Abstract

The old quantum theory and Schrödinger’s wave mechanics (and other forms of quantum mechanics) give the same results for the line splittings in the first-order Stark effect in hydrogen, the leading terms in the splitting of the spectral lines emitted by a hydrogen atom in an external electric field. We examine the account of the effect in the old quantum theory, which was hailed as a major success of that theory, from the point of view of wave mechanics. First, we show how the new quantum mechanics solves a fundamental problem one runs into in the old quantum theory with the Stark effect. It turns out that, even without an external field, it depends on the coordinates in which the quantum conditions are imposed which electron orbits are allowed in a hydrogen atom. The allowed energy levels and hence the line splittings are independent of the coordinates used but the size and eccentricity of the orbits are not. In the new quantum theory, this worrisome non-uniqueness of orbits turns into the perfectly innocuous non-uniqueness of bases in Hilbert space. Second, we review how the so-called WKB (Wentzel-Kramers-Brillouin) approximation method for solving the Schrödinger equation reproduces the quantum conditions of the old quantum theory amended by some additional half-integer terms. These extra terms remove the need for some arbitrary extra restrictions on the allowed orbits that the old quantum theory required over and above the basic quantum conditions.

Keywords: Stark effect; Bohr-Sommerfeld theory; Hamilton-Jacobi theory; Epstein; wave mechanics; WKB approximation.

1We dedicate this paper to the memory of Philip M. Stehle (1919-2013).
1 Introduction

In March of 1916, Epstein (1916a,b) and Schwarzschild (1916) showed that the old quantum theory of Bohr (1913) and Sommerfeld (1915a,b, 1916) can account for an effect discovered by and named after Stark (1913), the splitting of the spectral lines of hydrogen atoms placed an external electric field. This result was hailed as a tremendous success for the old quantum theory. Epstein (1916a, p. 150) boasted 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.” In the conclusion of the first edition of his Atombau und Spektrallinien, the bible of the old quantum theory, Sommerfeld (1919, p. 458) called the theory’s explanation of the Stark effect one of “the most impressive achievements in our field” and a “capstone on the edifice of atomic physics.”

However, as we noted in an earlier paper (Duncan and Janssen, 2014), the old quantum theory’s explanation of the Stark effect was not without its share of problems. These problems were solved when, shortly after the arrival of Schrödinger’s (1926a) wave mechanics, Schrödinger (1926b) and Epstein (1926) produced an account of the Stark effect in the new theory. In this paper, we focus on two of these problems and show how they are resolved in wave mechanics.

First, we show how the new quantum mechanics takes care of a fundamental problem one runs into when applying the old quantum theory to the Stark effect. It turns out that the allowed orbits of the electron in the hydrogen atom, with or without an external field, depend on the coordinates in which the quantum conditions are imposed. The allowed energy levels and hence the line splittings do not depend on the coordinates used but the size and eccentricity of the elliptical orbits do. In the new quantum theory, this worrisome non-uniqueness of orbits turns into the perfectly innocuous non-uniqueness of bases in Hilbert space.

Second, we show how wave mechanics does away with another problem in the old quantum theory, namely the need for extra restrictions on the allowed orbits over and above the basic quantum conditions. We review how the so-called WKB approximation method for solving the Schrödinger equation, named after Wentzel (1926), Kramers (1926) and Brillouin (1926), reproduces the quantum conditions of the old quantum theory amended by some additional half-integer terms. With these additional terms, there is no need anymore for extra restrictions on the allowed orbits.

We will proceed as follows. In section 2, we use the old quantum theory to find
the formula for the energy levels for the first-order Stark effect, i.e., the energy of the allowed orbits of an electron in a hydrogen atom placed in a weak electric field, to first order in the strength of that field. We show that the old quantum theory calls for some arbitrary restrictions on the allowed orbits over and above the basic quantum conditions. In section 3, we present the problem of the non-uniqueness of the orbits in the old quantum theory. In section 4, we sketch how the formula for the energy levels in the Stark effect is derived in wave mechanics. We only present the first part of this derivation in detail. This suffices to show how wave mechanics avoids the need for extra restrictions on the allowed quantum states. In section 5, we show how the problem of the non-uniqueness of the orbits is solved in modern quantum mechanics. In section 6, we use the WKB method to find approximate solutions to the Schrödinger equation to recover the quantum conditions of the old quantum theory from wave mechanics with correction terms of $\frac{1}{2}$. These correction terms remove the need for extra restrictions on the allowed orbits in the old quantum theory. In section 7, we summarize our conclusions.

## 2 The Stark effect in the old quantum theory

In Cartesian coordinates $(x, y, z)$, the Hamiltonian for an electron (reduced mass $\mu$, charge $-e$) in a hydrogen atom in an external electric field $E$ in the $z$-direction is given by (in Gaussian units):

$$H = \frac{p^2}{2\mu} - \frac{e^2}{r} + eEz,$$

where $p^2 \equiv p_x^2 + p_y^2 + p_z^2$, with $(p_x, p_y, p_z)$ the momenta conjugate to the coordinates $(x, y, z)$.

We switch to parabolic coordinates $(\xi, \eta, \varphi)$, related to $(x, y, z)$ via (Kramers, 1919, p. 301, Eq. 43)

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

This coordinate transformation is illustrated in Fig. 1. It follows from Eq. (2) that

$$r^2 = x^2 + y^2 + z^2 = \xi\eta + \frac{(\xi^2 - 2\xi\eta + \eta^2)}{4} = \frac{(\xi + \eta)^2}{4}, \tag{3}$$

Epstein (1916b, p. 492, Eqs. 19–20) defined parabolic coordinates slightly differently. In the notation of Eq. (2), he set $z = (\xi^2 - \eta^2)/2$ and $\sqrt{x^2 + y^2} = \xi\eta$. Moreover, Epstein called $x$ what we call $z$ and $y$ what we call $\sqrt{x^2 + y^2}$. The quantity $r \equiv \sqrt{x^2 + y^2}$ in Epstein’s notation is thus equal to $r \equiv \sqrt{x^2 + y^2 + z^2}$ in our notation. Instead of Eq. (4) below, Epstein found $r = (\xi^2 + \eta^2)/2$. 

$$E_{-\ell} = \frac{-\ell^2}{r} + \frac{1}{r} + \frac{1}{2}, \tag{4}$$
Figure 1: Parabolic coordinates. This figure is taken from Epstein (1916b, p. 498) but the labeling has been changed to reflect the definition of the coordinate transformation \((x, y, z) \rightarrow (\xi, \eta, \varphi)\) as given in Eq. (2), which follows Kramers (1919, p. 301, Eq. 43) rather than Epstein (1916b, p. 495, Eqs. 19–20). The figure shows what Epstein calls a “meridian plane” (ibid.), a plane through the \(z\)-axis and the position of the electron. This plane rotates around the \(z\)-axis as the electron orbits the nucleus. Within this plane, the electron stays between \(\xi_{\text{min}}\) and \(\xi_{\text{max}}\) and between \(\eta_{\text{min}}\) and \(\eta_{\text{max}}\).

or

\[
r = \frac{\xi + \eta}{2}.
\]  

In parabolic coordinates the Hamiltonian in Eq. (1) is given by:

\[
H = \frac{1}{2\mu} \left( \frac{4}{\xi + \eta} (p_\xi p_\xi) + \frac{4}{\xi + \eta} (p_\eta p_\eta) + \frac{1}{\xi \eta} p_\varphi^2 \right) - \frac{2e^2}{\xi + \eta} + \frac{1}{2} eE(\xi - \eta),
\]  

where \((p_\xi, p_\eta, p_\varphi)\) are the momenta conjugate to \((\xi, \eta, \varphi)\). In the old quantum theory, as in classical mechanics, \(p_\xi p_\xi = \xi p_\xi^2\) and \(p_\eta p_\eta = \eta p_\eta^2\). The reason we wrote these products the way we did in Eq. (5) is that in wave mechanics \(p_\xi\) becomes a differential operator, differentiation with respect to \(\xi\), that does not commute with multiplication by \(\xi\).

Using \(E\) to denote energy, we write

\[
H = E = \alpha_1.
\]
where $\alpha_1$ is some negative constant. Substituting $\alpha_1$ for $H$ in Eq. (5), multiplying both sides of by $2\mu(\xi + \eta)$, and making the substitutions

$$p_\xi \longrightarrow \frac{\partial S}{\partial \xi}, \quad p_\eta \longrightarrow \frac{\partial S}{\partial \eta}, \quad p_\varphi \longrightarrow \frac{\partial S}{\partial \varphi},$$

related to a canonical transformation generated by an as yet unknown function $S$, known as Hamilton’s principal function (Goldstein et al. [2002, p. 431), we obtain the Hamilton-Jacobi equation for this system in parabolic coordinates in the following form:

$$4\xi \left( \frac{\partial S}{\partial \xi} \right)^2 + 4\eta \left( \frac{\partial S}{\partial \eta} \right)^2 + \left( \frac{1}{\xi} + \frac{1}{\eta} \right) \left( \frac{\partial S}{\partial \varphi} \right)^2 - 4\mu e^2 + \mu e \mathcal{E} (\xi^2 - \eta^2) = 2\mu(\xi + \eta)\alpha_1. \quad (8)$$

where we used that

$$\frac{\xi + \eta}{\xi \eta} = \frac{1}{\xi} + \frac{1}{\eta}, \quad (\xi + \eta)(\xi - \eta) = \xi^2 - \eta^2. \quad (9)$$

The reason for using parabolic coordinates now becomes clear. The Hamilton-Jacobi equation (8) is separable in these coordinates. This means that its solution has the form:

$$S(\xi, \eta, \varphi) = S_\xi(\xi) + S_\eta(\eta) + S_\varphi(\varphi). \quad (10)$$

If we insert this expression for $S$ into Eq. (8) and multiply both sides by $\xi \eta/(\xi + \eta)$, the only term involving $\varphi$ in the resulting equation is $(dS_\varphi/d\varphi)^2$. It follows that $dS_\varphi/d\varphi$ must be a constant, which we will call $\alpha_3$. If Eq. (10) for $S$ is inserted into Eq. (8), with $dS_\varphi/d\varphi = \alpha_3$, the Hamilton-Jacobi equation splits into a part that depends only on $\xi$ and a part that depends only on $\eta$. Since the sum of these two parts must vanish, the two parts themselves must be equal but opposite constants. Writing the constant as $2\alpha_2$, we arrive at:

$$4\xi \left( \frac{dS_\xi}{d\xi} \right)^2 + \alpha_3^2 \xi - 2\mu e^2 + \mu e \mathcal{E} \xi^2 - 2\mu \alpha_1 \xi = -2\alpha_2, \quad (11)$$

$$4\eta \left( \frac{dS_\eta}{d\eta} \right)^2 + \alpha_3^2 \eta - 2\mu e^2 - \mu e \mathcal{E} \eta^2 - 2\mu \alpha_1 \eta = +2\alpha_2. \quad (12)$$

4For a detailed explanation of the rationale behind this recipe, see, e.g., Goldstein et al. (2002 Ch. 10) or Corben and Stehle (1994 Ch. 11).
The constants \( \alpha_1, \alpha_2, \) and \( \alpha_3 \) are called the separation constants (Goldstein et al., 2002, p. 445). It follows from Eqs. (11)–(12) that

\[
\begin{align*}
\frac{dS_\xi}{d\xi} &= \frac{1}{2\xi} \sqrt{-\alpha_3^2 + 2(\mu\varepsilon^2 - \alpha_2)\xi + 2\mu\alpha_1 \xi^2 - \mu\varepsilon\xi^3}, \\
\frac{dS_\eta}{d\eta} &= \frac{1}{2\eta} \sqrt{-\alpha_3^2 + 2(\mu\varepsilon^2 + \alpha_2)\eta + 2\mu\alpha_1 \eta^2 + \mu\varepsilon\eta^3}.
\end{align*}
\]

(13) (14)

The quantum conditions,

\[ \oint p_i dq_i = n_i h \]

(15)

(where integration is over one period of the motion, the \( n_i \)'s are integers, and \( h \) is Planck’s constant), must be imposed in coordinates in which the Hamilton-Jacobi equation is separable.\(^5\) Introducing the action variables \( I_\xi, I_\eta, \) and \( I_\phi, \) we thus have:

\[
\begin{align*}
I_\xi &= \oint p_\xi d\xi = \oint dS_\xi d\xi = n_\xi h, \quad (16) \\
I_\eta &= \oint p_\eta d\eta = \oint dS_\eta d\eta = n_\eta h, \quad (17) \\
I_\phi &= \oint p_\phi d\phi = \oint dS_\phi d\phi = n_\phi h. \quad (18)
\end{align*}
\]

The action variables are so-called adiabatic invariants, which means that their values in the presence of a small electric field \( \varepsilon \) are the same as their values in the absence of such a field.\(^6\) It is this property of action variables in classical mechanics that makes them suitable candidates for the quantities subjected to quantum conditions in the old quantum theory. Where the cases \( \varepsilon = 0 \) and \( \varepsilon \neq 0 \) differ is in how the separation constants depend on the action variables. As we have seen, one of these separation constants, \( \alpha_1, \) is just the energy \( E. \) So even though the action variables have the same values for \( \varepsilon = 0 \) and \( \varepsilon \neq 0, \) the energy does not. Put differently, when the electric field is switched on, the energy of the allowed orbits must change for the action variables to remain the same.

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\(^5\)It was Schwarzschild who, in a letter of March 1, 1916, alerted Sommerfeld to the connection between the phase integral quantum conditions (15) introduced by Sommerfeld (1915a,b) and elements of celestial mechanics, especially action-angle variables and the Hamilton-Jacobi equation (Eckert, 2013, pp. 44–45; also discussed briefly in Duncan and Janssen, 2014).

