The 2-dimensional hydrogen atom

In these notes we investigate a particular partial differential equation arising from the quantum mechanical description of a hydrogen atom. For simplicity we consider the atom in a 2-dimensional instead of a 3-dimensional universe. For convenience we put all fundamental constants of nature equal to 1.

The problem. In quantum mechanics the electron is described by a so called wave function. A wave function is a complex valued function Ψ on $\mathbf{R} \times \mathbf{R}^2$ that gives the probability to find the electron at a certain position. To be more precise, suppose the position x_0 of the electron is measured at time t_0 and assume that U is a compact subset of $\mathbf{R}^2$. Then the probability that the position x_0 of the electron is inside U is given by

$$P\big(x_0 \in U\big) = \int_U |\Psi(t_0, x)|^2 \, dx.$$

Since the probability to find the electron anywhere in $\mathbf{R}^2$ equals 1, the wave-function has to satisfy

$$\int_{\mathbf{R}^2} |\Psi(t, x)|^2 \, dx = 1 \qquad (t \in \mathbf{R}).$$

The evolution of the wave function of the electron is given by the Schrödinger equation

$$i \frac{\partial}{\partial t} \Psi = H\Psi. \tag{1}$$

Here H is the partial differential operator $H = -\Delta + V$, where

$$\Delta = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}$$

is the Laplacian and V is the potential of the electric field originating from the proton at the origin, i.e., the Coulomb potential

$$V : \mathbf{R}^2 \setminus \{0\} \to \mathbf{R}; \quad x \mapsto -\frac{1}{\|x\|}.$$

(there are good arguments for taking the potential $x \mapsto \log(\|x\|)$ instead, but that would make the 2-dimensional case deviate more from the 3-dimensional). In the physics literature, the operator H is called the Hamiltonian. The term $-\Delta$ is the quantum mechanical equivalent of kinetic energy. Since the total energy is the sum of the kinetic energy and the potential energy, the Hamiltonian is an operator describing the total energy of the electron.

We call a function $\psi : \mathbf{R}^2 \setminus \{0\} \to \mathbf{C}$ a (normalized) *eigenfunction* of H with eigenvalue E if it

- satisfies the so-called time-independent Schrodinger equation

$$H\psi = E\psi. \tag{2}$$

- is C^3 and bounded on $\mathbf{R}^2 \setminus \{0\}$ (because we need it in what follows)
- satisfies the normalization condition

$$\int_{\mathbf{R}^2} |\psi(x)|^2 \, dx = 1 \tag{3}$$

It can be shown that if ψ is an eigenfunction of H with eigenvalue E, then $E < 0$. The physical significance of eigenvalues of H is that these are the (negative) values that can occur as the outcome of an energy measurement.

It can also be shown that the wave function of the electron in a hydrogen atom can at any time t in good approximation be written as a linear combination of eigenfunctions of H. The mathematical problem to be solved first is then to determine these eigenfunctions. Let $E < 0$ and put $\lambda = 2\sqrt{-E}$.

Eigenfunctions. We want to find the non-zero solutions ψ to the Scrödinger equation (2), which satisfy the $\bullet$'s above. To do this we will first rewrite the equation using polar coordinates.

Let $\Phi : \mathbf{R}_{>0} \times (-\pi, \pi) \to \mathbf{R}^2 \setminus (\mathbf{R}_{\leq 0} \times \{0\})$ be given by

$$\Phi(r, \theta) = (r\cos\theta, r\sin\theta)\,.$$

Then for $f \in C^2(\mathbf{R}^2)$

$$(\Delta f) \circ \Phi(r, \theta) = \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} \right) (f \circ \Phi)(r, \theta).$$

Before we apply this to the eigenfunction with eigenvalue $E = -\lambda^2/4$, it is convenient to substitute $\rho = \lambda r$ and write $\tilde{\Phi}(\rho, \theta) = \Phi(\rho/\lambda, \theta)$. This leads instead to

$$(\Delta f) \circ \tilde{\Phi}(\rho, \theta) = \lambda^2 \left(\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial}{\partial \rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial \theta^2} \right) (\psi \circ \tilde{\Phi})(\rho, \theta)$$

Now we apply to the eigenequation $H\psi = E\psi$. We write ϕ for $\psi \circ \tilde{\Phi}$ and conclude (recall that $H = -\Delta - \frac{1}{r}$)

$$\left(\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial}{\partial \rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{\lambda\rho} - \frac{1}{4} \right) \phi(\rho, \theta) = 0 \qquad \big(\rho \in \mathbf{R}_{>0}, \theta \in (-\pi, \pi)\big). \tag{4}$$

It is this partial differential equation which we want to solve, and we shall do this by the method of separation of variables, in analogy with has been done previously for the Laplace equation.

