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Schrödinger and Dirac equations for the hydrogen atom, and Laguerre polynomials

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Abstract It is usually claimed that the Laguerre polynomials were popularized by Schrödinger when creating wave mechanics; however, we show that he did not immediately identify them in studying the hydrogen atom. In the case of relativistic Dirac equations for an electron in a Coulomb field, Dirac gave only approximations, Gordon and Darwin gave exact solutions, and Pidduck first explicitly and elegantly introduced the Laguerre polynomials, an approach neglected by most modern treatises and articles. That Laguerre polynomials were not very popular before their use in quantum mechanics, probably because they had been little used in classical mathematical physics, is confirmed by the fact that, as we show, they had been rediscovered independently several times during the nineteenth century, in published or unpublished studies of Abel, Murphy, Chebyshev, and Laguerre.

1 Introduction

In 1923, Louis de Broglie published three short communications (de Broglie 1923a,b,c), in which he proposed to associate a wave to any moving particle, thus extending the dual character of the photon. De Broglie's ingenious intuition was confirmed 4 years later by the experiments of Clinton J. Davisson , Lester H. Germer, and George P. Thomson on diffraction waves of the electron, but an equation describing this mysterious wave and taking into account its dynamics was still missing from de Broglie's study. Erwin Schrödinger, at the time a professor in Zürich, was told by

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Einstein about de Broglie's articles in 1925 and solved this problem in January 1926 (Schrödinger 1926a). His article built on his earlier presentation of his famous (stationary) equation, which had taken in three pages, four equations, and two fruitful and ingenious *Ansatz*, and became an important article of 15 pages, in which Schrödinger also solved his equation in the case of the hydrogen atom, using Fuchs' theory of linear differential equations and the Laplace transform. He also recovered in this way the formulae for the energy levels given by Bohr in 1913. Both his way of introducing the wave equation, and his way of solving it for the hydrogen atom have disappeared from standard treatises and textbooks on quantum mechanics.

One aim of this article is to clarify the claim of some mathematicians involved in the theory of special functions that the Laguerre polynomials were popularized by Schrödinger when creating wave mechanics. It is partly true, but the Austrian physicist did not immediately identify the polynomials occurring in the Hydrogenic wave functions with Laguerre polynomials. A part of this story is very well described and documented in the remarkable book of Mehra and Rechenberg (1987), and in Rechenberg (1988), but is not mentioned in the other famous history of quantum mechanics by Jammer (1966). In contrast, the fact is emphasized in Walter Moore's interesting biography of Schrödinger, (Moore 1989), who writes on p. 199:

> It is surprising that Schrödinger had so much difficulty in solving the radial equation. He was using as a reference the little book of Ludwig Schlesinger, *Introduction to the Theory of Differential Equations,* published in 1900. As the title indicates, it is not a book devoted to the practical problems of solving differential equations of mathematical physics. Schrödinger evidently was not yet using the book that became the *vade mecum* of theoretical physicists, *Methoden der Mathematische Physik I,* published in 1924 by Richard Courant and David Hilbert. On page 161 of this book, the equation satisfied by the Laguerre polynomials appears, and its form is very close to that of the radial equation for the H-atom, but the associated Laguerre polynomials, which actually provide the solutions for Schrödinger equation are not cited. The book of Frank and von Mises, *Die Differential-und Integralgleichungen der Mechanik und Physik* was published only at the end of 1925; this gave a complete account of the associated Laguerre polynomials and their corresponding differential equations, but it would have been just too late to help Schrödinger.

We discuss those questions in Sect. 2.

If the Laguerre polynomials are now universally accepted and used in solving Schrödinger equation with a Coulomb potential, then the situation is quite different in the case of the Dirac equations of relativistic quantum mechanics. The second aim of this study is to survey the various approaches used to solve the Dirac equations for the relativistic electron, in which the explicit use of Laguerre polynomials is far less popular. In the preface of the second edition of his monumental treatise (Frank and von Mises 1925–1935) written in collaboration with Richard von Mises, Philipp Frank mentions that the first edition of volume 2 was in print when Schrödinger's first articles on wave mechanics appeared. However, the second edition contains a new sixth part, more than one hundred pages long, entirely devoted to the new wave mechanics, including the relativistic wave equation of Paul Dirac. Laguerre polynomials are explicitly used in the solution of the problem of the electron in a Coulomb field for the Schrödinger equation, but not for the Dirac equations. In fact, Dirac (1928) did not solve his relativistic equations for the hydrogen atom exactly in his seminal article, but only discussed the first two approximations. A few months later, Walter Gordon and Charles G. Darwin independently solved the equations using power series, which Gordon recognized as confluent hypergeometric functions (related to Laguerre polynomials) (Gordon 1928; Darwin 1928). Those polynomials were explicitly introduced in the solution of the relativistic electron in a Coulomb field 1 year later by Pidduck (1929). We analyze these questions in Sect. 3.

Laguerre polynomials were not very popular before their use in quantum mechanics, as is confirmed by their own story, which seems to require some amplifications and corrections. We show in the Appendix that, although usually named after Edmond-Nicolas Laguerre, those polynomials were rediscovered independently several times during the nineteenth century, in published or unpublished studies of several mathematicians, such as Joseph-Louis Lagrange, Niels-Hendrik Abel, Robert Murphy in 1835, Pafnuti L. Chebyshev in 1859, and Laguerre himself in 1879. We analyze the corresponding contributions and their contexts in the Appendix. For a long time, Laguerre polynomials remained much less popular than other special functions such as Bessel or hypergeometric functions, and Legendre or Hermite polynomials, probably because they were less used in problems on classical mathematical physics of this time. This is confirmed by their late inclusion in classical treatises of analysis.

2 The Schrödinger equation for the hydrogen atom

2.1 Schrödinger equation

Schrödinger's first article on quantization and eigenvalues proposed a fairly surprising and nowadays almost forgotten method for obtaining the wave equation for the hydrogen atom (Schrödinger 1926a). This cited article and its genesis have been nicely analyzed (Bloch 1976; Gerber 1969; Kragh 1982; Kubli 1970; Wessels 1979), and we concentrate here on the essential aspects.

The classical Hamiltonian for the Keplerian motion of an electron around a positively charged fixed nucleus, with Coulomb potential $V(r) = -\frac{e^2}{r}$, is given by

$$H(q, p) = \frac{|p|^2}{2m} + V(r) = E,$$

where E is the energy, $q = (x, y, z)$ the position of the electron, $r = (x^2 + y^2 + z^2)^{1/2}$ its distance from the nucleus, $p = \left(m\frac{\mathrm{d}x}{\mathrm{d}t}, m\frac{\mathrm{d}y}{\mathrm{d}t}, m\frac{\mathrm{d}z}{\mathrm{d}t}\right)$ its linear momentum, and e and m, respectively, its charge and mass. The corresponding Hamilton–Jacobi equation for the action S of the classical motion of the electron is the nonlinear first-order partial differential equation

$$\left(\frac{\partial S}{\partial x}\right)^2 + \left(\frac{\partial S}{\partial y}\right)^2 + \left(\frac{\partial S}{\partial z}\right)^2 - 2m\left(E + \frac{e^2}{r}\right) = 0.$$

The first *Ansatz* in Schrödinger (1926a) consists in introducing a new function ψ linked to S by the relation

$$S = K \log \psi$$

for some constant K. Kubli (1970) has noticed that such a transformation had already appeared in 1911 in an article by Sommerfeld and Runge (the daughter of Carl Runge) (1911), who attributed the idea to the Dutch physicist Peter Debye. Kubli has suggested that Debye, then professor at the University of Zürich, could have passed this information on to Schrödinger, who quoted the article in later publications. Indeed, when approximating a wave equation

$$\Delta\psi + n^2k^2\psi = 0$$

for k large, the transformation

$$\psi = A\exp(ikS) \tag{1}$$

is used where A and S are considered as slowly varying functions to obtain, in first approximation, the eikonal equation

$$|\nabla S|^2 = n^2.$$

Schrödinger's *Ansatz* appears as the inverse of the transformation (1). Instead of solving the transformed equation

$$\left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 - \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi^2 = 0, \tag{2}$$

Schrödinger introduced without any comment, in a bold second *Ansatz*, the integral over the whole space of its left-hand member (keeping the same notation ψ!)

$$\iiint_{\mathbb{R}^3} \left[\left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 - \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi^2\right] \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$$

and studied its extrema over a suitable (but not very precisely defined) class of function ψ that vanish at infinity. The corresponding Euler–Lagrange equation is the second-order linear partial differential equation

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi = 0. \tag{3}$$

In a correction added at the end of the article, Schrödinger suggested imposing the normalization condition $\int\int\int_{\mathbb{R}^3} \psi^2 = 1$, without discussing its relations with the boundary conditions at infinity. Although Schrödinger gave no explanation and no heuristics for his second ***Ansatz***, one can think that, in his quest of an eigenvalue problem that would give Bohr's energy levels as eigenvalues, he realized that the quadratic left-hand member of (2) used as the argument in the integral functional of a variational problem gives as its Euler–Lagrange equation a linear partial differential equation of the second order.

