38. **The hydrogen atom, I**

38.1. **The Schrödinger equation.** Let us now apply our knowledge of non-abelian harmonic analysis to solve a basic problem in quantum mechanics – describe the dynamics of the hydrogen atom.

The mechanics of the hydrogen atom is determined by motion of a charged quantum particle (electron) in a rotationally invariant attracting electric field. The potential of such a field is $-\frac{1}{r}$, where $r^2 = x^2 + y^2 + z^2$ (since this theory does not have nontrivial dimensionless quantities, we may choose the units of measurement so that all constants are equal to 1). Thus, the wave function $\psi(x, y, z, t)$ for our particle obeys the **Schrödinger equation**

$$i\partial_t \psi = H\psi,$$

where H is the **quantum Hamiltonian**

$$H := -\frac{1}{2}\Delta - \frac{1}{r},$$

and $\Delta = \partial_x^2 + \partial_y^2 + \partial_z^2$ is the Laplace operator. Recall also that for each t, the function $\psi(-, -, -, t)$ is in $L^2(\mathbb{R}^3)$ and $||\psi|| = 1$. The problem is to solve this equation given the initial value $\psi(x, y, z, 0)$.[17]

The Schrödinger equation can be solved by separation of variables as follows. Suppose we have an orthonormal basis ψ_N of $L^2(\mathbb{R}^3)$ such that $H\psi_N = E_N\psi_N$. Then if

$$\psi(x, y, z, 0) = \sum_N c_N \psi_N(x, y, z)$$

(i.e., $c_N = (\psi, \psi_N)$) then

$$\psi(x, y, z, t) = \sum_N c_N e^{-iE_N t} \psi_N(x, y, z),$$

So our job is to find such basis ψ_N, i.e., diagonalize the self-adjoint operator H.

Note that the operator H is unbounded and defined only on a dense subspace of $L^2(\mathbb{R})$, and although it is symmetric ($(H\psi, \eta) = (\psi, H\eta)$ for compactly supported functions), it is very nontrivial to say what precisely it means that H is self-adjoint. Also, this operator turns out to have both discrete and continuous spectrum, which means that there is actually *no basis* with the desired properties – eigenfunctions of H which lie in $L^2(\mathbb{R}^3)$ span a *proper* closed subspace of this Hilbert space. However, this will not be a problem for our calculation.

[17]Recall that ψ determines the probability $p(U, t)$ to find the electron in a region $U \subset \mathbb{R}^3$ at a time t, which is given by the formula $p(U, t) = \int_U |\psi(x, y, z, t)|^2 dxdydz$.

38.2. **Bound states.** We first focus on **bound states**, i.e., solutions of the **stationary Schrödinger equation**

$$H\psi = E\psi$$

which belong to $L^2(\mathbb{R}^3)$ and thus decay at infinity in the sense of L^2-norm (this is the situation when the electron does not have enough energy to escape from the nucleus, i.e., it is "bound" to it and thus unlikely to be found far from the origin, which explains the terminology). In particular, such eigenfunctions must have negative energy, $E < 0$. To do so, let us utilize the rotational symmetry and write this equation in spherical coordinates. For this we just need to write the Laplacian Δ in spherical coordinates. Let us write $\mathbf{r} = r\mathbf{u}$, where $\mathbf{u} \in S^2$ (i.e., $|\mathbf{u}| = 1$). We have

$$\Delta = \Delta_r + \tfrac{1}{r^2}\Delta_{\rm sph}$$

where

$$\Delta_{\rm sph} = \tfrac{1}{\sin^2\phi}\partial_\theta^2 + \tfrac{1}{\sin\phi}\partial_\phi \sin\phi\partial_\phi$$

is a differential operator on S^2 (the **spherical Laplacian**, or the **Laplace-Beltrami operator**) and

$$\Delta_r = \partial_r^2 + \tfrac{2}{r}\partial_r$$

is the **radial part** of Δ (check it!). So our equation looks like

$$\partial_r^2\psi + \tfrac{2}{r}\partial_r\psi + \tfrac{2}{r}\psi + \tfrac{1}{r^2}\Delta_{\rm sph}\psi = -2E\psi.$$

This equation can be solved by again applying separation of variables. Namely, we look for solutions in the form

$$\psi(r, \mathbf{u}) = f(r)\xi(\mathbf{u}),$$

where

$$\Delta_{\rm sph}\xi + \lambda\xi = 0. \tag{38.1}$$

Then we obtain the following equation for f:

$$f''(r) + \tfrac{2}{r}f'(r) + (\tfrac{2}{r} - \tfrac{\lambda}{r^2} + 2E)f(r) = 0. \tag{38.2}$$

So now we have to solve equation (38.1) and in particular determine which values of λ occur.