We look for solutions in product form $\phi(\rho, \theta) = R(\rho)\Theta(\theta)$ and after division by $\frac{1}{\rho^2} R\Theta$ we find the following separated equation

$$\frac{R'' + \frac{1}{\rho}R' + \left(\frac{1}{\lambda\rho} - \frac{1}{4}\right) R}{\frac{1}{\rho^2} R} = -\frac{\Theta''}{\Theta}$$

which then has to be a constant κ. This leads to the equations

$$R'' + \frac{1}{\rho}R' + \left(\frac{1}{\lambda\rho} - \frac{1}{4}\right) R - \frac{\kappa}{\rho^2}R = 0$$

and

$$\Theta'' + \kappa\Theta = 0$$

As Θ has to be 2π-periodic in the angular variable θ, we conclude that $\Theta(\theta) = e^{in\theta}$ and $\kappa = n^2$ for some $n \in \mathbf{Z}$ (just as what we saw for the Laplace equation). We are thus led to look for a solution which is given by a Fourier series with respect to θ,

$$\phi(\rho, \theta) = \sum_{l\in\mathbf{Z}} c_l(\rho)e^{il\theta} \qquad (\theta \in \mathbf{R}), \tag{5}$$

where the coefficient $c_l : \mathbf{R}_{>0} \to \mathbf{C}$ is expected to satisfy the equation for R above. That this is possible for any eigenfunction ψ follows from the fact that $\phi(\rho, \cdot)$ can be extended to a 2π-periodic C^1 function for every $\rho > 0$ with Fourier coefficients

$$c_l(\rho) = \frac{1}{2\pi}\int_{-\pi}^{\pi} \phi(\rho, \theta)\, e^{-il\theta}\, d\theta. \tag{6}$$

If we insert (5) into (4), interchange differentiation and summation and use the uniqueness of the Fourier series, we obtain (as expected) the following differential equation for the c_l:

$$\Big(\frac{d^2}{d\rho^2} + \frac{1}{\rho}\frac{d}{d\rho} - \frac{l^2}{\rho^2} + \frac{1}{\lambda\rho} - \frac{1}{4}\Big)c_l(\rho) = 0 \qquad (\rho \in \mathbf{R}_{>0}). \tag{7}$$

This equation has a regular singularity at the origin and can be solved by the power series method of Frobenius. Rather than doing this directly, it turns out to be an advantage first to simplify it by a change of variables.

The change of variables we apply is

$$c_l(\rho) = e^{-\frac{\rho}{2}}\rho^{|l|}\gamma_l(\rho) \qquad (\rho \in \mathbf{R}_{>0})$$

for some function $\gamma_l(\rho)$. Then

$$\begin{aligned} e^{\frac{\rho}{2}}\rho^{-|l|}\frac{dc_l}{d\rho}(\rho) &= \frac{d\gamma_l}{d\rho}(\rho) + \Big(\frac{|l|}{\rho} - \frac{1}{2}\Big)\gamma_l(\rho) \\ e^{\frac{\rho}{2}}\rho^{-|l|}\frac{d^2c_l}{d\rho^2}(\rho) &= \frac{d^2\gamma_l}{d\rho^2}(\rho) + 2\Big(\frac{|l|}{\rho} - \frac{1}{2}\Big)\frac{d\gamma_l}{d\rho}(\rho) + \Big(\frac{l^2 - |l|}{\rho^2} - \frac{|l|}{\rho} + \frac{1}{4}\Big)\gamma_l(\rho). \end{aligned}$$

If we apply this and multiply by $e^{\frac{\rho}{2}}\rho^{1-|l|}$, we obtain

$$\rho\frac{d^2\gamma_l}{d\rho^2}(\rho) + \Big(2|l| + 1 - \rho\Big)\frac{d\gamma_l}{d\rho}(\rho) + \Big(\frac{1}{\lambda} - |l| - \frac{1}{2}\Big)\gamma_l(\rho) = 0. \tag{8}$$

Solutions to (8). We will now construct two linearly independent solutions to this differential equation. To find the first one, we make the Ansatz that for $\rho > 0$, we can write

