

## A generalization of the quantization conditions for the purpose of wave mechanics

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A method shall be developed in this note for solving the eigenvalue problem of **Schrödinger**'s “wave mechanics” by successive approximations, starting from the limiting case of classical mechanics (the previous quantum theory, resp.). In many cases, that process of approximation can be arranged so that it truncates off after a few steps. Applications of it ( $H$  atom and Stark effect) are found at the end of the article.

**§ 1. The Riccati equation that belongs to the wave equation.** – Let a problem in **Schrödinger**'s wave equation with one degree of freedom <sup>(1)</sup> be given:

$$\psi'' + \frac{4\pi^2}{h^2} p^2 \psi = 0, \quad (1)$$

$$p^2 = 2m [E - V(x)]. \quad (2)$$

It is known that with the substitution:

$$\psi = e^{\frac{2\pi i}{h} \int y dx}, \quad (3)$$

(1) will yield an equivalent **Riccati** differential equation:

$$\frac{h}{2\pi i} y' = p^2 - y^2. \quad (4)$$

In the limiting case of  $h = 0$ , this will go to an algebraic equation, and in fact, with:

$$\lim_{h=0} y = y_0 = \frac{dS}{dx}, \quad (5)$$

it will represent **Hamilton**'s differential equation of classical mechanics:

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<sup>(1)</sup> **E. Schrödinger**, Ann. Phys. (Leipzig) **79** (1926), 489, especially pp. 510.

$$\left(\frac{dS}{dx}\right)^2 = y_0^2 = p^2. \quad (6)$$

Now since  $y'$  enters into the differential equation (4) only with the “small” coefficient  $h / 2\pi i$ , that suggests the possibility of rigorously solving the equation with  $y$  presented as a power series in the **Planck** quantum  $h$ :

$$y = \sum_{\nu=0}^{\infty} \left(\frac{h}{2\pi i}\right)^{\nu} \cdot y_{\nu}. \quad (7)$$

Starting with the classical solution  $y_0 = \pm p$ , one will then get a recursion formula that reads:

$$y'_{\nu-1} + \sum_{\alpha=0}^{\nu} y_{\alpha} y_{\nu-\alpha} = 0. \quad (8)$$

One then computes, in succession:

$$y_1 = -\frac{y'_0}{2y_0}, \quad y_2 = -\frac{y'_1 + y_1^2}{2y_0}, \quad \dots \quad (9)$$

In that way, one will arrive at two unique particular solutions to the differential equation (4) that go continuously to the (positive or negative) mechanical impulse for  $h = 0$  (as long as  $y_0 \neq 0$ ). The general integral can be constructed from it in a known way; all integrals besides the two in (7) degenerate for  $h = 0$ . ( $h = 0$  is an essential singular point for them.) In regard to possible thoughts concerning the existence of the two solutions (7) (the convergence of the development in  $h$ , resp.), let it be pointed out that we require the solutions (7) only in the neighborhood of the singular points of the differential equation, where they yield at least asymptotic solutions of (4) (in the form of semi-convergent power series).

**§ 2. Establishing the eigenvalues** <sup>(1)</sup>. – Now, with **Schrödinger**, let us especially look for the eigenfunctions  $\psi_k$  of the wave equation – i.e., the entire transcendental solutions that satisfy certain boundary conditions; let  $E_k$  be the associated “eigenvalue” of the energy constant  $E$ . Corresponding to (3), set:

$$\psi_k = e^{\frac{2\pi i}{h} \int y dx}, \quad y = \frac{h}{2\pi i} \frac{\psi'_k}{\psi_k}. \quad (10)$$

The boundary conditions consist of demanding that the integral  $\psi_k$  should remain bounded (vanish, resp.) at the singular points of the differential equations. If we select

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<sup>(1)</sup> I have reworked the text in § 2 along with the editor with the use of written communications by **E. Fues** that contributed very greatly to the explanation of the connections.

