

CHAPTER 2.4

The Stark effect in the Bohr–Sommerfeld theory and in Schrödinger’s wave mechanics

Anthony Duncan and Michel Janssen***

Abstract

The explanation of the Stark effect in hydrogen, the splitting of the Balmer lines in an external electric field, was a major success of the old quantum theory of Bohr and Sommerfeld. Borrowing techniques from celestial mechanics, Epstein and Schwarzschild found frequencies for the Stark effect components of these lines that were in excellent agreement with Stark’s experimental data. Using Bohr’s correspondence principle, Kramers found the correct polarizations for these components and intensities that agreed, at least qualitatively, with the data. Shortly after the arrival of wave mechanics, Schrödinger and Epstein treated the Stark effect on the basis of the new theory. The two theories agree on the polarizations and, at least to first order in the strength of the external field, on the frequencies, but not on the intensities, where the new theory was soon found to be in reasonable quantitative agreement with new and better data. More importantly, the new theory eliminated the need for some additional assumptions that

* Department of Physics and Astronomy, University of Pittsburgh; E-mail: tony@dectony.phyast.pitt.edu

** Program in the History of Science, Technology, and Medicine, University of Minnesota; E-mail: janss011@umn.edu

had to be made in the old theory. Furthermore, although this was not explicitly noted at the time, the new theory solved a fundamental problem in the old quantum theory that manifested itself glaringly in the Stark effect: it depends on the coordinates in which the quantum conditions are imposed which orbits are allowed. In the new theory, this worrisome non-uniqueness of orbits turns into the completely innocuous non-uniqueness of bases of eigenfunctions.

Key words: Stark effect; Bohr-Sommerfeld theory; Hamilton-Jacobi theory; wave mechanics; Epstein; Kramers; Schrödinger.

1. Introduction

In 1913, the same year that Niels Bohr proposed his model of the hydrogen atom and showed that it correctly reproduces the frequencies of the lines of the Balmer series in the hydrogen spectrum, Johannes Stark published his detailed measurements of the splitting of these spectral lines when a hydrogen atom is placed in an external electric field.¹ The Stark effect, as it quickly came to be called, the splitting of spectral lines by electric fields, is the electric analogue of the Zeeman effect, the splitting of spectral lines by magnetic fields, discovered by Pieter Zeeman in 1896.² Stark recalled that at a dinner party at Heike Kamerlingh Onnes's house during a visit to Leyden shortly after he discovered the effect, the hostess was seated right between Zeeman and himself. This prompted a risqué joke on the part of another dinner guest, Paul Ehrenfest, who quipped: "Well, Mrs. Onnes, now you have a choice: do you want to be split electrically or magnetically?"³

Both splittings won their discoverers a Nobel Prize, Zeeman in 1902, Stark in 1919. In the case of the Zeeman effect, Zeeman shared

1. Bohr (1913), Stark (1913a).

2. Kox (1997).

3. Hermann (1965b), p. 13.

the award with Hendrik Antoon Lorentz, whose electron theory could account for Zeeman's original findings though not for the more complicated manifestations of the effect found in subsequent years. Stark won his Nobel Prize alone, even though the Italian experimentalist Antonino Lo Surdo could claim to have found the Stark effect independently.⁴ Three years before Stark won the Nobel Prize, Paul Epstein and Karl Schwarzschild showed that the effect could be accounted for on the basis of Arnold Sommerfeld's extension of Bohr's theory.⁵ Although Stark did not share his Nobel Prize with any of these theorists either, part of the significance of the Stark effect was undoubtedly that it supported the Bohr-Sommerfeld theory. Stark, however, was a staunch opponent of the theory and actually spent part of his Nobel lecture railing against it.⁶ We will draw the veil of charity over this sad production and focus instead on Epstein and Schwarzschild.

Not coincidentally, as we will see, Epstein, a Polish-born Russian citizen who had come to Munich in 1910 and taken his doctorate with Sommerfeld in 1914, and Schwarzschild, director of the Astrophysical Observatory in Potsdam, arrived at virtually identical accounts of the Stark effect at almost exactly the same time. Using Sommerfeld's extension of Bohr's theory, especially the notion of (as we would now call it) degeneracy that came with the introduction of multiple quantum numbers, and some powerful techniques from celestial mechanics, they derived the energy levels for a hydrogen atom in an electric field to first order in the field strength, exam-

4. See Leone, Paolette and Robotti (2004) for discussion of this case of simultaneous discovery. Lo Surdo only realized after he read a short note in *Nature* in which Stark (1913b) announced his discovery that he had been seeing the same effect. Lo Surdo's colleague, the Italian spectroscopist Antonio Garbasso, suggested that the effect be called the "Stark-Lo Surdo phenomenon." Stark vehemently opposed this suggestion and the name did not catch on (Leone, Paolette and Robotti, 2004, pp. 281–283).

5. Epstein (1916a,b), Schwarzschild (1916), Sommerfeld (1915a,b). For historical discussion, see Kragh (2012), pp. 154–156, and Eckert (2013a), sec. 4.2, pp. 44–48.

6. Kragh (2012), pp. 127–128, pp. 168–169. As is well-known, Stark later became a strong supporter of the Nazi movement in Germany. Lo Surdo likewise became a strong supporter of the fascist movement in Italy (Leone, Paolette and Robotti, 2004, p. 291).

ined the transitions between these energy levels, and found what most experts, *pace* Stark, considered excellent agreement with Stark's spectroscopic data.

This explanation of the (first-order) Stark effect was hailed, both at the time and by later commentators,⁷ as one of the signature achievements of the old quantum theory of Bohr and Sommerfeld. As Epstein put it in the concluding paragraph of the short note in which he first announced his explanation of the Stark effect:

We believe that the reported results prove the correctness of Bohr's atomic model with such striking evidence that even our conservative colleagues cannot deny its cogency. It seems that the potential of the quantum theory in its application to this model is almost miraculous and far from being exhausted.⁸

Sommerfeld went even further. By the time he published the first edition of *Atombau und Spektrallinien*,⁹ which was to become the "Bible" of the old quantum theory,¹⁰ Hendrik A. (Hans) Kramers, Bohr's right-hand man in Copenhagen, had shown in his dissertation that, with the help of Bohr's correspondence principle, the Bohr-Sommerfeld theory could also account for the polarization and, at least qualitatively, the intensities of the various components into which an electric field splits the Balmer lines.¹¹ Sommerfeld ended the final chapter of his book with a section on the work of Epstein, Schwarzschild, and Kramers on the Stark effect and confidently concluded that "the theory of the Zeeman effect and especially the theory of the Stark effect belong to the most impressive achievements of our field and form a beautiful capstone on the edifice of atomic physics."¹² In the next and final paragraph of the book, he suggested that the building of atomic physics was now essentially complete and prophesized that a "proud new wing" for

7. See, e.g., Jammer (1966), pp. 108–109, and Pais (1991), p. 183.

8. Epstein (1916a), p. 150; translation following Jammer (1966), p. 108.

9. Sommerfeld (1919).

10. Eckert (2013b).

11. Kramers (1919).

12. Sommerfeld (1919), pp. 457–458.

nuclear physics, built on the same plan as the “edifice of atomic physics,” would soon be added.¹³

Within a few years, it was recognized that Sommerfeld’s proclamation of success had been premature. The Zeeman effect turned out to be one of the most thorny problems facing the Bohr-Sommerfeld theory. The theory performed much better in the case of the Stark effect. In hindsight, it is clear that this is mainly because the Stark effect, unlike the Zeeman effect, does not involve spin, at least not in the regime of electric fields used by Stark.¹⁴ Yet, as we will show in this paper, the old quantum theory’s treatment of the Stark effect also had its share of problems, especially compared to the way the effect is handled in wave mechanics.

Shortly after the advent of wave mechanics and independently of one another, Erwin Schrödinger and Epstein, who had meanwhile moved from Munich to Pasadena, applied the new theory to the Stark effect.¹⁵ To first order in the strength of the electric field, wave mechanics gives the same splittings of the energy levels as the old quantum theory. However, whereas the old quantum theory required some ultimately arbitrary selection rules in addition to the basic quantum conditions to restrict the allowed energy levels and the allowed transitions between them to eliminate some pathological orbits and to match the experimental data, the new theory gives the correct energy levels and transitions without any further assumptions. Wave mechanics also predicts the polarizations and intensities of the various components without any appeal to the correspondence principle. The wave-mechanical values for the intensities differed from those calculated by Kramers on the basis of the correspondence principle and were soon found to be in satisfactory, if not perfect, quantitative agreement with new experimental data.¹⁶

13. Sommerfeld (1919), p. 458. For discussion of Sommerfeld’s Munich school in theoretical physics, see Eckert (1993, 2013c), Seth (2010), and Schweber (2012), Ch. 3.

14. Jammer (1966), p. 109.

15. Schrödinger (1926), Epstein (1926). Schrödinger’s notes and calculations for his paper can be found on reels 40 and 41 of the microfilms of the *Archive for History of Quantum Physics* (AHQP).

16. See Condon and Shortley (1963), pp. 400–402, for references to the experimental literature of the late 1920s.

Schrödinger and Epstein both emphasized these two advantages of their new explanation of the Stark effect.¹⁷ Neither of them, however, commented on another advantage, the solution offered by wave mechanics of a more fundamental problem in the old quantum theory's account of the Stark effect. Both Schwarzschild and Epstein in 1916 and Schrödinger and Epstein in 1926 used parabolic coordinates to find the allowed energy levels of a hydrogen atom in an electric field. In the old quantum theory, one would expect that, if the electric field is set to zero, the orbits in parabolic coordinates reduce to those readily found in polar coordinates for the case without an external electric field. However, even though the energy levels of the orbits are the same in the two coordinate systems, the actual orbits are not. Both Epstein and Sommerfeld dutifully recorded this problem and offered a rather unrealistic suggestion as to how it might be solved.¹⁸ Bohr also emphasized that which orbits are allowed in the old quantum theory depends on the coordinates in which the quantum conditions are imposed. He suggested, however, that this was a virtue rather than a liability of the theory.¹⁹ We side with Sommerfeld and with Epstein in particular, who clearly recognized it as a liability. In wave mechanics, as we will see, the worrisome non-uniqueness of orbits turns into the completely innocuous non-uniqueness of bases of eigenfunctions in degenerate systems. The old quantum theory's account of the Stark effect thus illustrates graphically one of that theory's most problem-

17. In the conclusion of his paper, Epstein (1926), p. 710, wrote that the agreement of the intensities he had calculated on the basis of wave mechanics with Stark's data was "fair and decidedly better than that obtained from Bohr's correspondence principle in Kramers' work." Both Epstein's calculations and some of Stark's data, however, turned out to be wrong (see note 98 and 129). Gordon and Minkowski (1929) showed that, once corrected, Epstein's calculations give the same results as Schrödinger's. These results agreed with the measurements of Foster and Chalk (1926, 1928), which deviated from the intensities reported by Stark, especially in the case of the first two lines of the Balmer series, H_α and H_β .

18. Epstein (1916b), p. 507; Sommerfeld (1919), pp. 502-503.

19. Bohr (1918), pp. 20-23.

atic features, a feature eliminated in the transition to modern quantum mechanics, namely the notion that electrons and other particles have well-defined trajectories.

