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THEN & NOW

The discovery of the Stark effect and its early theoretical explanations

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1 Woldemar Voigt

After Pieter Zeeman had discovered in the fall of 1896 that an external magnetic field causes spectral lines to split in several components,[1] the logical next step was to investigate whether an electric field would also have an influence on the shape or frequency of spectral lines. The first to publish the results of a systematic theoretical investigation of the possible effect of electric fields was the Göttingen physicist Woldemar Voigt [2]. Voigt used a modified version of the purely classical model for the explanation of spectral lines that was used for the description of magneto-optic effects. In this model, devised by Hendrik Lorentz, atoms contain electrons that are bound to a center with a harmonic force. In Voigt's version these forces are no longer purely harmonic, but contain an anharmonic part as well. This anharmonic component was needed because an electric field has no influence on the frequency of a harmonically vibrating charged particle, as can be easily seen from its equation of motion. On the basis of his model and estimates (based on experimental results for electric double refraction) for the value of the anharmonic force constant for various substances, Voigt came to the conclusion that the effect of an electric field would be far too small to be observable.

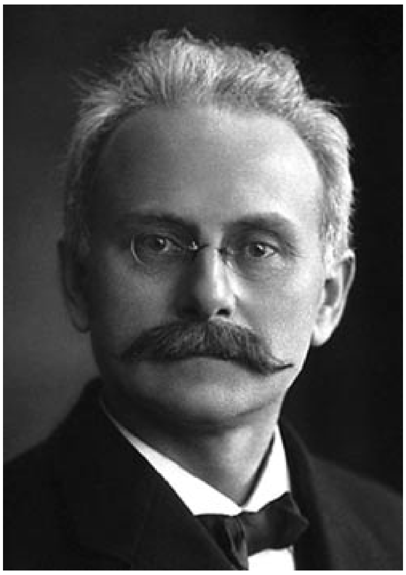

Figure 1 Johannes Stark (1874–1957). Photo: A. B. Lagrelius & Westphal, Stockholm.

2 Johannes Stark

In spite of Voigt's negative theoretical result, the Göttingen physicist Johannes Stark (Fig. 1) decided in 1906 that it would be worthwhile to investigate the matter experimentally. In particular after he had been shown an experimental setup by Voigt that had failed to detect an electric analogon of the Zeeman effect in the spectrum of sodium, Stark became convinced, as he recounts in his autobiographical notes [3], that one should look at light atoms like hydrogen and helium in very strong electric fields and that canal rays would provide the right experimental conditions.

At the time, Stark was becoming known through his experiments on the Doppler effect in the spectral lines emitted by canal rays. These experiments had started when Stark was still in Göttingen, and continued after he moved to Hannover in 1906 and then to Aachen in 1909. They lent strong support to the idea that canal rays consisted of fast-moving positively charged ionised atoms. (The work on the Doppler effect in canal rays, together with the discovery of the Stark effect would earn Stark a Nobel Prize in 1919.) Stark also tried to make a connection between his experimental results and Max Planck's still controversial quantum hypothesis.

Johannes Stark was a gifted experimenter, but also a difficult, abrasive personality, who easily took offense. Among his colleagues he acquired the reputation of someone who could react unnecessarily aggressively to imagined slights or injustices. In a typical example, after Hendrik Lorentz had received a very angry letter by Stark—the letter dealt with a World War I related public statement drawn up by Lorentz—Lorentz commented to his Leiden successor Paul Ehrenfest: "Knowing him, we won't take the matter too seriously."

[1] See [1] for an account of Zeeman's discovery.

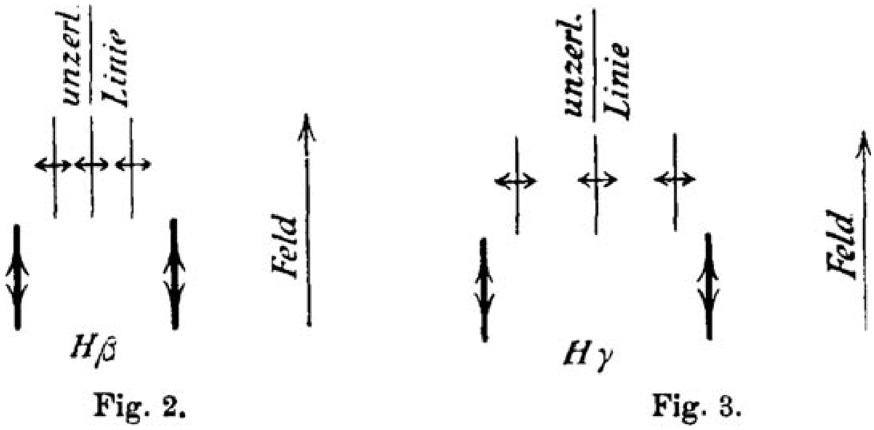

Figure 2 The splitting of the two hydrogen lines as illustrated in Stark's first paper (Ref. [6], p. 972). The arrows indicate the polarization direction.