such a singular location then we will get two particular solutions of the wave equation in its neighborhood when we substitute in (3) the two particular solutions (7) of the Riccati equation that were derived above for  $y$ . However, as one easily recognizes from the recursion formulas (8), (9), they will be pure imaginary for real  $x$  <sup>(1)</sup>, and in fact, one of them will be positive imaginary, while the other one will be negative imaginary. If one moves  $x$  along the real axis to the boundary point then one of the two functions (3) will become zero exponentially, while the other one will become infinite exponentially. The former is obviously the desired eigenfunction (in the event that such a thing even exists), so all other solutions that one obtains from linear combinations of the two particular solutions will likewise become infinite exponentially. In that way, we can control the behavior of the eigenfunction sufficiently at the singular locations of the differential equation.

The question is now, “Under what conditions can the solutions  $\psi$  that satisfy the boundary conditions at the singular points be associated with each other as analytic continuations of one and the same entire, transcendental function?” It is easy to give a necessary condition for that. It is known that any eigenfunction can be characterized by the number of its nodes (zero loci), and indeed from known theorems (“oscillation theorem”), those nodes all lie in an accessible region of  $x$ . However, the function  $\psi'_k / \psi_k$  has a simple pole of residue  $2\pi i$  at each of these nodal locations. If one then takes the integral  $\oint y dx$  along a closed path around the region in which all of the nodes of the oscillation lie then from (10), one will get the value of that integral from the number of nodes multiplied by  $h$ :

$$\oint y dx = k \cdot h \quad (k = \text{whole number} = \text{number of nodes}). \quad (11)$$

From **Cauchy**'s theorem, this equation is also true when one displaces the path of integration, and instead of it encircling the nodal locus one makes it encircle the remaining poles of  $y$  that are the singular points of the differential equation. However, from the above, in their vicinity,  $y$  is likewise given by one of the solutions (7), (8), and the integration can be performed directly. *The sum of the residues of these solutions at the singular points must then be a whole-number multiple of  $h$ .* That condition will suffice to establish the eigenvalue  $E_k$  of the energy constant. Naturally, a corresponding integral relation (11) is also true for non-eigenfunctions  $\psi$  when their number of nodes is finite, but with a different integrand  $y$ . It is only for eigenfunctions that  $y$  coincides with the distinguished solution to the **Riccati** equation that is calculated from (7), (8) at the two singular points, such that one can also write:

$$\sum_{\nu=0}^{\infty} \left( \frac{h}{2\pi i} \right)^{\nu} \oint y_{\nu} dx = k \cdot h, \quad (12)$$

instead of (11).

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<sup>(1)</sup>  $y_0 = \pm p$  is then pure imaginary outside of the domain of the classical path.

Since  $y_0 = \pm p$  <sup>(1)</sup>, in the limiting case  $h = 0$ , this condition is nothing but the **Sommerfeld** quantization prescription <sup>(2)</sup>:

$$\oint p dx = k \cdot h.$$

Furthermore, equation (12) teaches us that the “quantization condition,” as well as the residue method that **Sommerfeld** employed to evaluate it will preserve its meaning in wave mechanics when only the mechanical impulse  $p$  is replaced with the distinguished solution of the Riccati equation. The series development (12) permits a determination of the eigenvalues in successive approximations; moreover, in many problems (cf., § 5, 6), that development will truncate in such a way that the rigorous solution of the eigenvalue problem is attained by a finite number of approximations.

**§ 3. The connection with the eigenvalue problem for matrices.** – In an earlier paper <sup>(3)</sup>, I gave a solution of the eigenvalue problem for **Heisenberg**’s matrix mechanics, which likewise arose from an extension of **Sommerfeld**’s method of residues. Since **Schrödinger** <sup>(4)</sup> and **Pauli** <sup>(5)</sup> have established the complete identity of the matrix problem, on the one hand, and the wave problem, on the other, a closer connection between those two solutions of the eigenvalue problem must obviously exist. The disclosure of that connection is to be desired, in particular, due to the fact that the mathematical foundation of the matrix method was very flawed at the time <sup>(6)</sup>.