2. The Stark effect in the old quantum theory

Shortly after the discovery of the Zeeman effect, the Göttingen theoretical physicist Woldemar Voigt started to look into the theoretical possibility of an electric analogue of the effect.²⁰ From 1900 to 1906, Stark worked in Göttingen, in the same institute as Voigt. During those years he began a series of experiments to measure the effect of an external electric field on the spectra of (mainly) hydrogen and helium. His efforts finally bore fruit in 1913 in Aachen, where he had been appointed professor at the *Technische Hochschule* in 1909. Stark found that spectral lines emitted by hydrogen and helium split into a number of lines when an electric field is applied. In a series of papers published in 1914, Stark (and his co-authors Georg Wendt and Heinrich Kirschbaum) presented more detailed measurements of the effect in hydrogen, helium, and other elements.²¹ Like the magnetic field in the case of the Zeeman effect, the electric field typically turned spectral lines into multiplets with more than three components. Voigt's theory, like Lorentz's classical theory for the "normal" Zeeman effect, could only account for a splitting into three components. Moreover, unlike Lorentz's theory, Voigt's theory gave the wrong values for the frequencies of these components. So did a classical theory by Schwarzschild²² based on an analogy that he would put to better use two years later between the perturbation of an electron orbit by an electric field and the perturbation of a planetary orbit by a large but distant mass.²³ Early attempts to account for the Stark effect in hydrogen on the basis of Bohr's new quantum model of the hydrogen atom, by Emil War-

20. Hermann (1965a), Leone, Paolette and Robotti (2004), Kox (2013).

21. See the bibliography of Mehra and Rechenberg (1982) for detailed references.

22. Schwarzschild (1914).

23. Eckert (2013a), p. 47.

burg and Bohr himself, did not fare much better.²⁴ As one commentator notes: “Precondition for a successful treatment [of the Stark effect] was the extension of Bohr’s idea by Sommerfeld: the addition of elliptical orbits to the circular orbits of atomic electrons.”²⁵

Discrete sets of orbits, circular or elliptical, in and of themselves do not provide any new resources for the analysis of line splittings in electric and magnetic fields. An external field will affect the energy of the orbits. If the change in energy of one orbit is different from that of another, this will also change the frequency of the light emitted in a quantum jump from one to the other. So spectral lines would *shift*. But how would we explain that they *split*? Our only option, it seems, would be to establish that the effect of an external field on the energy of an orbit depends in just the right ways on the orientation of the orbit with respect to the field. Since the orbits in a gas of atoms will have different orientations with respect to the field, we could then use such dependence to explain the splitting of the spectral lines. It is unclear, however, whether that dependence would give us discrete multiplets or just a blurring of the spectral lines. In fact, Sommerfeld expected that this approach could only provide a natural explanation of triplets, as in Lorentz’s classical explanation of the Zeeman effect.²⁶

Sommerfeld’s extension of Bohr’s model,²⁷ by contrast, suggested a whole new kind of explanation of line splittings. The importance of the generalization from a discrete set of circular orbits to a discrete set of elliptical orbits in this context is that the latter require *two* quantum numbers whereas the former only required one.²⁸ Sommerfeld thereby introduced the key notion of degeneracy, to use the

24. Hermann (1965a), pp. 15–16; Kragh (2012), pp. 128–129; Eckert (2013a), pp. 18–20, pp. 26–27. See Darrigol (1992), pp. 90–92, for discussion of Bohr’s attempt.

25. Hermann (1965a), p. 16.

26. Sommerfeld (1915a), p. 450.

27. For brief overviews of this development, see, e.g., Eckert (2013c), sec. 7.4, and Kragh (2012), secs. 4.2–4.4.

28. Eckert (2013b), p. 32. Just adding elliptical orbits to circular orbits with discrete energies picked out by one quantum number gives a continuous set of orbits and does not provide a basis for an account of the discrete line splittings in the Stark effect.

modern term. The discrete set of allowed Kepler ellipses correspond to the exact same set of energy values as the original discrete set of allowed circular orbits, but the way in which these energy values and thus the transition frequencies are determined by quantum numbers is different in the two cases.

For circular orbits, the allowed energy levels are given by²⁹

$$E_n = -\frac{hR}{n^2}, \quad (1)$$

where h is Planck's constant, R is the Rydberg constant, and n is a non-negative integer. The frequency $\nu_{n_i \rightarrow n_f}$ of the radiation emitted when an electron jumps from an initial orbit with quantum number n_i to a final orbit with quantum number $n_f < n_i$ is given by $h\nu_{n_i \rightarrow n_f} = E_{n_i} - E_{n_f}$. Bohr thus arrived at the following formula for the frequencies of the spectral lines in hydrogen:

$$\nu_{n_i \rightarrow n_f} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right). \quad (2)$$

The well-known Balmer lines in the visible region of the spectrum are the ones for which $n_f = 2$. The most striking success of Bohr's model was that the Rydberg constant could be expressed in terms of more fundamental constants:

$$R = \frac{2\pi^2 \mu e^4}{h^3}, \quad (3)$$

where μ and $-e$ are the (reduced) mass and charge of the electron, respectively.

For a discrete set of elliptical orbits, Sommerfeld showed, Eq. (1) gets replaced by³⁰

$$E_{(n_r, n_\varphi)} = -\frac{hR}{(n_r + n_\varphi)^2}, \quad (4)$$

29. Bohr (1913). Here and in the rest of the paper we use our own modernized notation.

30. Sommerfeld (1915a), p. 439.

where the radial quantum number n_r is a non-negative integer and the azimuthal quantum number n_ϕ is a positive integer. Eq. (2) accordingly gets replaced by

$$\nu_{(n_r, n_\phi)_i \rightarrow (n_r, n_\phi)_f} = R \left(\frac{1}{(n_r + n_\phi)_f^2} - \frac{1}{(n_r + n_\phi)_i^2} \right), \quad (5)$$

where $(n_r + n_\phi)_i > (n_r + n_\phi)_f$. Sommerfeld found that, unless he quantized eccentricity as well as angular momentum, he did not get a discrete set of energy values for the allowed elliptical orbits. Commenting on Eq. (5), he wrote:

With the addition of our quantized elliptical orbits, the [Balmer] series has gained nothing in terms of number of lines and lost nothing in terms of sharpness. Instead of the diffuse bands discussed earlier [before eccentricity was quantized] we once again have the discrete Balmer lines, but now with an extraordinarily increased multiplicity of ways in which they can be generated.³¹

Sommerfeld only found new lines when he solved the Kepler problem relativistically in the next paper he presented to the Munich Academy.³² The fine structure of the hydrogen spectrum predicted by this relativistic calculation was confirmed within a few months by the Tübingen spectroscopist Friedrich Paschen in close consultation with Sommerfeld.³³ Compared to this triumph, the *non*-relativistic treatment of the Kepler problem was disappointing:

As long as Sommerfeld could not produce any tangible evidence [i.e., new lines] for the generalized Balmer formula [Eq. (5)], his theory compared to Bohr's atomic model had to appear as a very interesting but basically unnecessary extension.³⁴

31. Sommerfeld (1915a), p. 440.

32. Sommerfeld (1915b). This paper was presented in January 1916 but was still included in the proceedings volume for 1915.

33. Eckert (2013a), pp. 49–51.

34. Eckert (2013a), p. 33.

As Sommerfeld clearly realized, however, and as Michael Eckert proceeds to show, the extension from circular to elliptic orbits was of great importance even in the absence of “tangible evidence” deciding between Eq. (2) and Eq. (5).

Since the various energy levels in a hydrogen atom could be realized in many more ways with Sommerfeld’s ellipses than with Bohr’s circles, Sommerfeld’s theory provided a brand new tool for attempts to account for the Stark and Zeeman effects. The notion of degeneracy, which Sommerfeld in effect introduced by replacing Eq. (1) with Eq. (4), suggested that one try to explain these effects by showing that electric and magnetic fields lift the degeneracy in the energy of the orbits in just the right way. After all, an aggregate of hydrogen atoms with electrons jumping between all these different allowed elliptic orbits should be expected to start emitting light at many more frequencies than those given by the Balmer series as soon as an electric or a magnetic field changes the energies of those orbits and changes them in a way that is different from one orbit to another so that the radiation frequencies corresponding to transitions between orbits also change. Hence, even in the absence of “tangible evidence,” Sommerfeld’s generalization from circular to elliptic orbits had great heuristic potential.

Sommerfeld emphasized this potential in a section of his paper devoted to the Stark effect.³⁵ Although he acknowledged that a detailed theory of how the electric field lifts the degeneracy in this case had yet to be developed, he pointed to the large number of lines that Stark had found and argued that this made the approach he was proposing especially promising. “The hour has come for a true theory of the Zeeman effect,” he enthusiastically wrote to Wilhelm Wien on 31 December 1915,³⁶ a few weeks after submitting the first and a few weeks before submitting the second paper on his extension of Bohr’s theory to the Munich Academy. Sommerfeld turned out to be wrong about the Zeeman effect, but right about the Stark effect. By the end of March 1916, Epstein and Schwarzschild had worked out a theory of the Stark effect exploiting his notion of degeneracy.

35. Sommerfeld (1915a), pp. 449–451.

36. Quoted in Eckert (2013a), p. 44.

The other key insight that made it possible to account for the Stark effect was Schwarzschild's realization that the quantum conditions proposed by Sommerfeld could be connected to action-angle variables and Hamilton-Jacobi theory, both of which Schwarzschild was intimately familiar with because of his expertise in celestial mechanics.

Drawing on Max Planck's idea of quantizing the phase space spanned by a coordinate q and its associated momentum p , Sommerfeld had quantized what he called the "phase integral" for periodic systems, initially for systems with only one degree of freedom,³⁷

$$\int p dq = nh. \quad (6)$$

The integral is to be taken over one period of the motion. The quantum number n has to be a non-negative integer. In this way Sommerfeld could recover, in just a few lines and in a unified manner, both the quantization of the energy of the harmonic oscillator needed in black-body radiation theory and the quantization of angular momentum in the Bohr model of the hydrogen atom.

Consider a harmonic oscillator, a point mass m on a spring with spring constant k . The characteristic angular frequency of this system is $\omega = 2\pi\nu = \sqrt{k/m}$. The trajectory of the point mass in the phase space spanned by its position q and its momentum p is an ellipse the size of which is determined by the energy $E = p^2/(2m) + kq^2/2$. Using that $p = \sqrt{2mE}$ for $q = 0$ and that $q = \sqrt{2E/k}$ for $p = 0$, we see that the major and minor semi-axes, d_{major} and d_{minor} , of this ellipse are $\sqrt{2mE}$ and $\sqrt{2E/k}$, respectively. The phase integral over one period of the motion is equal to the area of this ellipse, $\pi d_{\text{major}} d_{\text{minor}}$. Sommerfeld's phase integral quantization condition (6) thus gives

$$\int p dq = \pi \sqrt{2mE} \sqrt{2E/k} = 2\pi E \sqrt{m/k} = E/\nu = nh,$$

which is the familiar quantization condition $E = nh\nu$ for the energy of the harmonic oscillator.

37. Sommerfeld (1915a), p. 429.

In the first installment of his famous trilogy,³⁸ Bohr had similarly quantized the total energy E of an electron in a hydrogen atom to select its allowed circular orbits (with radii r_n and orbital frequencies ν_n): $|E| = E_{\text{kin}} = nh\nu_n/2$.³⁹ The relation between the kinetic energy, $E_{\text{kin}} = \frac{1}{2}\mu(2\pi\nu_n r_n)^2$, of an electron in the n th orbit ($n = 1, 2, 3, \dots$) and its angular momentum, $L = \mu(2\pi\nu_n r_n)r_n$, in that orbit is simply $L = E_{\text{kin}}/\pi\nu_n$. Bohr could thus rewrite the quantization condition as $L = n\hbar$, where $\hbar \equiv h/2\pi$.⁴⁰ When (p, q) are chosen as (L, φ) , where φ is one of the polar coordinates (r, φ) , Sommerfeld's phase integral quantization condition (6) reproduces Bohr's quantization condition in the form $L = n\hbar$:

$$\int_0^{2\pi} L d\varphi = 2\pi L = nh.$$

Note, however, that we need to add to Sommerfeld's quantum condition (6) in this case that $n \neq 0$. There cannot be an orbit with vanishing angular momentum.

Since the Kepler problem involves two degrees of freedom, two phase integrals need to be quantized for the generalization from a discrete set of circular orbits to a discrete set of elliptical orbits.⁴¹ Solving the Kepler problem in polar coordinates, Sommerfeld arrived at the quantum numbers n_φ and n_r , given in Eq. (4):

$$\int p_\varphi d\varphi = n_\varphi h, \quad \int p_r dr = n_r h, \quad (7)$$

with $p_\varphi \equiv L$ and the additional condition $n_\varphi \neq 0$ (cf. Eq. (4)). Sommerfeld then applied this same approach to the relativistic Kepler problem.⁴² As he told Schwarzschild in a letter of 28 December

38. Bohr (1913).

39. The virial theorem says that, for a $1/r$ Coulomb potential, $\overline{E_{\text{kin}}} = -\frac{1}{2}\overline{E_{\text{pot}}}$, where $\overline{E_{\text{kin}}}$ and $\overline{E_{\text{pot}}}$ are the average kinetic and potential energies. For circular orbits, E_{kin} and E_{pot} are constant so it follows from the virial theorem that $E_{\text{kin}} = -\frac{1}{2}E_{\text{pot}}$. From $E = E_{\text{kin}} + E_{\text{pot}}$, it then follows that $E = -E_{\text{kin}}$.

