arguments (Born et al., 1926, p. 596). Neither had there been any attempt to derive selection rules from symmetry arguments before the publication of Wigner's group-theoretical work. In early 1926, symmetry considerations entered the new quantum mechanics only as far as a very special kind of symmetry was concerned: the invariance of quantum systems with respect to the permutation of identical particles. Since it was by this path that Wigner eventually came to his result, I will briefly state the problem, before shifting the focus to Wigner's work.

In the early 1920's, the interpretation of the spectra of the various elements in terms of quantum numbers and selection rules had allowed the development of increasingly elaborate theories of inner atomic structure (Hund, 1984, pp. 104-113). On this basis, Wolfgang Pauli formulated his exclusion principle, according to which no two electrons within the same atom could be in the same state. One year later, Werner Heisenberg and Paul Dirac contemporarily but independently showed that Pauli's exclusion principle was a consequence of the invariance of atomic states with respect to permutations of their electrons (Dirac, 1926 pp. 666-670, Heisenberg, 1926).

The new symmetry was formally expressed by requiring that the wave function of a many-electron system should be either symmetric or antisymmetric under permutation of the labels of the electrons. Heisenberg and Dirac argued that no transitions between symmetric and antisymmetric wave function could ever occur, and that in nature only antisymmetric functions were realized, giving rise to Pauli's exclusion principle. Heisenberg also showed how permutation symmetry explained the structure of the helium spectrum and, in a later paper, attempted to provide a rigorous proof of the non-combination principle for states of different symmetry in the case of a generic number of electrons (Heisenberg, 1927). According to Scholz, though, his argumentation was flawed (Scholz, 2006, pp. 443-447). Interesting for us is the fact that, although he had worked at developing selection rules for various kinds of "angular momentum" quantum numbers, Heisenberg did not come to the idea that, beside permutation symmetry, rotation symmetry, too, might be of help in explaining spectral structures. This connection was established by Wigner, to whose early career we now turn.

7. Wigner's experience with the group theory of crystallographers (1923-1925)

Eugene Paul (Jenő Pál) Wigner was born in 1902 in Budapest from a Hungarian Jewish family. Like his childhood friend John von Neumann, he was sent to study in Berlin and, between 1921 and 1925, he earned a diploma and a PhD in chemical engineering at the Technical University.[10] During his study, he worked under the supervision of Michael Polanyi in the laboratories of the newly-founded Kaiser Wilhelm Institute for Fiber Materials, where he also collaborated with Hermann Mark. In 1925, after receiving his PhD, Wigner followed the wishes of his family and went back to Hungary to work as a chemical engineer in a leather factory. In 1926, though, he received an offer to come back to Berlin as an assistant to Karl Weissenberg, a mathematician and crystallographer who had been collaborating with Mark and Polanyi at the Fiber Material Institute since the early 1920's (Polanyi, 1962, Wigner, 1992, pp. 101-103).[11]

Wigner gladly accepted the opportunity offered to him, and in 1926 he was back in Berlin, working as an assistant to Weissenberg. At the time, Weissenberg had already made a decisive contribution to X-ray crystallography in the form of a new method of structure determination, and had also published a series of theoretical articles developing a theory of crystalline solids in which symmetries and group theory played a central role (Buerger, 1990, p. 112, Weissenberg, 1925a-e).

At this point, it is important to raise a question: what was "group theory" in Wigner's time? As has been masterfully shown by Scholz (1989), in the first decades of the twentieth century, the group theory of the crystallographers was different from that of the mathematicians. It was not a case of the one being less advanced than the other: they were two different mathematical tools to be employed for different aims. The theory of symmetry groups had been one of the main tools for theoretical crystallographers since the nineteenth century (Scholz, 1989, pp. 110-153). Shortly before 1900, Evgraph Stephanovič Fedorov and Arthur Schoenflies had independently derived a complete classification of all possible symmetries of a crystal lattice - i.e. of a three-dimensional, discrete, space-filling, periodical structure - the so-called 230 "space groups" (Scholz, 1989, pp.

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[10] The most detailed discussion of this stage of Wigner's career is: (Chayut, 2001). On Wigner's life see (Hargittai, 2006, Wigner, 1992). I wish to thank Prof. Bretislav Friedrich for many fruitful discussions on Wigner's early work.