\(^6\)See the passage following Eq. (25) in Duncan and Janssen (2014) for a brief discussion of how Ehrenfest and his student Burgers connected quantum conditions such as those in Eqs. (16)–(18) to the notion of adiabatic invariants and for references to the historical literature on this topic.
We now evaluate the integrals in Eqs. (16)–(18) using Eqs. (13)–(14) and the simple equation $dS_\phi/d\phi = \alpha_3$ for the integrands. This will give us expressions for the action variables $I_\xi$, $I_\eta$, and $I_\phi$ in terms of the separation constants $\alpha_1$, $\alpha_2$, and $\alpha_3$. We then invert these relations to find the separation constants in terms of the action variables and thereby in terms of the quantum numbers $n_\xi$, $n_\eta$, and $n_\phi$. First, we do this for the case that $\mathcal{E} = 0$, then for the case that $\mathcal{E} \neq 0$.

As long as there is no external field ($\mathcal{E} = 0$), we can use the standard integral,

$$\int_a^b \frac{1}{x} \sqrt{(x-a)(b-x)} = \frac{\pi}{2} \left( a + b - 2\sqrt{ab} \right), \quad (19)$$

and Eqs. (13) and (14) to evaluate the integrals in Eqs. (16) and (17).

We first consider $I_\xi$. Using Eq. (13) with $\mathcal{E} = 0$ for $dS_\xi/d\xi$, we can write Eq. (16) as:

$$I_\xi = \sqrt{-2\mu \alpha_1} \int \frac{d\xi}{2\xi} \sqrt{\frac{\alpha_2^2 - \mu \epsilon^2}{2\mu \alpha_1} \frac{\alpha_3^2 - \epsilon^2 \alpha_2 - \xi - \xi^2}{\alpha_1}}. \quad (20)$$

The quadratic expression in $\xi$ under the square root sign can be written as

$$(\xi - \xi_\min)(\xi_\max - \xi) = -\xi_\min \xi_\max + (\xi_\min + \xi_\max)\xi - \xi^2, \quad (21)$$

where $\xi_\min$ and $\xi_\max$ are the roots of the quadratic equation that we obtain by setting the expression under the square root sign in Eq. (20) equal to zero. Comparing this expression to the right-hand side of Eq. (21), we find

$$\xi_\min + \xi_\max = \frac{\alpha_2 - \mu \epsilon^2}{\mu \alpha_1}, \quad \xi_\min \xi_\max = -\frac{\alpha_3^2}{2\mu \alpha_1}. \quad (22)$$

Replacing the loop integral in Eq. (20) by twice the line integral from $\xi_\min$ to $\xi_\max$, we can rewrite $I_\xi$ as

$$I_\xi = \sqrt{-2\mu \alpha_1} \int_{\xi_\min}^{\xi_\max} \frac{d\xi}{\xi} \sqrt{(\xi - \xi_\min)(\xi_\max - \xi)}. \quad (23)$$

Using Eqs. (19) and (22), we then find that

$$I_\xi = \frac{\pi}{2} \sqrt{-2\mu \alpha_1} \left[ \frac{\alpha_2 - \mu \epsilon^2}{\mu \alpha_1} - \frac{2\alpha_3 \sqrt{-2\mu \alpha_1}}{\sqrt{-2\mu \alpha_1}} \right]. \quad (24)$$

We now turn to $I_\eta$. Using Eq. (14) with $\mathcal{E} = 0$ for $dS_\eta/d\eta$, we can write Eq. (17) as:

$$I_\eta = \sqrt{-2\mu \alpha_1} \int \frac{d\eta}{2\xi} \sqrt{\frac{\alpha_3^2}{2\mu \alpha_1} \frac{\alpha_2^2 + \alpha_2}{\mu \alpha_1} \eta - \eta^2}. \quad (25)$$
The quadratic expression in $\eta$ under the square root sign can be written as

$$(\eta - \eta_{\text{min}})(\eta - \eta_{\text{max}}), \quad (26)$$

where $\eta_{\text{min}}$ and $\eta_{\text{max}}$ are the roots of the quadratic equation that we obtain by setting the expression under the square root sign in Eq. (25) equal to zero. Eq. (25) can thus be rewritten as

$$I_\eta = \sqrt{-2\mu \alpha_1} \int_{\eta_{\text{min}}}^{\eta_{\text{max}}} \frac{d\eta}{\eta} \sqrt{(\eta - \eta_{\text{min}})(\eta_{\text{max}} - \eta)}. \quad (27)$$

The quantities $\xi_{\text{min}}, \xi_{\text{max}}$ in Eqs. (21)–(23) and $\eta_{\text{min}}, \eta_{\text{max}}$ in Eqs. (26)–(27) are called the turning points of the motion or the apsidal distances (Goldstein et al., 2002, p. 78).

To evaluate the integral in Eq. (27), we simply note that $I_\eta$ only differs from $I_\xi$ in the sign of the term with $\alpha_2$ (compare Eqs. (20) and (25) or Eqs. (11) and (12) for $E = 0$). In analogy with Eq. (24), we thus find

$$I_\eta = \frac{\pi}{2} \sqrt{-2\mu \alpha_1} \left[ -\frac{\alpha_2 + \mu e^2}{\mu \alpha_1} - \frac{2\alpha_3}{\sqrt{-2\mu \alpha_1}} \right]. \quad (28)$$

Finally, inserting $dS/\varphi = \alpha_3$ into Eq. (18), we find that

$$I_\varphi = 2\pi \alpha_3 = n_\varphi h. \quad (29)$$

In other words, $\alpha_3 = n_\varphi h$ (with $h \equiv h/2\pi$). In fact, $n_\varphi$ is just the absolute value of the familiar azimuthal quantum number $m$, $I_\varphi = |m|h$ and $\alpha_3 = |m|h$.

To find $\alpha_1$ in terms of $I_\xi$, $I_\eta$, and $I_\varphi$ for the case that $E = 0$, we add Eqs. (24), (28), and (29). The terms with $\alpha_2$ and $\alpha_3$ cancel and the sum reduces to

$$I_\xi + I_\eta + I_\varphi = \pi \sqrt{-2\mu \alpha_1} \left( \frac{2\mu e^2}{-2\mu \alpha_1} \right) = \frac{2\pi \mu e^2}{\sqrt{-2\mu \alpha_1}}. \quad (30)$$

Solving for $\alpha_1$, we find

$$\alpha_1 = E = \frac{2\pi^2 \mu^2 e^4}{(I_\xi + I_\eta + I_\varphi)^2}. \quad (31)$$

This is the familiar Balmer formula, as long as the principal quantum number $n$ is set equal to the sum of the quantum numbers introduced in Eqs. (16)–(18):

$$n = n_\xi + n_\eta + n_\varphi. \quad (32)$$
To find \( \alpha_2 \) in terms of \( I_\xi, I_\eta, \) and \( I_\varphi \), we subtract Eq. (28) from Eq. (24). The terms with \( \alpha_3 \) cancel and the difference reduces to

\[
I_\xi - I_\eta = \pi \sqrt{-2\mu \alpha_1} \left( \frac{-2\alpha_2}{-2\mu \alpha_1} \right) = -\frac{2\pi \alpha_2}{\sqrt{-2\mu \alpha_1}}. \tag{33}
\]

Using Eq. (30) to eliminate \( \alpha_1 \), we arrive at:

\[
\alpha_2 = -\frac{\sqrt{-2\mu \alpha_1}}{2\pi} (I_\xi - I_\eta) = \mu e^2 I_\eta - \frac{I_\xi}{I_\xi + I_\eta + I_\varphi}. \tag{34}
\]

We now compute the integrals for \( I_\xi, I_\eta, \) and \( I_\varphi \) in Eqs. (16)–(18) for the case that \( \mathcal{E} \neq 0 \). As already noted above, the action variables \( I_\xi, I_\eta, \) and \( I_\varphi \) are adiabatic invariants so their values for \( \mathcal{E} \neq 0 \) are the same as for \( \mathcal{E} = 0 \). What changes is the dependence of the separation constants \( \alpha_1, \alpha_2, \) and \( \alpha_3 \) on these action variables and thus the values of these separation constants, including most importantly the energy \( \alpha_1 \).

Since \( S_\varphi \) does not depend on \( \mathcal{E} \), the integral in Eq. (18) gives the exact same result as before: \( I_\varphi = 2\pi \alpha_3 = n_\varphi \hbar \) or \( \alpha_3 = n_\varphi \hbar \) (see Eq. (29)). In the cases of \( I_\xi \) and \( I_\eta \) it suffices to compute the integrals in Eqs. (16)–(17) to first order in \( \mathcal{E} \) as the external field will be much smaller than the Coulomb field of the nucleus. We start with \( I_\xi \):

\[
I_\xi = \oint dS_\xi d\xi = \int \left( \frac{dS_\xi}{d\xi} \right) \bigg|_{\xi=0} d\xi + \int \frac{d}{d\mathcal{E}} \left( \frac{dS_\xi}{d\xi} \right) \bigg|_{\mathcal{E}=0} \mathcal{E} d\xi + O(\mathcal{E}^2). \tag{35}
\]

For the first integral, we can use Eq. (24), which gives \( I_\xi \) as a function of \( \alpha_1, \alpha_2, \) and \( \alpha_3 \) for the case that \( \mathcal{E} = 0 \). Using Eq. (13) for \( dS_\xi/d\xi \), we can write the second integral as:

\[
\int \frac{d}{d\mathcal{E}} \left( \frac{dS_\xi}{d\xi} \right) \bigg|_{\mathcal{E}=0} \mathcal{E} d\xi = \int \frac{1}{2\xi} \frac{-\mu e \xi^3 \mathcal{E}}{2\sqrt{-\alpha_3^2 + 2(\mu e^2 - \alpha_2)\xi + 2\mu \alpha_1 \xi^2}}. \tag{36}
\]

The expression under the square root in the denominator in Eq. (36) has the same form as the one under the square root in the numerator in Eq. (20). It can thus be written as

\[
\sqrt{-2\mu \alpha_1} \sqrt{\frac{-\alpha_3^2}{2\mu \alpha_1} - \frac{\mu e^2 - \alpha_2}{\mu \alpha_1} - \xi^2} = \sqrt{-2\mu \alpha_1} \sqrt{(\xi - \xi_{\text{min}})(\xi_{\text{max}} - \xi)}, \tag{37}
\]
with the same identification of $\xi_{\text{min}} + \xi_{\text{max}}$ and $\xi_{\text{min}}\xi_{\text{max}}$ in terms of $\alpha_1$, $\alpha_2$, and $\alpha_3$ as before (see Eq. (22)). The second integral in Eq. (35) can then be rewritten as:

$$\oint \frac{d}{dE} \left( \frac{dS_{\xi}}{d\xi} \right) \bigg|_{\xi=0} E \, d\xi = -\frac{\mu e E}{4\sqrt{-2\mu \alpha_1}} \oint \frac{\xi^2 \, d\xi}{\sqrt{(\xi - \xi_{\text{min}})(\xi_{\text{max}} - \xi)}}.$$  

(38)

The loop integral is twice the standard line integral

$$\int_a^b \frac{x^2 \, dx}{\sqrt{(x-a)(b-x)}} = \frac{\pi}{8} (3a + b)^2 - 4ab).$$  

(39)

Using this result along with Eq. (22), we can rewrite Eq. (38) as:

$$\oint \frac{d}{dE} \left( \frac{dS_{\xi}}{d\xi} \right) \bigg|_{\xi=0} E \, d\xi = -\frac{\mu e E}{16\mu \alpha_1 \sqrt{-2\mu \alpha_1}} \left[ 3(\alpha_2 - \mu e^2)^2 + 2\mu \alpha_1 \alpha_3^2 \right].$$  

(40)

Since this expression is of order $E$, we can use Eqs. (29), (31), and (34) giving $\alpha_1$, $\alpha_2$, and $\alpha_3$ as functions of $I_\xi$, $I_\eta$, and $I_\phi$ for the case that $E = 0$. Using these three equations, we find:

$$\alpha_2 - \mu e^2 = \mu e^2 \left( \frac{I_\eta - I_\xi}{I_\xi + I_\eta + I_\phi} - 1 \right) = -\mu e^2 \left( \frac{2I_\xi + I_\phi}{I_\xi + I_\eta + I_\phi} \right),$$  

(41)

$$2\mu \alpha_1 \alpha_3^2 = -\frac{\mu^2 e^4 I_\phi^2}{(I_\xi + I_\eta + I_\phi)^2},$$  

(42)

$$\alpha_1 \sqrt{-2\mu \alpha_1} = \left( \frac{2\pi^2 \mu e^4}{(I_\xi + I_\eta + I_\phi)^2} \right)^2 \cdot \left( \frac{2\pi \mu e^2}{I_\xi + I_\eta + I_\phi} \right) = \frac{8\pi^5 \mu^3 e^{10}}{(I_\xi + I_\eta + I_\phi)^5},$$  

(43)

where in the last line we used Eq. (30) along with Eq. (31). With the help of Eqs. (41) and (42) we can write the final expression in Eq. (40) as:

$$-\frac{(\pi e E)(\mu^2 e^4)}{16\mu \alpha_1^2 \sqrt{-2\mu \alpha_1}} \left[ 3 \left( \frac{2I_\xi + I_\phi}{I_\xi + I_\eta + I_\phi} \right)^2 - \left( \frac{I_\phi^2}{I_\xi + I_\eta + I_\phi} \right)^2 \right]$$

$$= -\frac{\pi e^5 \mu E}{16\alpha_1^2 \sqrt{-2\mu \alpha_1}} \left[ \frac{12I_\xi^2 + 12I_\xi I_\phi + 2I_\phi^2}{(I_\xi + I_\eta + I_\phi)^2} \right].$$  

(44)
Using Eq. (43), we can rewrite factor multiplying the expression in square brackets as

\[ \frac{\pi e^5 \mu E (I_x + I_y + I_\varphi)^5}{16} \approx \frac{E}{128\pi^4 \mu^2 e^5} (I_x + I_y + I_\varphi)^5. \]  (45)

With the help of Eqs. (44) and (45), we can rewrite Eq. (40) as

\[ \oint \frac{d\xi}{dE} \left( \frac{dS}{d\xi} \right) \bigg|_{E=0} d\xi = \oint \frac{d\eta}{dE} \left( \frac{dS}{d\eta} \right) \bigg|_{E=0} d\eta + \oint \frac{d\varphi}{dE} \left( \frac{dS}{d\varphi} \right) \bigg|_{E=0} d\varphi + O(E^3). \]  (46)