40. Bohr (1913), p. 15. For discussion, see Heilbron and Kuhn (1969), p. 280.

41. Sommerfeld (1915a), pp. 432-440.

42. Sommerfeld (1915b).

1915, he was “moving full steam ahead on spectral lines, with fairy-tale results.”⁴³

Two months later, on 1 March 1916, Schwarzschild sent Sommerfeld a letter in which he made the connection between phase integrals such as those in Eqs. (6)–(7) and action-angle variables.⁴⁴ Consider Hamilton’s equations for some multiply-periodic system with Hamiltonian H described in terms of generalized coordinates q_k and their conjugate momenta p_k :

$$\dot{q}_k = \frac{\partial H}{\partial p_k}, \quad \dot{p}_k = -\frac{\partial H}{\partial q_k}. \quad (8)$$

One way to solve these equations is to perform a canonical transformation to new variables, called action-angle variables and typically denoted by J and w , that have the desirable property that the Hamiltonian, written as a function of the new variables, only depends on the new momenta, the action variables J_k , and not on the new coordinates, the angle variables w_k . A generating function $S(q_k, J_k)$, which is known as Hamilton’s principal function and turns out to be equal to the action integral for the system, is used to implement the transformation $(q_k, p_k) \rightarrow (w_k, J_k)$:

$$w_k = \frac{\partial S}{\partial J_k}, \quad p_k = \frac{\partial S}{\partial q_k}. \quad (9)$$

In action-angle variables, Hamilton’s equations have the simple form:

$$\dot{w}_k = \frac{\partial H}{\partial J_k} = \nu_k, \quad \dot{J}_k = -\frac{\partial H}{\partial w_k} = 0, \quad (10)$$

where the ν_k ’s are the characteristic frequencies of the system. The equations for \dot{w}_k allow us to find these characteristic frequencies without fully solving the equations of motion. This explains much of the appeal of action-angle variables in celestial mechanics. Eqs. (10) can readily be solved. The hard part is finding the generating

43. Eckert (2013a), p. 29.

44. This letter is quoted in full in Eckert (2013a), pp. 44–45. See also Eckert (2014), p. 151.

function $S(q_k, J_k)$ that gets us from Eqs. (8) to Eqs. (10). This requires the solution of the so-called Hamilton-Jacobi equation for the system, which we obtain by making the substitutions

$$p_k \rightarrow \frac{\partial S}{\partial q_k}$$

(see Eq. (9)) in the Hamiltonian $H(q_k, p_k)$ and setting the result equal to some constant.⁴⁵

The equations for J_k in Eqs. (10) tell us that the action variables J_k are constants of the motion. This makes them suitable candidates to subject to quantum conditions. In fact, what Schwarzschild pointed out to Sommerfeld was precisely that his phase integrals can be seen as action variables.⁴⁶ Sommerfeld's quantization conditions can be written as:

$$J_k = \int p_k dq_k = \int \frac{\partial S}{\partial q_k} dq_k = n_k h. \quad (11)$$

As Schwarzschild told Sommerfeld, it was only after he had cast the quantization conditions in this new form that they had become truly compelling for him. He added that they now also provided a definite point of departure for the treatment of the Stark effect and the Zeeman effect. "There are violins hanging all over the quantum heavens," he rhapsodized in another letter to Sommerfeld four days later.⁴⁷

45. For further discussion of canonical transformations, action-angle variables, and Hamilton-Jacobi theory, we refer the reader to graduate textbooks in classical mechanics such as Goldstein et al. (2002), Matzner and Shepley (1991) and Corben and Stehle (1994). For an insightful discussion of the use of these techniques in the old quantum theory and wave mechanics, see Yourgrau and Mandelstam (1979), Chs. 10–11, pp. 97–126. See also Michiyo Nakane's contribution to this volume.

46. That this is true, for instance, in the case of the phase integrals in Eqs. (7), is because the Hamilton-Jacobi equation for the non-relativistic treatment of an electron orbiting the nucleus in a hydrogen atom is separable in polar coordinates (see the paragraph following Eq. (16) for a definition of the notion of separability of the Hamilton-Jacobi equation).

47. Eckert (2013a), p. 45.

Given how important we now know these techniques from celestial mechanics were for the development of the Bohr-Sommerfeld theory, Sommerfeld's reaction to Schwarzschild's communication may come as a surprise. In his reply of 9 March 1916, he admitted that he was unfamiliar with the techniques Schwarzschild was referring to and that this would probably be true for most physicists.⁴⁸ Sommerfeld, however, immediately recognized the importance of Schwarzschild's intelligence. He relayed the information to Epstein, now an enemy alien in wartime Munich, who, at Sommerfeld's suggestion, had taken up the problem of the Stark effect for a habilitation thesis. In his interview for the *Archive for History of Quantum Physics* (AHQP) in 1963, Epstein recalled the sinking feeling he had upon hearing that Schwarzschild had resumed work on the Stark effect: "Now I have no prospects unless Schwarzschild should go to Heaven."⁴⁹ Epstein would obviously have preferred Schwarzschild to fiddle with another problem in his quantum heaven, but he may not have known back in March 1916 that Schwarzschild had contracted pemphigus while serving on the Russian front, an autoimmune disease causing painful blisters on the skin that would kill him only two months later.

Whether or not he was aware of his rival's predicament, Epstein understood that there was no time to lose if he wanted to beat Schwarzschild to the punch. Fortunately, inspired perhaps by Schwarzschild's 1914 paper on the Stark effect, Epstein had already begun to bone up on celestial mechanics. On 21 March 1916, he handed in his solution for the Stark effect to Sommerfeld. Later that same day, Sommerfeld received a letter from Schwarzschild with a virtually identical solution.⁵⁰

Epstein submitted a preliminary note to *Physikalische Zeitschrift* on 29 March 1916, the day before Schwarzschild submitted his paper to the Berlin Academy.⁵¹ Epstein's note appeared on 15 April 1916,

48. Eckert (2013a), p. 46.

49. AHQP interview with Epstein, session 1, p. 11, quoted by Mehra and Rechenberg (1982), p. 225, note 355).

50. Eckert (2013a), p. 47.

51. Epstein (1916a), Schwarzschild (1916).

Schwarzschild's on 11 May 1916.⁵² Schwarzschild died that same day. He was only 42 years old. In a popular article published later that year, "The quantum theory of spectral lines and the last paper of Karl Schwarzschild," Sommerfeld highlighted and praised Schwarzschild's contributions to the old quantum theory.⁵³

A few days before Schwarzschild "went to Heaven," Epstein submitted a lengthy paper with the details of his explanation of the Stark effect to *Annalen der Physik*.⁵⁴ This paper appeared in July 1916. In what follows, we present the derivation of the formula for the energy levels in the (first-order) Stark effect in the form in which it appears in the dissertation by Kramers.⁵⁵ Kramers cites Epstein's *Annalen* paper as his source.

2.1. Solving the Hamilton-Jacobi equation to find the line splittings in the Stark effect in hydrogen

In Cartesian coordinates (x, y, z) , the Hamiltonian for an electron in a hydrogen atom in an external electric field \mathcal{E} in the z -direction is given by (in Gaussian units):

$$H = \frac{p^2}{2\mu} - \frac{e^2}{r} + \mathcal{E}z, \quad (12)$$

where $p^2 \equiv p_x^2 + p_y^2 + p_z^2$, with (p_x, p_y, p_z) the components of the momentum \mathbf{p} , and $r \equiv \sqrt{x^2 + y^2 + z^2}$. The external electric field applied by Stark was weak compared to that of the hydrogen nucleus keeping the electron in orbit, which means that it can be treated as a small perturbation, amenable to the standard techniques of canonical perturbation theory borrowed from celestial mechanics.

However, in this case these techniques could not be used in either Cartesian or polar coordinates. Instead, both Epstein and Schwarzschild used parabolic coordinates (ξ, η, φ) , related to (x, y, z) via

52. Mehra and Rechenberg (1982), p. 225.

53. Sommerfeld (1916).

54. Epstein (1916b).

55. Kramers (1919), pp. 16-18.

$$z = \frac{\xi - \eta}{2}, \quad x + iy = \sqrt{\xi\eta}e^{i\varphi}, \quad r = \frac{\xi + \eta}{2},$$

where we followed Kramers rather than Epstein.⁵⁶ In parabolic coordinates, the Hamiltonian in Eq. (12) is given by:

$$H = \frac{1}{2\mu} \left(\frac{4}{\xi + \eta} (p_\xi \xi p_\xi) + \frac{4}{\xi + \eta} (p_\eta \eta p_\eta) + \frac{1}{\xi\eta} p_\varphi^2 \right) - \frac{2e^2}{\xi + \eta} + \frac{1}{2} e\mathcal{E}(\xi - \eta), \tag{13}$$

where $(p_\xi, p_\eta, p_\varphi)$ are the momenta conjugate to (ξ, η, φ) . In the old quantum theory, as in classical mechanics, $p_\xi \xi p_\xi = \xi p_\xi^2$ and $p_\eta \eta p_\eta = \eta p_\eta^2$. It is with malice aforethought that we wrote these products the way we did in Eq. (13): in wave mechanics p_ξ is replaced by a differential operator, $(\hbar/i) \partial/\partial\xi$, that does not commute with multiplication by ξ .

Setting $H = \alpha_1$, where α_1 is some negative constant giving the energy of the system, multiplying both sides by $2\mu(\xi + \eta)$, using that

$$\frac{\xi + \eta}{\xi\eta} = \frac{1}{\xi} + \frac{1}{\eta}, \quad (\xi + \eta)(\xi - \eta) = \xi^2 - \eta^2, \tag{14}$$

and making the substitutions

$$p_\xi \rightarrow \frac{\partial S}{\partial \xi}, \quad p_\eta \rightarrow \frac{\partial S}{\partial \eta}, \quad p_\varphi \rightarrow \frac{\partial S}{\partial \varphi}, \tag{15}$$

we arrive at the Hamilton-Jacobi equation for this system in parabolic coordinates:

$$4\xi \left(\frac{\partial S}{\partial \xi} \right)^2 + 4\eta \left(\frac{\partial S}{\partial \eta} \right)^2 + \left(\frac{1}{\xi} + \frac{1}{\eta} \right) \left(\frac{\partial S}{\partial \varphi} \right)^2 - 4\mu e^2 + \mu e\mathcal{E}(\xi^2 - \eta^2) = 2\mu(\xi + \eta)\alpha_1. \tag{16}$$

At this point, the reason for using parabolic coordinates becomes clear: the Hamilton-Jacobi equation is *separable* in these coordinates, which means that its solution is the sum of three terms that each depend only on one of the three coordinates.⁵⁷

56. Kramers (1919), p. 17, Eq. 43; Epstein (1916b), p. 495, Eqs. 19–20. See Fig. 1, Eqs. (2)–(4) and note 2 in Duncan and Janssen (2014) for more detailed discussion of the difference between Epstein’s and Kramers’ definitions of the coordinates (ξ, η, φ) .

57. It had long been known that the corresponding problem in celestial mechanics,

$$S(\xi, \eta, \varphi) = S_\xi(\xi) + S_\eta(\eta) + S_\varphi(\varphi). \tag{17}$$

$S_\varphi(\varphi)$ can simply be set equal to $\alpha_3\varphi$. Hence,

$$\frac{dS_\varphi}{d\varphi} = \alpha_3. \tag{18}$$

When α_3 is substituted for $\partial S/\partial\varphi = dS_\varphi/d\varphi$ in Eq. (16), the equation splits into a part depending only on ξ and a part depending only on η . Since the sum of these two parts must vanish, the two parts themselves must be equal but opposite constants. Denoting these constants by $\mp 2\alpha_2$, we can schematically write the Hamilton-Jacobi equation (16) as⁵⁸

$$\underbrace{\text{Terms with } \frac{dS_\xi}{d\xi}, \alpha_1, \alpha_3 \text{ depending on } \xi}_{= -2\alpha_2} + \underbrace{\text{Terms with } \frac{dS_\eta}{d\eta}, \alpha_1, \alpha_3 \text{ depending on } \eta}_{= 2\alpha_2} = 0, \tag{19}$$

which splits into separate equations for S_ξ and S_η of the form

$$\frac{dS_\xi}{d\xi} = u(\xi, \alpha_1, \alpha_2, \alpha_3), \quad \frac{dS_\eta}{d\eta} = v(\eta, \alpha_1, \alpha_2, \alpha_3). \tag{20}$$

We now impose the Sommerfeld-Schwarzschild quantum conditions (11). So far, it may have looked as if we could impose these conditions in arbitrary coordinates. It turns out, however, that the conditions can only be imposed consistently in coordinates in which the Hamilton-Jacobi equation for the system under consideration is separable. As Albert Einstein pointed out, in a paper that did not attract much attention at the time,⁵⁹ this amounts to a severe limitation of the formalism of the Bohr-Sommerfeld theory, over and above its restriction to multiply-periodic systems, as there are many

the motion of a body attracted by two other bodies one of which has a very large mass and is at a very large distance, is separable in parabolic coordinates. This is noted, for instance, in Bohr (1918), pp. 20-21.