First, let us make a more formal remark. If one goes from the variables  $x, y, p$  that were used in § 1 to analogous matrices  $\mathbf{x}, \mathbf{y}, \mathbf{p}$  then the Riccati differential equation (4) will read:

<sup>(1)</sup> The integral around the domain of the zero locus of  $\psi$  is the counterpart to **Sommerfeld**’s integral around the branch cut of the double-valued function  $y_0 = \pm p$ , which characterizes the domain of the classical path. As **Schrödinger** emphasized, the oscillation process then takes place chiefly in the domain of the classical path. One can also see from our formula (3) that, in fact, all nodes lie in that region (or entirely in its vicinity) when one substitutes the distinguished solution  $y$  (7); it is, in fact, pure imaginary outside the classical path region ( $p^2 < 0$ ), so it will follow that  $\psi_k$  will die away on both sides of it, and indeed monotonically and with no zero points. By contrast,  $y$  is complex inside the path region, such that the real part of  $\psi_k$  will oscillate there like a type of cosine, but with alternating amplitudes and wave lengths; the meaning of the “phase integral” as a number of nodes will then become intuitively clear in that way. In the case for which (classically) two mechanical paths are possible for a given energy  $E$  (i.e., two branch cuts in the accessible domain), the amplitude of oscillation will die off in the region *between* two paths just as strongly as on one side, such that in fact both oscillation processes are basically realized simultaneously, but one of the two will be realized only with vanishingly small amplitude (in particular, in the limiting case of  $h = 0$ ). Moreover, from our current way of seeing things, the method of residues is also applicable to that case, which was not the case in the previous quantum theory, since that phase integral was extended around only *one* of the branch cuts at the time.

<sup>(2)</sup> In a letter, **W. Pauli** made me aware of the fact that in the limiting case of classical mechanics,  $\psi$  will come back to itself under a circuit around the branch cut of  $y_0$  (cf., the previous remark) if and only if the modulus of periodicity of the action function ( $\oint y_0 dx$ ) is a whole-number multiple of  $h$ . That remark, which **Pauli**, in turn, attributed to **O. Klein**, was one of the starting points for my investigation.

<sup>(3)</sup> **G. Wentzel**, Zeit. Phys. **37** (1926), 80.

<sup>(4)</sup> **E. Schrödinger**, Ann. Phys. (Leipzig) **79** (1926), 734.

<sup>(5)</sup> In a written communication.

<sup>(6)</sup> **G. Wentzel**, *loc. cit.*; cf., in particular, footnote 1, pp. 83.

$$\frac{h}{2\pi i} \mathbf{y}' = \mathbf{p}^2 - \mathbf{y}^2. \quad (13)$$

Now, in matrix mechanics, one has the commutation – or quantization – relation:

$$\frac{h}{2\pi i} \cdot \mathbf{1} = \mathbf{p} \cdot \mathbf{x} - \mathbf{x} \cdot \mathbf{p}, \quad (14)$$

and as a result, for the function  $\mathbf{y} = \mathbf{y}(\mathbf{x})$ , one will have:

$$\frac{h}{2\pi i} \cdot \mathbf{y}' = \mathbf{p} \cdot \mathbf{y} - \mathbf{y} \cdot \mathbf{p}. \quad (15)$$

However, equation (13) then goes to:

$$(\mathbf{y} + \mathbf{p})(\mathbf{y} - \mathbf{p}) = 0;$$

this will be satisfied by:

$$\mathbf{y} = \pm \mathbf{p}, \quad \mathbf{y}^2 = \mathbf{p}^2, \quad \mathbf{y}' = \mathbf{0}. \quad (16)$$

$\mathbf{y}$  and  $\mathbf{p}$  are then identical as matrices.