We can evaluate the integral (17) giving the action variable \( I_\eta \) in the presence of a small external electric field \( E \) in the same way as we calculated the integral (16) giving \( I_\xi \). In analogy with Eq. (35), we have

\[ I_\eta = \oint \frac{dS}{d\eta} d\eta = \oint \left( \frac{dS}{d\eta} \right) \bigg|_{E=0} d\eta \]  (47)

For the first integral, we can use Eq. (28), which gives \( I_\eta \) as a function of \( \alpha_1, \alpha_2, \) and \( \alpha_3 \) for the case that \( E = 0 \). Inserting Eq. (14) for \( dS/\eta \), we can write the second integral as:

\[ \oint \frac{d\eta}{dE} \left( \frac{dS}{d\eta} \right) \bigg|_{E=0} d\eta = \oint \frac{1}{4\eta} \sqrt{-\alpha_3^2 + 2(\mu e^2 + \alpha_2)\eta + 2\mu \alpha_1 \eta^2} \frac{\mu e \eta^3 E}{d\eta}. \]  (48)

Except for an overall minus sign and another minus sign in the term with \( \alpha_2 \), this equation has the exact same structure as Eq. (30). Proceeding along the same lines as in Eqs. (36)–(40), we arrive at:

\[ \oint \frac{d\eta}{dE} \left( \frac{dS}{d\eta} \right) \bigg|_{E=0} d\eta = \oint \frac{E}{128\pi^4 \mu^2 e^5} (I_x + I_y + I_\varphi)^3 (12I_\eta^2 + 12I_yI_\varphi + 2I_\varphi^2). \]  (49)

To find \( \alpha_1 \), the total energy in the presence of a small external electric field of strength \( E \), we calculate, as in the case without an electric field, the sum of the action variables (to first order in \( E \)):

\[ I_x + I_y + I_\varphi = \frac{2\pi \mu e^2}{\sqrt{-2\mu \alpha_1}} + \oint \frac{d\xi}{dE} \left( \frac{dS}{d\xi} \right) \bigg|_{E=0} d\xi + \oint \frac{d\eta}{dE} \left( \frac{dS}{d\eta} \right) \bigg|_{E=0} d\eta + O(E^2). \]  (50)

The first term on the right-hand side is just expression (30) for the sum \( I_x + I_y + I_\varphi \) in the case that \( E = 0 \). For the next two terms, we use Eqs. (46) and (49). Noting that

\[ I_\eta^2 + I_yI_\varphi - I_\eta I_x - I_\xi I_\varphi = (I_y - I_\xi)(I_y + I_\xi) + (I_\eta - I_\xi)I_\varphi = (I_y - I_\xi)(I_y + I_\xi + I_\varphi), \]  (51)
we can write these two terms as
\[
\frac{12E}{128\pi^4\mu^2e^5} (I_\eta - I_\xi) (I_\xi + I_\eta + I_\varphi)^4.
\]
Inserting this result into Eq. (50), we arrive at:
\[
I_\xi + I_\eta + I_\varphi = \frac{2\pi\mu e^2}{\sqrt{-2\mu\alpha_1}} + \frac{12E}{128\pi^4\mu^2e^5} (I_\eta - I_\xi) (I_\xi + I_\eta + I_\varphi)^4 + O(\mathcal{E}^2).
\]
To solve this equation for the energy \(\alpha_1\) it will be helpful to schematically write it as:
\[
x \approx \frac{y}{\sqrt{-2\mu\alpha_1}} + \mathcal{E}z,
\]
with the abbreviations
\[
x \equiv I_\xi + I_\eta + I_\varphi, \quad y \equiv 2\pi\mu e^2, \quad z \equiv \frac{12}{128\pi^4\mu^2e^5} (I_\eta - I_\xi) (I_\xi + I_\eta + I_\varphi)^4.
\]
Solving Eq. (54) for \(\alpha_1\), we find:
\[
\alpha_1 \approx -\frac{1}{2\mu} \left( \frac{y}{x(1 - \mathcal{E}z/x)} \right)^2.
\]
To first order in \(\mathcal{E}\), \(\alpha_1\) is given by:
\[
\alpha_1 \approx -\frac{1}{2\mu} \left( \frac{y}{x(1 - \mathcal{E}z/x)} \right)^2 \approx -\frac{y^2}{2\mu x^2} - \frac{\mathcal{E}y^2 z}{\mu x^3}.
\]
Inserting the expressions for \(x\), \(y\), and \(z\) in Eq. (55) into the final expression in Eq. (57), we arrive at:
\[
\alpha_1 = -\frac{(2\pi\mu e^2)^2}{2\mu(I_\xi + I_\eta + I_\varphi)^2} - \left( \frac{\mathcal{E}(2\pi\mu e^2)^2}{\mu} \right) \left( \frac{12}{128\pi^4\mu^2e^5} \right) (I_\eta - I_\xi) (I_\xi + I_\eta + I_\varphi)
\]
\[
= -\frac{2\pi^2\mu e^4}{(I_\xi + I_\eta + I_\varphi)^2} + \frac{3\mathcal{E}}{8\pi^2e\mu} (I_\xi - I_\eta) (I_\xi + I_\eta + I_\varphi).
\]
The first term on the right-hand side is just the Balmer term (cf. Eq. (31)), the second term gives the first-order Stark effect, the leading term in the splitting of the energy levels by an external electric field in the z-direction. Eq. (58) is exactly the result reported by Epstein (1916a, p. 508, Eq. (62)) and by Kramers (1919, p. 18, Eq. (46)). Imposing the quantum conditions (16)–(18) and setting the sum \(I_\xi + I_\eta + I_\varphi\)
equal to the principal quantum number \( n \) times \( h \), we find that the energy levels \( E = \alpha_1 \) of a hydrogen atom in an electric field are given by

\[
E = -\frac{\mu e^4}{2n^2\hbar^2} + \frac{3\mathcal{E}\hbar^2}{2e\mu} (n_{\xi} - n_{\eta}) n. \tag{59}
\]

The splitting of the energy levels of the first-order Stark effect in hydrogen is thus proportional to \( \mathcal{E}(n_{\xi} - n_{\eta})n \). Most experts agreed that the experimental data on the Stark effect were in excellent agreement with this formula, even though Stark, a staunch opponent of the old quantum theory, did not (Kragh 2012, pp. 127–128, 168–169).

Figure 2: The problem with orbits with \( n_{\varphi} = 0 \). This figure is taken from Epstein (1916b, p. 499) but relabeled the same way as Fig. 1.

As mentioned in the introduction, we focus on two problems with Epstein and Schwarzschild’s account of the Stark effect on the basis of the Bohr-Sommerfeld theory. First, as we will show in section 3, the orbits found in parabolic coordinates do not reduce to the orbits found in spherical coordinates if we let the strength \( \mathcal{E} \) of the external field go to zero. Second, this account of the Stark effect calls for extra restrictions on the allowed orbits over and above the quantum conditions.

---

See Fig. 1 in Duncan and Janssen (2014) for a graphical representation, based on tables given by Epstein (1916b, pp. 512–513), of the splittings both of the energy levels with principal quantum number \( n = 2 \) and \( n = 3 \) and of the Balmer line \( H_{\alpha} \) associated with transitions between those energy levels.
In wave mechanics, by contrast, the basic quantum condition (i.e., the 
normalizability of bound-state eigenfunctions) suffices to get the correct formula for
the Stark effect. In section 4, in which we will cover Schrödinger and Epstein’s
account of the Stark effect on the basis of wave mechanics, we will encounter
the same quantum numbers \( n_\xi, n_\eta, \) and \( n_\varphi \) that we encountered above (see Eqs. (16)–
(18)). However, the relation between these three quantum numbers and the principal
quantum number \( n \) is different in the two theories. In the old quantum theory, as
we saw above (see Eqs. (58)–(59)), the relation is given by:

\[
n = n_\xi + n_\eta + n_\varphi.
\]

(60)

In wave mechanics it gets replaced by

\[
n = n_\xi + n_\eta + n_\varphi + 1.
\]

(61)

The additional term of 1 obviates the need for extra restrictions required by the
old quantum theory. In section 5, we use the WKB method of finding approximate
solutions of the Schrödinger equation to derive amended versions of the quantum
conditions in the old quantum theory, which changes Eq. (60) to Eq. (61) so that
extra conditions are no longer needed.

To conclude this section, we review what these extra restrictions are. There are
two of them. First, it immediately follows from Eq. (60) that the three quantum
numbers \( n_\xi, n_\eta, \) and \( n_\varphi \) cannot simultaneously be zero, as that would result in the
energy, \( E \propto -1/n^2 \), becoming infinite. Second, even in cases where \( n_\xi \) and/or \( n_\eta \)
are non-zero, so that the energy is finite, a zero value for \( n_\varphi \) still needs to be ruled
out as that value would give rise to an unstable orbit. The problem is illustrated
in Fig. 2. If \( n_\varphi = 0 \), the orbit of the electron would be in the plane in the figure.
Contrary to the situation depicted in Fig. 1, this plane would not be rotating around
the \( z \)-axis. As long as there is no external electric field, such orbits are allowed.
However, as soon as the electric field in the \( z \)-direction is switched on, such orbits
become unstable and the electron will eventually hit the nucleus.

### 3 The non-uniqueness of orbits in the old quantum theory

In this section, we compare the orbits found by applying the quantum conditions of
the old quantum theory to the motion of the electron in a hydrogen atom without an
external electric field in two different sets of coordinates, spherical coordinates and
parabolic coordinates. In the presence of an external field, we cannot use spherical coordinates because the Hamilton-Jacobi equation for the system is not separable in those coordinates. This is why, in section 2, we used parabolic coordinates instead. As long as there is no electric field, however, the Hamilton-Jacobi equation is separable in both sets of coordinates. Proceeding in the same way that got us to Eqs. (16)–(18) in section 2, we set the action variables corresponding to the spherical coordinates \((r, \theta, \phi)\) equal to integral multiples of \(\hbar\) (Corben and Stehle, 1994, sec. 64, pp. 200–206):

\[
I_r = \oint p_r \, dr = n_r \hbar, \tag{62}
\]
\[
I_\theta = \oint p_\theta \, d\theta = n_\theta \hbar, \tag{63}
\]
\[
I_\phi = \oint p_\phi \, d\phi = n_\phi \hbar, \tag{64}
\]

where, at least at this point, \(n_r, n_\theta,\) and \(n_\phi\) can take on the values 0, 1, 2, \ldots. Examining the relation between quantum numbers and separation constants in this case (cf. Eqs. (64)–(32) in section 2), we find the relation between the quantum numbers \((n_r, n_\theta, n_\phi)\) and the usual quantum numbers \((n, l, m)\). As in the case of parabolic coordinates (see Eq. (31)), the energy \(E\) depends on the sum of the action variables:

\[
E = -\frac{2\pi^2 \mu e^4}{(I_r + I_\theta + I_\phi)^2} = -\frac{2\pi^2 \mu e^4}{(n_r + n_\theta + n_\phi)^2 \hbar^2} \tag{65}
\]

It follows that the principal quantum number \(n\) is given by

\[
n = n_r + n_\theta + n_\phi, \tag{66}
\]

and that \(n_r, n_\theta,\) and \(n_\phi\) cannot all be zero simultaneously. The total angular momentum, \(L = il\hbar\), and the \(z\)-component of the angular momentum, \(L_z = m\hbar\), it turns out, are equal to \((1/2\pi)\) times \(I_\theta + I_\phi\) and \(I_\phi\), respectively. It follows that

\[
l = n_\theta + n_\phi, \quad n_\phi = |m|. \tag{67}
\]

The total angular momentum cannot be zero as that would correspond to straight-line motion through the nucleus. Like the principal quantum number \(n\), the quantum number \(l\) can thus only take on the value 1, 2, 3, \ldots. The quantum number \(m\) can take on the values \(-l, \ldots, 0, \ldots, l\). Comparing Eqs. (66) and (67), we note that

\[
n = n_r + l. \tag{68}
\]
The orbits are ellipses characterized by their semi-major axes \( a \) and their eccentricities \( \epsilon \). In analogy to the minimum and maximum distance of a planet to the Sun at perihelion and aphelion, respectively, we consider the apsidal distances \( r_{\text{max}} \) and \( r_{\text{min}} \), the maximum and minimum distances of the electron to the nucleus at one of the focal points of the ellipse. These apsidal distances can be expressed in terms of \( a \) and \( \epsilon \) (Goldstein et al., 2002, p. 96):

\[
\begin{align*}
    r_{\text{max}} &= a(1 + \epsilon), \\
    r_{\text{min}} &= a(1 - \epsilon).
\end{align*}
\] (69)

Inverting these relations, we find

\[
\begin{align*}
    a &= \frac{1}{2}(r_{\text{max}} + r_{\text{min}}), \\
    \epsilon &= \frac{r_{\text{max}} - r_{\text{min}}}{r_{\text{max}} + r_{\text{min}}}. \quad (70)
\end{align*}
\]

The eccentricity can also be expressed in terms of the energy \( E \) and the angular momentum \( L \) (cf. Goldstein p. 94, Eq. (3.57); Corben and Stehle, 1994, p. 95, Eq. (37.8)):

\[
    \epsilon = \sqrt{1 + \frac{2EL}{\mu e^4}}. \quad (72)
\]

Inserting Eq. (65) for \( E \) and \( l\hbar \) for \( L \), we find that this equation reduces to:

\[
    \epsilon = \sqrt{1 - \frac{l^2}{n^2}}. \quad (73)
\]

This equation also allows us to compute \( l \) once we know \( n \) and \( \epsilon \):

\[
    l = n\sqrt{1 - \epsilon^2}. \quad (74)
\]

Table 1 shows the values of the angular momentum \( L \) (in terms of \( l = L\hbar \)) and the eccentricity \( (\epsilon) \) for orbits corresponding to low values for the principal quantum number \( n = n_r + l \), if we select the allowed orbits by imposing the quantum conditions in spherical coordinates.

We now compare the angular momenta and eccentricities of these orbits with the angular momenta and eccentricities of orbits that we find if we impose the quantum conditions in parabolic coordinates \((\xi, \eta, \varphi)\) (see Eq. (2)). The results are collected in Table 2.