$\gamma_l(\rho)$ as a power series $\sum_{m=0}^{\infty} a_m \rho^m$ for certain coefficients $a_m \in \mathbf{C}$. If we formally insert this series into (8) and interchange differentiation and summation, then we obtain

$$\begin{aligned} 0 &= \sum_{m=0}^{\infty} a_m \Big(m(m-1)\rho^{m-1} + m(2|l|+1)\rho^{m-1} + \big(-m + \frac{1}{\lambda} - |l| - \frac{1}{2}\big)\rho^m \Big) \qquad (9) \\ &= \sum_{m=1}^{\infty} \Big(a_m\big(m^2 + 2|l|m\big) - a_{m-1}\big(m + |l| - \frac{1}{\lambda} - \frac{1}{2}\big)\Big)\rho^{m-1}. \end{aligned}$$

The identity principle implies that the coefficients on the right-hand side of (9) are all zero, i.e.,

$$a_m = \frac{m + |l| - \frac{1}{\lambda} - \frac{1}{2}}{m^2 + 2|l|m}\, a_{m-1} \qquad (m \in \mathbf{N}). \tag{10}$$

This relation uniquely determines the a_m for $m \geq 1$ in terms of a_0. We choose $a_0 = 1$. Then

$$a_m = \left(\prod_{k=1}^{m} \frac{k + |l| - \frac{1}{\lambda} - \frac{1}{2}}{k^2 + 2|l|k} \right). \tag{11}$$

Note that if $a_m = 0$ for some $m \in \mathbf{N}$, then $a_{m+j} = 0$ for all $j \in \mathbf{N}$, and $\sum_{m=0}^{\infty} a_m \rho^m$ is a finite sum. Otherwise

$$\lim_{m\to\infty} \frac{a_m}{a_{m-1}} = \lim_{m\to\infty} \frac{m + |l| - \frac{1}{\lambda} - \frac{1}{2}}{m^2 + 2|l|m} = 0,$$

and the radius of convergence of the series $\gamma_{l,1}(\rho) = \sum_{m=0}^{\infty} a_m \rho^m$ is infinite. In any case the sum defines a solution of (8) on $\mathbf{R}$.

The linear equation (8) is of order 2, hence it has a 2-dimensional solution space. A solution $\gamma_{l,2}$, which is linearly independent of $\gamma_{l,1}$, can be found by an Ansatz that it has the form

$$\gamma_{l,2}(\rho) = c \ln(\rho)\gamma_{l,1} + \sum_{m=-2|l|}^{\infty} b_m \rho^m, \tag{12}$$

for some constant c and coefficients b_m. However, this solution is unbounded for $\rho \to 0$, and it will soon be discarded. Since we have found two linearly independent solutions to the second order linear differential equation (8), any other solution on $\mathbf{R}_{>0}$ is a linear combination of these two.

Behavior of the solutions. The function ψ is by assumption bounded. Therefore

$$|c_l(\rho)| = \left| \frac{1}{2\pi} \int_{-\pi}^{\pi} \psi \circ \Phi(\rho,\theta) e^{-il\theta}\, d\theta \right| \leq \frac{1}{2\pi} \int_{-\pi}^{\pi} |\psi \circ \Phi(\rho,\theta)|\, d\theta \leq \sup|\psi|.$$

Hence the c_l are bounded functions. Furthermore, they are linear combinations

$$c_l(\rho) = C_1 e^{-\frac{\rho}{2}} \rho^{|l|} \gamma_{l,1}(\rho) + C_2 e^{-\frac{\rho}{2}} \rho^{|l|} \gamma_{l,2}(\rho) \qquad (\rho \in \mathbf{R}_{>0}).$$

It follow that c_l is bounded if and only if $C_2 = 0$.