While still in Göttingen Stark began preparing an experiment to observe the influence of an electric field on spectral lines. He continued working on it in later years, but only in the fall of 1913, at the University of Aachen, was he successful. Using a modified discharge tube in which canal rays moved through a strong electric field, he found that the hydrogen lines H_β and H_γ were split in five components when observed in the direction perpendicular to the field, and in three components in the parallel direction. He also registered a less clear splitting in the stronger lines of helium. Stark's choice for hydrogen and helium was fortunate, because the effect is most prominent for light elements. Stark reported on his discovery in a letter to *Nature* [4], and in two more detailed papers, [5] (also published as [6]) and [7] (Fig. 2). Further experiments and publications followed. The new phenomenon discovered by Stark became soon known as the Stark effect.

3 Stark or Lo Surdo?

As soon as the Italian physicist Antonino Lo Surdo had read Stark's announcement in *Nature* he realized that he had observed the same phenomenon while doing experiments on the Doppler effect in a certain type of positive rays, without knowing, however, that the spectral line splitting that he had seen was caused by an external electric field. So, whereas Stark discovered an effect that he was actively looking for, Lo Surdo's discovery has more of a serendipitous character. It is perhaps for this reason that the name Stark-Lo Surdo effect, proposed by one of Lo Surdo's Italian colleagues, has never really taken root. Not unexpectedly, given his combative personality, Stark strongly rejected the suggestion that Lo Surdo had co-discovered the effect.[2]

4 Theoretical explanations

It is interesting to look a little more closely at the various consecutive theoretical explanations that were offered after Stark had announced his discovery, because they very clearly reflect the development of the ideas about how to construct a valid quantum theory.

After a first unsuccessful attempt by Emil Warburg [9], which will be skipped here, important theoretical papers on the Stark effect were published by Niels Bohr, Paul Epstein, and Karl Schwarzschild. In the following these will be discussed in some detail.

4.1 Niels Bohr

Niels Bohr first learned about Stark's results through the paper in *Nature* [4]. He immediately realized that the Stark effect would provide an excellent opportunity to apply his recent (1913) theory of atomic spectra and wrote to Stark to ask him for a reprint of his publication [5].[3] In [11], a paper that appeared in the spring of 1914, Bohr presented his ideas on the Stark effect. He claimed that an electric field would deform the circular orbits of his atomic model in such a way that only two rectilinear motions through the nucleus remained, parallel and antiparallel to the field. He also presented a derivation which showed that the frequency shift due to the electric field $\mathcal{E}$ of an atomic transition between the states characterized by the quantum numbers n_1 and n_2 (with n the quantum number from his theory of atomic spectra), was proportional to $\mathcal{E}$ and to the difference $n_1^2 - n_2^2$. But this result could not satisfactorily explain Stark's results.

4.2 Paul Epstein

Two years after Bohr's publication, both the Munich physicist Paul Epstein and the Potsdam astronomer

[2] See [8] for more on Lo Surdo's work and Stark's response to it.

[3] The letter is reproduced in [10], p. 606.

Karl Schwarzschild presented detailed quantum-theoretical calculations of the effect of an external electric field on the spectral lines of hydrogen [12, 13]. These authors used similar methods; I will only discuss Epstein's work, because it is slightly more general than Schwarzschild's. Epstein uses the quantization methods developed by Arnold Sommerfeld, in whose group at the University of Munich he was working. Basically, Sommerfeld's method is a hybrid one: the periodic motion of bound electrons in an atom is first described purely classically, and then quantized with the help of so-called quantum conditions. These conditions have the general form

$$\oint p\,dq = nh, \tag{1}$$

where q is a generalized coordinate and p its conjugate momentum, h Planck's constant and n an integer (quantum number). The integral is taken over one complete closed trajectory in (p, q)-space. For the case of the Stark effect Epstein first writes down the expression for the total potential energy U of an electron in the field of a nucleus of charge eZ, in the presence of a constant electric field $\mathcal{E}$ in the direction of the x-axis:

$$U = -\frac{Ze^2}{r} - ex\mathcal{E} \tag{2}$$

He then changes from cartesian coordinates to parabolic coordinates, and proceeds to integrate the Hamilton equations for the electron, using the traditional methods of Hamilton-Jacobi theory. The electron trajectory turns out to be a complicated modification of the original elliptic orbit of the electron. At this point Epstein introduces Sommerfeld's quantum conditions. If the parabolic coordinates are designated by (ξ, η, φ), with $x = \xi\eta\cos\varphi$, $y = \xi\eta\sin\varphi$, and $2z = (\xi^2 - \eta^2)$, the quantum conditions are

$$\oint p_\xi\, d\xi = n_1 h,$$
$$\oint p_\eta\, d\eta = n_2 h,$$
$$\oint p_\varphi\, d\varphi = n_3 h, \tag{3}$$