We will only present the calculations for the special case that one of the two quantum numbers \( n_\xi \) or \( n_\eta \) equals zero. Suppose \( n_\eta = 0 \). The case that \( n_\xi = 0 \) can
Table 1: Parameters characterizing orbits in hydrogen for low values of the principal quantum number $n = n_r + l$ (see Eq. (68)) when quantum conditions are imposed in spherical coordinates: angular momenta $L$ (in terms of $l = L/h$) and eccentricities $\epsilon$ (see Eq. (73)).

| $n$ | $n_r$ | $l$ | $\epsilon$ |
|-----|-------|-----|------------|
| 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   | $2\sqrt{2}/3$ |

be handled in the exact same way. If $n_\eta = 0$, the action variable $I_\eta = n_\eta h = 0$. This action variable is essentially equal to the integral of an expression of the form $\sqrt{(\eta - \eta_{\min})(\eta_{\max} - \eta)}$ from $\eta_{\min}$ to $\eta_{\max}$ (see Eq. (27)). This integral vanishes only if the integrand is identically zero, i.e., if the value of $\eta$ is fixed: $\eta = \eta_{\min} = \eta_{\max}$. In section 2, we saw that $\eta_{\min}$ and $\eta_{\max}$ are the roots of the quadratic equation obtained by setting the expression under the square root sign in the integral giving the action variable $I_\eta$ equal to zero:

$$\frac{\alpha_2^2}{2\mu\alpha_1} - \left(\frac{\mu e^2 + \alpha_2}{\mu\alpha_1}\right) \eta - \eta^2 = 0$$

(75)

(cf. Eq. (25)). If the two roots of this equation, which is of the form $a\eta^2 + b\eta + c = 0$, are the same, the discriminant, $b^2 - 4ac$, vanishes and the roots are simply equal to $-b/2a$. In other words,

$$\eta_{\min} = \eta_{\max} = -\frac{\mu e^2 + \alpha_2}{2\mu\alpha_1}.$$  

(76)

With the help of Eqs. (31) and (34), $\alpha_1$ and $\alpha_2$ can be expressed in terms of the action variables ($I_\xi, I_\eta, I_\phi$) and the quantum numbers ($n_\xi, n_\eta, n_\phi = |m|$) associated with them.

If $\eta$ is constant, then $r = (\xi + \eta)/2$ (see Eq. (4)) reaches its minimum and maximum value whenever $\xi$ reaches its minimum and maximum value. In section 2, we saw that $\xi_{\min}$ and $\xi_{\max}$ are the roots of the quadratic equation obtained by setting the expression under the square root sign in the integral giving the action variable $I_\xi$ equal to zero:

$$\frac{\alpha_3^2}{2\mu\alpha_1} - \left(\frac{\mu e^2 - \alpha_2}{\mu\alpha_1}\right) \xi - \xi^2 = 0$$

(77)
Solving this equation gives us expressions for $\xi_{\text{min}}$ and $\xi_{\text{max}}$ in terms of the separation constants $(\alpha_1, \alpha_2, \alpha_3)$. We can then use Eqs. (31), (34), and (29) to express $(\alpha_1, \alpha_2, \alpha_3)$ in terms of the quantum numbers $(n\xi, n\eta, n\varphi = |m|)$. Finally, we set $n\eta = 0$ and derive expressions for $r_{\text{max}} = \frac{1}{2}(\xi_{\text{max}} + \eta_{\text{max}})$ and $r_{\text{min}} = \frac{1}{2}(\xi_{\text{min}} + \eta_{\text{min}})$, using Eq. (76) for $\eta_{\text{min}} = \eta_{\text{max}}$. In this way we find:

$$r_{\text{min}} = \frac{nh^2}{\mu \pi e^2} \left( n - \sqrt{n\xi(n\xi + |m|)} \right),$$

(78)

$$r_{\text{max}} = \frac{nh^2}{\mu \pi e^2} \left( n + \sqrt{n\xi(n\xi + |m|)} \right).$$

Inserting these results into Eq. (71) for $\epsilon$, we find:

$$\epsilon = \frac{r_{\text{max}} - r_{\text{min}}}{r_{\text{max}} + r_{\text{min}}} = \sqrt{\frac{n\xi(n\xi + |m|)}{n^2}}. \tag{79}$$

A similar result holds for orbits for which $n\xi = 0$:

$$\epsilon = \sqrt{n\eta(n\eta + |m|)}.$$

(80)

If both $n\xi$ and $n\eta$ are non-zero, it is more difficult to determine $r_{\text{min}}$ and $r_{\text{max}}$. If $\xi$ oscillates between $\xi_{\text{min}}$ and $\xi_{\text{max}}$ and $\eta$ oscillates between $\eta_{\text{min}}$ and $\eta_{\text{max}}$, it depends on the phase difference $\delta$ between those two oscillations when $r = (\xi + \eta)/2$ reaches its minimum and maximum value and what those values are. We will not present the calculations of the eccentricities for such orbits but simply state the result. For arbitrary values of $n\xi$ and $n\eta$, the eccentricity is given by

$$\epsilon = \sqrt{\sigma_1^2 + \sigma_2^2 + 2\sigma_1 \sigma_2 \cos(2\pi\delta)}, \tag{81}$$

where $\sigma_1$ and $\sigma_2$ are defined as:

$$\sigma_1 \equiv \frac{1}{n} \sqrt{n\xi(n\xi + |m|)}, \quad \sigma_2 \equiv \frac{1}{n} \sqrt{n\eta(n\eta + |m|)}.$$

(82)

For $n\eta = 0$ and $n\xi = 0$, Eq. (81) reduces to Eq. (79) and Eq. (80), respectively.

Table 2 brings together the results for all possible values of $n\xi$ and $n\eta$ for orbits corresponding to low values of $n = n\xi + n\eta + |m|$ (cf. Eq. (32) with $n\varphi = |m|$), if we select the allowed orbits by imposing the quantum conditions in parabolic coordinates. The table shows the values of the eccentricity $\epsilon$ and the angular momentum
Table 2: Parameters characterizing orbits in hydrogen for low values of the principal quantum number \( n = n_\xi + n_\eta + |m| \) (cf. Eq. (32) with \( n_\phi = |m| \)) when quantum conditions are imposed in \textbf{parabolic coordinates}: angular momenta \( L \) (in terms of \( l = L/h \)) and eccentricities \( \epsilon \) (computed on the basis of Eqs. (79)–(82)).

\[
\begin{array}{|c|c|c|c|c|}
\hline
n & n_\xi & n_\eta & |m| & l & \epsilon \\
\hline
1 & 0 & 0 & 1 & 1 & 0 \\
2 & 0 & 0 & 2 & 2 & 0 \\
2 & 1 & 0 & 1 & \sqrt{2} & 1/\sqrt{2} \\
2 & 0 & 1 & 1 & \sqrt{2} & 1/\sqrt{2} \\
2 & 1 & 1 & 0 & 2 \sin (\pi \delta) & \cos (\pi \delta) \\
3 & 0 & 0 & 3 & 3 & 0 \\
3 & 1 & 1 & 1 & \sqrt{1 + 8 \sin^2 (\pi \delta)} & 2\sqrt{2} \cos (\pi \delta)/3 \\
3 & 2 & 0 & 1 & \sqrt{3} & \sqrt{2}/3 \\
3 & 0 & 2 & 1 & \sqrt{3} & \sqrt{2}/3 \\
3 & 1 & 0 & 2 & \sqrt{6} & 1/\sqrt{3} \\
3 & 0 & 1 & 2 & \sqrt{6} & 1/\sqrt{3} \\
\hline
\end{array}
\]

\( L \) (in terms of \( l = L/h \)) for these orbits. For those orbits for which either \( n_\eta = 0 \) or \( n_\xi = 0 \), we used Eqs. (79) and (80), respectively, to compute \( \epsilon \). In all cases, we inserted the values for \( \epsilon \) into Eq. (74) to compute \( l \).

Comparison of Tables 1 and 2 clearly shows that the allowed orbits depend on the coordinates in which the quantum conditions are imposed. For circular orbits, for which the eccentricity \( \epsilon \) equals zero, the orbits are the same. In all other cases, the orbits are different. If the quantum conditions are imposed in spherical coordinates, the angular momentum is always an integral multiple of \( h \). If they are imposed in parabolic coordinates, this is true only for circular orbits. The angular momentum is not even discrete in all cases. If both \( n_\xi \) and \( n_\eta \) are non-zero, it can take on a continuous range of values labeled by the phase factor \( \delta \).\(^8\)

Both Epstein (1916b, p. 507) and Sommerfeld (1923, p. 284) acknowledged the problem with the non-uniqueness of the orbits.\(^9\) The solution they proposed was

\(^{8}\)If the quantum conditions are imposed in so-called prolate spheroidal coordinates, another coordinate system in which the Hamilton-Jacobi equation for an electron in a hydrogen atom without external electric field is also separable, we find yet another set of different orbits. We leave this as an exercise to the reader.

\(^{9}\)See Duncan and Janssen (2014) for the passages in which Epstein and Sommerfeld stated the problem. The problem is also noted by Juvet (1926, p. 121), professor at the University of Neuchatel, in a book on analytical mechanics and the old quantum theory.
little more than wishful thinking. Their hope was that, if relativistic effects were
included in the Hamiltonian in Eq. (1), there would only be one coordinate system
left in which the Hamilton-Jacobi equation would be separable. The actual orbits
would then be the orbits found if the quantum conditions were imposed in those
coordinates. Unfortunately, as Einstein (1917) suspected early on, there is in general
simply no coordinate system in which the Hamilton-Jacobi equation for a Hamilto-
nian containing a variety of physical effects is separable. So the solution suggested
by Epstein and Sommerfeld does not work. There are either two or more coordinate
systems in which the Hamilton-Jacobi can be separated or none at all.

4 The Stark effect in wave mechanics

Shortly after Schrödinger (1926a) introduced wave mechanics, Schrödinger (1926b)
and Epstein (1926), independently of one another, applied the new wave mechanics
to the Stark effect. For our purposes, it suffices to solve the Schrödinger equation
for the hydrogen atom without an external electric field in parabolic coordinates.
This amounts to a derivation of the extra term of 1 in the relation (61) between the
principal quantum number and the quantum numbers in parabolic coordinates that
we mentioned at the end of section 2. We will only sketch the derivation of the actual
formula for the first-order Stark effect, i.e., the formula for the energy levels in the
presence of an external electric field.

As in the old quantum theory, the starting point for the derivation of the formula
for the Stark effect in hydrogen is the Hamiltonian (5) in parabolic coordinates.
Instead of the substitutions (7) of $\frac{\partial S}{\partial \xi}$ for $p_\xi$ etc., we now make the substitutions

$$p_\xi \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial \xi}, \quad p_\eta \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial \eta}, \quad p_\phi \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial \phi}, \quad (83)$$

to form the Hamilton operator entering into the time-independent Schrödinger equa-
tion

$$H\psi = \alpha_1 \psi, \quad (84)$$

where $\psi(\xi, \eta, \phi)$ is the wave function in parabolic coordinates and where, to bring
out the family resemblance of the calculation in wave mechanics to the one in the

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10Schrödinger’s paper was received by Annalen der Physik on May 10 and published July 13,
1926. Epstein’s paper is signed July 29 and appeared in Physical Review in October 1926. Epstein
had moved from Munich to Pasadena in 1921. In his paper, Epstein (1926, p. 695, note 1) cited
Schrödinger’s first and second “communication” (Mitteilung) on wave mechanics but not the third.
Presumably, the July 13 issue of Annalen der Physik had not reached Pasadena by July 29.

11For the main steps in the derivation below, see Condon and Shortley (1963, pp. 398–399).
old quantum theory given in section 2, we used $\alpha_1$ to label the eigenvalues of energy. With the substitutions (83) the Hamiltonian (5) becomes:

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

(85)

Inserting this Hamilton operator into Eq. (84), dividing both sides by $\psi$ and multiplying by $2\mu(\xi + \eta)$ (using relations (9)), we arrive at the Schrödinger equation:

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

(86)

Note the similarity between this equation and the Hamilton-Jacobi equation (8). The Schrödinger equation, like the Hamilton-Jacobi equation for this system, is separable in parabolic coordinates. In the case of the Schrödinger equation, this means that its solution factorizes as follows:

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

(87)

The wave function $\psi$ 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 $(\xi, \eta, \varphi)$, $\psi$ must be the product of three such functions:

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

(88)

with

$$\psi_\xi(\xi) = e^{iS_\xi(\xi)/\hbar}, \quad \psi_\eta(\eta) = e^{iS_\eta(\eta)/\hbar}, \quad \psi_\varphi(\varphi) = e^{iS_\varphi(\varphi)/\hbar}.$$  

(89)

Just as we could set $S_\varphi(\varphi)$ equal to $\alpha_3 \varphi$, we can now set $S_\varphi(\varphi)$ equal to $e^{i\alpha_3 \varphi/\hbar}$, with $\alpha_3 = |m|\hbar$ (cf. Eq. (29)). After we substitute $-m^2 \psi$ for $\partial^2 \psi/\partial \varphi^2$ in Eq. (86), we are left with an equation that splits into a part that only depends on $\xi$ and a part that only depends on $\eta$. The two parts must therefore each be constant. Denoting these constants by $\pm 2\alpha_2$ as we did in the corresponding Eqs. (11)–(12) in the old quantum theory, we arrive at

$$-\frac{4\hbar^2}{\psi_\xi} \frac{d}{d\xi} \left( \xi \frac{d\psi_\xi}{d\xi} \right) + \frac{m^2 \hbar^2}{\xi} - 2\mu e^2 + \mu e \mathcal{E} \xi^2 - 2\mu \alpha_1 \xi = -2\alpha_2,$$

(90)

$$-\frac{4\hbar^2}{\psi_\eta} \frac{d}{d\eta} \left( \eta \frac{d\psi_\eta}{d\eta} \right) + \frac{m^2 \hbar^2}{\eta} - 2\mu e^2 - \mu e \mathcal{E} \eta^2 - 2\mu \alpha_1 \eta = +2\alpha_2.$$  

(91)