[11] On Weissenberg's life and research, see the summary and references in Chayut (2001). I am deeply indebted to Prof. H. Gutfreund for leading me to appreciate the significance of Weissenberg's theoretical work.

114-148). At the beginning of the twentieth century, though, the group theory of crystallographers and that of mathematicians started drifting apart, as mathematicians focused on more abstract aspects, such as how to extend the crystallographic classification to lattices of *n* dimensions (Scholz, 1989, pp. 150-153, Wussing, 1969, pp. 182-183). Crystallographers were instead primarily interested in physically relevant symmetries of three-dimensional, discrete, periodical structures. In 1912, experiments by von Laue had shown that X-rays passing through crystals produced regular, geometrical diffraction patterns and, since then, physicists had developed increasingly refined methods to extract from those patterns information about the inner structure of crystal solids (Ewald, 1962). This subject is of particular interest to us, because Wigner's earliest research was in X-ray crystallography, one of the main field of activities of Polanyi, Mark and Weissenberg at the Kaiser Wilhelm Institute for Fiber Materials.

Chayut (2001) has already noted that the origin of Wigner's innovative style in joining quantum mechanics and group theory may be sought in his work in a "peripheral" area of science, namely chemistry and crystallography. While acknowledging the role played by crystallography, and especially by Weissenberg, in shaping Wigner's research interests, Chayut saw only a generic framework alerting Wigner to the power of symmetry and of group theory, and remarked: "Wigner's work is very different from Weissenberg's sketchy theory" (Chayut, 2001, p. 68). In the following pages, I will argue that, contrary to Chayut's claim, there are a number of specific features which connect the use of group theory in crystallography to its employment to explain spectroscopic data. Moreover, I will try to show that Weissenberg's theory of crystalline matter, while relying on the group theory of the crystallographers and not on the latest innovations of the mathematicians, yet focused on the kind of symmetry arguments which would be relevant for Wigner's work. In my discussion, I do not aim at proving any "influences", but only wish to contribute to making plausible why it was Wigner, and not for example Hermann Weyl, who first asked whether group theory might help explain spectroscopic selection rules. I will first shortly discuss the role of group theory in X-ray crystallography and then, in the next section, I will focus on Weissenberg's theory of crystalline matter.

To earn his diploma in chemical engineering, Wigner had studied the structure of rhombic sulfur with X-ray diffraction under the supervision of Hermann Mark (Mark/Wigner, 1924, Wigner, 1992, pp. 80-81). When extracting information about the inner structure of a crystal from its X-ray diffraction patterns, a key step is determining to which of the 230 space groups the crystal belongs (Ewald (1962), pp. 102-116). As P.P. Ewald explained, "This [...] does not require a quantitative discussion of intensities [in the diffraction pattern], but only the observation of certain zero intensities occurring systematically, the '*absences*'." (Ewald, 1962, p.107) Thus, inner symmetry became visible in form of an "absence" ("Auslöschung") of radiation, and this method was employed also by Wigner and Mark in their work on rhombic sulphur (Mark/Wigner, 1924, 410-411). More in general, X-ray crystallography was based on the notion that the group-theoretical properties of crystal lattices determined the intensity patterns of diffracted X-ray radiation. By 1928, the laws governing the structure of these patterns were referred to as "selection rules" ("Auswahlregeln"), although this was a different notion from the one which we had earlier emerged in spectroscopy. (Brandenberger et al., 1928, especially p. 303). A further contact point between the use of group theory in crystallography and its later employment in quantum spectroscopy was the focus on linear transformation of discrete sets of objects. Finally, mirror inversions, which are hardly relevant in classical mechanics, play a very important role both in crystallography and in quantum theory. As we shall see presently, the first one to note their relevance for quantum system was Wigner.

8. Group theory in Karl Weissenberg's research program

The story of how Wigner learned about group theory by trying to solve problems posed to him by Weissenberg has often been told: Weissenberg assigned Wigner problems in group theory, to solve which Wigner, with the help of von Neumann, learned and applied the newest result of the mathematicians (Chayut, 2001, pp. 57-58, pp. 68-72, Scholz, 2006, p. 447, Wigner, 1992, pp. 104-106). According to Wigner, Weissenberg did not really understand these abstract solutions, but this is not what interests us here. I will instead try to fill in some background to this story as far as Weissenberg's theory of matter structure is concerned, because I wish to make some light on the kind of problems which Weissenberg asked Wigner to solve.