2.2 The solution for the hydrogen atom

Schrödinger passed from (x, y, z) to spherical coordinates (r, θ, φ), and obtained the radial equation for $\chi(r)$

$$\frac{\mathrm{d}^2\chi}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}\chi}{\mathrm{d}r} + \left(\frac{2mE}{K^2} + \frac{2me^2}{K^2 r} - \frac{n(n+1)}{r^2}\right)\chi = 0. \tag{4}$$

by taking Eq. 3, written in those coordinates, and setting $\psi(r, \theta, \varphi) = Y_{n,k}(\theta, \varphi)\chi(r)$, where $Y_{n,k}$ is the spherical harmonic and $|k| \leq n$; n, k are integers.

In order to apply the Laplace transform with kernel e^{zr} to (4) (Ince 1927), the centrifugal term in $\frac{1}{r^2}$ is eliminated through the change of unknown $\chi(r) = r^n U(r)$, which gives the following Laplace-type equation:

$$\frac{\mathrm{d}^2U}{\mathrm{d}r^2} + \left(\delta_0 + \frac{\delta_1}{r}\right)\frac{\mathrm{d}U}{\mathrm{d}r} + \left(\epsilon_0 + \frac{\epsilon_1}{r}\right)U = 0, \tag{5}$$

for U, where

$$\delta_0 = 0, \quad \delta_1 = 2(n+1), \quad \epsilon_0 = \frac{2mE}{K^2}, \quad \epsilon_1 = \frac{2me^2}{K}.$$

Then, Schrödinger took the solution as given in a textbook of 1900 by Schlesinger (1900), and used the same notation:

$$U(r) = \int_L e^{zr}(z - c_1)^{\alpha_1 - 1}(z - c_2)^{\alpha_2 - 1}\,\mathrm{d}z,$$

where the integral is taken along a path L such that the function

$$\int_L \frac{\mathrm{d}}{\mathrm{d}z}[e^{zr}(z - c_1)^{\alpha_1}(z - c_2)^{\alpha_2}]\,\mathrm{d}z$$

is a solution of (5). In those integrals,

$$\alpha_1 = \frac{\epsilon_1 + \delta_1 c_1}{c_1 - c_2}, \quad \alpha_2 = \frac{\epsilon_2 + \delta_1 c_2}{c_2 - c_1},$$

and c_1, c_2 are solutions of the quadratic equation (leading term in the equation in z)

$$z^2 + \delta_0 z + \epsilon_0 = 0.$$

Some delicate arguments based on the condition at infinity, and suitable manipulations of the signs of E, allowed him to deduce the existence of "discrete states," implying that $\alpha_1 - (n+1) = \frac{me^2}{K\sqrt{-2mE}}$ is a positive integer $l > n$. Now, with $\alpha_1 - 1 = l + n$, $\alpha_2 = -l + n$, the computation of $U(r)$ after expansion of the algebraic factor gave

$$\chi(r) = f\left(r\sqrt{-2mE}K\right), \tag{6}$$

with

$$f(x) = x^n \mathrm{e}^{-x} \sum_{j=0}^{l-n-1} \frac{(-2x)^j}{j!} \binom{l+n}{l-n-1-j},$$

where

$$\binom{p}{q} = \frac{\Gamma(p+1)}{\Gamma(q+1)\Gamma(p-q+1)}$$

is the binomial coefficient, with

$$\Gamma(x) = \int_0^{+\infty} \mathrm{e}^{-t} t^{x-1}\, \mathrm{d}t \quad (x > 0)$$

Euler's Gamma function.

In his first article, Schrödinger did not recognize the polynomial part of $f(x)$, essentially a Laguerre polynomial. He focused his interest on the energy spectrum $\{E_l\}$, rather than on the eigenfunctions, giving the formulae

$$-E_l = \frac{2\pi^2 me^4}{h^2 l^2}$$

after setting $K = \frac{h}{2m}$ for dimensional reasons, h being Planck's constant (see Mehra and Rechenberg 1987, p. 494, last paragraph). One should notice that, in a footnote of his first article, Schrödinger thanked Hermann Weyl, then professor at the University of Zürich, for having provided him with the necessary information for treating equation (4), and sent the reader to Schlesinger's book mentioned above. Therefore, we see that Weyl himself, an outstanding mathematician, did not recognize Laguerre polynomials.

2.3 The occurrence of Laguerre polynomials

In a footnote of his second (and longer) article, Schrödinger thanked Erwin Fues, at this time, his assistant in Zürich, for identifying the eigenfunctions of Planck's oscillator with Hermite polynomials, and observed that he has identified the polynomials obtained in his first article with the $(2n + 1)$th derivative of the $(n + l)$th Laguerre polynomial (Schrödinger 1926b). Thus, Schrödinger definitely abandoned Schlesinger's approach and, following a suggestion of Weyl and Fues, referred to the recent *Methoden der mathematischen Physik* of Richard Courant and David Hilbert published in 1924, with the aim of providing the mathematical foundations of classical physics (Courant and Hilbert 1924). In the French translation of Schrödinger (1927) published in 1933, Schrödinger advised the reader to forget about his first approach, and suggested it would be rather better to consult recent books on wave mechanics, instead of his articles, for a clearer and simpler approach.

The explicit definition of the *Laguerre polynomials of degree n* (up to a multiplicative constant A_n) is

$$L_n^{(\alpha)}(x) = A_n \left[\sum_{m=0}^{n} (-1)^m \binom{n+\alpha}{n-m} \frac{x^m}{m!} \right] \tag{7}$$

where α is a real or complex parameter (Rainville 1960). In the past, the functions $L_n^{(0)} := L_n$ were called *Laguerre polynomials* and the functions $L_n^{(\alpha)}$ ($\alpha \neq 0$) *associated* or *generalized Laguerre polynomials*. The expression *Sonine polynomials* (see below) was also sometimes used when $\alpha = m$, was a positive integer. This distinction is now abandoned, and the expression *Laguerre polynomial* is used for $L_n^{(\alpha)}$ for any value of α.

The choice $A_n = 1$ comes from the *generating function*

$$F_\alpha(x, t) = (1 - t)^{-\alpha-1} \mathrm{e}^{\frac{xt}{t-1}} \tag{8}$$

giving, by expansion in powers of t,

$$F_\alpha(x, t) = \sum_{n=0}^{\infty} L_n^{(\alpha)}(x) t^n \quad (|t| < 1). \tag{9}$$

Easy consequences of (9) are the relations

$$(n+1)L_{n+1}^{(\alpha)}(x) - (2n + \alpha + 1 - x)L_n^{(\alpha)}(x) + (n + \alpha)L_{n-1}^{(\alpha)}(x) = 0,$$

$$x \frac{\mathrm{d}L_n^{(\alpha)}}{\mathrm{d}x}(x) = nL_n^{(\alpha)}(x) - (n + \alpha)L_{n-1}^{(\alpha)}(x), \tag{10}$$

$$\frac{\mathrm{d}L_n^{(\alpha)}}{\mathrm{d}x}(x) = -L_{n-1}^{(\alpha+1)}(x), \tag{11}$$

so that $L_n^{(\alpha)}$ satisfies *Laguerre differential equation*

$$x\frac{d^2y}{dx^2} + (\alpha + 1 - x)\frac{dy}{dx} + ny = 0. \tag{12}$$

Iteration of formula (11) gives

$$\frac{d^p L_n^{(\alpha)}}{dx^p} = (-1)^p L_{n-p}^{(\alpha+p)},$$

but physicists prefer to write

$$\frac{d^p L_n}{dx^p} = L_n^p \tag{13}$$

(without parenthesis for p), taking into account that the degree of $L_n^p(x)$ is no longer n but $n-p$. Another interesting expression of $L_n^{(\alpha)}$ is *Rodrigues' representation formula*:

$$L_n^{(\alpha)}(x) = \frac{1}{n!}e^x x^{-\alpha}\frac{d^n}{dx^n}[e^{-x}x^{n+\alpha}].$$

When α is real and larger than -1, the Laguerre polynomials $L_n^{(\alpha)}$ satisfy the *orthogonality conditions*

$$\int_0^\infty e^{-x}x^\alpha L_n^{(\alpha)}(x)L_m^{(\alpha)}(x)\,dx = (A_n)^2\frac{\Gamma(n+\alpha+1)}{\Gamma(n+1)}\delta_{m,n}, \tag{14}$$

where $\delta_{m,n}$ denotes Kronecker's symbol. Concerning the constant A_n, mathematicians often prefer to consider *monic Laguerre polynomials* $\overline{L}_n^{(\alpha)}$ with leading term 1, such that

$$L_n^{(\alpha)} = \frac{(-1)^n}{n!}\overline{L}_n^{(\alpha)},$$

but physicists, who work in the orthogonality domain $\alpha > -1$, prefer the *orthonormed Laguerre polynomials* $L_n^{*(\alpha)}$ such that

$$\int_0^\infty e^{-x}x^\alpha \left[L_n^{*(\alpha)}(x)\right]^2 dx = 1.$$

Equation 12 is the special case of the *confluent hypergeometric* or *Kummer equation*, introduced in 1836 by Ernst Eduard Kummer

$$x\frac{d^2y}{dx^2} + (c - x)\frac{dy}{dx} - ay = 0, \tag{15}$$

with $a = -n$ and $c = \alpha + 1$ (Kummer 1836). The solution of (15) analytic at $x = 0$ is the *confluent hypergeometric function* ${}_1F_1(a, c; x)$ (Buchholz 1969; Slater 1960), given for $c \neq -N$, N positive integer, by

$$ {}_1F_1(a, c; x) = \sum_{k=0}^{\infty} \frac{(a)_k}{(c)_k} \frac{x^k}{k!}, \tag{16}$$

where $(a)_k := a(a+1)\cdots(a+k-1) = \Gamma(a+k)/\Gamma(a)$. Therefore,

$$L_n^{(\alpha)}(x) = \frac{\Gamma(n+\alpha+1)}{n!\Gamma(\alpha+1)}\, {}_1F_1(-n, \alpha+1; x). \tag{17}$$

For more details, see, for example, the classical treatises in the area (Buchholz 1969; Henrici 1974–1986; Lavrentiev and Shabat 1977; Lebedev 1965; Nikiforov and Ouvarov 1976; Rainville 1960; Slater 1960).