---

12 Condon and Shortley use $F$ and $G$ for what we call $\psi_\xi$ and $\psi_\eta$, respectively.
These last two equations can be rewritten as

\[ \xi \frac{d^2 \psi_\xi}{d\xi^2} + \frac{d\psi_\xi}{d\xi} + \frac{1}{4} \left[ \frac{2\mu e^2}{\hbar^2} - \frac{2\alpha_2}{\hbar^2} - \frac{m^2}{\xi} + \frac{2\mu \alpha_1}{\hbar^2} - \frac{\mu e E}{\hbar^2} \xi^2 \right] \psi_\xi = 0, \quad (92) \]

\[ \xi \frac{d^2 \psi_\eta}{d\eta^2} + \frac{d\psi_\eta}{d\eta} + \frac{1}{4} \left[ \frac{2\mu e^2}{\hbar^2} + \frac{2\alpha_2}{\hbar^2} - \frac{m^2}{\eta} + \frac{2\mu \alpha_1}{\hbar^2} + \frac{\mu e E}{\hbar^2} \eta^2 \right] \psi_\eta = 0. \quad (93) \]

We now solve Eq. (92) for \( \psi_\xi(\xi) \) for the case that \( E = 0 \). It will be convenient to introduce the quantity \( n \) defined as

\[ na \equiv \frac{\hbar}{\sqrt{-2\mu \alpha_1}}, \quad (94) \]

where \( a \equiv \hbar^2 / \mu e^2 \) is the Bohr radius. The notation \( n \) was chosen with malice aforesight as \( n \) will turn out to be the principal quantum number (cf. Eqs. (30)–(32)). Eq. (94) allows us to write

\[ \alpha_1 = -\frac{\hbar^2}{2\mu a^2 n^2}. \quad (95) \]

With the help of Eqs. (94) and (95), Eq. (92) for \( E = 0 \) can be rewritten as:

\[ \xi \frac{d^2 \psi_\xi}{d\xi^2} + \frac{d\psi_\xi}{d\xi} + \frac{1}{4} \left[ \frac{2\mu e^2}{\hbar^2} - \frac{2\alpha_2}{\hbar^2} - \frac{m^2}{\xi} - \frac{\xi}{n^2 a^2} \right] \psi_\xi = 0. \quad (96) \]

To solve this equation we first need to examine its asymptotic behavior. The upshot of that is that \( \psi_\xi \) can be written in the form

\[ \psi_\xi(\xi) = \xi^{|m|/2} e^{-\xi/2na} f(\xi), \quad (97) \]

where \( f(\xi) \) should be finite as \( \xi \to 0 \) and power bounded for \( \xi \to \infty \). Given this factorization, we can write the first derivative of \( \psi_\xi \) and \( \xi \) times the second derivative of \( \psi_\xi \) as

\[ \frac{d\psi_\xi}{d\xi} = \left( \frac{|m|}{2} \xi^{|m|-1} e^{-\xi/2na} - \xi^{|m|/2} f' \right) e^{-\xi/2na}, \quad (98) \]

\[ \frac{d^2 \psi_\xi}{d\xi^2} = \left( \frac{|m|}{2} \xi^{|m+1|-2} f - \frac{1}{2na} \xi^{|m|/2} f + \xi^{|m|/2} f' \right) e^{-\xi/2na}, \quad (99) \]

\[ \frac{d^2 \psi_\eta}{d\eta^2} = \left( \frac{|m|}{2} \eta^{|m|-1} e^{-\eta/2na} - \eta^{|m|/2} f' \right) e^{-\eta/2na}. \quad (100) \]

\[ \frac{d\psi_\eta}{d\eta} = \left( \frac{|m|}{2} \eta^{|m|-1} e^{-\eta/2na} - \eta^{|m|/2} f' \right) e^{-\eta/2na}, \quad (101) \]

\[ \frac{d^2 \psi_\eta}{d\eta^2} = \left( \frac{|m|}{2} \eta^{|m+1|-2} f - \frac{1}{2na} \eta^{|m|/2} f + \eta^{|m|/2} f' \right) e^{-\eta/2na}. \quad (102) \]
\[
\xi \frac{d^2 \psi}{d \xi^2} = \left( \frac{|m|}{2} \left( \frac{|m|}{2} - 1 \right) \xi^{\frac{|m|}{2} - 1} - \frac{|m| \xi^{\frac{|m|}{2}}}{2na} + |m| \xi^{\frac{|m|}{2}} f' + \frac{\xi^{\frac{|m|}{2} + 1}}{4n^2 a^2} \right) \xi^{\frac{|m|}{2} - 1} \left( 1 - \frac{1}{n} \right) + \frac{\alpha_2}{2h^2} - \frac{|m|}{2na} \right) + \xi^{\frac{|m|}{2} + 1} f'' e^{-\xi/2na}. \tag{99}
\]

When these results are inserted into Eq. (96), the last two terms in \(\frac{1}{4} \ldots \psi_{\xi}\) cancel against the terms \(\left( \frac{|m|}{4} \xi \right) \psi_{\xi}\) and \(\frac{|m|}{2a^2} \psi_{\xi}\) in \(\xi \frac{d^2 \psi_{\xi}}{d \xi^2}\); and the first term in \(\frac{d \psi_{\xi}}{d \xi}\) cancels against the term \(-\left( \frac{|m|}{2} \right) \psi_{\xi}/\xi\) in \(\xi \frac{d^2 \psi_{\xi}}{d \xi^2}\). Dividing the remainder of Eq. (96) by \(\xi^{\frac{|m|}{2}} e^{-\xi/2na}\) and grouping terms with \(f, f',\) and \(f''\), we find:

\[
\xi f'' + \left( |m| + 1 - \frac{\xi}{na} \right) f' + \left( \frac{1}{2a} \left( 1 - \frac{1}{n} \right) - \frac{\alpha_2}{2h^2} - \frac{|m|}{2na} \right) f = 0. \tag{100}
\]

The solution of this equation will be a polynomial in \(\xi\):

\[
f(\xi) = \sum_k c_k \xi^k. \tag{101}
\]

Inserting this polynomial into Eq. (100), we find:

\[
\sum_k c_k \left( k(k-1)\xi^{k-1} + (|m|+1)k \xi^{k-1} - \frac{k}{na} \xi^k + \left( \frac{1}{2a} \left( 1 - \frac{|m|+1}{n} \right) - \frac{\alpha_2}{2h^2} \right) \xi^k \right) = 0. \tag{102}
\]

Replacing the summation variable \(k\) by \(k+1\), we can rewrite the terms of order \(k-1\) in \(\xi\) in Eq. (102) as terms of order \(k\):

\[
\sum_k k c_k (k + |m|) \xi^{k-1} = \sum_k (k + 1) c_{k+1} (k + 1 + |m|) \xi^k \tag{103}
\]

For Eq. (102) to hold, the coefficients of \(\xi^k\) must vanish for all \(k\). Inserting Eq. (103) into Eq. (102), we thus find the following recursion relation for the coefficient \(c_k\):

\[
\frac{c_{k+1}}{c_k} = \frac{k - \frac{n}{2} \left( 1 - \frac{|m|+1}{n} \right) + \frac{\alpha_2 na}{2h^2}}{na(k+1)(k + 1 + |m|)}. \tag{104}
\]

As the polynomial in Eq. (101) needs to break off for finite \(k\) to get a legitimate wave function (otherwise \(\psi_{\xi}(\xi) \approx e^{+\xi/2na}\) as \(\xi \to \infty\), leading to a non-normalizable wave function), there must be some value \(n_\xi\) for \(k\) such that \(c_{k+1} = 0\). Eq. (104) tells us that this quantum number is given by:

\[
n_\xi = \frac{n}{2} \left( 1 - \frac{|m|+1}{n} \right) - \frac{\alpha_2 na}{2h^2}. \tag{105}
\]

23
To find the solution of equation (93) for $\psi_\eta(\eta)$ for $E = 0$, we proceed in the exact same way as we did in Eqs. (96)–(105) for $\psi_\xi(\xi)$. Given its behavior at small and large $\eta$, we write $\psi_\eta(\eta)$ as (cf. Eq. (97))

$$\psi_\eta(\eta) = \eta^{m|/2} e^{-\eta/2} n a g(\eta).$$

We then derive an equation for $g(\eta)$, analogous to Eq. (100) for $f(\xi)$. The solution of this equation will be a polynomial $\sum_k \hat{c}_k \eta^k$ (where the ‘hat’ is used to distinguish the coefficients from those in Eq. (101) for $f(\xi)$) that will break off if and only if there is a value $n_\eta$ for $k$ such that (cf. Eq. (105)):

$$n_\eta = \frac{n}{2} \left(1 - \frac{|m|+1}{n}\right) + \frac{\alpha_n a^2}{2\hbar^2}.$$  

Combining Eq. (105) and Eq. (107), we find

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

or

$$n = n_\xi + n_\eta + |m| + 1.$$  

Comparing this result in wave mechanics with the corresponding result (32) in the old quantum theory, we notice that the difference between the two is the final term $+1$ in Eq. (109). This extra term obviates the need for a special condition to rule out $|m| = 0$ (cf. Eqs. (60)–(61) and Fig. 2). As Epstein (1926, p. 708) noted toward the end of his paper on the Stark effect in wave mechanics:

> 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.

To conclude this section, we sketch how the formula for the energy levels in the first-order Stark effect is recovered in wave mechanics. The power-series solutions discussed above for the wave functions $\psi_\xi(\xi)$ and $\psi_\eta(\eta)$ turn out to be Laguerre polynomials. The full normalized energy eigenfunction solutions $\psi_{n_\xi n_\eta m}(\xi, \eta, \varphi)$ for the state characterized by quantum numbers $n_\xi, n_\eta, m$ (with principal quantum number
\[ n = n_\xi + n_\eta + |m| + 1 \] in the unperturbed case (i.e., a hydrogen atom in zero electric field) take the form

\[
\psi_{n_\xi n_\eta m} = C_{n_\xi n_\eta m} \left( \frac{\xi}{na} \right)^{|m|/2} e^{-\xi/2na} \left( \frac{\eta}{na} \right)^{|m|/2} e^{-\eta/2na} L_{n_\xi}^{|m|} \left( \frac{\xi}{na} \right) L_{n_\eta}^{|m|} \left( \frac{\eta}{na} \right) e^{im\varphi},
\]

(110)

where \( C_{n_\xi n_\eta m} \) is an explicitly known normalization constant which we will not give here (see, e.g., Condon and Shortley, 1963, p. 399). Introducing the Stark perturbation operator \( H^{\text{Stark}} \equiv \frac{1}{2} e E (\xi - \eta) \), the standard procedure of first-order degenerate perturbation theory instructs us to calculate the matrix of the perturbing operator in the basis of the \( n^2 \) degenerate states of identical unperturbed energy corresponding to a given principal quantum number \( n \). The calculation, using standard properties of Laguerre functions, gives

\[
\langle n'_\xi n'_\eta m' | e E \left( \frac{\xi - \eta}{2} \right) | n_\xi n_\eta m \rangle = \frac{3}{2} e E n(n_\xi - n_\eta) a \delta_{n'_\xi n_\xi} \delta_{n'_\eta n_\eta} \delta_{m'm}. \]

(111)

The perturbation matrix is, in fact, diagonal in this basis, so the Stark energy shifts can be read off directly and are seen to be identical to the results obtained in the old quantum theory (see Eq. 59).

### 5 Orbits versus eigenfunctions

In this section, we show how the problematic non-uniqueness of orbits that we ran into in the old quantum theory (see section 3) turns into the totally unproblematic non-uniqueness of bases in Hilbert space in the new quantum theory—more specifically: the non-uniqueness of bases of eigenfunctions in wave mechanics.

In wave mechanics, the stationary states are associated with eigenfunctions of the Hamilton operator of the system. Thus, to solve the problem of the hydrogen atom in spherical coordinates \((r, \vartheta, \varphi)\), we need to find normalizable (square-integrable) solutions of the time-independent Schrödinger equation,

\[
-\frac{\hbar^2}{2\mu} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial \psi}{\partial \vartheta} \right) + \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial^2 \psi}{\partial \varphi^2} \right) - \frac{e^2}{r} \psi = E \psi,
\]

(112)

for energy eigenvalues \( E < 0 \), where the wavefunction \( \psi \) is a function of \((r, \vartheta, \varphi)\). We highlight this choice of coordinates by using the notation \( \psi_{\text{spherical}}(r, \vartheta, \varphi) \) for solutions of Eq. (112). The negative-energy normalizable solutions of Eq. (112) correspond to the discrete energies \( E_n \) labeled by the value of the principal quantum
number \( n \). The Schrödinger equation can be separated in spherical coordinates, which means that Eq. (112) has solutions of the form \( \psi_n(r) \psi_{n_\theta}(\vartheta) \psi_{n_\varphi}(\varphi) \). For each value of the principal quantum number \( n = n_r + l \), the angular momentum quantum number \( l = n_\theta \) can take on the values 0, 1, 2, \ldots, \( n - 1 \) and, for each value of \( l \), the azimuthal quantum number \( m \) (where \( |m| = n_\varphi \)) can take on the values \(-l, -l+1, \ldots, l-1, l\). For each value of \( n \), there are \( \sum_{l=0}^{n-1}(2l+1) = n^2 \) degenerate orthogonal solutions of Eq. (112). We can conveniently label these solutions with the values of \( n \) and \( m \) but a fixed value of \( l \) and \( n \) must be a linear combination of the solutions \( \psi_{nlm}^{\text{spherical}}(r, \vartheta, \varphi) \) for different values of \( l \) and \( m \) but a fixed value of \( n \).