58. See Sec. 2 of Duncan and Janssen (2014) for a detailed self-contained version of the derivation only sketched here.

59. Einstein (1917). "In spite of its general and novel approach, Einstein's paper was ignored by most" (Einstein, 1987-2012, Vol. 6, p. xxv).

systems for which the Hamilton-Jacobi equation is not separable in *any* coordinates. The formalism, however, does work for the case at hand. Introducing the notation I_ξ , I_η , and I_φ for the action variables, we thus impose the quantum conditions

$$\begin{aligned} I_\xi &= \int p_\xi d\xi = \int \frac{dS_\xi}{d\xi} d\xi = n_\xi h, \\ I_\eta &= \int p_\eta d\eta = \int \frac{dS_\eta}{d\eta} d\eta = n_\eta h, \\ I_\varphi &= \int p_\varphi d\varphi = \int \frac{dS_\varphi}{d\varphi} d\varphi = n_\varphi h, \end{aligned} \quad (21)$$

where n_ξ , n_η , and n_φ are non-negative integers. Both Epstein and Schwarzschild assumed that the values of I_ξ , I_η , and I_φ in the presence of a weak electric field \mathcal{E} are the same as their values in the absence of such a field. Where the cases $\mathcal{E}=0$ and $\mathcal{E} \neq 0$ differ is in how the separation constants α_1 and α_2 depend on the action variables. Recall that α_1 is equal to the energy E . So even though the action variables have the same values for $\mathcal{E} = 0$ and $\mathcal{E} \neq 0$, the energy does not.

The justification of the assumption that action variables have the same values for $\mathcal{E} = 0$ and $\mathcal{E} \neq 0$ is that they are what Ehrenfest called adiabatic invariants. In June 1916, Ehrenfest presented a paper to the Amsterdam academy connecting the adiabatic principle, which he had already been working on for a number of years, to the Bohr-Sommerfeld theory.⁶⁰ In July, he submitted a similar paper to *Annalen der Physik*.⁶¹ In September he added a postscript to the latter responding to Schwarzschild's combination of the Bohr-Sommerfeld theory and Hamilton-Jacobi theory:

The beautiful researches of Epstein, Schwarzschild, and others⁶² which have appeared in the meantime, show the great importance that cases integrable by means of Stäckel's method of "separation of

60. Ehrenfest (1916a).

61. Ehrenfest (1916b). See Pérez (2009), pp. 83–84, for a concise overview of Ehrenfest's papers on the topic in 1916.

62. Such as Peter Debye (Eckert, 2013a, p. 52)

the variables” have for the development of the theory of quanta.⁶³ Hence the question arises: to what extent are the different parts into which these authors separate the integral of action according to Stäckel’s method adiabatic invariants?⁶⁴

Ehrenfest’s question was taken up by one of his students in Leyden, Johannes (Jan) Burgers, who showed that action variables such as those in Eqs. (21) are indeed adiabatic invariants.⁶⁵

We now return to the calculation for the Stark effect. The next step is to evaluate the integrals in Eqs. (21) after substitution of the right-hand sides of Eqs. (18) and (20) for the integrands. For I_φ , we find with the help of Eq. (18):

$$I_\varphi = \int \frac{dS_\varphi}{d\varphi} d\varphi = 2\pi\alpha_3 = n_\varphi h. \quad (22)$$

In other words, $\alpha_3 = n_\varphi h$, so n_φ is the familiar azimuthal quantum number typically denoted nowadays by m . Similarly, although performing the integrals now requires some effort, we can express the action variables I_ξ and I_η in terms of the separation constants α_1 , α_2 , and α_3 . We then invert these relations to find the α ’s in terms of the I ’s and thereby in terms of the quantum numbers n_ξ , n_η , and n_φ . We need to do this twice, first for $\mathcal{E} = 0$, then to first order in $\mathcal{E} \neq 0$. We will not go through these calculations in detail but only state the end results.⁶⁶

In the absence of an external field ($\mathcal{E} = 0$), the sum of I_ξ , I_η , and I_φ for $\mathcal{E} = 0$ is given by

$$I_\xi + I_\eta + I_\varphi = \frac{2\pi\mu e^2}{\sqrt{-2\mu\alpha_1}}.$$

Solving for α_1 , we find

63. Staeckel (1891).

64. Ehrenfest (1916b), translation based on Pérez (2009), p. 93

65. Burgers (1917a,b,c). For discussion, see Klein (1970), pp. 290–291; Yourgrau and Mandelstam (1979), pp. 110–111; and Pérez (2009), pp. 93–102.

66. See Sec. 2 of Duncan and Janssen (2014) for a self-contained version of these calculations.

$$\alpha_1 = -\frac{2\pi^2\mu e^4}{(I_\xi + I_\eta + I_\varphi)^2}.$$

This reduces to the expression $-hR/n^2$ for the allowed energy levels in a hydrogen atom in the absence of an electric field found earlier (see Eqs. (1) and (4)), if the sum of the quantum numbers introduced in Eqs. (21) is set equal to the principal quantum number n :

$$n = n_\xi + n_\eta + n_\varphi. \quad (23)$$

As in Sommerfeld's calculation for elliptical orbits in polar coordinates (cf. Eq. (4)), the calculation for elliptical orbits in parabolic coordinates for $\mathcal{E} = 0$ thus leads to the same energy levels as Bohr's original calculation for circular orbits (cf. Eq. (1)) but does reveal the degeneracy of those energy levels:

$$E_{(n_\xi, n_\eta, n_\varphi)} = \alpha_1 = -\frac{2\pi^2\mu e^4}{h^2(n_\xi + n_\eta + n_\varphi)^2} = -\frac{hR}{n^2}, \quad (24)$$

where in the last step we used expression (3) for the Rydberg constant. As in Sommerfeld's formula for the allowed energy levels in polar coordinates (see Eq. (4)), we need to impose further restrictions on the allowed values of the quantum numbers in Eqs. (21).⁶⁷ First, n_ξ , n_η , and n_φ cannot all three be zero as the principal quantum number n would then be zero. Second, even if $n_\xi \neq 0$ and/or $n_\eta \neq 0$, n_φ cannot be zero. As long as $\mathcal{E} = 0$ there is no problem, but when $\mathcal{E} \neq 0$ this orbit becomes unstable and the electron will eventually hit the nucleus.

The degeneracy in the energy levels in Eq. (24) is lifted once the electric field is switched on. The integrals in Eqs. (21) now have to be evaluated to first order in \mathcal{E} (where in terms of order \mathcal{E} we can use the relations between α 's and I 's found for $\mathcal{E} = 0$). In this approximation, Eq. (24) gets replaced by

$$E_{(n_\xi, n_\eta, n_\varphi)} = \alpha_1 = -\frac{hR}{n^2} + C\mathcal{E}n(n_\xi - n_\eta),$$

67. Epstein (1916b), sec. 4, pp. 497-501.

where $C \equiv 3h^2/8\pi^2\epsilon\mu$. The electric field thus produces the splittings

$$\Delta E_{(n_\xi, n_\eta, n_\varphi)} = C\mathcal{E}n(n_\xi - n_\eta) \quad (25)$$

of the energy levels and the splittings

$$\Delta\nu_{(n_\xi, n_\eta, n_\varphi)_i \rightarrow (n_\xi, n_\eta, n_\varphi)_f} = \frac{C\mathcal{E}}{h} \left([n(n_\xi - n_\eta)]_i - [n(n_\xi - n_\eta)]_f \right) \quad (26)$$

of the transition frequencies.⁶⁸ The splittings ΔE in Eq. (25) are symmetric around the values for E without an external field. The splittings $\Delta\nu$ in Eq. (26) are likewise symmetric around the values for ν without an external field. As Epstein noted, this is in accordance with Stark's experimental results.⁶⁹

Figure 1 illustrates the Stark effect for the Balmer line H_α in the hydrogen spectrum.⁷⁰ It shows the splittings ΔE of the energy levels $n = 2$ and $n = 3$ in the presence of an external electric field of strength \mathcal{E} and the splittings $\Delta\nu$ of the frequencies of the radiation emitted in transitions from $n = 3$ to $n = 2$. Similar though increasingly more complicated diagrams can be drawn for H_β ($n = 4 \rightarrow n = 2$), H_γ ($n = 5 \rightarrow n = 2$), and H_δ ($n = 6 \rightarrow n = 2$).⁷¹

The electric field splits the lower level ($n = 2$) into three levels. For $\mathcal{E} = 0$, the energies of the orbits picked out by the values (101), (002), and (011) for the quantum numbers $(n_\xi, n_\eta, n_\varphi)$ are all the same. For $\mathcal{E} \neq 0$, the energy of the orbit (101) is raised by $2C\mathcal{E}$, while the energy of the orbit (011) is lowered by that same amount (cf. Eq. (25)). The electric field splits the upper level ($n = 3$) into five levels. For $\mathcal{E} = 0$, the energies of the orbits (201), (102), (111), (003), (012), and (021) are all the same. For $\mathcal{E} \neq 0$, the energies of the orbits (102) and (201) are raised by $3C\mathcal{E}$ and $6C\mathcal{E}$, respectively, while the energies of the orbits (012) and (021) are lowered by those same amounts.

For $\mathcal{E} = 0$, a quantum jump of an electron from any of the six pos-

68. The equivalents of Eqs. (25) and (26) in Epstein (1916b) are Eq. 62 on p. 508 and Eq. 65 on p. 509, respectively.

69. Epstein (1916b), pp. 509-510.

70. This figure is based on the numbers in Epstein (1916b), p. 512, Table I.

71. Epstein (1916b), pp. 512-513, Tables II-IV.

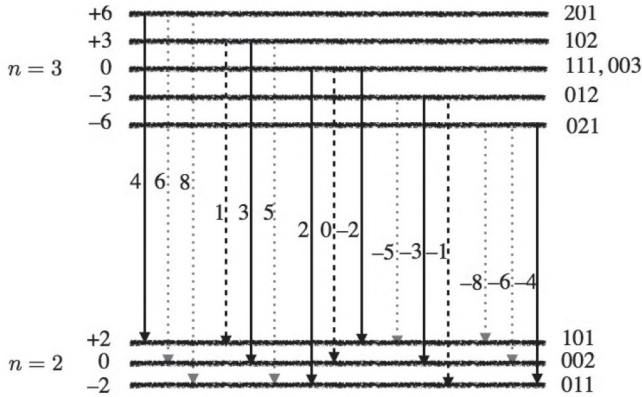


Figure 1: Stark effect for the Balmer line H_α in the hydrogen spectrum: splittings ΔE (in units of $C\mathcal{E}$ with \mathcal{E} the strength of the electric field and $C \equiv 3h^2/8\pi^2e\mu$) of energy levels for $n = 2$ and $n = 3$ [horizontal lines with values of ΔE to the left and values of quantum numbers (n, n_η, n_θ) to the right]; splittings $\Delta\nu$ (in units of $C\mathcal{E}/h$) of the frequency of the radiation emitted in transitions from $n = 3$ to $n = 2$ [arrows with values of $\Delta\nu$ to the left - solid arrows: parallel polarization; dashed arrows: perpendicular polarization; dotted arrows: violation of selection rule]. The figure is not drawn to scale: the energy gap between the $n = 2$ and $n = 3$ levels is much greater than the level splittings.

sible $n = 3$ orbits to any of the three possible $n = 2$ orbits is accompanied by the same energy loss and therefore by emission of radiation of the same frequency. For $\mathcal{E} \neq 0$, as indicated by the arrows in Figure 1, the energy loss in a quantum jump from $n = 3$ to $n = 2$ can take on fifteen different values, resulting in frequency shifts $\Delta\nu$ ranging from $-8C\mathcal{E}/h$ to $+8C\mathcal{E}/h$. This means that the frequency of the Balmer line H_α , emitted in the transition from $n = 3$ to $n = 2$, splits into fifteen different frequencies. Illustrating Epstein’s general observation noted above, the fourteen shifted frequencies lie symmetrically on opposite sides of the unshifted one.