With the notation of (13), the function $f(x)$ in formula (6) is written, up to a multiplicative constant, as the *Laguerre function* $x^n e^{-(x/2)} L_{n+l}^{2n+1}(x)$ instead of $x^n e^{-(x/2)} L_{n-l-1}^{2n+1}(x)$. Let us also notice that in books on quantum physics, n and l are permuted and, therefore, the quantum number l becomes smaller than n. Following Schrödinger's theory, the probability that the electron is located at a distance r from the nuclei is controlled by $L_{n+l}^{2n+1}(\lambda r)$, where the constant λ depends on the choice of units and the quantum number l. This probability vanishes, therefore, at the zeros of those Laguerre polynomials. For each l, the $n - l - 1$ zeros $x_{N,i}^l$ of $L_{n+l}^{2n+1}(x)$, where $N = n - l - 1$, generate the "universal" sequences of "excited nodes":

$$S_N^l = \left(1, \frac{x_{N,2}^l}{x_{N,1}^l}, \frac{x_{N,3}^l}{x_{N,1}^l}, \ldots, \frac{x_{N,N}^l}{x_{N,1}^l}\right).$$

In his third article, where he introduced his famous perturbation method, Schrödinger used parabolic coordinates to study Stark's effect, when a constant electric field is added to the Coulomb force (Schrödinger 1926c). In this case, the separation of variables introduces two different Laguerre polynomials with different arguments. This article contains in a *Mathematical appendix*, a section called *The orthogonal functions and the generalized Laguerre polynomials* where Schrödinger summarizes, with reference to the treatise Courant-Hilbert mentioned above, the definition and main properties of Laguerre polynomials, and explicitly evaluates the two important integrals:

$$J_1 = \int_0^{\infty} x^p e^{-x} L_{n+k}^{(n)}(x) L_{n'+k'}^{(n')}(x)\, dx$$

$$J_2 = \int_0^{\infty} x^p e^{-\frac{\alpha+\beta}{2}x} L_{n+k}^{(n)}(\alpha x) L_{n'+k'}^{(n')}(\beta x)\, dx,$$

using the generating function of Laguerre polynomials,

In order to sum up, Schrödinger did not seem to be very familiar with special functions at the time he developed his wave mechanics, even if he checked that the polynomial part of $f(x)$ was not that of Legendre's, and even though he had earlier solved the problem of the infinite vibrating string with the Bessel functions J_n. His reference book (Schlesinger 1900) contained a whole chapter on Gauss's differential equation for hypergeometric functions, but did not cover the confluent form that contains, as we have seen, Laguerre's differential equation as a special case. Like many other first class scientists, Schrödinger first solved his equation for the hydrogen atom using the mathematical tools he had learned at university, instead of searching more recent information. The same attitude also appears in the way that the equation in $\chi(r)$ is solved in the famous Lectures on physics (Feynman et al. 1966) of Richard P. Feynman, where power series are used, thereby avoiding the explicit introduction of Laguerre polynomials, in this case for pedagogical reasons linked to the mathematical level of the students.

3 Dirac equations for the hydrogen atom

3.1 Dirac: a perturbation approach

The history of Dirac's relativistic theory of electrons is nicely described in Kragh's studies (1981; 1990). Dirac's system of equations for an electron in an electromagnetic field with scalar potential A_0 and vector potential $A = (A_1, A_2, A_3)$ is

$$\left[p_0 I + \sum_{j=1}^{3} \alpha_j p_j + \alpha_4 mc \right] \psi = 0, \tag{18}$$

where $\psi = (\psi_1, \psi_2, \psi_3, \psi_4)$,

$$p_0 = -\frac{h}{2\pi i c}\frac{\partial}{\partial t} + \frac{e}{c}A_0, \quad p_j = \frac{h}{2\pi i}\frac{\partial}{\partial x_j} + \frac{e}{c}A_j \quad (j = 1, 2, 3),$$

and $\alpha_1, \ldots \alpha_4$ are (4×4)-matrices satisfying the relations (Dirac 1928)

$$\alpha_r \alpha_s + \alpha_s \alpha_r = 2\delta_{r,s} I \quad (r, s = 1, 2, 3, 4).$$

In the special case of a central field of force, where $A_1 = A_2 = A_3 = 0$ and $A_0 = \frac{c}{e} V(r)$, with solutions periodic in time (so that p_0 is now a parameter equal to $1/c$ times the energy level E), Dirac showed, after lengthy considerations based on arguments drawn from noncommutative algebra instead of the classical separation of variables, that the radial part of the first and the third components ψ_1 and ψ_3 of ψ must satisfy the system of first-order differential equations

$$
\begin{aligned}
&[p_0 + V(r)]\,\psi_1 - \frac{h}{2\pi}\frac{\mathrm{d}\psi_3}{\mathrm{d}r} - \frac{jh}{2\pi r}\psi_3 + mc\psi_1 = 0\\
&[p_0 + V(r)]\,\psi_3 + \frac{h}{2\pi}\frac{\mathrm{d}\psi_1}{\mathrm{d}r} - \frac{jh}{2\pi r}\psi_1 - mc\psi_3 = 0
\end{aligned}
\tag{19}
$$

where j is an integer (Dirac's quantum number). The two other components of ψ satisfy the same system.

The elimination of ψ_1 implies that ψ_3 satisfies a second-order differential equation of the form

$$
\frac{\mathrm{d}^2\psi_3}{\mathrm{d}r^2} + \left[\frac{(p_0+V)^2 - m^2c^2}{h^2} - \frac{j(j+1)}{r^2}\right]\psi_3 - \frac{1}{Bh}\frac{\mathrm{d}V}{\mathrm{d}r}\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{j}{r}\right)\psi_3 = 0, \tag{20}
$$

where $B = (p_0 + V + mc)/h$. The acceptable values of the parameter $p_0 = \frac{E}{c}$ are those for which (20) has a solution that is finite at $r = 0$ and at $r = \infty$. In order to compare this equation with those of previous theories, Dirac put $\psi_3 = r\chi$, so that χ must be solution of

$$
\begin{aligned}
&\frac{\mathrm{d}^2\chi}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}\chi}{\mathrm{d}r} + \left[\left(\frac{p_0+V}{h}\right)^2 - \left(\frac{mc}{h}\right)^2 - \frac{j(j+1)}{r^2}\right]\chi\\
&\quad - \frac{1}{Bh}\frac{\mathrm{d}V}{\mathrm{d}r}\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{j+1}{r}\right)\chi = 0.
\end{aligned}
\tag{21}
$$

By neglecting the last term, which is small because hB is large, one recovers the Schrödinger equation (4) for $V(r) = \mathrm{e}^2/cr$, with a relativistic correction included. Dirac then showed that the next approximation gave corrections $-\frac{\mathrm{e}^2}{2mc^2r^3}(j+1)$ and $\frac{\mathrm{e}^2}{2mc^2r^3}j$, which coincided with the ones given by the earlier theory of Wolfgang Pauli and of Darwin, thus incorporating the spin in Schrödinger's theory (Pauli 1927; Darwin 1927).

We see that Dirac did not solve his equation for the hydrogen atom exactly but restricted himself to the first two approximations. Why did such a mathematically gifted theoretical physicist refrain from solving Eq. 21 exactly for the Coulomb field? Kragh (1981, 1990) has suggested the following explanation:

> According to Dirac's own account, he did not even attempt to solve the equation (21) exactly, but looked for an approximation from the start. Dirac explains it [...] : 'I was afraid that maybe they [i.e., the higher order corrections] would not come out right.' [...] I shall propose a somewhat different version [...]. Having found equation (21) and having realized that it contained the correct spin, Dirac was in a hurry to publish and was not prepared to waste time in a detailed examination of the exact energy levels of the hydrogen atom. He realized that it was not a mathematically simple problem and decided to publish the first approximation. [...] Dirac knew that other physicists were also on the trail, so he may indeed have been motivated by [...] fear of not being first to publish, not any fear that the theory have serious shortcomings. This conjecture is substantiated

by the fact that he did not *attempt* to obtain the exact agreement, not even after he had published his theory.

3.2 Gordon: using confluent hypergeometric functions

It did not take long for other physicists to obtain the complete solution. The first was Gordon, and the story is pleasantly told on p. 63 of Kragh's monograph (Kragh 1990):

> Within two weeks following submission of the article, Walter Gordon in Hamburg was able to report to Dirac that he had derived the exact fine structure formula from the new equation and that Heisenberg's first question [getting the Sommerfeld formulas in all approximations] could thus be answered affirmatively. Reporting the main steps in the calculation, Gordon wrote : 'I should like very much to learn if you knew these results already and if not, if you think I should publish them.'