In parabolic coordinates \((\xi, \eta, \varphi)\) (see Eq. (2)), the time-independent Schrödinger equation for the same system is (cf. Eqs. (85)–(86)):

\[
-\frac{\hbar^2}{2\mu} \left( \frac{4}{\xi + \eta} \frac{\partial}{\partial \xi} \left( \xi \frac{\partial \psi}{\partial \xi} \right) + \frac{4}{\xi + \eta} \frac{\partial}{\partial \eta} \left( \eta \frac{\partial \psi}{\partial \eta} \right) + \frac{1}{\xi \eta} \frac{\partial^2 \psi}{\partial \varphi^2} \right) - \frac{2e^2}{\xi + \eta} \psi = E \psi, \tag{113}
\]

where the wave function \( \psi \) is now a function of \((\xi, \eta, \varphi)\). We highlight this choice of coordinates by adopting the notation \( \psi_{\text{parabolic}}^{\text{parabolic}}(\xi, \eta, \varphi) \) for solutions of Eq. (113).\(^{14}\)

The Schrödinger equation can once again be separated in parabolic coordinates, which means that Eq. (113) has solutions of the form \( \psi_{n_\xi}(\xi) \psi_{n_\eta}(\eta) \psi_{n_\varphi}(\varphi) \) (see Eq. (87)). For \( E < 0 \), there are normalizable solutions only for discrete energies \( E_n \) labeled by the principal quantum number \( n = n_\xi + n_\eta + n_\varphi + 1 \) (see Eq. (109)). For any fixed value of \( n \), there are \( n^2 \) degenerate orthogonal solutions, labeled by the values of the integer quantum numbers \( n_\xi, n_\eta, \) and \( n_\varphi = |m| \) (where \( m \) is the same as in spherical coordinates). We introduce the notation \( \psi_{\text{parabolic}}^{\text{parabolic}}(\xi, \eta, \varphi) \) for these solutions. For a given value of \( n \), all combinations of positive or zero values of \( n_\xi, n_\eta, \) and \( |m| \) consistent with \( n = n_\xi + n_\eta + |m| + 1 \) are possible. The number of such combinations is \( n^2 \). Any solution of Eq. (113) for \( E = E_n \) must be a linear combination of the solutions \( \psi_{n_\xi n_\eta n_\varphi}^{\text{parabolic}}(\xi, \eta, \varphi) \) with different values of \( n_\xi, n_\eta, \) and \( |m| \) but a fixed value of \( n \).

Any solution \( \psi_{\text{spherical}}^{\text{spherical}}(r, \vartheta, \varphi) \) of Eq. (112) can be immediately converted into a solution \( \psi_{\text{parabolic}}^{\text{parabolic}}(\xi, \eta, \varphi) \) of Eq. (113) simply by expressing \((r, \vartheta, \varphi)\) in terms of \((\xi, \eta, \varphi)\). The allowed physical states are therefore identical, whichever coordinate system we use, unlike the orbits selected by the quantum conditions in the old quantum theory. However, the individual separated solutions (labeled by definite triples of quantum numbers) in parabolic coordinates...
numbers in either coordinate system) are not in one-to-one correspondence. Since we are dealing with different representations of one and the same self-adjoint operator, any solution \( \psi_{nlm}^{\text{spherical}}(r, \vartheta, \varphi) \) of Eq. (112) must be a linear combination of the solutions \( \psi_{n\xi n\eta m}^{\text{parabolic}}(\xi, \eta, \varphi) \) of Eq. (113). After all, any solution \( \psi_{nlm}^{\text{spherical}}(r, \vartheta, \varphi) \) —with \((r, \vartheta, \varphi)\) expressed in terms of \((\xi, \eta, \varphi)\) —of Eq. (112) must also be a solution of Eq. (113) for the same energy \( E = E_n \). The lack of a one-to-one correspondence between the separated solutions in two different coordinate systems can be regarded as the "residue" in wave mechanics of the problem of the non-uniqueness of the orbits in the old quantum theory. This residue, of course, is no problem at all in wave mechanics.

The explicit separated solutions are as follows. In spherical coordinates, they are

\[
\psi_{nlm}^{\text{spherical}}(r, \vartheta, \varphi) = C_{nlm} \left( \frac{2r}{na} \right)^l e^{-r/na} L_{n-l-1}^{2l+1} \left( \frac{2r}{na} \right) P_l^m(\cos \vartheta) e^{im\varphi},
\]

while in parabolic coordinates, they are

\[
\psi_{n\xi n\eta m}^{\text{parabolic}}(\xi, \eta, \varphi) = C_{n\xi n\eta m} \left( \frac{\eta \xi}{n^2 a^2} \right)^{|m|/2} e^{-(\xi+\eta)/2na} L_n^{|m|} \left( \frac{\xi}{na} \right) L_{|m|}^{|m|} \left( \frac{\eta}{na} \right) e^{im\varphi},
\]

where \( P_l^m \) and \( L_{\cdot \cdot \cdot} \) are the associated Legendre and Laguerre polynomials. \( C_{nlm} \) and \( C_{n\xi n\eta m} \) are normalization constants. Dropping these, and the identical exponential radial dependence \( e^{-r/na} = e^{-(\xi+\eta)/2na} \) and azimuthal dependence \( e^{im\varphi} \) in both cases, we find that

\[
\psi_{nlm}^{\text{spherical}}(r, \vartheta, \varphi) \propto r^l L_{n-l-1}^{2l+1} \left( \frac{2r}{na} \right) P_l^m(\cos \vartheta),
\]

and that

\[
\psi_{n\xi n\eta m}^{\text{parabolic}}(\xi, \eta, \varphi) \propto r^{|m|} \sin^{|m|} \vartheta L_n^{|m|} \left( \frac{\xi}{na} \right) L_{|m|}^{|m|} \left( \frac{\eta}{na} \right).
\]

As discussed above, the functions in Eq. (116) must be linear combinations of those in Eq. (117) (and conversely). This is tedious to demonstrate algebraically in complete generality, but easy to see for the special case of maximal azimuthal quantum number, \(|m| = l\). In this case, using the addition formula

\[
\sum_{n_\xi=0}^{n-|m|-1} L_{n_\xi}^{|m|} \left( \frac{\xi}{na} \right) L_{n-|m|-1-n_\xi}^{|m|} \left( \frac{\eta}{na} \right) = L_{n-|m|-1}^{2|m|+1} \left( \frac{\xi+\eta}{na} \right) = L_{n-l-1}^{2l+1} \left( \frac{2r}{na} \right)
\]

and

\[
P_l^l(\cos \vartheta) = (2l - 1)!! \sin^l \vartheta,
\]
we find very simply that

$$\varphi_{\text{spherical}}^{\text{all}} = (2l - 1)!! \sum_{n_\xi = 0}^{n_l - 1} \varphi_{n_\xi, n_l - 1 - n_\xi, m = l}^{\text{para}}.$$  \hspace{1cm} (120)

For example, for the 2p states with maximal $|m| = 1$, the sum in Eq. (120) degenerates to a single term and we have a one-one correspondence between normalized states in spherical coordinates, which we will denote as $|nlm\rangle$, and normalized states in parabolic coordinates, which we will denote as $|n_\xi n_\eta m\rangle$:

$$|2 \ 1 + 1\rangle = |00 + 1\rangle, \quad |2 \ 1 - 1\rangle = |00 - 1\rangle.$$  \hspace{1cm} (121)

For the 2s state, $m = l = 0$ and the sum in Eq. (120) contains two terms and we have

$$|2 \ 0 \ 0\rangle = \frac{1}{\sqrt{2}} \{ |1 \ 0 \ 0\rangle + |0 \ 1 \ 0\rangle \}.$$  \hspace{1cm} (122)

The remaining state (2p with $m = 0$) is evidently

$$|2 \ 1 \ 0\rangle = \frac{1}{\sqrt{2}} \{ |1 \ 0 \ 0\rangle - |0 \ 1 \ 0\rangle \}.$$  \hspace{1cm} (123)

Once the term $eE \cos \vartheta = \frac{1}{2} eE (\xi - \eta)$, describing an external field in the $z$-direction, is added to the Hamilton operator of the system, the problem is no longer separable in spherical coordinates, neither in the old quantum theory $[S(r, \vartheta, \varphi) \neq S_{n_r}(r) + S_{n_\vartheta}(\vartheta) + S_{n_\varphi}(\varphi)]$ nor in wave mechanics $[\psi(r, \vartheta, \varphi) \neq \psi_{n_r}(r) \psi_{n_\vartheta}(\vartheta) \psi_{n_\varphi}(\varphi)]$. However, the problem continues to be separable in parabolic coordinates, both in the old quantum theory $[S(\xi, \eta, \varphi) = S_{n_\xi}(\xi) + S_{n_\eta}(\eta) + S_{n_\varphi}(\varphi); \text{ cf. Eq. (10)}]$ and in wave mechanics $[\psi(\xi, \eta, \varphi) = \psi_{n_\xi}(\xi) \psi_{n_\eta}(\eta) \psi_{n_\varphi}(\varphi); \text{ cf. Eq. (87)}]$. From the point of view of the old quantum theory, this means that the dynamics must be analyzed in parabolic coordinates. In wave mechanics, the separated eigenfunctions in spherical coordinates are no longer eigenfunctions of the new Hamilton operator, but linear combinations of them give, at least to first order, the separated eigenfunctions in parabolic coordinates! To account for the first-order Stark effect, the quantum conditions of the old quantum theory had to be imposed in parabolic coordinates. From the point of view of the new quantum theory, this is directly related to the fact that, in standard first-order degenerate perturbation theory, the matrix of the perturbing part of the Hamilton operator (here the term with the external electric field) is diagonal in the basis of the (unperturbed) states $|n_\xi n_\eta m\rangle$ in parabolic coordinates (cf. Eq. (111)).
6 The WKB approximation: recovering the old quantum conditions with half-integer instead of integer quantum numbers from wave mechanics

Our analysis of the treatment of the Stark effect in hydrogen in the old quantum theory, typically hailed as one of its great successes, has turned up some serious problems. In section 3, we showed that which sets of electron orbits are allowed, even in the absence of an external electric field, depends on the coordinates in which the quantum conditions are imposed. Even though the energy levels and the level of degeneracy (both determined by the principal quantum number $n$) are the same in different coordinate systems, the eccentricities and angular momenta are not. In section 5, we saw that in wave mechanics this problem is resolved by replacing the old quantum theory’s representation of physical states in terms of orbits by a representation in terms of wave functions. In view of this, it may seem almost miraculous that the old quantum theory worked even to the extent that it did.\footnote{A well-known related puzzle, which is beyond the scope of our paper, is how Sommerfeld could get the right formula for the fine-structure constant in the old quantum theory. See [Eckert 2013, p. 59] for a brief discussion of this issue. [Yourgrau and Mandelstam 1979] argue that the neglect of wave-mechanical effects and the neglect of spin canceled each other out. [Biedenharn 1983] takes issue with this assessment.}

This becomes even more puzzling when we consider that, in the Bohr model of the atom, the ground state of the electron (with principal quantum number $n = 1$) has angular momentum $l\hbar$ with $l = n = 1$, whereas in the correct theory the angular momentum of the electron is actually zero. Despite this glaring distortion of the physical situation, the theory gave the correct value for the binding energy of the electron. As we saw in sections 2 and 4, the mismatch between the angular momentum values and energy levels in the original Bohr model persisted in the old quantum theory of Bohr and Sommerfeld (see Eqs. (60)–(61) and (109) and Fig. 2), resulting in a good deal of convoluted argumentation where certain states of zero angular momentum had to be ruled ineligible on the grounds of instability.

The seemingly accidental success of the old quantum theory can be explained on the basis of the new quantum theory. This explanation is based on an approximation scheme known as the WKB or JWKB approximation, named after [Wentzel 1926], [Kramers 1926] and [Brillouin 1926], who developed it shortly after the transition from the old to the new quantum theory in 1925–26, and [Jeffreys 1924] who developed it right before that watershed in a different context.\footnote{See [Mehra and Rechenberg 2000] pp. 8–9 and pp. 20–36) for a brief history of the (J)WKB method and references to the most important contributions to the further development of the...}
The WKB method, as we will refer to it hereafter, can be seen as providing a “halfway house” between the old and the new theory. It amends the quantum conditions of the old quantum theory, replacing many integer quantum numbers of the original theory by half-integer quantum numbers. In fact, before the advent of the new quantum mechanics, several physicists, including Reiche and Pauling, had made use of half-integer quantum numbers, which typically gave better results than integer ones (e.g., in the case of the specific heat of hydrogen), though in at least one case (that of the electric susceptibility of some diatomic gases) it only made matters worse.\textsuperscript{17} With the WKB amendment of the quantum conditions of the old quantum theory, the connection between the values of the energy and angular momentum is the same as in the new quantum theory (e.g., Eq. (60), \( n = n_{\xi} + n_{\eta} + |m| \), changes to Eq. (61), \( n = n_{\xi} + n_{\eta} + |m| + 1 \)). As we will see in this section, the WKB approximation is key to understanding the remarkable, if partial, success of the old quantum theory.

The first inklings of the semi-classical analysis that would eventually evolve into the WKB method can be found in a heuristic argument that Schrödinger (1926a) used in his first paper on wave mechanics. This is especially clear in the case of Wentzel (1926) and Brillouin (1926), who both took the classical Hamilton-Jacobi equation as the starting point of their analysis. Kramers (1926) only made the connection between his approximation scheme for the Schrödinger equation and the classical Hamilton-Jacobi equation explicit in sec. 3 of his paper, in which he compared his approach to that of Brillouin and Wentzel (ibid., pp. 834–836).

Schrödinger showed that the reformulation of the classical Hamilton-Jacobi equation in terms of a variational principle leads to the Schrödinger equation if we demand that the functional being varied be extremal rather than simply zero, as in the classical case. The connection requires that we express the wave-function \( \psi(x) \) in terms

\textsuperscript{17} See Gearhart (2010, especially pp. 158, 166) for the case of Reiche and specific heat and Midwinter and Janssen (2013) for the case of Pauling and electric susceptibilities (see p. 186 for an explanation of why in this case half-integer quantum numbers only made matters worse). In both cases, the quantization rule for angular momentum in the old quantum theory, \( L = l \hbar \) was changed to \( L = (l + \frac{1}{2}) \hbar \). Kramers (1926) explicitly mentioned half-integer quantization in his paper on the new approximation scheme. However, as we will see, the half-quantum numbers in the two examples mentioned above are not the half-quantum numbers dropping out of the WKB scheme (see Eq. (154) below). Other instances of factors of \( \frac{1}{2} \) cropping up in the late teens and early twenties turned out to be related to spin and have no connection to WKB either. However, the \( \frac{1}{2} \hbar \nu \) term in the energy \( E = \hbar \nu (n + \frac{1}{2}) \) of the harmonic oscillator, i.e., its zero-point energy, is reproduced by the WKB approximation scheme.
of a phase function $S(x)$, which is complex though its leading term (which does not contain $\hbar$) is real:

$$\psi(x) \equiv \exp\left(\frac{i}{\hbar} S(x)\right). \tag{124}$$

As the notation suggests and as will become clear below, the phase function $S(x)$ is closely related to Hamilton’s principal function $S(x)$ in Hamilton-Jacobi theory.