One can prove this identity more rigorously when one starts with the **Schrödinger-Pauli** construction of the matrices from the eigenfunctions  $\psi_k$ . It gives:

$$(\mathbf{x})_{kl} = \int_{-\infty}^{+\infty} x \psi_k \psi_l dx, \quad (\mathbf{p})_{kl} = \int_{-\infty}^{+\infty} \psi_k \psi_l' dx. \quad (17)$$

From the “completeness relation” for the eigenfunctions  $\psi_k$ :

$$\int f g dx = \sum_k \int f \psi_k dx \cdot \int g \psi_k dx,$$

one easily proves <sup>(1)</sup>, firstly, that the quantities (17) multiply like matrices, secondly, that the commutation relation (14) is fulfilled, and thirdly, that the energy matrix is a diagonal matrix (i.e., temporally constant), and that its elements are identical with the eigenvalues  $E_k$ . However, as a result of the first of those statements, the matrix that belongs to  $y$  (as a function of only  $x$ ) will be equal to:

$$(\mathbf{y})_{kl} = \int y \psi_k \psi_l dx.$$

If one replaces the  $l^{\text{th}}$  eigenfunction  $\psi_l$  in this with the corresponding solution  $y$ , in particular, then according to the definitions (10) and (17), it will become simply:

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<sup>(1)</sup> When one identifies  $f$  ( $g$ , resp.) with  $x \psi_l$  ( $\psi_l'$ , resp.) as required.

$$(\mathbf{y})_{kl} = \frac{h}{2\pi i} \int \psi_k \psi_l' dx = (\mathbf{p})_{kl}, \quad (18)$$

which was to be proved.

In § 2, it was shown that the sum of the residues of  $y$  must be equal to  $l \cdot h$ , while in the previous method, the sum of the residues of the matrix  $\mathbf{p}$  was set equal to  $(l + \alpha) h$ . Both methods will obviously become identical <sup>(1)</sup> when one sets the previously-undetermined constant  $\alpha = 0$ . Therefore, the absolute normalization of the quantum numbers is also established, which was left open in my earlier process.

**§ 4. Generalization to several degrees of freedom.** – The process that was given in § 1 of successive approximations to quantum mechanics starting from classical mechanics can always be carried out for separable systems; the formulas generally read somewhat differently, though. One gets a differential equation of the type:

$$y'' + f(x) y' + \frac{4\pi^2}{h^2} \cdot g(x) \psi = 0 \quad (1')$$

for the individual degrees of freedom, instead of (1). By the substitution (3), this goes to the somewhat more general Riccati differential equation:

$$\frac{h}{2\pi i} y' = g(x) - \frac{h}{2\pi i} f(x) y - y^2, \quad (4')$$

and one immediately derives a recursion formula that is similar to (8), (9) (cf., § 5, 6). The arguments in § 2 are valid for each degree of freedom individually.

**§ 5. Application to the  $H$  atom.** – In order to prove the simplicity of the new calculation procedure, we treat the problem of the  $H$  atom as the first example. After splitting off the equation for spherical functions <sup>(2)</sup>, the wave equation in that case will read <sup>(3)</sup>:

$$\psi'' + \frac{2}{r} \psi' + \frac{4\pi^2}{h^2} \left[ 2mE + \frac{2me^2}{r} + \left( \frac{h}{2\pi i} \right)^2 \frac{l(l+1)}{r^2} \right] \psi = 0, \quad l = 0, 1, \dots \quad (19)$$

With **Sommerfeld**'s abbreviations:

<sup>(1)</sup> In fact, the elements of the diagonal matrices that appear in the development of the matrix  $\mathbf{y}$  in powers of the matrix  $\mathbf{x} - \mathbf{x}_0$  are identical with the numerical coefficients of the development of  $y$  in powers of  $x - x_0$ .

<sup>(2)</sup> **E. Schrödinger**, Ann. Phys. (Leipzig) **79** (1926), 361.