Chayut's (2001) judgment that Weissenberg's theory was "sketchy" is based on the general introductory remarks made by Weissenberg in the very first paper he published on the subject (Chayut, 2001, p. 67; Weissenberg, 1925a, pp. 406-414). In those pages, the author expounded his idea that the formal transformation properties of physical objects with respect to a change of system of reference provided information on the physical behavior of the system. As noted by Chayut, this approach is similar to Wigner's later research program, but too vague to be regarded as a significant element in shaping his physical-mathematical techniques. The gist of Weissenberg's theory, though, is a proposal for a classification of crystalline structures which Weissenberg regarded as physically highly significant addition (“Zusatz”) to the 230 space groups (Weissenberg, 1925a-e, quote from Weissenberg, 1925d, p. 14). A witness to the non-triviality of Weissenberg's work was the expert in crystallographic group theory Schoenflies who, in 1926, wrote a report "On the most recent crystallographic works of K. Weissenberg", with the aim of improving the reception of what he considered a promising theory by expounding it in a more accessible terms (Schoenflies, 1926). The key notion in Weissenberg's classification of crystal structures was that of an "island" ("Insel"), later called a "particle group" ("Partikelgruppe") (Weissenberg, 1925c, p. 433, Weissenberg, 1925e, p. 57). Weissenberg's island was a set of particles in a crystal structure which possessed the following property: when the crystal was subjected to a transformation which left it invariant as a whole (i.e. a transformation belonging to some subgroup of the crystal's space group), then, either the particles of the island transformed into each other, or the whole island was transformed into another, equivalent, island.

Purely on the basis of symmetry considerations, Weissenberg was able to show that islands displayed a very important physical property: each particle in an island was always more strongly bound to the other particles in the same island than to any other particle in the crystal (Schoenflies, 1926, pp. 217-219, Weissenberg, 1925c, pp. 445-446, Weissenberg, 1925e, pp. 95-96). Weissenberg believed that a classification of crystal structures according to different kinds of islands would be more effective for physical and chemical research than the 230 space groups, and claimed to have given such a complete systematic (Weissenberg, 1926e, p. 102). According to Schoenflies' summary, the task Weissenberg had set himself amounted to providing an overview of all subgroups of each of the 230 space groups (Schoenflies, 1926, p. 206). At that time, the theory of subgroups of space groups was not well developed, and its beginning is usually associated with a paper published in 1929 by Carl Hermann (Aroyo et al., 2006, p. 3, Hermann, 1929, Senechal, 1990, p. 51). In that paper, Hermann referred to Weissenberg's work as the most recent and complete classification of a part of the subgroups of space groups (Hermann, 1929, p. 534). Thus, in 1926, to bring forward his research program, Weissenberg had to cope with a kind of group-theoretical problems which, until then, had not been of much interest to crystallographer: how to classify regular point systems by decomposing them into subsystems transforming into each other under a symmetry leaving invariant the system as a whole. It was in all probability this kind of problems which Weissenberg expected Wigner to solve for him, and it was in this way that Wigner, thanks to von Neumann's advice, discovered the tools which mathematicians had developed to deal with such questions: the theory of group representations. Wigner never published any results of the group-theoretical computations undertaken when working for Weissenberg, but his recollections on the subject are quite vivid and, even though they have often been cited, it is worth quoting them here once more:

> My boss, Dr. Weissenberg, also did fine work. He wanted to learn why atoms hold positions in the crystal lattice corresponding to symmetry axes and planes. He told me to read up on group theory, try to resolve this questions, and then report to him. "Here is Weber's *Algebra*," he would say. "Read it and then prove to me that stable positions in crystals are symmetry points."[12]
>
> I spent about three weeks reading Weber's book and I found a crude solution. Though Weissenberg was a fine crystallographer, he hardly followed my answer. He told me it was not general enough and sent me back to refine it.
>
> This grew into a routine. Weissenberg gave me what seemed to be simple problems to solve. They *were* simple to solve in an elementary way. But then Weissenberg would look into my answers and ask for more elegant ones. Though I often doubted I could do better, the search for a suitable elegance led me increasingly deeper into group theory.
>
> [...] In group theory, Weissenberg gave me one highly exasperating problem. I worked diligently at it and got exactly nowhere. So I turned for help to my childhood friend from Budapest, Jancsi von Neumann. [...] Jancsi considered my group theory problem for about half an hour's time. Then he said, "Jenö, this involves representation theory".
>
> Jancsi gave me a reprint of a decisive 1905 [sic] article by Frobenius and Schur. [...] This reprint was my primary introduction to representation theory, and I was charmed by its beauty and clarity. I saved the article for many years out of a certain piety that these things create. (Wigner, 1992, p. 104-107)