We will only consider systems in one dimension. This restriction is less constraining than it may seem, as the success of the Bohr-Sommerfeld approach depended on the existence of coordinate systems in which the three-dimensional classical motion could be separated into three effectively independent one-dimensional motions.

Consider a Hamiltonian of the form $H = p^2/2\mu + V(x)$. Replacing $p$ by $(\hbar/i) d/dx$, we find the Schrödinger equation in one dimension

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + V(x)\right) \psi(x) = E \psi(x). \tag{125}$$

This can be rewritten as

$$\psi''(x) + \frac{2\mu}{\hbar^2} (E - V(x)) \psi(x) = 0. \tag{126}$$

We now insert the expression for $\psi(x)$ in Eq. (124), using that

$$\psi'(x) = \frac{i}{\hbar} S'(x) \psi(x), \quad \psi''(x) = \left(\frac{i}{\hbar} S''(x) - \frac{1}{\hbar^2} S'(x)^2\right) \psi(x), \tag{127}$$

and divide by $\psi(x)$:

$$\frac{i}{\hbar} S''(x) - \frac{1}{\hbar^2} S'(x)^2 + \frac{2\mu}{\hbar^2} (E - V(x)) = 0. \tag{128}$$

Multiplying by $-\hbar^2$ and rearranging terms, we find

$$S'(x)^2 - 2\mu (E - V(x)) - i\hbar S''(x) = 0. \tag{129}$$

We recover this equation—except for the term depending on $\hbar$—if we substitute $S'(x)$ for $p$ in the equation $H(p, x) = E$, with $H = p^2/2\mu + V(x)$. In other words, if the

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18As we saw in section 4 (see especially Eq. (83)), this substitution is similar to the replacement of $p$ by $dS/dx$ in Hamilton-Jacobi theory.
term with $\hbar$ is neglected, Eq. (129) is just the classical Hamilton-Jacobi equation for the system.\footnote{This relation between the Schrödinger equation and the classical Hamilton-Jacobi equation is emphasized, for instance, in the opening paragraph of the paper in which \cite{Jordan1927} introduced transformation theory.}

We introduce the quantities

$$f(x) \equiv S'(x)$$

and

$$p(x) \equiv \sqrt{2\mu(E - V(x))}.$$  \hspace{1cm} (131)

Note that $2\mu(E - V(x))$ gives the square of the momentum as a function of $x$. Also note that $p$ is real only if $E > V(x)$. Substituting Eqs. (130) and (131) into Eq. (129), we find

$$f(x)^2 - p(x)^2 - \i \hbar f'(x) = 0.$$ \hspace{1cm} (132)

Treating $\hbar$ as a small parameter, we can solve Eq. (132) iteratively. Using that $f(x) = \pm p(x)$ to zeroth order, we obtain at the next level of approximation:

$$f^2 = p(x)^2 \pm \i \hbar p'(x).$$ \hspace{1cm} (133)

Squaring and then differentiating both sides of Eq. (131), we see that $2p(x)p'(x) = -2\mu V''(x)$ or that

$$p'(x) = -\frac{\mu V'(x)}{p(x)}.$$ \hspace{1cm} (134)

Using this relation, we can rewrite Eq. (133) as

$$f^2 = p(x)^2 \pm \i \hbar \frac{\mu V'(x)}{p(x)}.$$ \hspace{1cm} (135)

It follows that, to first order in $\hbar$,

$$f(x) = \sqrt{p(x)^2 \pm \i \hbar \frac{\mu V'(x)}{p(x)}}$$

$$= \pm p(x) \left(1 \mp \frac{\i \hbar \mu V'(x)}{2p(x)^3}\right)$$ \hspace{1cm} (136)

$$= \pm p(x) - \i \hbar \mu V'(x) \frac{2}{2p(x)^2}.$$
The semi-classical approximation that we are considering here is valid only if the second term on the right-hand-side of (136) is small compared to the first, i.e., if 

\[ \left| \frac{\hbar \mu V'(x)}{2p(x)^3} \right| \ll 1. \]  

(137)

This condition may look peculiar at first sight but it amounts to the perfectly natural requirement that the relative change in the “local” momentum \( p(x) \) (due to the variation of the potential) over a single de Broglie wavelength be small (Stehle, 1966, p. 131). The “local” de Broglie wavelength \( \lambda(x) \) is given by \( \hbar/p(x) \). The relative change in \( p(x) \) over this distance can be written as

\[ \frac{\delta p(x)}{p(x)} = \frac{p'(x)\lambda(x)}{p(x)} = -\frac{\hbar \mu V'(x)}{p(x)^3}, \]  

(138)

where we used Eq. (134) for \( p'(x) \). Comparing Eqs. (137) and (138), we see that the condition for the validity of our semi-classical approximation is just that \( |\delta p(x)| \ll |p(x)| \).

In order to find the Schrödinger wave function \( \psi(x) \) in Eq. (124) in this semi-classical approximation, we need to integrate Eq. (136) to get from the derivative \( S'(x) \equiv f(x) \) of the phase factor in the wave function to this phase factor \( S(x) \) itself:

\[ S(x) = \pm \int_x^p \frac{p(y)dy}{p(x)} - \frac{i\hbar \mu}{2} \int_x^p \frac{V'(y)}{p(y)^2}dy. \]  

(139)

Using Eq. (131) for \( p(y) \) in the second integral, we can rewrite this as

\[ S(x) = \pm \int_x^p \frac{p(y)dy}{p(x)} - \frac{i\hbar}{4} \int_x^p \frac{V'(y)}{E-V(y)}dy. \]  

(140)

The second integral is equal to

\[ -\ln(E-V(x)) = -\ln \left( \frac{p(x)^2}{2\mu} \right) = -2\ln p(x) + \ln 2\mu. \]  

(141)

Substituting this expression into Eq. (140), we find

\[ S(x) = \pm \int_x^p p(y)dy + \frac{i\hbar}{2} \ln p(x) + \text{constant}. \]  

(142)

Inserting this result into the expression for the Schrödinger wave function \( \psi(x) \) in Eq. (124), one finds, apart from (at this point uninteresting) normalization factors:

\[ \psi(x) \propto \frac{1}{\sqrt{p(x)}} \exp \left( \pm \frac{i}{\hbar} \int_x^p p(y)dy \right). \]  

(143)
In general, the wave-function will be a linear combination of the two possibilities for \( \psi(x) \) in Eq. (143):

\[
\psi(x) = \frac{1}{\sqrt{p(x)}} \left( A \exp\left( +\frac{i}{\hbar} \int_{x}^{\infty} p(y) \, dy \right) + B \exp\left( -\frac{i}{\hbar} \int_{x}^{\infty} p(y) \, dy \right) \right), \tag{144}
\]

with the (in general complex) coefficients \( A \) and \( B \) and the lower bounds of the integrals (not shown here) chosen to respect the relevant physical boundary conditions.

The preceding analysis should be regarded as holding in the region in which \( E > V(x) \) so that \( p(x) = \sqrt{2\mu(E - V(x))} \) (see Eq. (131)) is real. In the region where \( E < V(x) \), which is classically forbidden but critical in quantum mechanics, it is more convenient to write Eq. (144) in terms of \( \pi(x) \equiv \sqrt{2\mu(V(x) - E)} \), which is real when \( E < V(x) \). Since \( p(x) = i\pi(x) \), the exponentials in Eq. (144) now are real:

\[
\psi(x) = \frac{1}{\sqrt{\pi(x)}} \left( C \exp\left( -\frac{1}{\hbar} \int_{x}^{\infty} \pi(y) \, dy \right) + D \exp\left( +\frac{1}{\hbar} \int_{x}^{\infty} \pi(y) \, dy \right) \right). \tag{145}
\]

Once again, the (complex) coefficients \( C \) and \( D \) (and the lower bounds of the integrals) must be chosen so that the wave function has the right asymptotic behavior (e.g., vanishes appropriately at spatial infinity).

Figure 3: Potential energy plot for a classically bound particle.
The semi-classical approximations to the wave function in Eqs. (144) and (145) cannot be expected to hold at points where \( p(x) \approx 0 \), i.e., near the classical turning points where \( E = V(x) \). This can be seen upon inspection of the original expansion in Eq. (136). Consider, for example, the case of a classically bound particle of energy \( E \) moving in the potential shown in Fig. 3. The particle executes oscillatory motion between the points \( x_A \) and \( x_B \), coming to a stop at precisely those points. In wave mechanics, the de Broglie wavelength goes to infinity when the momentum vanishes, so the assumption that the potential only varies slightly over a single wavelength must certainly fail at such points. Instead, a more careful analysis of the original Schrödinger equation in the immediate neighborhood of the turning point(s) shows that the solutions take the form of Airy functions (Bessel functions of order 1/3). These solutions can then be extended to a form that matches the semi-classical forms given in Eqs. (144) and (145) that are correct far from the turning point(s). The details of this procedure are irrelevant for our purposes. We should emphasize, however, that this is the central technical problem facing the WKB approach. Without a careful treatment of the solution in the neighborhood of turning points, essential features of the semi-classical quantization are missed.

We examine the behavior of the WKB solution for a bound state as we go from \( x = -\infty \) to \( x = +\infty \) (cf. Fig. 3). For \( x \ll x_A \), the solution has the form of Eq. (145), with the lower bound of the integrals chosen as \( x_A \) and the constant \( C \) set to zero. The term involving the coefficient \( D \) will vanish exponentially as \( x \to -\infty \) (as the exponent is the integral of a positive quantity from \( x_A \) to \( x \)). The extension of the appropriate combination of Airy functions to the region to the right of the turning point \( x_A \) then yields an oscillatory solution of the form of Eq. (144). We must here assume that we are able to go far to the right (many wavelengths) of \( x_A \), while remaining to the left of the turning point \( x_B \). The specific form of this solution (the overall constant is irrelevant) is (see, e.g., Kramers, 1926, p. 831, Eq. 12)

\[
\psi(x) \propto \cos \left( \frac{1}{\hbar} \int_{x_A}^{x} p(y)dy - \frac{\pi}{4} \right), \quad x_A \ll x \ll x_B, \quad (146)
\]

where the much-greater-than signs imply many wavelengths.

The same procedure can be applied at the right turning point \( x_B \). For \( x \gg x_B \), the solution once again has the form of Eq. (145), now with the lower bound of the integrals chosen as \( x_B \) and the constant \( D \) set to zero. In this case, the term involving the coefficient \( C \) will vanish exponentially as \( x \to \infty \). Once again, we need to connect the exponentially decreasing solution for \( x \gg x_B \) to an oscillatory

\footnote{For a careful treatment, see, e.g., Morse and Feshbach (1953, Vol. 2, pp. 1092–1099) and the monographs mentioned in note 16}
solution to the left of \(x_B\) similar to the one in Eq. (146) (not surprisingly, from the symmetry of the situation)
\[
\psi(x) \propto \cos \left( \frac{\pi}{4} - \frac{1}{\hbar} \int_x^{x_B} p(y) dy \right), \quad x_A \ll x \ll x_B.
\]

(147)

As the solutions in Eqs. (146) and (147) must agree, the arguments of the cosine in these two equations must be equal to one another modulo \(n\pi\), where \(n\) is an arbitrary integer:
\[
\frac{1}{\hbar} \int_{x_A}^x p(y) dy - \frac{\pi}{4} = \frac{\pi}{4} - \frac{1}{\hbar} \int_x^{x_B} p(y) dy + n\pi.
\]

(148)

Rearranging and renaming the integration variable, we can rewrite this as
\[
\frac{1}{\hbar} \int_{x_A}^{x_B} p(x) dx = (n + \frac{1}{2}) \pi.
\]

(149)

Taking an integral over a complete cycle of the classical motion, from \(x_A\) up to \(x_B\) and back again, we find:
\[
\oint p(x) dx = 2 \int_{x_A}^{x_B} p(x) dx = (n + \frac{1}{2}) 2\pi \hbar = (n + \frac{1}{2}) \hbar.
\]

(150)

This is precisely the quantum condition of the old quantum theory (cf. Eqs. (15)–(18)) with the critical addition of the \(\frac{1}{2}\) piece (cf. note 17).

Of course, the conditions of validity of the derivation really require \(n \gg 1\), as the left-hand-side of Eq. (149) is just the phase change of the wave function between the turning points. Nevertheless, for the special case of the Coulomb potential, this extra term—now referred to as a Maslov index (Gutzwiller, 1990, p. 211)—is precisely what is needed to restore the consistency between the angular momentum and energy quantum numbers lost in the old quantum theory.\(^{21}\)

The improvement in the situation is seen most directly if we impose the quantum conditions of the old quantum theory in parabolic coordinates in the case of the hydrogen atom. The motion in the coordinates \(\xi\) and \(\eta\) involve the Coulomb potential and each have turning points qualitatively of the form indicated in Fig. 3. In section 2, we labeled these turning points \((\xi_{\text{min}}, \xi_{\text{max}})\) and \((\eta_{\text{min}}, \eta_{\text{max}})\), respectively (see Eqs. (21) and (26)). The WKB amendment of the quantum conditions of the old quantum

\(^{21}\)As mentioned above (see note 17), the extra term in the quantum condition (150) can also be used to justify the zero-point energy term of the harmonic oscillator. It changes the quantum condition on the energy of the harmonic oscillator from \(E = n\hbar\nu\) to \(E = (n + \frac{1}{2})\hbar\nu\).
theory requires that we replace $n_\xi$ and $n_\xi + \frac{1}{2}$ in Eq. (16) for the action variable $I_\xi$ and, likewise, that we replace $n_\eta$ by $n_\eta + \frac{1}{2}$ in Eq. (17) for the action variable $I_\eta$. The third coordinate, the azimuthal angle $\varphi$, does not contain the potential. The motion in this coordinate corresponds to free angular motion.