<sup>(3)</sup> I inverted **Schrödinger**'s notation for  $n, l$  in order to remain in agreement with the currently-accepted notation for "quantum numbers." Cf., say: **Grimm** and **Sommerfeld**, Zeit. Phys. **36** (1926), 36, pp. 37, footnote 5, or **F. Hund**, Zeit. Phys. **36** (1926), 657, pp. 658, footnote 2.

$$A = 2m E, \quad B = me^2, \quad C = \left( \frac{lh}{2\pi i} \right)^2,$$

the **Riccati** differential equation (4') will read:

$$\frac{h}{2\pi i} \left[ y' + \frac{2}{r} y - \frac{\sqrt{C}}{r^2} \right] = \left[ A + \frac{2B}{r} + \frac{C}{r^2} \right] - y^2. \quad (20)$$

For  $h = 0$ , one will have:

$$y_0 = \sqrt{A + \frac{2B}{r} + \frac{C}{r^2}},$$

and the developments at the poles  $r = 0$  and  $r = \infty$  will read:

$$\begin{aligned} \text{at } r = 0: \quad y_0 &= \frac{\sqrt{C}}{r} + \dots, \\ \text{at } r = \infty: \quad y_0 &= \sqrt{A} + \frac{B}{\sqrt{A}} \cdot \frac{1}{r} + \dots \end{aligned}$$

If one substitutes the series (7) in (20) then the first approximation will read:

$$y_1 = - \frac{1}{2y_0} \left[ y_0' + \frac{2}{r} y_0 - \frac{\sqrt{C}}{r^2} \right].$$

However, from the foregoing series for  $y_0$ , one easily sees that  $y_1$  will behave regularly for  $r = 0$  (the poles that originate in the three terms cancel each other precisely) and that the development of  $y_1$  for  $r = \infty$  will begin with:

$$y_1 = - \frac{1}{r} + \dots$$

$y_1 \cdot h / 2\pi i$  then contributes  $(-h)$  to the sum of the residues. All higher corrections  $y_2, y_3, \dots$  etc., will behave regularly for  $r = 0$ , as well as  $r = \infty$ . Since the corrections  $y_2, y_3, \dots$  only contribute a whole number to the sum of the residues then, the general quantization condition (12) will reduce to **Sommerfeld's**:

$$\frac{1}{h} \oint y_0 dr = \text{whole number}, \quad (21)$$

which verifies the validity of the Balmer formula in wave mechanics.

If one adds a term  $c / r^2$  to the potential energy then the calculation will proceed in an entirely analogous manner when one determines  $C$  from the quadratic equation:

$$C + \frac{h}{2\pi i} \sqrt{C} = \left( \frac{h}{2\pi i} \right)^2 l(l+1) + e.$$

That will then yield a formula for a term with a “half-integer azimuthal quantum number”  $l + 1/2$ :

$$\frac{2\pi i}{h} \frac{B}{\sqrt{A}} = n - \left( l + \frac{1}{2} \right) + \sqrt{\left( l + \frac{1}{2} \right)^2 - \text{const.}}$$

(This is an extension of the **Balmer** formula to the **Rydberg** formula.)

Finally, we would like to convince ourselves that the solutions (10) to the wave equation that belong to the energy values  $E_{nl}$  actually have no singularities at  $r = 0$  and  $r = \infty$ . If one substitutes the development for  $y$  that one then obtains into (10) then it will follow directly that:

$$\text{For } r = 0: \quad \psi_{nl} = \text{const.} \cdot r^l + \dots,$$

$$\text{For } r = \infty: \quad \psi_{nl} = \text{const.} \cdot e^{-\frac{2\pi}{h}\sqrt{-2mE} \cdot r} (r^{n-1} + \dots),$$

which coincides with the complete expression for  $\psi_{nl}$  that **Schrödinger** gave <sup>(1)</sup>.

**§ 6. Application to the Stark effect.** – As a second example, one might treat the  $H$  atom in a homogeneous electric field. **Schrödinger** <sup>(2)</sup> carried out the separation of the wave equation in question in parabolic coordinates; in that way, one will arrive at two ordinary differential equations of the type:

$$\psi'' + \frac{1}{x} \psi' + \frac{4\pi^2}{h^2} \left[ a + \frac{b}{x} + \frac{c}{x^2} + d \cdot x \right] \psi = 0; \quad (22)$$

$$a = 2mE, \quad b = m(e^2 \pm b), \quad c = \frac{1}{4} \left( \frac{mh}{2\pi i} \right)^2 (m = 0, 1, \dots), \quad d = \pm 2meF.$$

The associated **Riccati** equation reads:

$$\frac{h}{2\pi i} \left[ y' + \frac{y}{x} \right] = \left[ a + \frac{b}{x} + \frac{c}{x^2} + d \cdot x \right] - y^2. \quad (23)$$

<sup>(1)</sup> *Loc. cit.*, pp. 369, equation (18).