Notice that for sufficiently large m the expression $m + |l| - \frac{1}{\lambda} - \frac{1}{2}$ is strictly positive. Therefore, for those m the a_m are either all non-negative or all non-positive. Moreover,

$$\frac{m + |l| - \frac{1}{\lambda} - \frac{1}{2}}{m^2 + 2|l|m}$$

behaves like $\frac{1}{m}$ for large m, hence it follows from (10) that $|a_m| \geq \frac{1}{2m}|a_{m-1}|$ for sufficiently large m. Since a_m and a_{m-1} carry the same sign (or are both zero) for sufficiently large m, we have the three possibilities, $a_m = a_{m-1} = 0$, $a_m \geq \frac{1}{2m}a_{m-1} > 0$, or $a_m \leq \frac{1}{2m}a_{m-1} < 0$ for such m. It follows that there are the possibilities:

- there exists a m_0 such that $a_m = 0$ for $m \geq m_0$.
- there exists a m_0 and a constant $c > 0$ such that $a_m > \frac{c}{2^m m!}$ for $m \geq m_0$
- there exists a m_0 and a constant $c > 0$ such that $a_m < \frac{-c}{2^m m!}$ for $m \geq m_0$.

We will now exclude the last two cases. They both imply

$$\begin{aligned}
|\sum_{m=0}^{\infty} a_m \rho^m| &\geq |\sum_{m=m_0}^{\infty} a_m \rho^m| - \sum_{m=0}^{m_0-1} \frac{1}{2^m m!}|a_m|\rho^m \\
&\geq c \sum_{m=m_0}^{\infty} \frac{1}{2^m m!}\rho^m - \sum_{m=0}^{m_0-1} \frac{1}{2^m m!}|a_m|\rho^m \\
&= c\sum_{m=0}^{\infty} \frac{1}{2^m m!}\rho^m - \sum_{m=0}^{m_0-1} \frac{1}{2^m m!}(c + |a_m|)\rho^m = ce^{\frac{\rho}{2}} - P(\rho)
\end{aligned}$$

with a polynomial P. Since the exponential function dominates the polynomial for ρ sufficiently large, we conclude that there exists $c_1 > 0$ and $\rho_0 > 0$ such that

$$|\sum_{m=0}^{\infty} a_m \rho^m| \geq c_1 e^{\frac{\rho}{2}}$$

for all $\rho \geq \rho_0$. Hence

$$|c_l(\rho)| = |C_1|e^{-\frac{\rho}{2}}\rho^{|l|}|\sum_{m=0}^{\infty} a_m \rho^m| \geq c_1|C_1|\,\rho^{|l|}. \qquad (\rho \in \mathbf{R}_{>0}).$$

In particular it follows that in that case $\int_{\mathbf{R}_{>0}} \rho|c_l(\rho)|^2\,d\rho$ is infinite. By the Plancherel formula for the fourier series $\sum_l c_l(\rho)e^{il\theta}$,

$$|c_l(\rho)|^2 \leq \sum_{l\in\mathbf{Z}} |c_l(\rho)|^2 = \int_{\theta\in(-\pi,\pi)} |\phi(\rho,\theta)|^2\,d\theta$$

and hence

$$\int_{\rho\in\mathbf{R}_{>0}} \rho|c_l(\rho)|^2\,d\rho \leq \int_{\rho\in\mathbf{R}_{>0}} \int_{\theta\in(-\pi,\pi)} |\phi(\rho,\theta)|^2\,d\theta\,\rho\,d\rho = \lambda^2 \int_{\mathbf{R}^2} |\psi(x)|^2\,dx,$$

which is finite. This is a contradiction, and the last mentioned cases have been excluded.

We conclude that $a_m = 0$ for sufficiently large m, or equivalently γ_l is a polynomial. These polynomials are called *associated Laguerre polynomials*. Note that if γ_l is a polynomial, then

$$\int_{\rho\in\mathbf{R}_{>0}} \rho|e^{-\frac{\rho}{2}}\rho^{|l|}\gamma_l(\rho)|^2\,d\rho < \infty$$

so that the contradiction of before is not reached in this case.

Quantization of energy. Since the power series has to break off, it follows from (10) that if c_l is non-zero, then $m_1 + |l| - \frac{1}{\lambda} - \frac{1}{2} = 0$ for some $m_1 \geq 1$. Equivalently,

$$E = -(\frac{\lambda}{2})^2 = \frac{-1}{(2m_1 + 2|l| - 1)^2}$$

Since $m_1 + |l| \in \mathbf{N}$, this means that not all negative real numbers are eigenvalues. Let $n = m_1 + |l| - 1$, then $n \in \mathbf{Z}_{\geq 0}$ and

$$E_n = \frac{-1}{(2n+1)^2}.$$

Since the set of eigenvalues is discrete, and this set is the set of all negative values that can occur as the possible outcomes of energy measurements, the energy of the hydrogen atom is said to be *quantized*.