Dirac's answer must have been positive, and, in an article received on February 23th 1928, Gordon started from the system of equations (19) obtained by Dirac with $V(r) = \frac{e^2}{cr}$, namely

$$\begin{aligned} \frac{d\psi_1}{dr} &= \frac{j}{r}\psi_1 + \left[\frac{2\pi}{h}mc\left(1 - \frac{E}{mc^2}\right) - \frac{\alpha}{r}\right]\psi_3 \\ \frac{d\psi_3}{dr} &= \left[\frac{2\pi}{h}mc\left(1 + \frac{E}{mc^2}\right) + \frac{\alpha}{r}\right]\psi_1 - \frac{j}{r}\psi_3 \end{aligned} \tag{22}$$

where E was the energy of the electron including the energy at rest mc^2, $\alpha = \frac{2\pi}{h}\frac{e^2}{c}$ was Sommerfeld's fine structure constant, and j is the quantum number introduced by Dirac (Gordon 1928). Letting

$$\psi_1 = \sqrt{1 - \frac{E}{mc^2}}\,(\sigma_1 - \sigma_2), \quad \psi_3 = \sqrt{1 + \frac{E}{mc^2}}\,(\sigma_1 + \sigma_2)$$

and then

$$\sigma_1 = e^{-k_0 r} f_1, \quad \sigma_2 = e^{-k_0 r} f_2,$$

with $k_0 = \frac{2\pi}{h}mc\sqrt{1 - \frac{E}{mc^2}}$ ($k_0 > 0$ for the discrete spectrum), Gordon obtained the system

$$\begin{aligned} \frac{df_1}{dr} &= \left(2k_0 - \frac{\alpha/mc^2}{\sqrt{1-(E/mc^2)^2}}\frac{1}{r}\right)f_1 - \left(j + \frac{\alpha}{\sqrt{1-(E/mc^2)^2}}\right)\frac{f_2}{r} \\ \frac{df_2}{dr} &= -\left(j - \frac{\alpha}{\sqrt{1-(E/mc^2)^2}}\right)\frac{f_1}{r} + \frac{\alpha/mc^2}{\sqrt{1-(E/mc^2)^2}}\frac{f_2}{r}. \end{aligned} \tag{23}$$

He then searched for solutions of the form:

$$f_1(r) = r^\rho \sum_{\nu=0}^{\infty} c_\nu^{(1)} r^\nu, \quad f_2(r) = r^\rho \sum_{\nu=0}^{\infty} c_\nu^{(2)} r^\nu$$

which gave, by identification,

$$\rho = \sqrt{j^2 - \alpha^2} \tag{24}$$

and

$$\frac{c_0^{(1)}}{c_0^{(2)}} = -\frac{n}{\frac{\alpha}{\sqrt{1-(E/mc^2)^2}} - j}$$

$$c_\nu^{(1)} = \frac{(-2k_0)^\nu (n-1)(n-2)\cdots(n-\nu)}{\nu!(2\rho+1)(2\rho+2)\cdots(2\rho+\nu)} c_0^{(1)},$$

$$c_\nu^{(2)} = \frac{(-2k_0)^\nu n(n-1)\cdots(n-\nu+1)}{\nu!(2\rho+1)(2\rho+2)\cdots(2\rho+\nu)} c_0^{(1)},$$

$(\nu = 1, 2, \ldots)$, where

$$n = \frac{\alpha E}{mc^2\sqrt{1-(E/mc^2)^2}} - \rho. \tag{25}$$

From this, Gordon concluded that

$$\begin{aligned} \sigma_1(r) &= c_0^{(1)} \mathrm{e}^{-k_0 r} r^{\sqrt{j'^2-\alpha^2}} \, {}_1F_1(-n+1, 2\rho+1; 2k_0 r), \\ \sigma_2(r) &= c_0^{(2)} \mathrm{e}^{-k_0 r} r^{\sqrt{j'^2-\alpha^2}} \, {}_1F_1(-n, 2\rho+1; 2k_0 r), \end{aligned} \tag{26}$$

where ${}_1F_1$ is the confluent hypergeometric function defined in (16); (Gordon wrote F instead of the more recent notation ${}_1F_1$). He noticed that the σ_j are of the same type as Schrödinger's eigenfunctions for the hydrogen atom, which can be written as $\chi(r) = \mathrm{e}^{-k_0 r} r^l \, {}_1F_1(-n, 2l+2, 2k_0 r)$. Excluding the case where $\beta = 0$ or a negative integer, Gordon observed that ${}_1F_1(\alpha, \beta, r)$ was a polynomial in r of degree $-\alpha$ when α is a negative integer, so that, for $n = 1, 2, 3, \ldots$, one obtains a solution. When α and β are real numbers that are not non-positive integers, Gordon showed that the corresponding solutions grow exponentially, and cannot satisfy the normalization condition. This is also in the case when $n = 0$ and $j > 0$, although an acceptable solution exists when $n = 0$ and $j \leq -1$. Taking into account the relation (17) between the Laguerre polynomials and confluent geometric functions, one can say that Gordon *implicitly* solved the hydrogen problem for Dirac equations with Laguerre polynomials.

3.3 Darwin: using power series

The same problem was treated independently the same year in an article by Darwin, received March 6th 1928 (2 weeks later than Gordon!) (Darwin 1928). As mentioned by Kragh (1990), Darwin went to Cambridge a few days before Christmas 1927, and wrote a letter to Niels Bohr about his surprise at learning of Dirac's new electron theory:

> I was at Cambridge a few days ago and saw Dirac. He has now got a completely new system of equations for the electron which does the spin right in all cases and seems to be 'the thing.' His equations are first order, not second, differential equations ! He told me something about them but I have not yet even succeeded in verifying that they are right for the hydrogen atom.

In contrast to Gordon, whose article is purely technical, Darwin started with some comments about Dirac's abstract approach to relativistic quantum mechanics:

> There are probably readers who will share the present writer's feeling that the methods of non-commutative algebra are harder to follow, and certainly much more difficult to invent, than are operations of types long familiar to analysis. Wherever it is possible to do so, it is surely better to present the theory in a mathematical form that dates from the time of Laplace and Legendre, if only because the details of the calculus have been so much more thoroughly explored. Therefore, the object of this study is to take Dirac's system and treat it by ordinary methods of wave calculus.

The same opinion was also expressed in a letter of Darwin to Niels Bohr quoted by Kragh (1990):

> I continue to find that though Dirac evidently knows all about everything the only way to get it out of his writings is to think of it all for oneself in one's own way and afterwards to see it was the same thing.

In order to find the energy levels in the radial field of force, Darwin set $p_0 = \frac{1}{c}[E + eV(r)]$, omitted the vector potentials, wrote the corresponding Dirac equations as an explicit system of four equations in four stationary wave functions ψ_j ($j = 1, 2, 3, 4$)

$$\begin{aligned}
&\frac{2\pi i}{hc}\left(E + \frac{e^2}{r} + mc^2\right)\psi_1 + \left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right)\psi_4 + \frac{\partial}{\partial z}\psi_3 = 0 \\
&\frac{2\pi i}{hc}\left(E + \frac{e^2}{r} + mc^2\right)\psi_2 + \left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right)\psi_3 - \frac{\partial}{\partial z}\psi_4 = 0 \\
&\frac{2\pi i}{hc}\left(E + \frac{e^2}{r} + mc^2\right)\psi_3 + \left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right)\psi_2 + \frac{\partial}{\partial z}\psi_1 = 0 \\
&\frac{2\pi i}{hc}\left(E + \frac{e^2}{r} + mc^2\right)\psi_4 + \left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right)\psi_1 - \frac{\partial}{\partial z}\psi_2 = 0,
\end{aligned} \tag{27}$$

and, this time using the classical method of separation of variables, expressed the four functions as spherical harmonics multiplied by radial functions. He showed that ψ_1, ψ_2 must involve the same radial function $F(r)$, and ψ_3, ψ_4 the same radial function $G(r)$. Taking as trial solutions

$$\begin{aligned} \psi_1 &= -ia_1F(r)P_{k+1}^u, \quad & \psi_2 &= -ia_2F(r)P_{k+1}^{u+1}, \\ \psi_3 &= a_3G(r)P_k^u, & \psi_4 &= a_4G(r)P_k^{u+1}, \end{aligned}$$

where P_k^u denotes the whole spherical harmonic (called $Y_{u,k}$ in Sect. 2.2), and trying to adjust the a_j so that all four equations in (27) are satisfied, Darwin found

$$a_1 = 1, \quad a_2 = 1, \quad a_3 = k+u+1, \quad a_4 = -k+u$$

with F and G solutions of the following system of equations

$$\begin{aligned} \frac{2\pi}{hc}\left[E + eV(r) + mc^2\right]F + \frac{\mathrm{d}G}{\mathrm{d}r} - \frac{k}{r}G &= 0 \\ -\frac{2\pi}{hc}\left[E + eV(r) - mc^2\right]F + \frac{\mathrm{d}F}{\mathrm{d}r} + \frac{k+2}{r}G &= 0. \end{aligned} \tag{28}$$

The corresponding solution was named (F_k, G_k). Another way of elimination gave

$$a_1 = k+u, \quad a_2 = -k+u+1, \quad a_3 = 1, \quad a_4 = 1,$$

with F and G solutions of the system.

$$\begin{aligned} \frac{2\pi}{hc}\left[E + eV(r) + mc^2\right]F + \frac{\mathrm{d}G}{\mathrm{d}r} + \frac{k+1}{r}G &= 0 \\ -\frac{2\pi}{hc}\left[E + eV(r) - mc^2\right]F + \frac{\mathrm{d}F}{\mathrm{d}r} - \frac{k-1}{r}G &= 0. \end{aligned} \tag{29}$$

Observing that (29) is the same as (28) after the substitution $k \to -k-1$, Darwin denoted the solution of (29) by (F_{-k-1}, G_{-k-1}).