<sup>(2)</sup> **E. Schrödinger**, *Ann. Phys. (Leipzig)* **80** (1926), 437.



Only  $y_0$  will produce a residue  $(2\pi i\sqrt{c})$  at  $x = 0$ , while all remaining  $y_i$  will be regular. At  $x = \infty$ , one must first develop them in powers of the field strength  $F$  ( $d$ , resp.). The series in question reads:

$$\begin{aligned}
y_0 &= \left[ a^{1/2} + \frac{1}{2} b a^{-1/2} x^{-1} + \dots \right] \\
&\quad + \frac{1}{2} d \left[ a^{-1/2} x - \frac{1}{2} b a^{-3/2} + \left( \frac{3}{8} b^2 a^{-5/2} - \frac{1}{2} c a^{-3/2} \right) x^{-1} + \dots \right] \\
&\quad - \frac{1}{8} d^2 \left[ a^{-3/2} x^2 - \frac{3}{2} b a^{-3/2} x + \left( \frac{15}{8} b^2 a^{-7/2} - \frac{3}{2} c a^{-5/2} \right) \right. \\
&\quad \quad \left. + \left( -\frac{35}{16} b^3 a^{-9/2} + \frac{15}{4} b c a^{-7/2} \right) x^{-1} + \dots \right] + \dots, \\
y_1 &= \left[ -\frac{1}{2} x^{-1} + \frac{1}{4} b a^{-1} x^{-2} + \dots \right] + d \left[ -\frac{1}{4} a^{-1} + 0 \cdot x^{-1} + \dots \right] \\
&\quad + d^2 \left[ \frac{1}{4} a^{-2} x - \frac{1}{4} b a^{-3} + 0 \cdot x^{-1} + \dots \right] + \dots, \\
y_2 &= \left[ -\frac{1}{2} a^{-1/2} x^{-2} + \dots \right] + d \left[ \frac{1}{16} a^{-3/2} x^{-1} + \dots \right] \\
&\quad + d^2 \left[ -\frac{13}{64} a^{-5/2} + \frac{25}{128} b a^{-7/2} x^{-1} + \dots \right] + \dots
\end{aligned}$$

All higher  $y_2, y_4, \dots$  behave regularly (for  $x = \infty$ ) in the terms in  $d^2$  and up. The residue at:

$$y \approx y_0 + y_1 \cdot h / 2\pi i + y_2 (h / 2\pi i)^2$$

is then:

$$\begin{aligned}
&2\pi i \left\{ \left[ \frac{1}{2} b a^{-1/2} - \frac{1}{2} \frac{h}{2\pi i} \right] \right. \\
&\quad + d \left[ \frac{3}{16} b^2 a^{-5/2} - \frac{1}{4} c a^{-3/2} + \frac{1}{16} \left( \frac{h}{2\pi i} \right)^2 a^{-3/2} \right] \\
&\quad \left. + d^2 \left[ \frac{35}{128} b^3 a^{-9/2} - \frac{15}{32} b c a^{-7/2} + \frac{25}{128} \left( \frac{h}{2\pi i} \right)^2 b a^{-7/2} \right] + \dots \right\}.
\end{aligned}$$