In the writings he published in 1926-1927, Wigner did not cite any joint paper by Georg Ferdinand Frobenius and Issai Schur. However, Frobenius and Schur only wrote two papers together, both published in the 1906 (!) issue of the Proceedings of the *Königlich Preussischen Akademie der Wissenschaften*.[13] Both papers dealt with the theory of group representations, the first one was "On the real representations of finite groups", while the second one had the title "On the equivalence of groups of linear substitutions" (Frobenius and Schur, 1906a and 1906b) and was cited by Weyl in his textbook on "Group theory and quantum mechanics" (Weyl, 1928, p. 126 and p. 277). It remains open to discussion which of the two papers Wigner preserved with such piety, although the first one had a more introductive character.

It would lead us too far, if we tried to explore specific hypotheses on how Wigner's problem

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[12] Heinrich Weber's "Lehrbuch der Algebra" was at the time the standard textbook for algebra and group theory in German language (Wussing, 1969, p. 184). Weber introduced group theory in the second volume of his textbook (Weber, 2nd ed. 1899), but he did not discuss the theory of group representations, which was developed between the last decades of the nineteenth century and the early twentieth century.

[13] The papers of Frobenius and Schur are collected respectively in: Frobenius, 1968; Schur, 1973 (on Schur’s joint papers with Frobenius see the remark in Schur, 1973, vol. 1, p. IV).

might have looked like and how the Frobenius/Schur paper might have helped him solve it. However, I have gone into some detail in discussing Weissenberg's research beyond Wigner's scanty reference to "symmetry axes and planes" and "group theory", as I believe that it provides important elements to understand the origin of Wigner's group-theoretical arguments. Although it is true that Wigner only learnt about representation theory from von Neumann, this is still only half of the story: the other, essential half of the historical and epistemological picture is that Wigner came to know representation theory along a path that made him aware of a specific kind of questions that could be asked and answered with its help. As we shall see in the next section, there were remarkable structural similarities between the kind of problems Wigner tackled when working with Weissenberg and his later use of group theory in atomic spectroscopy.

9. Wigner's use of group theory in explaining selection rules as a signature of symmetry (1926-1927)

In section 5 above, we left Heisenberg and Dirac claiming - but not proving - the impossibility of transitions between quantum states described by wave functions with different transformation properties with respect to permutations of identical particles. To prove this claim, as Dirac and Heisenberg noted, one would have had to classify wave functions according to how they behaved under permutation: a trivial task for the case of two particles, but already complex for $n=3$. Given Wigner's background as discussed in the previous sections, it is hardly surprising that he realized how the problem of classifying the solutions of Schrödinger's equation according to their permutation symmetry properties could be solved by group-theoretical methods, in particular representation theory. Wigner immediately set himself to work and, on November 12th, submitted to *Zeitschrift für Physik* the first part of a study on "Non-combining terms in the new quantum theory", in which an explicit computation for $n=3$ was given and a general solution was announced (Wigner, 1927a). The second part of the study was submitted only two weeks later, and it contained a rigorous - although relatively obscure - group-theoretical proof of Dirac's and Heisenberg's claim (Wigner, 1927b).

At this point, one might say that it "only" remained for Wigner to generalize his approach from permutations to generic linear transformations. Yet, this further step was at the time anything but obvious, and the fact that Wigner took it represented an innovative breakthrough setting in motion the synergy between selection rules and group theory. A generalization from permutations to other linear transformation was at the time not obvious because permutations seemed to stand on a different epistemological footing than other symmetries. Pauli's exclusion principle was regarded as expressing a significant, if obscure, physical law, and the newly established connection between that principle and permutation symmetry was therefore regarded as a decisive, unique step towards understanding the non-classical features of quantum systems. As for rotation symmetry and symmetry arguments in general, however, there was no reason to consider them as a promising starting point for gaining a deeper understanding of quantum mechanics. Moreover, as we have seen, selection rules were by this time considered as rather uninteresting from the theoretical point of view.