In order to discuss system (28) in the case of the Coulomb potential $V(r) = \frac{e}{r}$, Darwin introduced the positive numbers A and B defined by

$$A^2 := \frac{2\pi}{hc}(E + mc^2), \quad B^2 := \frac{2\pi}{hc}(-E + mc^2)$$

and the fine structure constant $\gamma := \frac{2\pi}{h}\frac{e^2}{c}$. Then, system (28) becomes

$$\begin{aligned} \left(A^2 + \tfrac{\gamma}{r}\right)F + \frac{\mathrm{d}G}{\mathrm{d}r} - \frac{k}{r}G &= 0 \\ \left(B^2 - \frac{\gamma}{r}\right)G + \frac{\mathrm{d}F}{\mathrm{d}r} + \frac{k+2}{r}F &= 0, \end{aligned} \tag{30}$$

and Darwin tried to solve this system in series of the form:

$$F(r) = e^{-\lambda r}\left(a_0 r^{\beta} + a_1 r^{\beta-1} + a_2 r^{\beta-2} + \cdots\right)$$
$$G(r) = e^{-\lambda r}\left(b_0 r^{\beta} + b_1 r^{\beta-1} + b_2 r^{\beta-2} + \cdots\right).$$

This gave him

$$b_s = c_s\left[\gamma\frac{B}{A} + \beta + k + 2 - s\right]$$
$$a_s = c_s\frac{B}{A}\left[\gamma\frac{A}{B} - \beta + k + s\right]$$

with the c_s such that, with $k' = \sqrt{(k+1)^2 - \gamma^2}$ supposed positive,

$$2AB(s+1)c_{s+1} = -c_s(\beta + 1 - s - k')(\beta + 1 - s + k'),$$

and so

$$c_s = (-1)^s\frac{(\beta - k' + 1)\cdots(\beta - k' - s + 2)(\beta + k' + 1)\cdots(\beta + k' - s + 2)}{2^s \cdot s!(AB)^s}.$$

In order that those solutions remain finite throughout space, the series must terminate for some value of s such that $\beta - s \geq 0$. It is, therefore, necessary that $\beta = k' + n' - 1$ for some integer $n' \geq 0$, which determines the energy levels

$$E = mc^2\left[1 + \frac{\gamma^2}{(k' + n')^2}\right]^{-1/2}. \tag{31}$$

Observing that the positivity of k was nowhere used in the process above, Darwin concluded that the same solution holds for (29) with Coulomb potential provided that k is replaced by $-k - 1$.

Formula (31) was the same as the one already obtained by Sommerfeld in the frame of the old relativistic theory of quanta. As pertinently observed by Kragh (1990, p. 63),

> The fact that Dirac equations yielded exactly the same formula for the hydrogen atom that Sommerfeld had found 13 years earlier was another great triumph. It also raised the puzzling question of how Sommerfeld's theory, based on the old Bohr's theory and without any notion of spin, could give exactly the same energy levels as Dirac's theory. However, this was a historical curiosity that did not bother the physicists.

In contrast to Gordon, Darwin did not relate his solutions to any special functions.

3.4 Pidduck: using Laguerre polynomials

Less than 1 year after Gordon and Darwin, Pidduck, in the article, (Pidduck 1929) received November 6th, 1928, solved the Dirac equations for the hydrogen atom using Laguerre polynomials *explicitly* and *elegantly*. Let us first write a few words on this scientist, who is somewhat less known than the other ones mentioned already. Frederick Bernard Pidduck was born on July 17th, 1885, in Southport, England. After high school in Manchester Grammar School, he proceeded to Exeter College, Oxford, in 1903. He took a First Class degree in Maths Moderations in 1904, was awarded a Johnson University Scholarship in 1907, took a First Class degree in physics in 1907, his MA in 1910 and Dr. Sci. in 1923. His thesis included two important contributions to the kinetic theory of gases. Between 1907 and 1921, he was a Fellow at Queen's College, Oxford, and was then a Fellow of Corpus Christi College, Oxford from 1921 until his retirement in 1950. He served twice as Vice-President of the College (1924–1926; 1931–1932), and was University of Oxford Pro-Proctor (1923–1924). During the First World War, he was a Ballistic Research Officer at the Woolwich Arsenal (1916–1919), where his study gained official commendation. It seems that Pidduck entered a little later into the life of his Colleges and University and was apt to dwell on grievances (Anonymous obituary 1952). His lack of social contacts may have contributed to his somewhat justified feeling that he lacked public recognition for his notable achievements. After retirement, he lived at Keswick. An all-the-year round swimmer and amateur photographer, Pidduck died June 18th, 1952 and his body was found on July 1st on a Lakeland mountainside (Anonymous obituary 1952).

More than a theoretical physicist, Pidduck was an applied mathematician in the pure British tradition, and contributed mostly to the mathematical theory of electricity, with special attention to diffraction of waves and the magnetron oscillator. He published a *Treatise on Electricity* in 1916 that was translated into Spanish in 1921 and re-edited in 1925, his *Lectures on Mathematical Theory of Electricity* in 1937, and his *Currents in aerials and high-frequency networks* in 1946. He was an enthusiast for the M.K.S. system of electrical units, co-authoring with R. K. Sas a pamphlet on *The Metre-kilogram-second System of Electrical Units* in 1947. All this study, of course, made Pidduck familiar with the use of orthogonal polynomials and special functions, and indeed in 1910, he introduced a class of polynomials that he denoted (n, λ), and which were generated by the function $\frac{(1+z)^{\lambda}}{(1-z)^{\lambda+1}}$ (Pidduck 1910), in a contribution to fluid mechanics, The polynomials (n, λ) are now sometimes referred as *Pidduck polynomials* (Bacry and Boon 1985), and are related to others such as the Mittag-Leffler, Hardy, and Pollaczek polynomials (Pollaczek 1956).

Let us now come to Pidduck's contribution to the solution of Dirac equations for the electron. He started his article as follows:

> The radial functions in Dirac's theory of the electron were found by Gordon for the field of a single nucleus and shown to be degenerate hypergeometric functions of the type used by Schrödinger. Gordon's results are obtained here by a slightly different method, in which the two functions are made to depend on a single function satisfying Laguerre's differential equation.

Strangely, Pidduck did not quote Darwin's article of 1928, but, when writing the equations for the radial functions supposedly taken from Gordon's article of 1928, he in fact started from Darwin's system (30) (with F replaced by $-F$), not from Gordon's system (23). He defined j to be $k+1$ when it is positive, and $-k$ when it is negative (the value zero being excluded), to obtain

$$\frac{2\pi}{hc}\left(h\nu + mc^2 + \frac{e^2}{r}\right)F - \frac{dG}{dr} + \frac{j-1}{r}G = 0 \tag{32}$$

$$\frac{dF}{dr} + \frac{j+1}{r}F - \frac{2\pi}{hc}\left(-h\nu + mc^2 - \frac{e^2}{r}\right)G = 0, \tag{33}$$

and stated: "write, with a small modification of *Darwin*'s notation" (our emphasis),

$$\gamma = \frac{2\pi e^2}{hc},\ h\nu = \frac{mc^2 N}{n},\ n = (N^2+\gamma^2)^{1/2},\ \alpha = \frac{h}{4\pi mc\gamma} = \frac{h^2}{8\pi^2 me^2}. \tag{34}$$

He then changed the independent variable by letting $x = \frac{r}{an}$ to obtain the system

$$\begin{aligned} &\left[\frac{n+N}{2\gamma}x + \gamma\right]F - x\frac{dG}{dx} + (j-1)G = 0 \\ &x\frac{dF}{dx} + (j+1)F - \left[\frac{n-N}{2\gamma}x - \gamma\right]G = 0. \end{aligned} \tag{35}$$

Pidduck's ingenious idea consisted then in looking for F and G in the form

$$\begin{aligned} F(x) &= e^{-Kx}x^{J-1}\left(Px\frac{dz}{dx}(x) + Qz(x)\right) \\ G(x) &= e^{-Kx}x^{J-1}\left(Rx\frac{dz}{dx}(x) + Sz(x)\right), \end{aligned} \tag{36}$$

which involve the single function z, where K, J, P, Q, R, S are undetermined constants. The identification of the two second-order differential equations generated by introducing (36) into (35) allowed him to compute those constants, namely

$$K = \frac{1}{2},\quad J = (j^2 - \gamma^2)^{1/2},\quad \frac{Q}{S} = -\frac{\gamma}{j+J},\quad \frac{P}{R} = \frac{\gamma}{n+N},\quad \frac{S}{R} = n - N + j + S.$$

Now, the first equation reduces to

$$x\frac{d^2z}{dx^2} + (q+1-x)\frac{dz}{dx} + pz = 0 \quad (p = N - J, q = 2J)$$

and so $z = L_p^q$, to insure that F and G vanish at infinity.