This expression, when augmented with the residue at  $x = 0$ :

$$-2\pi i \sqrt{c} = -\frac{1}{2} m h,$$

is set equal to  $n_1 h$  in one case [namely, for  $b = m (e^2 + \beta)$ ,  $d = + 2me F$ ], and equal to  $n_2 h$  in another case [namely, for  $b = m (e^2 - \beta)$ ,  $d = - 2me F$ ], corresponding to the two differential equations that one obtains from the separation. If one then eliminates the integration constant  $\beta$  in a known way then one will get the eigenvalues of the energy constants:

$$\left. \begin{aligned} E_{n_1 n_2 n_3} &= -\frac{2\pi^2 m e^4}{h^2 n^2} - \frac{3h^2 F}{8\pi^2 m e} \cdot n(n_1 - n_2) \\ &- \frac{h^6 F^2}{2^{10} \pi^6 m^3 e^6} \cdot n^4 [17n^2 - 3(n_1 - n_2)^2 - 9(n_3 - 1)^2 + 19] + \dots, \end{aligned} \right\} \quad (24)$$

in which one sets <sup>(1)</sup>:

$$n = n_1 + n_2 + m + 1 = n_1 + n_2 + n_3 = 1, 2, \dots, \quad n_3 = m + 1 = 1, 2, \dots$$

The first-order Stark effect naturally agrees with the one that was predicted before by the earlier quantum theory; **Pauli** <sup>(2)</sup> and **Schrödinger** <sup>(3)</sup> have already established that. By contrast, the second-order term deviates from the one that **Epstein** <sup>(4)</sup> calculated; using the old quantum theory, **Epstein** found, not the bracketed expression [cf., (24)]:

$$[17 n^2 - 3 (n_1 - n_2)^2 - 9 (n_3 - 1)^2 + 19], \quad (25)$$

but the expression:

$$[17 n^2 - 3 (n_1 - n_2)^2 - 9 n_3^2]. \quad (26)$$

Naturally, both expressions will go to each other for large quantum numbers; however, the new expression will be noticeably larger than **Epstein**'s for small quantum numbers.

As is known, the quadratic term in (24) means that the splitting of the hydrogen lines in large field strengths is no longer symmetric to the field-free lines, but is shifted to the red. This “quadratic Stark effect” was known to **Sommerfeld** <sup>(5)</sup>, in conjunction with **Takamine** and **Kokubo**, and further investigated experimentally by **M. Kiuti** <sup>(6)</sup> and **J. S. Foster** <sup>(7)</sup>. The most precise measurements are the ones that pertain to the middle components of  $H_\gamma$ . **Takamine** <sup>(8)</sup> and **Kiuti** agreed that the redshift is larger than was expected from **Epstein**'s formula, and in fact, judging from **Kiuti**'s graphical representation, the discrepancy amounts to about 20 percent. However, that is precisely what one would expect from formula (24). The middle components in question arise, in fact, from the two transitions  $(n_1, n_2, n_3)$ :

<sup>(1)</sup> As **W. Pauli** already pointed out [Zeit. Phys. **36** (1926), 336],  $n_3 = m + 1 = 0$  is excluded from the outset.

<sup>(2)</sup> *Loc. cit.*

<sup>(3)</sup> *Loc. cit.*

<sup>(4)</sup> **P. Epstein**, Ann. Phys. (Leipzig) **51** (1916), 184.

<sup>(5)</sup> **A. Sommerfeld**, Ann. Phys. (Leipzig) **65** (1921), 36.

<sup>(6)</sup> **M. Kiuti**, Japanese Journ. Phys. **4** (1925), 13.

<sup>(7)</sup> **J. S. Foster**, Astrophys. Journ. **63** (1926), 191.

<sup>(8)</sup> Cf., **A. Sommerfeld**, *loc. cit.*

$$1, 2, 3 \rightarrow 0, 0, 2 \quad \text{and} \quad 2, 2, 1 \rightarrow 0, 0, 2.$$

However, for the first of the two lines, the deviation of the expression (25) from that of **Epstein** (26) amounts to 19 percent, while it is 7 percent for the other one, which is, however, much weaker in intensity calculations <sup>(1)</sup>. **Foster**'s measurements relate to  $H_\delta$  and  $H_\varepsilon$ , but they are less precise; he found a deviation of around + 30 percent compared to **Epstein** for  $H_\delta$ , but no noticeable deviation for  $H_\varepsilon$  (middle component). Equation (24) leads one to expect + 5 to 10 percent.