Wigner, however, knew that, in crystallography, group-theoretical properties of linear transformations allowed to predict the regular diffraction patterns on the basis of the transformation properties of a given crystal lattice. While working on quantum permutations, he became aware that the situation in quantum mechanics was in principle very similar, due to the linearity of Schrödinger's equation. The considerations which had been valid for permutations of particle positions x_i could be extended to rotations and mirror inversions, and Wigner did so in his next paper: "Some conclusions from Schrödinger's theory for the structure of [spectral] terms" (Wigner, 1927c). The paper began with the words:

> The simple form of Schrödinger's differential equation allows the application of some methods of groups, more precisely, of the theory of representations. [...] In this way, it is possible to explain a large part of our qualitative spectroscopic experience.[14]

Wigner stated clearly his aim: explaining spectroscopic evidence, and particularly the selection rules for azimuthal and magnetic quantum numbers, without however dealing with the "spinning electron" (Wigner, 1927c, pp. 624-625, p. 643, pp. 648-694). He subdivided his paper into a "general" and a "special" part and, in the first one, he set the group-theoretical stage for the later computations. Given a generic function $\psi(x_1, x_2, ...x_n)$, he assumed its variables x_i to undergo a generic linear transformation into the new variables $x_i' = R(x_i)$. The function $\psi(x_1, x_2, ...x_n)$ would then transform into $\psi(R(x_1, x_2, ...x_n))$. If the function $\psi(x_1, x_2, ...x_n)$ was a solution of Schrödinger's eigenvalue equation for energy ε (i.e. $H(\psi, \varepsilon) = 0$), and if also $\psi(R(x_1, x_2, ...x_n))$ turned out to be a solution of the same equation, then one could state that the transformation R was contained in the symmetry group of the differential equation $H(\psi, \varepsilon) = 0$ (Wigner, 1927c, p. 626). Thus, Wigner associated with each type of Schrödinger equation a symmetry group, just like in

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[14] "Die einfache Gestalt der Schrödingerschen Differentialgleichung gestattet die Anwendung einiger Methoden der Gruppen , genauer gesagt, der Darstellungstheorie. [...] Es ist auf dieser Weise möglich, einen großen Teil unserer qualitativen spektroskopischen Erfahrung zu erklären" (Wigner, 1927c, p. 624).

crystallography each crystal lattice was linked with a space group.

Since the Schrödinger equation was itself linear, under a linear transformation its solutions became linear combinations of each other. In group theory, Wigner explained, the coefficients of such linear combinations were called "representations" of the relevant group (Wigner, 1927c, p. 627). He then introduced the notion of "irreducible representations", which I shall not discuss here further, and showed how one could classify the solutions of a given Schrödinger equation in terms of the irreducible representations of the symmetry group of the equation (Scholz, 2006, pp. 448-451, Wigner, 1927c, p. 629). Each complete, linearly independent set of solutions corresponding to the same energy transformed according to one of the irreducible representations of the symmetry group, so that its members only combined with each other under any transformation leaving the Schrödinger equation invariant.

Wigner offered a first example of how such a group-theoretical classification would be physically significant: the case of a system subjected to a perturbation which reduced its symmetry to a subgroup of the original group. (Wigner, 1927c, pp. 632-633) For example, an external field introduced a privileged direction and thus broke spherical invariance, leaving a residual rotation symmetry with respect to its direction. As a consequence, each set of same-energy-solutions of the unperturbed equations split into subsets of different energy, each of which transformed according to an irreducible representation of the residual symmetry group. One could estimate the energy splitting by expressing the representations of the original group in terms of those of the residual subgroups (Wigner, 1927c, p. 633). It is not difficult to see how similar this reasoning was to the kind of problems that Wigner had earlier tackled and eventually solved with the help of representation theory, when he was working with Weissenberg. It is in this sense that, earlier on, I claimed that the path taken by Wigner on his way to learning representation theory was just as important as the fact that he eventually learned it: that specific path made him aware of the potential physical applications of the theory. This use of representation theory played a key role in Wigner's paper, which devoted much space to spectra in electric, magnetic and crossed electric and magnetic fields (Wigner, 1927c, pp. 643-652).