An explicit use of the structure relation (10) for Laguerre polynomials allowed Pidduck to write the solutions F and G as a linear combination of two Laguerre polynomials

$$F(x) = -\frac{\gamma}{n+N} e^{-\frac{x}{2}} x^{J-1} \left[(n+j) L_q^p(x) + (N+J) L_{p-1}^q(x) \right] \tag{37}$$

$$G(x) = e^{-\frac{x}{2}} x^{J-1} \left[(n+j) L_q^p(x) - (N+J) L_{p-1}^q(x) \right]. \tag{38}$$

Pidduck concluded by observing that

> one can now calculate the integrals required in the theory of perturbations with the same facility as in Schrödinger's theory, since the methods of Schrödinger (1926c) do not require q to be an integer.

In order to compare Pidduck's results with Gordon's, we notice that, Gordon's α is Pidduck's γ (Sommerfeld's fine structure constant), and writing $E = h\nu$ in (34) we obtain

$$N = \frac{\gamma E}{mc^2 \sqrt{1-(E/mc^2)^2}},$$

and

$$p = \frac{\gamma E}{mc^2 \sqrt{1-(E/mc^2)^2}} - (j^2 - \gamma^2)^{1/2}, \quad q = 2(j^2 - \gamma^2)^{1/2}.$$

Hence, (25) shows that p is equal to Gordon's n, and (24) shows that q is equal to two times Gordon's ρ. Consequently, relation (17) implies that Gordon's solution (26) and Pidduck's solution (37) indeed does imply the same Laguerre polynomials.

3.5 Further literature

In contrast to the case of the Schrödinger equation, Laguerre polynomials do not seem to have been adopted by classical textbooks on relativistic quantum mechanics when solving the Dirac equations for the hydrogen atom. In his epoch-making monograph of 1930, Dirac included a solution of his equation for the hydrogen atom and only quoted Gordon's article of 1928 (Dirac 1930). However, Dirac's approach is closer to Darwin's, as he solved the radial equation through a series, without any mention of confluent hypergeometric functions or Laguerre polynomials. Darwin's approach was chosen by Louis de Broglie to explain the fine structure of hydrogen atom in his monograph (de Broglie 1934), which describes Dirac's theory and gives a very clear and detailed exposition of Darwin's contribution. Weyl's monograph and the well-known survey articles of E. L. Hill-R. Landshoff and of Hans A. Bethe and Edwin E. Salpeter (born in 1924) in the *Handbuch der Physik*, all follow Gordon in representing the two functions as a linear combination of confluent hypergeometric functions ${}_1F_1(a, b; x)$ with polynomial coefficients, although Hill-Landshoff also describe Darwin's article

(Weyl 1928; Hill and Landshoff 1938; Bethe and Salpeter 1957). The volume 4 of the monumental treatise of Landau and Lifchitz (1972) only quotes Gordon and Darwin, and gives Gordon's solution in terms of the confluent hypergeometric functions, although the well-known monograph of Schiff (1968) follows essentially Darwin's approach.

A clear and detailed treatment of Dirac equations for the Coulomb field is given in the book of Nikiforov and Uvarov (1988). Starting from Dirac equations in the form given in Bethe and Salpeter (1957), they look for solutions of the form:

$$\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = f(r)\Omega_{jlm}(\theta,\phi)$$
$$\begin{pmatrix} \psi_3 \\ \psi_4 \end{pmatrix} = (-1)^{(l-l'+1)/2} g(r)\Omega_{jl'm}(\theta,\phi)$$

where j is a quantum number specifying the total angular momentum of the particle ($j = 1/2, 3/2, \dots$); l and l' are orbital angular momentum quantum numbers, which, for given j, can have the values $j - \frac{1}{2}$ and $j + \frac{1}{2}$, with $l' = 2j - l$; the quantum number m takes half-integral values between the numbers $-j$ and j. The functions Ω_{jlm} and $\Omega_{jl'm}$, called *spherical spinors*, are connected to spherical harmonics Y_{lm}. Substitution gives a system of first-order linear equations in f and g whose solution must be such that $rf(r)$ and $rg(r)$ are bounded near 0 and

$$\int_0^{+\infty} r^2[f^2(r) + g^2(r)]\,\mathrm{d}r = 1.$$

A careful and detailed elimination procedure leads to the solution of a differential equation of the form

$$xy'' + (2\nu - x)y' + ny = 0$$

whose only polynomial solutions are the Laguerre polynomials $B_n L_n^{2\nu-1}$. This makes it possible to express f and g in terms of products of $x^{\nu-1}e^{-x/2}$ with suitable linear combinations of $xL_{n-1}^{2\nu+1}(x)$ and $L_n^{2\nu-1}(x)$. Notice that no reference is made to Gordon or Pidduck, and that Nikiforov-Uvarov's treatment is less elegant and more complicated than Pidduck's.

Pidduck's contribution was also overlooked by Leverett Davis Jr, who started his article (Davis 1939) as follows :

> It does not appear to have been noticed that the radial functions that arise in the treatment of Dirac's relativistic hydrogenic atom can be expressed in terms of generalized Laguerre polynomials.

He wrongly believed that he was the first to express the radial functions in terms of Laguerre polynomials L_n^α for values of α and n related to the quantum numbers. He quoted neither Gordon nor Darwin. That the situation has not improved since is testified by the recent article (Auvil and Brown 1978), where the Dirac equation for the hydrogen atom is solved in terms of Laguerre polynomials, using a procedure used by Schiff (1968) for Klein-Gordon equation. The authors pertinently observe that

> A number of well-known quantum-mechanics texts derive the energy spectrum, but do not derive, or even quote, the eigenfunctions.

In a more recent article devoted to the role of orthogonal polynomials in the hydrogen atom, Dehesa et al. (1991) noticed that

> For the Dirac equation, [...] the corresponding radial wave functions do not involve any longer a single Laguerre polynomial but a combination of two Laguerre polynomials [see also (Auvil and Brown 1978)], which receive the name of Dirac polynomials.

If we remember that Dirac did not find a rigorous solution of his equation (21), then the name *Pidduck polynomials* should be historically more appropriate! Laguerre polynomials are also absent in the quoted articles on the history of Dirac equations, and in Dirac's authoritative scientific biography (Kragh 1990).

Let us end with a very recent development related to Dirac equations and Laguerre polynomials, due to Antonio J. Durán and F. Alberto Grünbaum. In 1949, Mark G. Krein developed a theory of matrix-valued orthogonal polynomials without any reference to differential equations (Krein 1949). In 2004, Durán and Grünbaum developed a method for producing matrix-valued polynomials associated to second-order differential operators with matrix coefficients (Durán and Grünbaum 2004). Observing that the Schrödinger equation is solved in several special problems through the use of orthogonal polynomials, and that Dirac equations can be seen as a first-order differential equation with matrix coefficients acting on a four-component vector function, they established a connection between the solution of Dirac equations for a central Coulomb potential and the theory of matrix-valued orthogonal polynomials initiated by Krein (Durán and Grünbaum 2006). They quoted Darwin's article, but neither Gordon's nor Pidduck's ones, despite the fact that both Laguerre polynomials and hypergeometric confluent functions are mentioned there, and absent in Darwin's treatment. They grounded their discussion on the solutions of Dirac equations given in recent treatises (Rose 1961; Nikiforov and Ouvarov 1976).

The systematic lack of reference to Pidduck's article has a possible explanation. After 1926, most of the fundamental articles in quantum mechanics were published in the journals *Zeitschrift für Physik* or *Proceedings of the Royal Society of London*. Pidduck's article appeared in the *Journal of the London Mathematical Society*, which was not very popular among contemporary physicists, and was completely forgotten until the publication in 1940 of Hille–Shohat–Walsh's important bibliography on orthogonal polynomials (Hille et al. 1940).

4 Conclusion

In spite of their multiple paternity (see the Appendix), Laguerre polynomials have taken more time to penetrate the classical treatises of analysis of the end of the nineteenth and the beginning of the twentieth century than other special functions such as Legendre polynomials, Bessel functions, hypergeometric functions, Chebyshev, or Hermite polynomials. For example, there is no trace of Laguerre polynomials in the monumental treatises of analysis of the French mathematicians Laurent (1885–1991), Jordan (1887), Picard (1891–1897), Goursat (1910–1915), or Hadamard (1927–1930). The same is true for the classical *Modern Analysis* of the British mathematicians Whittaker and Watson (1902), concentrating on special functions, and the comprehensive book *Die partiellen Differential-Gleichungen der Mathematischen Physik* of the German mathematician Weber (1900–1901) devoted to mathematical physics.