The difference between the expressions (25) and (26) for small quantum numbers is more definitive, and especially in the ground state  $n_1 = n_2 = 0, n_3 = 1$ ; the expressions (25) and (26) then have a ratio of 4.5 : 1. In that case, there is, in fact, no direct experimental criterion, but there is an interesting connection with the problem of the stimulated helium atom. The failure of the earlier quantum theory in the context of that problem <sup>(2)</sup> is, in fact, partially based in the fact that it yielded a value for the induced dipole moment in the outer electron shell in  $\text{He}^+$  that was much too small. However, the constant of the quadratic term in (24) is precisely a measure for the polarization that is produced in the  $\text{He}^+$  shell by the external field. Due to the magnitude of the aforementioned ratio 4.5 : 1, one must then hope that quantum mechanics will be much more fruitful in the helium problem. If one, with **Unsöld** <sup>(3)</sup>, makes the assumption that the magnitudes of the terms in the He spectrum are, in the final analysis, determined by the polarizability of the  $\text{He}^+$  shell (and not by its quadrupole moment) then formula (24) will allow one to make a first approximation of the constants in the series formula that might read:

$$\nu = \frac{R}{(n - \delta)^2}, \quad \text{with} \quad \delta = \frac{27}{128} \cdot \frac{1}{k^5}, \quad k = \frac{1}{2}, \frac{3}{2}, \dots$$

One then gets the numerical values:

$$\delta = 0.028, \quad 0.0022, \quad 0.0004$$

for the series  $p, d, f$  ( $k = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$ , resp.) in the He line spectrum. Those numbers lie almost exactly at the mean of the empirical series constants for ortho-helium:

$$\delta = 0.069, \quad 0.003, \quad 0.001$$

on the one hand, and para-helium:

$$\delta = -0.011, \quad 0.002, \quad 0.001,$$

on the other. (Cited by **Unsöld**, *loc. cit.*)

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<sup>(1)</sup> Perhaps four or five times the corresponding calculations of **H. A. Kramers** (Diss. Copenhagen 1919) and around 4.4 times those of **Schrödinger**, *loc. cit.*

<sup>(2)</sup> Cf., **M. Born** and **W. Heisenberg**, *Zeit. Phys.* **16** (1923), 229.

<sup>(3)</sup> **A. Unsöld**, *Zeit. Phys.* **36** (1926), 92.

## Summary

§ 1. The **Riccati** differential equation that is associated with the **Schrödinger** equation can be integrated by means of a series in increasing powers of  $h$ , in such a way that zeroth-order approximation corresponds to the classical mechanics (earlier quantum theory, resp.), while the addition of the higher powers of  $h$  allows one to arrive at a progressive approximation to the new quantum – or wave – mechanics.

§ 2. The **Sommerfeld** quantization condition  $\oint y dx = k \cdot h$  remains true when one replaces  $y$  (instead of the impulse  $p$ ) with the solution to the **Riccati** differential equation that was obtained in § 1.

§ 3. The solution to the eigenvalue problem that this yields is identical with that of the residue method that the author previously introduces in matrix mechanics; the absolute normalization of the quantum numbers that was left open in it proves to be unique here.

§ 4. The method for one degree of freedom that was developed in § 1 and § 2 was generalized to arbitrary separable systems.

§ 5. The application to the  $H$  atom yields a very simple derivation of the **Balmer** series formula.

§ 6. The calculation of the Stark effect confirms the known formula for the linear effect; by contrast, **Epstein**'s formula for the second-order effect was modified. For  $H_\gamma$ , this difference in the middle components amounts to 19 percent theoretically, and around 20 percent experimentally. For the ground state, the quadratic effect proves to be 4.5 times bigger than what **Epstein** calculated, which might be interesting in a future theory of the helium line spectrum.

**Munich**, Institut für theoretische Physik, June 1926.

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