In the "special" part of the paper, Wigner began by listing all symmetries which came into questions as possible symmetry groups of the Schrödinger equation in different physical contexts: permutations, rotations in three-dimensional space - with or without a privileged axis - and mirror inversions. As I have already noted, Wigner's attention to mirror transformations can be connected to his experience in crystallography, where they were an essential component of space groups. A summary of Wigner's results in modern terms has already been given by various authors (Mehra et al., 2000, pp. 492-496, Scholz, 2006). I will focus on some peculiarities of Wigner's computations which are particularly revealing of his style of thinking. Since all computations were based on the same formula, I will only discuss those valid in absence of external field.

If no external force is acting on a system, Wigner said, the symmetry group *R* of the relevant Schrödinger equation will include all rotations leaving fixed the origin of the coordinate system, as well as all mirror transformations with respect to the same point. Given any integer *l* - which is here purely a group-theoretical parameter - there exist two irreducible representation of the group *R*, each containing *2l+1* linearly independent elements. One representation corresponds to proper rotations, the other to improper ones, which include a mirror inversion (Wigner, 1927c, p. 636). Wigner computed explicitly the coefficients of the representations of *R* for a generic value of *l* and, as he himself noted in later a correction to the paper, committed a serious error, forgetting some terms in the expressions (Wigner, 1927c, pp. 638-639, Wigner, 1927d). Without noticing his mistake, Wigner went on to try and derive the selection rule for the group-theoretical parameter *l*, which he already planned to identify with the azimuthal quantum number (Wigner, 1927c, pp. 641-643). To describe the intensity of a radiation process, he used the absolute value of the usual dipole formula from wave mechanics, which he wrote in the (rather sketchy) form:

$\left| \int x \ \psi_i \psi_k \ \right|$ (Wigner, 1927c, p. 641).

The variable *x* represented here one coordinate of any of the electrons and, following Heisenberg, Wigner assumed it to be proportional to the corresponding component of the electric dipole moment ("lineare Polarisation") due to that electron (Wigner, 1927c, p. 641-642). The indexes *i* and *k* corresponded to two different values of the group-theoretical parameter *l* and Wigner's aim was to show that, unless *i* and *k* satisfied specific conditions, the integral would vanish, leading to a selection rule assigning intensity zero to (i.e. theoretically forbidding) that transition. For clarity, it may be useful to write down the integral in a more explicit form:

$\int x_1 \ \psi_i(x_1, ..., x_n) \ \psi_k(x_1, ..., x_n) \ dx_1 ...dx_n.$

Here, I have chosen as x the variable x_1: as Wigner noted, the value of the integral is the same for any choice of x_i and need therefore be computed only once (Wigner, 1927c, p. 842). The straightforward group-theoretical approach to solve this problem would have been to consider the transformation properties of x_1 under rotations, and argue from there at an abstract group-theoretical level.[15] Wigner, instead, took another path: he used the explicit form of the transformation coefficients which he had previously computed to formulate a very convoluted argument in which

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[15] The full-fledged group-theoretical argument was given first by Weyl in his textbook "Gruppentheorie und Quantenmechanik" (Weyl, 1928, pp. 157-158). The proof hinges on the fact that the integral is different from zero only if the group-theoretical product of the two representations corresponding respectively to ψ_i and ψ_k contains at least one element which transforms like x, i.e. like the component of a vector. Such a term exists only if $i - k = 0$ or ± 1 .

some of the variables x_i were expressed in terms of the parameters defining a generic rotation (Wigner, 1927c, pp. 641-644). Wigner's argument exploited the fact that the dependence of the functions ψ_i and ψ_k from the variables x_i was subject to specific restrictions due to their group-theoretical transformation properties. By taking into account these restrictions when computing the dipole integral, one could see that it would be different from zero only for certain values of i and k. The reasoning, which I shall not discuss here in detail, was carried out by visually representing and manipulating the n variables x_i as n points in three-dimensional space, and in my opinion showed how well Wigner could cope with such complex geometrical problems, partly thanks to his own talent and partly to his experience in X-ray crystallography. However, this method of computation is also evidence that, at this stage, Wigner still had a relatively small grasp of the power of the abstract group theory of the mathematicians.