Using these quantum conditions, and taking into account only terms linear in the electric field (Stark had found that the magnitude of the effect was directly proportional to the electric field strength), Epstein finds for the atomic energy levels $E_{(n_1,n_2,n_3)}$ in the field $\mathcal{E}$:

$$E_{(n_1,n_2,n_3)} = \frac{A_1}{(n_1+n_2+n_3)^2} + \mathcal{E} A_2 (n_1+n_2+n_3)(n_1-n_2), \tag{4}$$

with

$$A_1 = -\frac{2\pi^2 Z^2 me^4}{h^2} \tag{5}$$

and

$$A_2 = \frac{3h^2}{8\pi^2 Zme}. \tag{6}$$

From (4), (5), and (6) it is easily seen that an electric field causes a frequency shift for any transition from (n_1, n_2, n_3) to (m_1, m_2, m_3). The calculated shifts for hydrogen turn out to be in agreement with the values observed by Stark.

4.3 Matrix mechanics and wave mechanics

As one might expect, the formalisms of matrix mechanics and wave mechanics, developed in 1925–1926 by Werner Heisenberg and Erwin Schrödinger, respectively, offered new opportunities for a quantum theoretical treatment of the Stark effect. In the case of matrix mechanics, this was done by Wolfgang Pauli [14]; wave mechanics was applied by Schrödinger himself [15] and independently by Epstein [16]. The approach taken in the latter two papers resembles the earlier one by Epstein, in the sense that a change from cartesian to parabolic coordinates is performed and the Hamiltonian for the hydrogen atom in an external field is written in terms of these variables. But instead of solving the Hamilton-Jacobi equation for this system, Schrödinger and Epstein now insert this Hamiltonian in the wave equation and solve it, retaining only terms linear in $\mathcal{E}$. In this approximation, they both arrive at Epstein's earlier result. In addition, they also calculate the intensities of the shifted spectral lines.

5 Stark and Lo Surdo: physics and politics

It is ironic that in the years after World War I Stark, whose work had provided so much support to quantum theory, became more and more hostile towards the new developments in physics—not only quantum theory, but also relativity. It is well known how he, and his ideological partner Philipp Lenard, converted to nazism and tried to make physics pure and aryan by getting rid of quantum theory and relativity (see, e.g., [17] for more details). Even more ironic is that his co-discoverer followed a similar path. Lo Surdo became embittered by what he considered lack of recognition, especially after Stark had been awarded the Nobel Prize, and he enthusiastically embraced the ideas of Italian fascism. Both Stark and Lo Surdo lived to see the demise of their respective ideologies and ended their lives as pariahs in the scientific world of their home countries.

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References

[1] A. J. Kox, Eur. J. Phys. **18**, 139 (1997).
[2] W. Voigt, Ann. Phys. (Berlin) **309**, 197 (1901).
[3] J. Stark, Erinnerungen eines deutschen Naturforschers. A. Kleinert, ed. (Bionomica, Mannheim, 1987).
[4] J. Stark, Nature **92**, 401 (1913).
[5] J. Stark, Sitz. ber. Preuss. Akad. Wiss. (Berlin), 932 (1913).
[6] J. Stark, Ann. Phys. (Berlin) **348**, 965 (1914).
[7] J. Stark, and J. Wendt, Ann. Phys. (Berlin) **348**, 983 (1914).
[8] M. Leone, A. Paoletti, and N. Robotti, Phys. Perspect. **6**, 271 (2004).
[9] E. Warburg, Verh. Deutsch. Phys. Ges. **15**, 1259 (1913).
[10] N. Bohr, Collected Works, Vol. 2. U. Hoyer, ed. (North-Holland, Amsterdam, 1981).
[11] N. Bohr, Phil. Mag. **27**, 506 (1914).
[12] P. S. Epstein, Ann. Phys. (Berlin) **355**, 489 (1916).
[13] K. Schwarzschild, Sitz. ber. Preuss. Akad. Wiss. (Berlin), 548 (1916).
[14] W. Pauli, Z. Phys. **36**, 336 (1926).
[15] E. Schrödinger, Ann. Phys. (Berlin) **385**, 437 (1926).
[16] P. S. Epstein, Phys. Rev. **28**, 695 (1926).
[17] D. Hoffman, and M. Walker, eds. The German Physical Society in the Third Reich (Cambridge University Press, Cambridge, 2012).