Epstein eliminated six of these fourteen shifted frequencies, three on each side of the unshifted one. He adopted, at least initially, a selection rule proposed by Sommerfeld, which requires that⁷²

72. Sommerfeld (1915a), pp. 447–448; Epstein (1916b), p. 511, Eq. (69)

$$n_{\xi}^f \leq n_{\xi}^i, \quad n_{\eta}^f \leq n_{\eta}^i, \quad n_{\varphi}^f \leq n_{\varphi}^i. \quad (27)$$

According to this selection rule, the six transitions in which one of the three quantum numbers increases are forbidden. These are the transitions represented by dotted arrows in Figure 1.⁷³ The corresponding lines were either absent or exceedingly faint in Stark's spectroscopic data, which supported Sommerfeld's selection rule. The nine remaining transitions all matched lines clearly present in Stark's data: the six transitions indicated by solid arrows (with Δv equal to $\pm 2, \pm 3, \pm 4$ times $C\mathcal{E}/h$) producing light polarized parallel to the field; the three transitions indicated by dashed arrows (with Δv equal to $0, \pm 1$ times $C\mathcal{E}/h$) producing light polarized perpendicular to the field.

The splittings of other Balmer lines found by Stark violated Sommerfeld's selection rule. To match Stark's data, Epstein eventually settled on a modified version of the rule,⁷⁴

$$n_{\xi}^f \leq n_{\xi}^i, \quad n_{\eta}^f \leq n_{\eta}^i, \quad n_{\varphi}^f \leq n_{\varphi}^i + 1, \quad (28)$$

and emphasized that transitions violating this rule are not strictly forbidden, just highly improbable. As we mentioned in the introduction, the explanation of the Stark effect in the Bohr-Sommerfeld theory thus requires what in the final analysis are rather arbitrary restrictions, both on the allowed energy levels (see our comments following Eq. (24)) and on the allowed transitions between them (see Eqs. (27) and (28)).

With the help of these additional conditions, Schwarzschild and Epstein could account for the frequencies of all components into which the Balmer lines were observed to split in the Stark effect. This was rightfully celebrated as a tremendous success for the Bohr-Sommerfeld theory. However, neither Schwarzschild nor Epstein

73. Under this selection rule, the transitions '(003) \rightarrow (011)' and '(003) \rightarrow (101)' are also forbidden but $E_{(003)} = E_{(111)}$ even if $\mathcal{E} \neq 0$ and the transitions '(111) \rightarrow (011)' and '(111) \rightarrow (101)' are allowed, so this does not affect the number of lines.

74. Epstein (1916b), p. 516.

could account for the polarizations or the intensities of these components.

2.2. Using the correspondence principle to find the polarizations and the intensities of the Stark effect components of the Balmer lines

Epstein devoted a section of his paper to polarizations and intensities.⁷⁵ He began that section with the following disclaimer:

The theory of Bohr's atomic model in its current form is based on the consideration of stationary orbits at the beginning and at the end of every individual radiation process. What happens during the transition of an electron from one orbit to another is still very unclear to us. Accordingly, the goal of this section is not to draw theoretical conclusions about polarization and intensities . . . but only to extract lawlike regularities from the available empirical material.⁷⁶

For the polarizations Epstein stated the following empirical law. Even values of $\Delta n_\varphi \equiv n_\varphi^i - n_\varphi^f$ give rise to parallel polarization, odd values to perpendicular polarization. Note that for the dashed arrows in Figure 1 (polarization perpendicular to the field), $\Delta n_\varphi = \pm 1$, while for the solid arrows (polarization parallel to the field), $\Delta n_\varphi = 0$. Turning to intensities, Epstein wrote:

[T]he following hypothesis seems to fit the facts best: *a component . . . is stronger, caeteris paribus, the greater the largest of the three differences* [between initial and final quantum numbers] . . . the idea behind this is that the situation is similar to when there is a difference in altitude: the greater the difference in quantum numbers the greater the tendency to eliminate that difference.⁷⁷

Bohr's correspondence principle⁷⁸ provided a much more promis-

75. Epstein (1916b), sec. 8, pp. 514–518.

76. Epstein (1916b), p. 514.

77. Epstein (1916b), p. 515, emphasis in the original.

78. See, e.g., Kragh (2012), Ch. 5, for a recent discussion of the correspondence prin-

ing starting point for dealing with polarizations and intensities of spectral lines than Epstein’s “evening out differences in altitude” analogy. Consider the Fourier expansion of the position \mathbf{x} of a particle:⁷⁹

$$\mathbf{x} = \sum_{\tau_1 \dots \tau_s} C_{\tau_1 \dots \tau_s} \cos 2\pi \left\{ (\tau_1 \omega_1 \dots \tau_s \omega_s) t + c_{\tau_1 \dots \tau_s} \right\}. \quad (29)$$

Commenting on this expression, Bohr wrote:

Now on ordinary electrodynamics the coefficients $C_{\tau_1 \dots \tau_s}$ in the expression [Eq. (29)] for the displacement of the particles in the different directions would in the well known way determine the intensity and polarization of the emitted radiation of the corresponding frequency $\tau_1 \omega_1 + \dots + \tau_s \omega_s$. As for systems of one degree of freedom we must therefore conclude that, in the limit of large values for the n ’s, the probability of spontaneous transition between two stationary states of a conditionally periodic system, as well as the polarization of the accompanying radiation, can be determined directly from the values of the coefficient $C_{\tau_1 \dots \tau_s}$ in (31) corresponding to a set of τ ’s given by $\tau_k = n_k' - n_k''$ if n_1', \dots, n_s' and n_1'', \dots, n_s'' are the numbers which characterize the two stationary states.⁸⁰

In other words, Bohr suggested that, in the limit of large quantum numbers, the intensity of the radiation of frequency $\nu_{i \rightarrow f}$ emitted in the transition from an initial orbit with the values $(n_1, n_2, n_3)_i$ for the quantum numbers to a final orbit with the values $(n_1, n_2, n_3)_f$ should be equal to the square of the coefficient $C_{\tau_1 \dots \tau_s}$ of a term in the Fourier expansion of that orbit such that

$$\nu_{i \rightarrow f} = \frac{1}{h} (E_i - E_f) = \sum_{k=1}^s \omega_k \tau_k,$$

ciple. See the Nobel lecture by Bohr (1923), pp. 38–39, for a concise statement of it. Insightful contributions to the more recent literature on the correspondence principle are Fedak and Prentis (2002), and, building on their paper, Bokulich (2008), sec. 4.2, pp. 80–94. See also the contributions of Martin Jähnert, Enric Pérez Canals and Blai Pie Valls, and Robert Rynasiewicz to this volume.

79. Bohr (1918), p. 31, Eq. (31).

80. Bohr (1918), pp. 31–32.

and $\tau_k = n_k^i - n_k^f$.⁸¹ Bohr now took the leap of faith that this asymptotic connection between his own theory and classical electrodynamics would continue to hold if we go from high to low quantum numbers. With this general prescription, both intensities and polarizations could be handled. A transition between two orbits will be accompanied by radiation with a certain polarization and a certain intensity whenever the relevant coefficient in the orbit's Fourier expansion is non-vanishing. For very large quantum numbers it does not matter whether we consider the Fourier expansion of the initial or of the final orbit. For low quantum numbers, however, this does matter, rendering Bohr's prescription ambiguous. Should we consider the Fourier expansion of the initial or of the final orbit? Some average of the two perhaps? Or an average over initial and final orbit and all orbits in between?⁸²

Despite this ambiguity, this approach based on the correspondence principle was much more promising than the one taken by Epstein based on Sommerfeld's selection rule (27), which Bohr rejected:

Thus, from the fact that in general negative as well as positive values for the τ 's appear in [Eq. (29)], it follows that we must expect that in general not only such transitions will be possible in which all the n 's [e.g., the quantum numbers n_ξ , n_η , and n_ρ] decrease, but that also transitions will be possible for which some of the n 's increase while others decrease. This conclusion, which is supported by observations on the fine structure of the hydrogen lines as well as on the Stark effect, is contrary to the suggestion by Sommerfeld . . . that every of the n 's must remain constant or decrease under a transition.⁸³

81. Bohr (1918), p. 30, Eq. 30.

82. As Foster and Chalk (1929), two experimentalists who made important measurements of the intensities of Stark effect components (see note 93), put it: "The correspondence principle was indefinite . . . in that there were the two amplitudes in each case which should, perhaps, be averaged in some manner not obviously expressed. Kramers used, for convenience, the arithmetical mean" (p. 109). As we will see, there is no such indefiniteness in wave mechanics (see Eq. (41)).

83. Bohr (1918), p. 32.

In his dissertation, Bohr's assistant Kramers adopted and elaborated Bohr's correspondence-principle approach to account for the polarizations and intensities of the Stark effect components of the Balmer lines.⁸⁴ By distinguishing Fourier expansions of the motion in the direction of the field (z) and in the plane perpendicular to the field ($x+iy$), Kramers could account for the polarizations found by Stark. The exponent for the Fourier expansion of z ,⁸⁵ both for initial and final orbit, does not contain τ_3 , which according to Bohr's correspondence principle should be set equal to $n_\phi^i - n_\phi^f$. This suggests that $\Delta n_\phi = 0$ for all transitions in which radiation polarized parallel to the field is emitted. Similarly, only terms with $\tau_3 = \pm 1$ are present in the exponent of the Fourier expansion of $x + iy$.⁸⁶ This suggests that $\Delta n_\phi = \pm 1$ for all transitions in which radiation polarized perpendicular to the field is emitted. Figure 1 illustrates that these conclusions based on the correspondence principle are supported by Stark's findings. The solid-arrow transitions (parallel polarization) all have $\Delta n_\phi = 0$; the dashed-arrow transitions (perpendicular polarization) all have $\Delta n_\phi = \pm 1$.

Kramers could also account, at least qualitatively, for the intensities of the various components Stark had found.⁸⁷ In principle, Kramers used the average of the squares of coefficients of the relevant Fourier components of the initial and the final orbits to estimate the intensity of the corresponding line. However, even in cases where a certain frequency was completely absent from the Fourier expansion of both the initial and the final orbit, Kramers left open the possibility that the corresponding line might appear in the spectrum, albeit only faintly, as its frequency might be present in the Fourier expansion of some orbit in between. Kramers thus allowed several lines that are forbidden by the selection rules (27) and (28) of Sommerfeld and Epstein. As we saw above, Epstein had ruled out six possibilities for the transition $n = 3 \rightarrow n = 2$ (see the dotted

84. Kramers (1919). For discussion, see Dresden (1987), Ch. 11, sec. IV (pp. 107-110).

85. Kramers (1919), p. 21, Eq. (60).

86. Kramers (1919), p. 23, Eq. (67).

87. Kramers (1919), pp. 55-57, Tables I-IV.

arrows in Figure 1 with values ± 5 , ± 6 , ± 8 times $C\mathcal{E}/h$ for Δv). Kramers predicted (correctly as it turned out) that these Stark effect components of H_α had just escaped notice so far because of their low intensity.⁸⁸

In his 2012 book on the Bohr model, Helge Kragh observes: “Kramers arrived at theoretical values for the relative intensities that he modestly described as ‘convincing’. In fact the agreement between theory and experiment was nearly perfect.”⁸⁹ Kragh reproduces a diagram from Bohr’s Nobel lecture showing remarkably close agreement between Kramers’ theoretical values and Stark’s experimental results for the relative intensities of the Stark effect components of H_γ .⁹⁰ Discussing this diagram, Bohr stated that “the theory reproduces completely the main feature of the experimental results.”⁹¹ Kragh proceeds to quote from a *Bulletin* of the National Research Council on quantum theory, in which Kramers’ results are hailed as “most convincing evidence for the value of [Bohr’s] principles.”⁹² Finally, he cites a 1924 paper by John Stuart Foster with the results of measurements of the relative intensities of some Stark effect components of H_ϵ , the Balmer line corresponding to the transition $n = 7 \rightarrow n = 2$.⁹³ Foster wrote:

88. Kramers (1919), Appendix, Fig. 1 (Kramers (1956), p. 105).

89. Kragh (2012), p. 205. Similarly, Dresden (1987) writes that “[t]he agreement between theory and experiment is surprisingly good” and that “Kramers describes this impressive agreement in his customary guarded manner” (p. 109). Leone, Paolette and Robotti (2004) reproduce a diagram from Kramers’ dissertation showing observed and calculated relative intensities of the Stark effect components of the first three Balmer lines, H_α , H_β , and H_γ , and comment: “Kramers’s theoretical predictions were in excellent agreement with Stark’s measurements” (p. 288).