This may be the reason why Laguerre polynomials were not immediately identified by Schrödinger when solving his equation for the hydrogen atom. However, besides their presence in the solution of this important physical problem, the role of Hermite's polynomials in solving the linear oscillator in wave mechanics showed that further developments and computational successes of Schrödinger's quantum mechanics strongly depended on the appropriate tools developed by mathematicians involved in special functions and spectral theory, as surveyed in volume 1 of the *Methoden der mathematischen Physik* of Courant and Hilbert (1924). In return, those physical applications popularized mathematical concepts that had remained rather little known. It is the case of Laguerre polynomials, where this is examplified, for example, by their systematic inclusion in subsequent treatises on analysis, such as those of Valiron (1942–1945), Favard (1960–1963), Smirnov (1969–1984), Lavrentiev and Shabat (1977), or Chatterji (1997–1998), and in most recent study on special functions (Erdélyi et al. 1953; Nikiforov and Ouvarov 1976). One can also consult the historical and technical articles contained in a conference devoted to orthogonal polynomials (Brezinski et al. 1985).

The fruitful interplay between mathematics and physics always is a two-winners game.

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Appendix: Laguerre polynomials: a historical survey

Introduction

At the end of nineteenth century, the polynomials (7) with $\alpha = 0$ were called *polynomials of E. N. Laguerre*, an expression switching to *Laguerre polynomials* at the beginning of the twentieth century. Richard Askey, in his comments on Szëgo's article (Szegö 1968), given in the *Collected Papers* of Szegö, observed (Askey 1982):

> There is no adequate historical treatment of orthogonal polynomials which is a shame for many reasons. First, a number of important parts of mathematics are directly related to orthogonal polynomials. Many of the methods developed to study orthogonal polynomials have been used in other parts of mathematics.

> Finally, a source exists which makes it easy to find most of the important early article. This is (Hille et al. 1940). I think it is the best bibliography that has been compiled on any large part of mathematics. I have not found it very useful for research study but for historical study it is invaluable. [...] The classical orthogonal polynomials are mostly attributed to someone other than the person who introduced them. Szegö refers to Abel and Lagrange and Tschebyscheff in Szegö 1959, Chapter 5, for study on the Laguerre polynomials $L_n^0(x)$. Abel's study was published posthumously in 1881. Probably the first published study on these polynomials that uses their orthogonality was by Murphy (Murphy 1833–1835).

The same names are quoted by Gautschi (1981). In the special case of Laguerre polynomials, we shall try to amplify and complete this historical sketch.

Lagrange

In a section of his memoir *Solution de différents problèmes de calcul intégral* of 1762 entitled *Recherche des cas d'intégration de l'équation* $\frac{\mathrm{d}^2y}{\mathrm{d}t^2} + ayt^{2m} = T$ (with $2m$ erronously replaced by m), Lagrange (1762) first considered the equation

$$\frac{\mathrm{d}^2z}{\mathrm{d}t^2} + azt^{2m} = 0, \tag{39}$$

and substituted the independent variable $u = \frac{t^{m+1}}{m+1}$ to reduce (39) to

$$\frac{\mathrm{d}^2z}{\mathrm{d}u^2} + \frac{n}{u}\frac{\mathrm{d}z}{\mathrm{d}u} + az = 0,$$

where $n = \frac{m}{m+1}$. Introducing the new unknown given by $z = x\mathrm{e}^{ku}$, with $k^2 + a = 0$, Lagrange obtained the differential equation

$$\frac{\mathrm{d}^2x}{\mathrm{d}u^2} + \left(2k + \frac{n}{u}\right)\frac{\mathrm{d}x}{\mathrm{d}u} + \frac{nk}{u}x = 0, \tag{40}$$

and searched for a solution in the form:

$$x = Au^r + Bu^{r+1} + Cu^{r+2} + \cdots.$$

In modern terminology, Eq. 40 is a confluent hypergeometric equation (15), which can be written in the more standard form:

$$t\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + (n-t)\frac{\mathrm{d}x}{\mathrm{d}t} - \frac{n}{2}x = 0$$

through the change of variable $u = -\frac{t}{2k}$. Polynomial solutions of degree $n = -\frac{n}{2}$ can effectively be written as Laguerre polynomials $L_{-n/2}^{(n-1)}(t)$, but with a parameter

$\alpha = n - 1$ depending upon $n!$ Kummer polynomials would probably be more appropriate (see Humbert 1922). It seems, therefore, more accurate to say that Lagrange reduced the integration of Eq. 39 to a Kummer equation, and gave a polynomial solution of it. The link with Laguerre polynomials is not very strong. Notice that in Lagrange's transformation for passing from (39) to (40), the chosen constants $\frac{1}{m+1}$ and $k^2 = -a$ could be arbitrary without changing the Kummer-type character of the equation for $x(u)$.

Abel

Now, as can be seen on p. 284 of volume II of his complete studies, (Sylow and Lie 1881) an unpublished manuscript of Abel written in 1826 and entitled *Mémoires de mathématiques par N. H. Abel* contains, on pp. 75–79 a sequence of computations entitled *Sur une espèce particulière de fonctions entières nées du développement de la fonction* $\frac{1}{1-v}e^{-\frac{xv}{1-v}}$ *suivant les puissances de* v. Writing

$$\frac{1}{1-v}e^{-\frac{xv}{1-v}} = \sum \varphi_m(x)v^m,$$

Abel found

$$\varphi_m(x) = 1 - mx + \frac{m(m-1)}{2}\frac{x^2}{2} - \frac{m(m-1)(m-2)}{2.3}\frac{x^3}{2.3} + \cdots \pm m\frac{x^{m-1}}{2.3\cdots(m-1)} \mp \frac{x^m}{2.3\cdots m}.$$

Thus, Abel's φ_m is identical to the L_m given in (7) with $\alpha = 0$, and is obtained through the generating function (8) with $\alpha = 0$. Furthermore, multiplying each member of the identity

$$\frac{1}{(1-v)(1-u)}e^{-\frac{xv}{1-v}-\frac{xu}{1-u}} = \sum\sum \varphi_m(x)\varphi_n(x)v^m u^n$$

by e^{-x} and integrating over $(0, \infty)$, Abel obtained

$$\frac{1}{1-vu} = \sum\sum u^n v^m \int_0^\infty e^{-x}\varphi_m(x)\varphi_n(x)\,dx,$$

from which he concluded, because of the identity

$$\frac{1}{1-vu} = \sum u^n v^n,$$

that the integral

$$\int_0^\infty e^{-x}\varphi_m(x)\varphi_n(x)\,dx$$

is equal to one if $m = n$, and to zero if $m \neq n$. This is the orthogonality condition (14) with $\alpha = 0$. Finally, Abel also gave the development of x^μ in terms of $\varphi_0(x), \ldots, \varphi_\mu(x)$, namely

$$x^\mu = A_0\varphi_0(x) + A_1\varphi_1(x) + \cdots + A_\mu\varphi_\mu(x) \tag{41}$$

with

$$A_m = (-1)^m \frac{\Gamma(\mu+1)}{\Gamma(m+1)} \cdot \frac{\Gamma(\mu+1)}{\Gamma(\mu-m+1)}.$$

This link with Laguerre polynomials seems to have been first noticed by Milne (1915).

Murphy

The contribution of Robert Murphy is quite remarkable. In the second of the three memoirs quoted in Murphy (1833–1835, p. 146), he introduced a family of polynomials $T_n(z)$, of degree n, with $z = \ln t$ (written as h.l.t for hyperbolic logarithm of t):

$$T_n(z) = \sum_{k=0}^{n} \binom{n}{k} \frac{z^k}{k!}$$

and computed the integrals

$$I(n,m) = \int_0^1 T_n(\ln t)(\ln t)^m\,dt, \tag{42}$$

using $\int_0^1 (\ln t)^r\,dt = (-1)^r r!$ Now $I(n,m)$ becomes

$$(-1)^m m! \sum_{k=0}^{n} (-1)^{k+m} \binom{n}{k} \frac{(k+m)!}{k!},$$

and Murphy proved, and used, the interesting combinatorial identity

$$\sum_{k=0}^{n} (-1)^{k+m} \binom{n}{k} \frac{(k+m)!}{k!} = 0 \quad \text{for} \quad m < n,$$

showing in that way, from (42), the orthogonality of the families $T_n(\ln t)$ on $]0, 1[$. With $L_n(x) = T_n(-\ln t)$, $t = e^x$, Laguerre's orthogonality formula (14) (for $\alpha = 0$) is recovered. Murphy's trick in proving the combinatorial identity came from the expansion of the product, in powers of h, of

$$(1+h)^n\left(1+\frac{1}{h}\right)^{-(m+1)},$$

for which the constant term, equal to zero for $n > m$ coincides with the left-hand side of the identity. Murphy also obtained a Rodrigues-type representation formula (14) and a generating function for the family $T_n(\ln t)$. The technique used here was based on Lagrange's inversion theorem, exactly in the same way as in the article of James Ivory and Carl Gustav Jacobi, published 2 years later (Ivory and Jacobi 1837), and dealing with the generating function and Rodrigues-type representation formula for Legendre polynomials (see Ronveaux and Mawhin 2005).