The wave function must be single-valued in $\varphi$, so the solutions $e^{2\pi i n_\varphi \varphi}$ require that the corresponding action variable (see Eq. (18))

$$I_\varphi = \oint p_\varphi d\varphi = n_\varphi \hbar,$$

(151) (with $n_\varphi$ and integer) lack the extra term of $\frac{1}{2}$. The difference in character between the motion in the coordinates $\xi$ and $\eta$ and the motion in the coordinate $\varphi$ has a classical correlate in the distinction between libration and rotation (Goldstein et al., 2002, p. 453, Fig. 10.2).

The upshot then is that the relation between the principal quantum number $n$ and the quantum numbers $n_\xi$, $n_\eta$, and $n_\varphi = |m|$ in the old quantum theory changes from

$$n = n_\xi + n_\eta + |m|$$

(152) (see Eq. (32)) to

$$n = n_\xi + n_\eta + |m| + 1,$$

(153) which is precisely the result obtained in wave mechanics (see Eq. (109); see also Eqs. (60) and (61)). The contorted reasoning needed in the old quantum theory to remove certain states with $m = 0$ is rendered moot.

The efficacy of the WKB treatment in bringing the quantum conditions of the old quantum theory into closer compliance with the results of wave mechanics is not restricted to the use of parabolic coordinates. However, the analysis for the more commonly used polar coordinates requires, somewhat unexpectedly, a more careful treatment than that given above for parabolic coordinates. One result of this analysis is a clearer understanding of the semi-classical “Langer modification” (Langer, 1937) in which the centrifugal term in the radial Schrödinger equation is changed in the following way:

$$\frac{\hbar^2 l(l + 1)}{2\mu r^2} \rightarrow \frac{\hbar^2 (l + \frac{1}{2})^2}{2\mu r^2}.$$  

(154)

We conclude our discussion of the WKB approach with a brief discussion of its application in this case (for more details, see, e.g., Morse and Feshbach, 1953, Vol. 2, p. 1101). The starting point is the familiar radial Schrödinger equation in a central

\footnote{This modification explains the efficacy of the introduction of half-quantum numbers in several instances in the early 1920s (cf. note 17).}
potential, where, for simplicity, we take the Coulomb potential \( V(r) = -\frac{2}{ar} \) of the hydrogen atom (where \( a \equiv \hbar^2/\mu e^2 \) is the Bohr radius):

\[
\frac{d^2R(r)}{dr^2} + \left( \frac{2\mu E}{\hbar^2} + \frac{2}{ar} - \frac{l(l+1)}{r^2} \right) R(r) = 0.
\] (155)

We introduce some substitutions to transform this equation into one of the form of the one-dimensional Schrödinger equation (126), which we analyzed at the beginning of this section. First, we define a rescaled energy

\[-\kappa^2 \equiv \frac{2\mu E}{\hbar^2}\] (156)

(the negative sign as we are considering bound-state solutions only). More importantly, we introduce a rescaled dimensionless coordinate variable \( x \) defined by

\[r = ae^x.\] (157)

The range of this new variable \( x \) is \(-\infty < x < +\infty\), just as in the example discussed above (cf. Fig. 3), whereas the range of the original variable \( r \) is \( 0 < r < \infty \). As explained by Langer (1937, p. 674), the WKB approximation method fails for Eq. (155) because of difficulties one runs into when examining the behavior of the solution at \( r = 0 \). Finally, we redefine the dependent variable by introducing a new one-dimensional wave function \( \psi(x) \) given by

\[R(r) \equiv e^{x/2}\psi(x).\] (158)

With the help of Eqs. (157) and (158), \( R''(r) \) in Eq. (155) can be expressed in terms of \( \psi(x) \) and its second-order derivative \( \psi''(x) \). From Eq. (157) it follows that \( x = \ln (r/a) \) and that

\[\frac{d}{dr} = \frac{dx}{dr} \frac{d}{dx} = \frac{1}{r} \frac{d}{dx} = \frac{1}{a} e^{-x} \frac{d}{dx}.\] (159)

Hence, \( R'(r) \) can be written as

\[
R'(r) = \frac{1}{a} e^{-x} \frac{d}{dx} \{ e^{x/2} \psi(x) \} = \frac{1}{a} e^{-x/2} \left\{ \frac{1}{2} \psi(x) + \psi'(x) \right\},
\] (160)
and \( R''(r) \) as

\[
R''(r) = \frac{1}{a^2} e^{-x} \frac{d}{dx} \left\{ \frac{e^{-x/2}}{2} \left( \frac{1}{2} \psi(x) + \psi'(x) \right) \right\}
\]

\[
= \frac{1}{a^2} e^{-3x/2} \left\{ -\frac{1}{2} \left[ \frac{1}{2} \psi(x) + \psi'(x) \right] + \frac{1}{2} \psi'(x) + \psi''(x) \right\}
\]

\[
= \frac{1}{a^2} e^{-3x/2} \left\{ \psi''(x) - \frac{1}{2} \psi(x) \right\}.
\] (161)

Inserting Eqs. (156)–(158) and (161) into Eq. (155), we find:

\[
\frac{1}{a^2} e^{-3x/2} \left\{ \psi''(x) - \frac{1}{2} \psi(x) \right\} + \left( -\kappa^2 + \frac{2}{a^2 e^x} - \frac{l(l+1)}{a^2 e^{2x}} \right) e^{x/2} \psi(x) = 0.
\] (162)

If this equation is multiplied by \( a^2 e^{3x/2} \), it reduces to

\[
\psi''(x) + \left( -\kappa^2 a^2 e^{2x} + 2 e^x - (l + \frac{1}{2})^2 \right) \psi(x) = 0.
\] (163)

Note that the terms with \(-\frac{1}{2} \psi(x)\) and \(l(l+1)\psi(x)\) in Eq. (162) combine to give the term \((l + \frac{1}{2})^2 \psi(x)\) in Eq. (163). This is the “Langer modification” mentioned above (see Eq. (154)).

In going from Eq. (155) for \( R(r) \) (with \( 0 < r < +\infty \)) to Eq. (163) for \( \psi(x) \) (with \( -\infty < x < +\infty \)), we have transformed the radial Schrödinger equation into an equation of the form of Eq. (126). We can thus apply the same WKB techniques that we applied to Eq. (126) to Eq. (164).

It will be convenient to introduce the rescaled binding energy \( \mathcal{E} \equiv \kappa^2 a^2 \) (not to be confused with the strength of the external electric field for which we used the notation \( E \above above)). This quantity takes on the values \( 1/n^2 \) for the quantized energy levels of the hydrogen atom, where \( n = 1, 2, 3, \ldots \) is the principal quantum number. Eq. (163) thus becomes

\[
\psi''(x) + \left( -\mathcal{E} e^{2x} + 2 e^x - (l + \frac{1}{2})^2 \right) \psi(x) = 0.
\] (164)

Just as we defined the momentum \( p(x)^2 \) in Eq. (131) as \( \hbar^2 \) times the factor multiplying \( \psi(x) \) in Eq. (126), we now define \( p(x)^2 \) as \( \hbar^2 \) times the factor multiplying \( \psi(x) \) in Eq. (164)

\[
p(x)^2 \equiv \hbar^2 \left( -\mathcal{E} e^{2x} + 2 e^x - (l + \frac{1}{2})^2 \right).
\] (165)

As in the case of Eq. (126), this problem corresponds to a classical motion between turning points \( x_{\text{min}} \) and \( x_{\text{max}} \) (cf. Fig. 3). It is easier to find \( x_{\text{min}} \) and \( x_{\text{max}} \) if we...
switch from $x$ to $\rho \equiv e^x$ and determine $\rho_{\text{min}} \equiv e^{x_{\text{min}}}$ and $\rho_{\text{max}} \equiv e^{x_{\text{max}}}$ instead. In terms of $\rho$, Eq. (165) becomes

$$\frac{p(\rho)^2}{\hbar^2} \equiv -E \rho^2 + 2\rho - \left(l + \frac{1}{2}\right)^2.$$  

(166)

The turning points occur at the roots $\rho_{\text{min}}$ and $\rho_{\text{max}}$ of the quadratic equation obtained by setting the right-hand side of Eq. (166) equal to zero. The right-hand side of Eq. (166) can be written in the form $E(\rho - \rho_{\text{min}})(\rho_{\text{max}} - \rho)$, where

$$\rho_{\text{max}} + \rho_{\text{min}} = \frac{2}{E}, \quad \rho_{\text{max}}\rho_{\text{min}} = \left(l + \frac{1}{2}\right)^2/E$$  

(167)

(cf. Eqs. (21)-(22)). The WKB quantization rule (149) therefore gives

$$\frac{1}{\hbar} \int_{x_{\text{min}}}^{x_{\text{max}}} p(y) dy = \sqrt{E} \int_{\rho_{\text{min}}}^{\rho_{\text{max}}} \sqrt{(\rho - \rho_{\text{min}})(\rho_{\text{max}} - \rho)} \frac{d\rho}{\rho}$$  

(168)

$$= \sqrt{E} \frac{\pi}{2} \left( \rho_{\text{max}} + \rho_{\text{min}} - 2\sqrt{\rho_{\text{max}}\rho_{\text{min}}} \right) = (n_r + \frac{1}{2})\pi,$$

where we used Eq. (19) to evaluate the integral. With the help of Eq. (167), we can rewrite the last equation as

$$\frac{1}{2} \left( \frac{2}{\sqrt{E}} - 2(l + \frac{1}{2}) \right) = (n_r + \frac{1}{2}).$$  

(169)

Substituting the principal quantum number $n$ for $1/\sqrt{E}$ and rearranging terms, we obtain:

$$n = (n_r + \frac{1}{2} + l + \frac{1}{2}) = n_r + l + 1.$$  

(170)

This agrees exactly with the expression for the principal quantum number in terms of the radial and angular quantum numbers in the new theory. Just as in the case of parabolic coordinates, the needed extra term of $+1$ arises from two separate terms of $\frac{1}{2}$ arising from a careful WKB analysis of the solutions. The non-zero Maslov index appearing in the radial quantization integral in Eq. (169) has an interesting

23For these roots to be real, the discriminant condition requires $\frac{1}{2} = n^2 > (l + \frac{1}{2})^2$, which is obviously true for the hydrogen atom (see, e.g., Eq. (170) below).

24The peculiar character of the Coulomb potential in conveniently yielding the correct values for the quantized energies in the first non-trivial order of the semi-classical expansion has been examined in detail by Hainz and Grabert (2011), who show explicitly why the semi-classical energy levels obtained above remain untouched, as we know they must, in higher orders in a systematic expansion in powers of Planck’s constant.
consequence in terms of an orbit interpretation: the possibility of a circular orbit, with degenerate roots $\rho_{\text{max}} = \rho_{\text{min}}$ (and therefore vanishing radial action integral) is removed. Even in the case of the ground state, with $n_r = 0, n = 1, l = 0$, the associated classical motion involves a libration between two distinct radial distances $r = (1 \pm \sqrt{3}/2)a$. Such a motion, with zero angular momentum, is classically impossible, of course, but we have left the realm of the classical Hamilton-Jacobi equation by including (in a limited way) quantum-mechanical effects.

7 Conclusion: Stark contrasts between the old and the new quantum theory

In the mid-1920s, a number of physicists working on the old quantum theory became increasingly suspicious of the notion of electron orbits. In the transition from the old quantum theory to both matrix mechanics and wave mechanics, orbits were discarded altogether (see Duncan and Janssen (2007) for the case of matrix mechanics). What we have shown in this paper, using the account of the Stark effect in the old and the new quantum theory as a striking example, is that orbits had become highly problematic well before the developments of the mid-1920s. The most important theorists working on the Stark effect—Sommerfeld, Epstein, and Kramers (Schwarzschild died shortly after making his contribution)—were well aware of these difficulties, especially of the two problems that we focused on in this paper. Yet, they offered only stopgap solutions for one of these problems and essentially ignored the other.

The two problems were the following. First, the relation between the quantum numbers for energy and angular momentum was such that the basic quantum conditions had to be supplemented by some ad-hoc extra conditions to rule out various pathological orbits (see section 2). Second, the orbits selected by the quantum conditions of the old quantum theory depend on the coordinates in which these conditions are imposed (see section 3).

The new quantum theory avoids both problems (see section 4). In sections 5 and 6, we used the new theory to elucidate the problems in the old one. The first problem could be fixed systematically with the help of the new theory (see section 6). The new theory, however, also makes it painfully clear that the second problem just goes to show that orbits are ill-suited to represent physical states in atomic physics.

The problematic relation between the quantum numbers for energy and angular momentum could be fixed by amending the basic quantum conditions of the old quantum theory, replacing many but not all integer quantum numbers by half-integer
ones. In section 6, we reviewed how these amendments can be derived using the WKB approximation method for finding approximate semi-classical solutions of the Schrödinger equation. If the motion in a particular coordinate is a libration, half-integer quantum numbers should be used; if it is a rotation, integer quantum numbers should be used. Even though physicists in the early 1920s realized that one often obtained better results with half-integer quantum number than with integer ones, they did not provide any systematic justification for using one rather than the other. In fact, the extra terms and factors of $\frac{1}{2}$ introduced in this period turned out to come from a variety of sources, including the as yet undiscovered electron spin. It was only with the arrival of the new quantum theory that a systematic justification for these extra terms and factors could be given. As we saw in section 6, the WKB method provided an important part of that justification.

The other problem, the non-uniqueness of the quantized orbits, strikes right at the heart of the old quantum theory. Its residue in the new quantum theory is that the eigenstates found by separating and solving the Schrödinger equation in one set of coordinates can always be written as a superposition of the eigenstates found by doing so in another set of coordinates. This, of course, is no problem at all. But rather than showing how to solve the non-uniqueness problem in the old quantum theory, this evaporation of the problem in the new quantum theory merely shows that, contrary to one of the main articles of faith of the old quantum theory, orbits cannot be used to represent physical states in atomic physics.

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