90. Bohr (1923), p. 39, reproduced in Kragh (2012), p. 206.

91. Bohr (1923), p. 39.

92. Adams (1923), p. 88, quoted in Kragh (2012), p. 206.

93. See the biographical memoir by Bell (1966), for a discussion (pp. 150–153) and a bibliography of Foster’s work on the Stark effect, which he started as a graduate student at Yale in the early 1920s and continued until the late 1930s as a professor at McGill. As his biographer points out, “[d]uring all of his work on the Stark effect he brooded over the design of Lo Surdo discharge tubes, and he was able to make them behave better than anyone else” (Bell, 1966, p. 151). See Leone, Paolette and Robotti (2004), especially Figs. 4, 6, 9, and 10, for a comparison between the experi-

At the time Kramers' dissertation was published there were no observations with which to compare his theoretical estimates of the relative intensities of the Stark effect components of H_ϵ . Two of the plates exposed . . . during this investigation show many components of this line . . . The relative intensities of the stronger inner components are very close to the predicted values.⁹⁴

In subsequent experiments, however, undertaken with his graduate student Laura Chalk,⁹⁵ Foster found relative intensities for some Stark effect components of H_α and H_β that differed markedly from those reported by Stark and from the theoretical values found by Kramers. The new experimental values, however, generally agreed with the intensities predicted by wave mechanics.⁹⁶ As Foster and Chalk reported:

By means of wave mechanics, Schrödinger [1926] has made quantitative calculations of the intensities of Stark components in hydrogen which are commonly considered to be an improvement on the earlier estimates based on the correspondence principle [Kramers (1919)]. That this is so in the case of H_β was shown recently by the writers in a quantitative experimental investigation [Foster and Chalk (1926)].

The greatest variation of the new theory from Prof. Stark's results,

mental setups used by Lo Surdo and Stark. In 1926, Foster spent almost a year in Copenhagen on an International Education Board fellowship, which gave him "the chance to publish his most important single paper" (Bell, 1966, p. 148). In this paper, communicated by Bohr, Foster (1927) presented both theoretical and experimental results on the Stark effect in helium.

94. Foster (1924), p. 675.

95. In 1928, Chalk became the first woman to earn her Ph.D. in physics at McGill.

96. See the diagrams in Condon and Shortley (1963), p. 401, based on the experimental work of Foster and Chalk, Mark and Wierl and others in the late 1920s, which show that in most cases the quantum-mechanical predictions for the intensities of the Stark effect components of H_α , H_β , H_γ , and H_δ agree within a few percent with experiment. Condon and Shortley (1963), p. 402, caution that these measurements "do not agree in detail with the theory, but provisionally we shall regard this as due to the large number of variations in physical conditions in the experimental work." The dependence of the results of measurements of the intensities of the Stark effect components of the Balmer lines on the experimental setup is emphasized by Mark and Wierl (1929), p. 538.

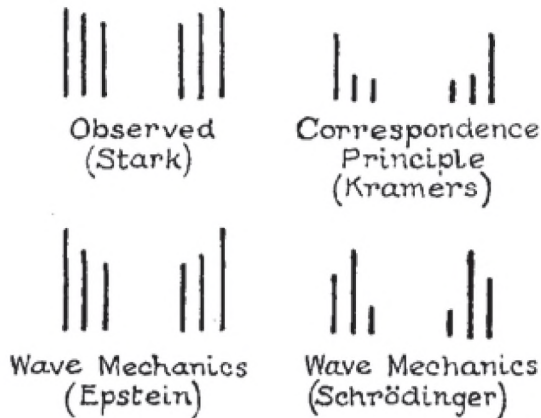


Figure 2: Four sets of values (one experimental, three theoretical) for the intensities of the six parallel Stark effect components of H_α (cf. Figure 1). From Foster and Chalk (1928), p. 830, Figure 1.

however, occurs in the parallel components of H_α . There are three pairs of such components which have been photographed; and in the original experiments, as well as in the older quantum theory, the outside components were found to be the strongest. This is further supported by the recent calculations of Epstein [1926] on wave mechanics. In contrast to these results, Schrödinger finds the greatest intensity for the pair with intermediate displacements. The difference between Schrödinger's calculations and the observations of Stark is obviously rather large to be considered as an experimental error. Yet this is what it appears to be according to numerous plates obtained by the junior author in an extension to the earlier experiments, the new results being in general agreement with the calculations of Schrödinger.⁹⁷

The three pairs of parallel Stark effect components of H_α mentioned by Foster and Chalk correspond to the six solid lines in our Figure 1, with $\Delta v = \pm 2, \pm 3, \pm 4$ (in units of $C\mathcal{E}h$). Figures 2 and 3 show the diagrams with which Foster and Chalk illustrated their claims.

Foster and Chalk suspected that Epstein's calculations only

97. Foster and Chalk (1928), p. 830. In square brackets are the papers cited by Foster and Chalk in this passage.

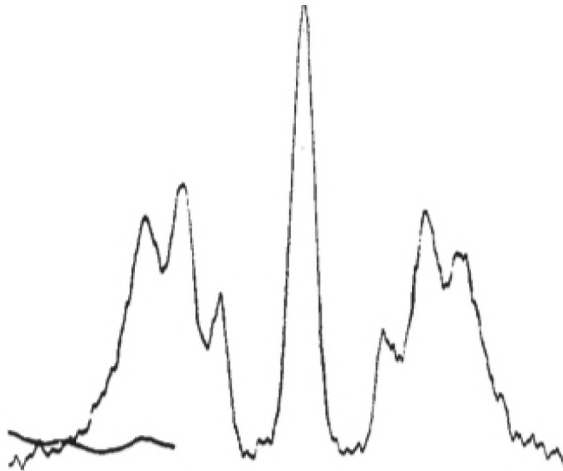


Figure 3: Foster and Chalk's measurements of the intensities of the six parallel Stark effect components of H_α corresponding to those shown in Figure 2. The peak at the center, the authors explain, may suggest that there is "a strong undisplaced parallel component, but, in reality, this is due to the overlapping of the images on the slit." From Foster and Chalk (1928), p. 831, Figure 2.

agreed with Stark's old data because Epstein had made some errors. This suspicion was confirmed the following year when Walter Gordon and Rudolph Minkowski corrected Epstein's calculations and showed that they led to the same results as Schrödinger's.⁹⁸

Foster and Chalk concluded that the intensities found by Schrödinger agreed well with their experimental findings:

Within the limits of experimental error the new results agree, we believe, with the calculations by Schrödinger. The well-marked agreement in the lines H_α and H_β is of especial importance, since it is in the case of low quantum numbers that the new quantum-theoretical calculations show the greatest departure from the estimates of the older theory.⁹⁹

98. Gordon and Minkowski (1929), cited by Condon and Shortley (1963), p. 400 (cf. note 129 below).

99. Foster and Chalk (1928), p. 116-118.

In a paper on the Stark effect in helium (cf. note 93), Foster gave the following assessment of the experimental situation concerning the intensities of the Stark effect components of hydrogen's Balmer lines: "The question of the intensity of the components has been fully treated by Schrödinger, whose results form a *quantitative extension of the qualitative estimate given earlier by Kramers* on the basis of the correspondence principle."¹⁰⁰

2.3. *The non-uniqueness of orbits*

To conclude our discussion of the Stark effect in the old quantum theory, we turn to the problem mentioned in the introduction that the electron orbits allowed by the quantization conditions depend on the coordinates in which these conditions are imposed. Although one finds the same energy levels in different coordinate systems, one does not always find the same orbits.¹⁰¹ The analysis of the Stark effect in hydrogen provides a dramatic illustration of this problem. The orbits found in parabolic coordinates when the electric field is set equal to zero differ sharply from those found without an external electric field in polar coordinates. Both Epstein and Sommerfeld acknowledged this discrepancy.¹⁰² Both of them expressed the (idle) hope that the problem would disappear once relativistic effects were taken into account.

In an appendix to the first edition of *Atombau und Spektrallinien*, "Quantization of elliptical motion according to the method of separation of variables," Sommerfeld showed how to solve the Kepler problem in the old quantum theory (one electron orbiting a nucleus) by separating the Hamilton-Jacobi equation for the problem in polar coordinates. He then raised the issue of the uniqueness of this choice of coordinates

Are polar coordinates . . . the only variables in which [the Hamilton-

100. Foster (1927), p. 139 (our emphasis).

101. Jammer (1966), p. 101.

102. Epstein (1916b), p. 507; Sommerfeld (1919), p. 502-503 (see also Sommerfeld (1923), p. 284).

Jacobi equation for the Kepler problem] can be separated? Do other coordinates, should there be any, lead to the same result [for the expression for the energy of the quantized orbits]?

The first question is to be answered negatively. When treating the Stark effect . . . we saw that [the Hamilton-Jacobi equation] for the Kepler problem with an external electric field (and hence also for the problem without one) can be separated through the introduction of so-called parabolic coordinates. The quantum conditions that obtain in these coordinates and the quantized orbits that result from them are different from those found in polar coordinates. The main result of our treatment, however, remains unaffected, for the expression for the energy quantized in parabolic coordinates [our Eq. (24)] has the same form as the one found here [our Eq. (4)].

The ambiguity disappears when we treat the problem more completely, i.e., by taking into account the relativistic variability of the electron mass . . . For this problem, the nature of our task makes polar coordinates the preferred ones. As we must think of ordinary mechanics as the limiting case of relativistic mechanics, we can also consider our treatment of the Kepler problem in polar coordinates as the legitimate limiting case of the complete and non-arbitrary relativistic solution of the problem.¹⁰³

Note that Sommerfeld sidestepped the question about which coordinates to use for the relativistic Kepler problem *with* an external electric field. Epstein did address that question, even if he did not have a satisfactory answer to it:

Even though this does not lead to any shifts in the line series, the notion that a preferred direction introduced by an external field, no matter how small, should drastically (*in einschneidender Weise*) alter the form and orientation of stationary orbits seems to me to be unacceptable. The solution of this apparent paradox is to be expected from a theory in which relativity and external field are taken into account at the same time . . . This would involve an extension of the quantum conditions for situations with a superposition of two effects that individually can be handled through a separation of variables.¹⁰⁴

103. Sommerfeld (1919), pp. 502-503.

104. Epstein (1916b), p. 507.

It is not clear what such an extension would look like. One might have held out hope that an exact treatment would lead to a Hamilton-Jacobi equation that is only separable in one unique set of coordinates. One could then argue that the real orbits of the system are the ones found in those coordinates. Alas, the exact treatment of any but the simplest systems will result in Hamilton-Jacobi equations that are not separable in *any* coordinates.¹⁰⁵

In the first installment of his 1918–1922 trilogy on the old quantum theory, Bohr also discussed the non-uniqueness of orbits in cases where the Hamilton-Jacobi equation is separable in more than one coordinate system.¹⁰⁶ Bohr argued that this will typically be the case for ‘degenerate systems’:¹⁰⁷

In the cases of degeneration . . . the conditions [$I_k = n_k h$ (cf. our Eqs. (21))] involve an ambiguity, since in general for such systems there will exist an infinite number of different sets of coordinates which allow of a separation of variables, and which will lead to different motions in the stationary states, when these conditions are applied. As we shall see below, this ambiguity will not influence the fixation of the total energy in the stationary states which is the essential factor in the theory of spectra.¹⁰⁸

105. As Epstein (1916b) had noted a few pages earlier: “Unfortunately, the relativistic motion around a center of attraction under the simultaneous influence of an external field does not belong to the class of problems that can be solved through separation of variables” (p. 500).

106. Before we present our gloss on Bohr’s remarks, a word of caution seems in order. As Helge Kragh (2012) explains: “While the trilogy of 1913 was clearly structured and fairly easy to follow [though Heilbron and Kuhn (1969) showed that even that text is not nearly as straightforward as it may appear to be at first sight], the new trilogy of 1918–1922 was anything but. It was, as Bohr said with understatement to Ehrenfest, ‘somewhat unmanageable’. Both the structure and style of the memoir – Bohr did not bother to split up sections into smaller bits or to limit the length of his sentences – made it something of a nightmare for the reader. Important as it was, it was definitely not a lucid work” (p. 192).

107. See Bohr (1918), p. 20, for his definition of “degenerate systems.” For our purposes, all that matters is that Bohr treats the hydrogen atom without an external electric field as an example of such a degenerate system (see Bohr (1918), p. 21).

108. Bohr (1918), p. 20.

Note that Bohr's first line of defense is the same as Sommerfeld's: the ambiguity does not affect the expression for the total energy. Also note that, while it is true that there are, e.g., infinitely many different polar coordinate systems or parabolic coordinate systems, these are still very special coordinates.¹⁰⁹ Bohr's statement thus gives a misleading impression about the range of problems to which the method of separation of variables can be applied. Most importantly, however, Bohr, unlike Epstein and Sommerfeld, saw the non-uniqueness of orbits as an asset rather than an embarrassment for the old quantum theory.