Chebychev

Chebyshev's fundamental article on orthogonal polynomials (Chebyshev 1859) is a continuation of a previous article on approximation (Chebychev 1858). There, given $n+1$ values $F(x_0), F(x_1), \ldots, F(x_n)$ of a function $F(x)$ defined on an interval I, and a probability law $\theta(x)$, Chebyshev searched for a polynomial approximation $P(x)$ of degree $m < n$ minimizing the expression

$$\sum_{i=0}^{n} \theta(x_i)[F(x_i) - P(x_i)]^2.$$

He showed that if $f(x) := \prod_{i=0}^{n}(x - x_i)$, and if the expression $\frac{f'(x)\theta(x)}{f(x)}$ was expanded in a continued fraction, its j^{th} member ψ_j was a polynomial of degree j such that

$$\sum_{i=0}^{n} \theta(x_i)\psi_j(x_i)\psi_k(x_i) = \delta_{j,k}.$$

In his article of 1859, Chebyshev extended his approach to different cases where the sums above are replaced by integrals, and showed that the corresponding sequence of polynomials could be used to obtain developments of functions in series of those polynomials 'analogous to Fourier series'. In particular, when $I = [0, \infty)$ and $\theta(x) = ke^{-kx}$. Chebychev's method provided the development

$$F(x) = \frac{\int\limits_0^\infty k\mathrm{e}^{-kx}\psi_0(x)F(x)\,\mathrm{d}x}{\int\limits_0^\infty k\mathrm{e}^{-kx}\psi_0^2(x)\,\mathrm{d}x}\psi_0(x) + \frac{\int\limits_0^\infty k\mathrm{e}^{-kx}\psi_1(x)F(x)\,\mathrm{d}x}{\int\limits_0^\infty k\mathrm{e}^{-kx}\psi_1^2(x)\,\mathrm{d}x}\psi_1(x) + \cdots,$$

where $\psi_0(x)$, $\psi_1(x)$, ... are the denominators of the convergents in the development in continued fraction of the function $\int_0^\infty \frac{k\mathrm{e}^{-ku}}{x-u}\,\mathrm{d}u$. Chebyshev found the following simple expressions for the functions $\psi_0(x)$, $\psi_1(x)$, ...,

$$\psi_0(x) = \mathrm{e}^{kx}\cdot\mathrm{e}^{-kx}, \quad \psi_1(x) = \mathrm{e}^{kx}\frac{\mathrm{d}(x\mathrm{e}^{-kx})}{\mathrm{d}x}, \ldots, \psi_l(x) = \mathrm{e}^{kx}\frac{\mathrm{d}^l(x^l\mathrm{e}^{-kx})}{\mathrm{d}x^l}.$$

Hence, referring to formula (14) with $\alpha = 0$, we see that, for $k = 1$, $\psi_n(x) = n!L_n(x)$. Some recent studies give a nice description of Chebyshev's contributions (Akhieser 1998; Steffens 2006). The priority of Chebyshev over Hermite (for Hermite's polynomials) and over Laguerre (for Laguerre's polynomials) was also noticed by Dieudonné (1985). In the Russian mathematical literature, Laguerre polynomials are frequently called *Chebychev–Laguerre polynomials* (Lavrentiev and Shabat 1977).

4.1 Laguerre

It remained for Laguerre to be the first to give the main properties of L_m in the same article: orthogonality, the three-term recurrence relations, the differential equation, the generating function, and the inversion formula

$$x^n = n!\sum_{k=0}^{n}(-1)^k\binom{n}{k}L_k(x),$$

which is nothing but Abel's unpublished formula (41) (Laguerre 1879a). Laguerre obtained his polynomials as denominators of the convergents of a development in continued fractions of the function $f(x) = \mathrm{e}^x\int_x^\infty \frac{\mathrm{e}^{-t}}{t}\,\mathrm{d}t$. He did not quote any of the authors we have just mentioned.

However, in another article, Laguerre gave a general second-order differential equation satisfied by a larger class of orthogonal polynomials $\{P_n(x)\}$ (Laguerre 1885), called today *semi-classical orthogonal polynomials* (Hendriksen and van Rossum 1985). This equation, rediscovered by Oskar Perron in the context of Padé approximants, is now sometimes called *Laguerre–Perron's equation* (Perron 1929). Using Laguerre's notation, this equation for the semi-classical orthogonal polynomial $y = P_n$ is

$$w(x)\theta_n(x)\frac{d^2y}{dx^2} + \left[\left(2v(x) + \frac{dw}{dx}(x)\right)\theta_n(x) - w(x)\frac{d\theta_n}{dx}(x)\right]\frac{dy}{dx} + \kappa_n(x)y = 0,$$

where $v(x)$ and $w(x)$ are polynomials occurring in a first-order linear inhomogeneous differential equation for the Stieltjes function f linked to the orthogonality weight ρ by the relation

$$f(x) = \int \frac{\rho(z)}{x - z}\,dz.$$

The polynomials θ_n and κ_n, with degree independent of n, are in general difficult to compute from v and w. Laguerre developed the case where $w(x) = x$ and $2v(x) = \alpha - x$ in detail, finding $\theta_n(x) = 1$ and $\kappa_n(x) = n$, discovering in the cited article the generalized Laguerre polynomials $L_n^\alpha(x)$, and giving their explicit representations. Hence, it is incorrect to write, as in Lebedev (1965, p. 76), that Laguerre only studied the case where $\alpha = 0$.

This important article, which was published 1 year before Laguerre's death, was omitted by Eugène Rouché from the list of Laguerre's scientific articles that concluded Laguerre's obituary (Rouché 1886) and was forgotten by the editors when compiling Volume I of Laguerre's *Oeuvres* (Hermite et al. 1898–1905) devoted to algebra and the integral calculus. It was, however, added at the end of Volume II, which is otherwise devoted to geometry. This omission can possibly be explained by the existence of two earlier short publications of Laguerre (1879b, 1884) that have (almost) the same title and are reproduced in Volume I of the *Oeuvres*. They were published, respectively, in the *Bulletin de la Société mathematique de France*, and the *Comptes Rendus des séances de l'Académie des Sciences*, and were both related to the longer important article of Volume II of the *Oeuvres*. There is some confusion about the three titles, in the articles and in the table of contents of the *Oeuvres*: "fonction" and "fraction" appear randomly in "Sur la réduction en fractions continues d'une fraction (or fonction)...." In fact "fraction" is probably a misprint, "fonction" being more appropriate. Furthermore, the 1884 note is wrongly dated from 1879 on p. 445 of the *Oeuvres*, and refers to the longer article of 1885. The version of this 1885 article given in the *Oeuvres*, vol. II, corrects the incorrect numbering of the sections and formulas in the original article, but omits its last sentence, where Laguerre promises to come back to the integration of some systems of difference equations, already considered, in special cases, by Jacobi and Carl Wilhelm Borchardt, using elliptic and abelian functions:

> Je reviendrai du reste sur ce point particulier, en essayant de compléter à certains égards les résultats obtenus par ces illustres géomètres.

Observe that, in his observation on Laguerre, Michael Bernkopf insists on the fact that this edition of the *Oeuvres* "teems with errors and misprints," but also misses introduction of the general family L_n^α in Laguerre (1879b) (Bernkopf 1991).

Sokhotskii and Sonine

The same extension of L_n was given in 1873 by Yulian V. Sokhotskii in his thesis (Sokhotskii 1873), and, 7 years later, in a long article of Sonine (1880) on cylindrical Bessel functions. There, in Section 40, the polynomials T_m^n of degree n, still sometimes referred as *Sonine polynomials*, are defined via the generating functions

$$\varphi_m(r, x) = \frac{e^{-r} J_m(2i\sqrt{rx})}{(i\sqrt{rx})^m} = \sum_{n=0}^{\infty} T_m^n(x) r^n,$$

where J_m is the Bessel function of first kind, and m is an integer. From the differential equation obtained by Sonine, it is easy to identify $T_m^n(x)$ (up to a constant factor) with the polynomials ${}_1F_1(-n, m+1; x)$ or $L_n^{(m)}(x)$. As Sonine's article was submitted in August 1879 and Laguerre's article (1879a) was published the same year, it is not surprising that Sonine did not quote Laguerre.

Fejér

In an article of 1909, announced in a short note at the *Comptes Rendus*, Leopold Fejér, without any mention of Laguerre or any of the other authors above, obtained the asymptotic development of the function:

$$\frac{e^{\frac{1}{z-1}}}{(1-z)^{\rho}} = \gamma_0 + \gamma_1 z + \cdots + \gamma_n z^n + \cdots,$$

where ρ is a real number (Fejér 1908, 1909). Fejér gave the expression

$$\gamma_n \simeq \frac{1}{\pi e} \frac{\sin\left[2\sqrt{n} + \left(\frac{3}{4} - \frac{\rho}{2}\right)\pi\right]}{n^{\left(\frac{3}{4} - \frac{\rho}{2}\right)}}. \tag{43}$$

In a note to those articles, Turán observed that $\frac{e^{-\frac{xw}{1-w}}}{(1-w)^{\alpha+1}}$, being the generating function of the Laguerre polynomials $L_n^{(\alpha)}$, (43) provides the first asymptotic development of those polynomials, which, is explicitly given by (Turán 1970)

$$L_n^{(\alpha)}(x) \simeq \frac{1}{\sqrt{\pi}} e^{\alpha/2} x^{-\frac{\alpha}{2}-\frac{1}{4}} n^{\frac{\alpha}{2}-\frac{1}{4}} \cos\left[2\sqrt{nx} - (2\alpha+1)\frac{\pi}{4}\right].$$

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