In the end, using his (wrong) coefficients, Wigner could prove that the integral was different from zero only for transitions $i \rightarrow k$ where $i - k = \Delta l = \pm 1$. As we have seen above, this result fitted spectroscopic evidence on the azimuthal quantum number, and Wigner remarked that it constituted an improvement with respect to the theoretical computations of Heisenberg, Born and Jordan, because it excluded transitions with $\Delta l = 0$ (Wigner, 1927c, p. 641, note 2). This fact, he said, confirmed the identification of his group-theoretical parameter l with the azimuthal quantum number usually indicated by the same letter, which was known to obey the selection rule $\Delta l = \pm 1$. In fact, though, the absence of $\Delta l = 0$ transitions was only due to Wigner's above-mentioned computational mistake: by adding the missing terms, he would later obtain the correct result $\Delta l = 0, \pm 1$, in accordance with the fact that, since spin is not taken into account, the group-theoretical parameter l must be regarded as corresponding to the quantum number representing total angular momentum, i.e. j, whose selection rule is $\Delta j = 0, \pm 1$ (Wigner, 1927d).

Wigner's error suggests that, while computing the representation coefficients, he already had his aim in mind: reproducing the selection rules $\Delta l = \pm 1$. Thus, when he (erroneously) obtained this result, he felt satisfied that it was correct. Wigner used group theory - and mathematics in general - as an effective tool to connect to experimental evidence, and not as a means of exploring and refining the formal structures of quantum mechanics, as mathematicians like Weyl or von Neumann would do. It was this peculiar approach which led Wigner to take an interest in the "empirical" selection rules and connect them with the structures of group theory. In this way, a very fruitful heuristic method which had emerged in the context of the old quantum theory could be taken over into the new quantum mechanics. Thus, after having passed from the status of a theoretical notion to that of a purely empirical one, spectroscopic selection rules had now found a new connection to mathematical physics. Even though the selection rules of empirical spectroscopy were in principle something distinct from those of group-theoretical analysis, the first ones could be regarded as the observable signature of the second ones - just like the "absences" and "selection rules" of X-ray crystallography were the visible evidence of inner crystal symmetries. I would like to suggest that it was precisely this ambiguity that allowed the notion of "selection rules" to develop into a productive means of connecting theory and experiment.

10. Epilogue: Selection rules, conservations laws and symmetry arguments

In 1913, Bohr had introduced the notions of stationary states and quantum transitions, as well as the frequency conditions linking the two. Subsequently, Bohr's model had been expanded into a theory which led to the interpretation of some spectra in terms of "missing lines". To account for these, physicists proposed theoretically-based "selection principles". Eventually, this theoretical scheme to fit spectroscopic data to a theory came to work also in the opposite direction: having theoretically assumed that spectra could be interpreted in terms of quantum numbers and selection principles, one could use them to formulate hypotheses on how those quantum numbers and selection principles should look like. Thanks to group theory, this deceptively simple interpretive scheme could be taken over in expanded form into quantum mechanics, and eventually also in quantum field theory. The encounter between spectroscopic selection rules and group theory in atomic spectroscopy provided the template for a new kind of symmetry argument, in which the observable signature of a (known or unknown) symmetry is sought in the form of a "selection rule": a missing radiation frequency, decay or scattering product. This heuristic scheme relies on two general theoretical premises - quantum states and perturbative transitions - and can be used to connect theory and experiment starting from both directions. One can employ it to classify experimental data, individuating regularities and interpreting them in terms of group representations. On the other hand, one can tentatively assume the validity of some symmetries, formulate predictions in terms of quantum states and allowed transitions, and compare them with experiment.

Moreover, Wigner himself showed how this kind of argument can be linked to the quantum equivalent of the classical connection between symmetries and conservation laws. In early 1928, he published a short study "On conservation laws in quantum mechanics" in which the connection between conservation laws and symmetries in quantum system was explicitly stated (Wigner, 1928). This relation had been known already in matrix mechanics, but, once again, Wigner was the first one to draw attention to its wide-ranging physical implications, as for example the possibility of defining a new, purely quantum-theoretical conserved quantity, later known as "parity" (Wigner, 1928, p. 387). Thanks to the encounter of selection rules and group theory, many other new physical quantities would follow later on, as for example baryon number, strangeness, charm or beauty (Michel, 1989).

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