A few pages later, in a maddeningly dense passage, Bohr describes what happens to orbits when an external field is switched on. Below are a few intriguing clauses from this passage:

Consider now a periodic system in some stationary state . . . and let us assume that an external field is slowly established . . . and that the motion at any moment during this process allows of a separation of variables in a certain set of coordinates . . . we must expect that the motion of a periodic system . . . under the establishment of the external field cannot be determined by ordinary mechanics, but that the field will give rise to effects of the same kind as those which occur during a transition between two stationary states accompanied by emission or absorption of radiation. Consequently we shall expect that, during the establishment of the field, *the system will in general adjust itself in some unmechanical way* until a stationary state is reached . . .¹¹⁰

This passage seems to suggest that, say, an electron in a hydrogen atom in an initially field-free region moving on one of the orbits found by imposing the quantum conditions in polar coordinates would, at the appearance of an arbitrarily small homogeneous electric field, immediately and stochastically jump to one of the orbits

109. In the parameter space of all physically reasonable Hamiltonian functions to which an actual electron might be subjected, the set of Hamiltonians amenable to separation in polar or parabolic coordinates – or indeed, any of the eleven “canonical” coordinate systems in which the Laplacian separates (Morse and Feshbach (1953), pp. 655-665) – occupy a set of measure zero.

110. Bohr (1918), p. 23 (emphasis in the original).

“adapted” to the direction of the field at that moment, i.e., one of the orbits found by imposing the quantum conditions in parabolic coordinates. As soon as the direction of the field is changed, it would jump to another adapted orbit found by imposing the quantum conditions in different parabolic coordinates. This picture, unattractive in and of itself, requires, as Bohr seems to acknowledge in the passage quoted above, that the external field experienced at any moment by the electron is such that there are coordinates in which the Hamilton-Jacobi equation for the system is separable. This requirement cannot be met as soon as there is any inhomogeneity in the electric field in the space traversed by the orbit. Worse yet, the inclusion of relativistic effects removes the possibility of separation of variables even in the case of an exactly homogeneous and constant external field. In short, what seems to emerge when we strip away Bohr’s obfuscating language is nothing but a rather bizarre proposal for the behavior of electrons in atoms. Had Bohr expressed himself more clearly, his proposal might actually have undermined rather than enhanced support for his theory! In the end, Bohr’s proposal mainly serves to reinforce Epstein’s point that “the notion that a preferred direction introduced by an external field, no matter how small, should drastically alter the form and orientation of stationary orbits would seem to be unacceptable.”^{III}

n	n_r	l	ϵ
1	0	1	0
2	0	2	0
2	1	1	$\sqrt{3}/2$
3	0	3	0
3	1	2	$\sqrt{5}/3$
3	2	1	$2\sqrt{2}/3$

Table 1: Angular momentum (l times \hbar) and eccentricity (ϵ) for low-lying orbits in polar coordinates.

III. Epstein (1916b), p. 507.

n	n_ξ	n_η	n_φ	l	ϵ
1	0	0	1	1	0
2	0	0	2	2	0
2	1	0	1	$\sqrt{2}$	$1/\sqrt{2}$
2	0	1	1	$\sqrt{2}$	$1/\sqrt{2}$
3	0	0	3	3	0
3	1	1	1	$\sqrt{1 + 8 \sin^2(\pi\delta)}$	$2\sqrt{2} \cos(\pi\delta)/3$
3	1	0	2	$\sqrt{6}$	$1/\sqrt{3}$
3	2	0	1	$\sqrt{3}$	$\sqrt{2/3}$
3	0	1	2	$\sqrt{6}$	$1/\sqrt{3}$
3	0	2	1	$\sqrt{3}$	$\sqrt{2/3}$

Table 2: Angular momentum (l times \hbar) and eccentricity (ϵ) for low-lying orbits in parabolic coordinates.

Tables 1 and 2 illustrate just how different the allowed orbits of the electron in a hydrogen atom in the absence of an external electric field are depending on whether the quantum conditions are imposed in polar or in parabolic coordinates. The first three columns in Table 1 and the first four columns in Table 2 give the quantum numbers – (n_r, l) and $(n_\xi, n_\eta, n_\varphi)$, respectively – for orbits with principal quantum number $n = 1, 2, 3$ (where $n = n_r + l = n_\xi + n_\eta + n_\varphi$). The last two columns in both tables give the values for the angular momentum and the eccentricity for the orbits characterized by these quantum numbers. These entries are based on the following relations, which we will not derive here but just state.¹¹² The size l of the angular momentum in units of \hbar and the eccentricity ϵ are related via

$$l = n\sqrt{1 - \epsilon^2}, \quad \epsilon = \sqrt{1 - \frac{l^2}{n^2}}. \tag{30}$$

We used the latter expression to find the numbers in the column for ϵ in Table 1. To find the corresponding entries in parabolic coordinates, we introduce the quantities σ_1 and σ_2 :

¹¹². See sec. 3 of Duncan and Janssen (2014) for a derivation of Eqs. (30)–(32) (the last one only for the special case that either σ_1 or σ_2 vanishes).

$$\sigma_1 \equiv \frac{1}{n} \sqrt{n_\xi(n_\xi + n_\varphi)}, \quad \sigma_2 \equiv \frac{1}{n} \sqrt{n_\eta(n_\eta + n_\varphi)}. \quad (31)$$

The eccentricity can be written as a function of these quantities and a phase parameter δ , which can take on a continuum of values:

$$\epsilon = \sqrt{\sigma_1^2 + \sigma_2^2 + 2\sigma_1\sigma_2 \cos(2\pi\delta)}. \quad (32)$$

We used this expression to find the numbers in the column for ϵ in Table 2. To obtain the values in the column for l , we substituted these values for ϵ into the first of Eqs. (30).

Comparing Tables 1 and 2, we see that only the circular orbits (with $n_r = n_\xi = n_\eta = 0$) are the same in polar and parabolic coordinates. All other orbits are different.

The appearance of the phase δ in Table 2 shows that, in many cases, the values of $(n_\xi, n_\eta, n_\varphi)$ do not even pick out discrete orbits but rather continuous sets of orbits. Orbits were abandoned in the transition from the old quantum theory to matrix mechanics in 1925, largely because of problems in dispersion theory.¹¹³ In hindsight, we can see that one of the most celebrated successes of the old quantum theory, the Stark effect, should have made proponents of the theory suspicious of the notion of well-defined electron orbits in atoms well before 1920.

3. The Stark effect in wave mechanics

The derivation of the formula for the Stark effect in wave mechanics shows a strong family resemblance to the derivation of Epstein and Schwarzschild in the old quantum theory.¹¹⁴ Independently of one another, Schrödinger and Epstein applied the new wave mechanics to the Stark effect.¹¹⁵ Schrödinger's paper was published in *Annalen der Physik* on 13 July 1926. Epstein's paper is signed 29 July 1926 and was published in *Physical Review* in October 1926. Epstein had moved

¹¹³. Duncan and Janssen (2007).

¹¹⁴. Epstein (1916b), Schwarzschild (1916).

¹¹⁵. Schrödinger (1926), Epstein (1926).

to Pasadena in 1921. In his paper, Epstein cited Schrödinger's first and second "communication" (*Mitteilung*) on wave mechanics as well as Schrödinger's paper on the equivalence of wave and matrix mechanics (which appeared in May 1926), but not the third communication.¹¹⁶ Presumably, the issue of 13 July 1926 of the *Annalen* had not reached Pasadena by 29 July 1926.

In the abstract of his paper, Epstein emphasized the advantages of the new theory of the Stark effect over the old one:

(1) *Positions of lines* practically coincide with those obtained in the writer's old theory which gave an excellent agreement with experiment.

(2) *Intensity expressions* are obtained in a simple closed form: (a) Components which, in the old theory, had to be ruled out by a special postulate now drop out automatically. (b) The computed intensities of the remaining components check the observed within the limits of experimental error.¹¹⁷

In the introduction, he elaborated:

The positions of the lines turn out to be practically the same as in the writer's old theory. The first order terms are identical with the old expressions, the second order terms [which we are ignoring in this paper (AD & MJ)] show a very slight difference. The main interest of the paper lies, therefore, in the intensity formulas, which are remarkably simple in their structure and agree with the observed values better than Kramers' intensity expressions derived from Bohr's correspondence principle.¹¹⁸

To bring out the close analogy between the calculations in the old and the new quantum theory, we sketch the derivation of the for-

116. Epstein (1926), p. 695, note 1.

117. Epstein (1926), p. 695. Claim (2b), however, was based in part on a comparison of erroneous calculations with spurious data (cf. notes 98 and 129).

118. Epstein (1926), p. 695.

mula for the Stark effect in hydrogen in wave mechanics.¹¹⁹ As in the old quantum theory, the starting point is the Hamiltonian (13) in parabolic coordinates. Instead of the substitutions (15) of $\partial S/\partial \xi$ for p_ξ etc., we now make the substitutions

$$p_\xi \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial \xi}, \quad p_\eta \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial \eta}, \quad p_\varphi \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial \varphi}, \quad (33)$$

to form the Hamilton operator \hat{H} entering into the time-independent Schrödinger equation,

$$\hat{H}\psi = \alpha_1\psi, \quad (34)$$

where $\psi(\zeta, \eta, \varphi)$ is the wave function in parabolic coordinates. Following the notation used in our calculation in the old quantum theory, we use α_1 to label the energy eigenvalues. With the substitutions (33) the Hamiltonian (13) becomes the Hamilton operator

$$\hat{H} = -\frac{\hbar^2}{2\mu} \left(\frac{4}{\xi + \eta} \left(\frac{\partial}{\partial \xi} \xi \frac{\partial}{\partial \xi} \right) + \frac{4}{\xi + \eta} \left(\frac{\partial}{\partial \eta} \eta \frac{\partial}{\partial \eta} \right) + \frac{1}{\xi \eta} \frac{\partial^2}{\partial \varphi^2} \right) - \frac{2e^2}{\xi + \eta} + \frac{1}{2} e\mathcal{E}(\xi - \eta). \quad (35)$$

Inserting this expression into Eq. (34), dividing both sides by ψ and multiplying by $2\mu(\xi + \eta)$ (using relations (14)), we arrive at:

$$-\frac{\hbar^2}{\psi} \left(4 \frac{\partial}{\partial \xi} \xi \frac{\partial}{\partial \xi} + 4 \frac{\partial}{\partial \eta} \eta \frac{\partial}{\partial \eta} + \left(\frac{1}{\xi} + \frac{1}{\eta} \right) \frac{\partial^2}{\partial \varphi^2} \right) \psi - 4\mu e^2 + \mu e\mathcal{E}(\xi^2 - \eta^2) = 2\mu(\xi + \eta)\alpha_1. \quad (36)$$

Note the similarity between the Schrödinger equation (36) and the Hamilton-Jacobi equation (16) in the old quantum theory.¹²⁰ Hamilton-Jacobi theory played an important role in the development of wave mechanics. It was the embodiment of the optical-mechanical

119. See, e.g., Condon and Shortley (1963), pp. 398–404, for a modern textbook treatment that follows Schrödinger (1926) and Epstein (1926).

120. See sec. 6 of Duncan and Janssen (2014) for a more detailed exploration of the connection between the Schrödinger equation and the Hamilton-Jacobi equation.

analogy that guided Schrödinger’s search for a new wave mechanics underlying ordinary particle mechanics the way wave optics underlies ray optics.¹²¹ Schrödinger’s account of the Stark effect shows that the connection between wave mechanics and Hamilton-Jacobi theory also enabled him to transfer important mathematical techniques from the old quantum theory to his new theory.

Eq. (36), like Eq. (16), is separable in parabolic coordinates. In the case of the Schrödinger equation, this means that its solution has the form

$$\psi(\xi, \eta, \varphi) = \psi_\xi(\xi)\psi_\eta(\eta)\psi_\varphi(\varphi).$$

The wave function ψ and the generating function S are related via $\psi = e^{iS/\hbar}$. Hence, if S is the sum of three functions, each of which depends on only one of the three coordinates $\xi, \eta,$ and φ (see Eq. (17)), ψ will be the product of three such functions:

$$\psi(\xi, \eta, \varphi) = e^{i(S_\xi(\xi)+S_\eta(\eta)+S_\varphi(\varphi))/\hbar} = \psi_\xi(\xi)\psi_\eta(\eta)\psi_\varphi(\varphi),$$

Just as we could set $S_\varphi(\varphi) = \alpha_3\varphi$ (see Eq. (22)), we can set $\psi_\varphi(\varphi) = e^{i\alpha_3\varphi/\hbar}$, with $\alpha_3 = n_\varphi\hbar$ and $n_\varphi = m$. Upon substitution of $-m^2\psi$ for $\partial^2\psi/\partial\varphi^2 = d^2\psi_\varphi/d\varphi^2$ in Eq. (36), we are left with an equation that splits into a part depending only on ξ and a part depending only on η . Both parts must therefore be constant. Denoting these constants by $\mp 2\alpha_2$ as we did in the corresponding Eq. (19) in the old quantum theory, we arrive at equations of the form

$$\xi \frac{d^2\psi_\xi}{d\xi^2} + \frac{d\psi_\xi}{d\xi} + (\dots)\psi_\xi = 0, \quad \eta \frac{d^2\psi_\eta}{d\eta^2} + \frac{d\psi_\eta}{d\eta} + (\dots)\psi_\eta = 0. \quad (37)$$

The expressions in parentheses are functions of ξ and η , respectively, containing the separation constants $\alpha_1, \alpha_2, \alpha_3,$ and the field strength \mathcal{E} .