Associated Laguerre polynomials and eigenfunctions Let α and β be non-negative integers. The unique solution $L = L_\alpha^\beta$ of

$$x\frac{d^2L}{dx^2} + (\beta + 1 - x)\frac{dL}{dx} + \alpha L = 0 \tag{13}$$

that is polynomial and satisfies the initial condition $L(0) = \binom{\alpha+\beta}{\alpha}$, is called the associated Laguerre polynomial of degree α and parameter β. An alternative description of these polynomials is given by the *Rodrigues' formula*

$$L_\alpha^\beta(x) = \frac{x^{-\beta}e^x}{\alpha!}\frac{d^\alpha}{dx^\alpha}(e^{-x}x^{\alpha+\beta})$$

From the previous discussion and comparison of (8) with (13) it follows that the eigenfunctions of H with eigenvalue E_n are linear combinations of the functions $\psi_{n,l}$ given by

$$\psi_{n,l}\circ\Phi(\rho,\theta) = \frac{1}{N_{n,l}}e^{il\theta}e^{-\frac{\rho}{2}}\rho^{|l|}L_{n-|l|}^{2|l|},$$

with l an integer between $-n$ and n and $N_{n,l}$ chosen such that $\int_{\mathbf{R}^2}|\psi_{n,l}(x)|^2\,dx = 1$. If $\psi = \sum_{l=-n}^n d_l\psi_{n,l}$ and $\sum_{l=-n}^n |d_l|^2 = 1$, then ψ satisfies (3), hence ψ is an eigenfunction of H with eigenvalue E_n. In fact every eigenfunction with eigenvalue E_n is of this form (the eigenspace is $2n+1$-dimensional, and the functions $\psi_{n,l}$ form an orthonormal basis).

Having determined the eigenfunctions for H, the next step is to solve (1) with a prescribed initial value $\Psi(0,x) = \psi(x)$ by the Ansatz that $\Psi(t,x)$ is a sum of eigenfunctions for H with t-dependent coefficients. This is done in Exercise 1 below in the case where the sum is finite.

Exercises

Exercise 1. *Assume that* $\psi = \sum_{k=0}^{n} c_k \psi_k$*, where the* $c_k \in \mathbf{C}$ *and the* ψ_k *are eigenfunctions of* H *with eigenvalues* E_k*. Find a solution to the initial value problem given by (1) and*

$$\Psi(0, x) = \psi(x) \qquad (x \in \mathbf{R}^2)$$

in terms of the c_k *and the* ψ_k*.*

Exercise 2. *Use the integral formula for* c_l *to prove that for every* $l \in \mathbf{Z}$ *the function* c_l *is* C^2*. Now use (7) to prove that the* c_l *are in fact* C^∞*. Prove that*

$$\frac{d^k}{d\rho^k}\phi(\rho, \theta) = \sum_{l \in \mathbf{Z}} \frac{d^k}{d\rho^k} c_l(\rho) e^{il\theta}$$

for $k = 1, 2$*.*

Exercise 3. *Use the differential equation and the initial value condition to show that*

$$L_\alpha^\beta(x) = \sum_{m=0}^{\alpha} \frac{(-1)^m}{m!} \binom{\alpha + \beta}{\alpha - m} x^m$$

Use this to prove Rodrigues' formula.

Exercise 4. *Let* $\alpha \in \mathbf{R}$*. Consider the Hermite equation of order* α

$$y'' - 2xy' + 2\alpha y = 0. \tag{14}$$

(a) Find the recursive formula for a power series solution.

(b) Show that the radius of convergence of the power series

$$y_1(x) = 1 + \sum_{n=1}^{\infty} \frac{(-2)^n \prod_{k=0}^{n-1}(\alpha - 2k)}{(2n)!} x^{2n}$$

and

$$y_2(x) = x + \sum_{n=1}^{\infty} \frac{(-2)^n \prod_{k=0}^{n-1}(\alpha - 2k - 1)}{(2n+1)!} x^{2n+1}$$

is infinite. Show that y_1 *and* y_2 *are two solutions and prove that they are linearly independent.*

(c) Show that y_1 *is a polynomial if* α *is a non-negative even integer and* y_2 *is a polynomial if* α *is a positive odd integer.*

The polynomial solutions of (14) of degree n *such that the top coefficient* a_n *equals* 2^n*, are called Hermite polynomials. They occur in quantum physics as the eigenfunctions for the Schrödinger equation of the harmonic oscillator.*