As in the old quantum theory, we first solve these equations for $\mathcal{E} = 0$ and then to first (and second) order in \mathcal{E} . For our purposes, the first step, with $\mathcal{E} = 0$, turns out to be the most interesting one, and

¹²¹I. Joas and Lehner (2009).

we will focus on that part of the calculation.¹²² We begin by studying the behavior of $\psi_\xi(\xi)$ and $\psi_\eta(\eta)$ at small and large ξ and η , respectively. This leads us to write these functions in the form

$$\psi_\xi(\xi) = \xi^{|m|/2} e^{-\xi/2na} f(\xi), \quad \psi_\eta(\eta) = \eta^{|m|/2} e^{-\eta/2na} g(\eta), \quad (38)$$

where f and g are as yet unknown functions. In the process we replaced a_1 by

$$na \equiv \frac{\hbar}{\sqrt{-2\mu\alpha_1}} \quad \text{with} \quad a \equiv \frac{\hbar^2}{\mu e^2},$$

anticipating that n will eventually be identified as the principal quantum number. Inserting Eqs. (38) for ψ_ξ and ψ_η into Eqs. (37), we find equations for f and g of the form:

$$\xi f'' + (\dots) f' + (\dots) f = 0, \quad \eta g'' + (\dots) g' + (\dots) g = 0.$$

The solution of these equations will be polynomials in ξ and η , respectively:

$$f(\xi) = \sum_{k=0}^{n_\xi} a_k \xi^k, \quad g(\eta) = \sum_{l=0}^{n_\eta} b_l \eta^l, \quad (39)$$

with recursion relations on their coefficients (of the form $a_{k+1}/a_k = \dots$ and $b_{l+1}/b_l = \dots$). For the wave function to be square-integrable, the polynomials in Eq. (39) have to break off at some point, i.e., there must be values n_ξ and n_η of k and l such that $c_{n_\xi+1} = 0$ and $c_{n_\eta+1} = 0$. This leads to the conditions:

$$n_\xi = \frac{n}{2} \left(1 - \frac{|m|+1}{n} \right) - \frac{\alpha_2 na}{2\hbar^2}, \quad n_\eta = \frac{n}{2} \left(1 - \frac{|m|+1}{n} \right) + \frac{\alpha_2 na}{2\hbar^2}.$$

Combining these two conditions, we find

$$\frac{n}{2} \left(1 - \frac{|m|+1}{n} \right) - n_\xi = n_\eta - \frac{n}{2} \left(1 - \frac{|m|+1}{n} \right),$$

¹²². See sec. 4 of Duncan and Janssen (forthcoming) for a more detailed version of this calculation.

or, equivalently,

$$n = n_\xi + n_\eta + |m| + 1. \quad (40)$$

Comparing this result in wave mechanics with the corresponding result (23) in the old quantum theory, we notice that the difference between the two results is the final term +1 in Eq. (40). This extra term obviates the need for a special condition to rule out $|m| = 0$. Both Schrödinger and Epstein emphasized this point.¹²³ Elaborating on point (2a) in his abstract (quoted above), Epstein commented:

It will be remembered that the restriction for the azimuthal quantum number [$|m| > 0$] was an additional one, not following from the dynamical conditions. It was introduced by Bohr for the purpose of eliminating plane orbits, moving in which the electrons would sooner or later undergo a collision [sic] with the nucleus. In our new theory an additional restriction is not necessary.¹²⁴

In the so-called WKB approximation,¹²⁵ conditions similar to the quantum conditions (11) of the Bohr-Sommerfeld theory emerge from the requirement that different parts of the approximate solutions of the Schrödinger equation constructed according to the WKB method merge properly. In the regime of large quantum numbers, one finds conditions of the form $\int p_i dq_i = (n_i + \alpha)h$ in this way, where α is equal to $\frac{1}{4}$ times an integer (now called the Maslov index¹²⁶). In the analysis of the Stark effect in parabolic coordinates, α turns out to be equal to $\frac{1}{2}$ and the quantum numbers n_ξ and n_η in the old quantum theory are replaced by $n_\xi + \frac{1}{2}$ and $n_\eta + \frac{1}{2}$, respectively. This explains the extra term 1 in Eq. (40) for the principal quantum number.¹²⁷

123. Schrödinger (1926), p. 463; Epstein (1926), p. 708.

124. Epstein (1926), p. 708.

125. The WKB or WKBJ approximation is named after Gregor Wentzel (1926), Léon Brillouin (1926), and Kramers (1926), who developed it independently of one another shortly after the formulation of wave mechanics, and Harold Jeffreys (1924), who had introduced it earlier in a different context.

126. Gutzwiller (1990), p. 211.

127. See sec. 6 of Duncan and Janssen (2014) for a more detailed discussion of how

As we saw at the end of Section 2, experimentalists established very quickly that the values given by Schrödinger for the intensities of the Stark effect components of the Balmer lines agreed better with their data than those given by Kramers. Despite the notorious animosity between proponents of wave and matrix mechanics, Schrödinger, who had just published his paper on the equivalence of the two formalisms, borrowed freely from matrix mechanics to calculate intensities. As he explained at the beginning of the section on intensities in his paper:

According to Heisenberg, if q is a Cartesian coordinate, the square of the matrix element ... should be a measure for the “transition probability from the r^{th} to the r'^{th} state,” more precisely speaking the intensity of that part of the radiation connected to this transition that is polarized in the direction of q .¹²⁸

In modern Dirac notation, this matrix element would be written as¹²⁹

$$\langle n_{\xi}^{r'}, n_{\eta}^{r'}, m^{r'} | q | n_{\xi}^r, n_{\eta}^r, m^r \rangle$$

Neither Epstein nor Schrödinger seems to have realized that the new account of the Stark effect was superior to the old one in yet another respect. As we mentioned in the introduction, quantum mechanics replaces the embarrassing non-uniqueness of orbits in the old quantum theory (see Tables 1 and 2 at the end of Section 2.3) by a completely innocuous non-uniqueness of bases of eigenfunctions. Consider, for example, the three orbits for the lower level ($n = 2$) in Figure 1, with the values (011), (002), and (101) for the quantum numbers $(n_{\xi}, n_{\eta}, n_{\varphi})$ associated with the use of parabolic coordinates in the old quantum theory. In wave mechanics, these three

the WKB approximation can be used to amend the quantum conditions of the old quantum theory.

128. Schrödinger (1926), p. 465.

129. As Gordon and Minkowski (1929) pointed out, the most serious mistake in Epstein’s calculation (cf. note 98 above) was that he equated the intensity with the norm of this matrix element rather than with its square.

levels do not correspond to orbits but to three (orthonormal) wave functions characterized by those same quantum numbers. All three are eigenfunctions (at least to first order in the electric field strength \mathcal{E}) of the Hamiltonian (35) for the hydrogen atom in an external electric field. These wave functions can be written as linear combinations of three (orthonormal) wave functions characterized by quantum numbers in polar coordinates. As long as there is no external electric field ($\mathcal{E} = 0$), these wave functions are eigenfunctions of the Hamiltonian as well. However, as soon as the field is switched on ($\mathcal{E} \neq 0$), they no longer are; only linear combinations of these wave functions in polar coordinates that correspond to the eigenfunctions of the Hamiltonian in parabolic coordinates are. This is no problem at all. In the old quantum theory, we get a different set of allowed physical states (represented by orbits in a miniature solar system) depending on whether we use polar or parabolic coordinates. In the new quantum theory, we get the same set of allowed physical states (now represented by wave functions or, more generally, by vectors or rays in Hilbert space) regardless of which coordinates we use. We just have the freedom of writing any state as a linear combination of any orthonormal basis of states in the Hilbert space.¹³⁰

4. Conclusion: Stark contrasts between the old and the new quantum theory

The explanation of the Stark effect by Epstein and Schwarzschild in 1916 was a triumph for the old quantum theory. In *Atombau und Spektrallinien*, from which we already quoted a few passages in the introduction, Sommerfeld wrote that this explanation was in such complete agreement with the empirical data that “any doubt about the correctness and uniqueness of the solution is no longer possible.”¹³¹ “[T]he classical theory,” he pointed out, “failed com-

¹³⁰. See sec. 5 of Duncan and Janssen (2014) for a more detailed discussion of how the non-uniqueness of orbits in the old quantum theory turns into the non-uniqueness of bases of eigenfunctions.

¹³¹. Sommerfeld (1919), p. 440.

pletely in the case of the Stark effect. By contrast, the quantum theory fully reproduces the observations in all their rich detail (including recently the polarizations)."¹³² A few pages later, after covering the work of Epstein, Schwarzschild, and Kramers on the Stark effect, he wrote in the concluding paragraphs of his book:

The frequencies, especially those of the electric splittings could be derived with extraordinary certainty and completeness from the principles of Bohr's theory of the hydrogen atom and of quantum emission. With a sensible extension of the theory, [the polarization] could also be explained in a way that hardly leaves any gaps. The ravine that originally seemed to open up between the quantum theory and the wave theory of spectral lines could therefore on essential points already be bridged. Not much is missing for it to be definitively filled in. In this sense, the theory of the Zeeman effect and especially that of the Stark effect belong to the most impressive achievements of our field and form a beautiful capstone on the edifice of atomic physics.¹³³

As we showed in Section 2, however, even the Stark effect revealed some serious cracks in Sommerfeld's edifice. To account for the effect in the old quantum theory, one had to make some arbitrary assumptions in addition to the Bohr-Sommerfeld quantum conditions to rule out certain orbits. To calculate intensities of lines on the basis of Bohr's correspondence principle, one had to make at least one more arbitrary assumption. It was not enough to stipulate that the intensity of a line of a given frequency is given by the square of the coefficient of the term in the Fourier expansion of the orbit with that frequency. One also had to decide whether to use the Fourier expansion of the initial orbit, the final orbit, or some weighted average of both and everything in between. Moreover, contrary to the calculations of the frequencies of the various lines, the calculations of their intensities only gave qualitative agreement with the (admittedly also less secure) experimental data. Most worrisome of all, we saw that the actual orbits predicted by the old quantum the-

¹³². Sommerfeld (1919), p. 440.

¹³³. Sommerfeld (1919), pp. 457–458.

ory depend on the coordinates chosen to impose the quantum conditions (see Tables 1 and 2). Both Sommerfeld and Epstein clearly identified this problem but their response to it was little more than wishful thinking that the problem would somehow go away. Bohr made an unconvincing attempt to turn this weakness into a strength of the theory.

As we showed in Section 3, all these problems were solved in 1926 when Schrödinger and Epstein explained the Stark effect on the basis of the new wave mechanics. The old explanation was certainly helpful as the mathematical techniques needed to solve the problem in the two theories are very similar, as we also saw in Section 3. In particular, it suggested that the Schrödinger equation, like the Hamilton-Jacobi equation, would be separable in parabolic coordinates (cf. Eqs. (16)–(20) and Eqs. (36)–(37)). The new theory determines all allowed states and transitions without any additional assumptions. In particular, the principal quantum number picked up an extra term of +1 (see Eq. (40)), which obviated the need to rule out certain combinations of values of the three parabolic quantum numbers. Wave mechanics also replaced the ambiguous guidelines based on the correspondence principle for calculating intensities by the straightforward and definite prescription that intensities are given by the squares of the matrix elements of position, leading to results in reasonable quantitative agreement with the experimental data. Finally, the embarrassing non-uniqueness of orbits in the old quantum theory was replaced by a completely innocuous non-uniqueness of bases of eigenfunctions in wave mechanics.

The Stark effect is remembered to this day as one of the few admittedly qualified successes of the old quantum theory. We suspect that this is largely because after 1926 it became just one of many unqualified successes of the new quantum theory.

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