To this end, recall that the operator $\Delta_{\rm sph}$ is rotationally invariant, so it preserves the space $L^2_{\rm alg}(S^2)$ of functions on S^2 belonging to finite dimensional representations of $SO(3)$. Moreover, it preserves the decomposition $L^2_{\rm alg}(S^2) = \oplus_{\ell\ge 0} L_{2\ell}$ of this space into irreducible representations of $SO(3)$ (Exercise 35.7(ii)), and on each $L_{2\ell}$ it acts by a certain scalar $-\lambda_\ell$. To compute this scalar, consider the vector Y_ℓ^0 in $L_{2\ell}$ of weight zero. This vector is invariant under $SO(2)$ changing θ, so it depends only on ϕ; in fact, it is a polynomial of degree ℓ in $\cos\phi$: $Y_\ell^0 = P_\ell(\cos\phi)$. Also orthogonality of the decomposition implies that

$$\int_{-1}^{1} P_k(z)P_n(z)dz = 0,\ \ k \neq n.$$

This means that P_n are the **Legendre polynomials**. Also

$$\Delta_{\mathrm{sph}} P_\ell(z) = \partial_z(1-z^2)\partial_z P_\ell(z) = -\lambda_\ell P_\ell(z),$$

which shows (by looking at the leading term) that

$$\lambda_\ell = \ell(\ell+1),\ \ \ell \in \mathbb{Z}_{\geq 0},$$

and the space of solutions of (38.1) with $\lambda = \lambda_\ell$ is $2\ell+1$-dimensional and is isomorphic to $L_{2\ell}$ as an $SO(3)$-module.

Consider now the vector $Y_\ell^m \in L_{2\ell}$ of any integer weight $-\ell \leq m \leq \ell$. We will be interested in these vectors up to scaling. We have

$$Y_\ell^m(\phi,\theta) = e^{im\theta}P_\ell^m(\cos\phi),$$

where P_ℓ^m are certain functions. These functions are called **spherical harmonics**. Moreover, it follows from representation theory of $SO(3)$ that Y_ℓ^m are trigonometric polynomials which are even for even m and odd for odd m (check it!), so $P_\ell^m(z)$ are polynomials in z when m is even and are of the form $(1-z^2)^{1/2}$ times a polynomial in z when m is odd.

Let us calculate the functions P_ℓ^m. Since they are eigenfunctions of the spherical Laplacian, we obtain that P_ℓ^m satisfy the **Legendre differential equation**

$$\partial_z(1-z^2)\partial_z P - \frac{m^2}{1-z^2}P + \ell(\ell+1)P = 0.$$

Exercise 38.1. Show that this equation has a unique up to scaling continuous solution on $[-1,1]$ when $-\ell \leq m \leq \ell$ and m is an integer, given by the formula

$$P_\ell^m(z) = (1-z^2)^{m/2}\partial_z^{\ell+m}(1-z^2)^\ell.$$

These functions are called **associated Legendre polynomials** (even though they are not quite polynomials when m is odd).

Now we can return to equation (38.2). It now has the form

$$f''(r) + \tfrac{2}{r}f'(r) + (\tfrac{2}{r} - \tfrac{\ell(\ell+1)}{r^2} + 2E)f(r) = 0. \tag{38.3}$$

To simplify this equation, write

$$f(r) = r^\ell e^{-\frac{r}{n}}h(\tfrac{2r}{n}),$$

where n can be chosen at our convenience. Then for h we get the equation

$$\rho h''(\rho) + (2\ell + 2 - \rho)h'(\rho) + (n - \ell - 1 + \tfrac{1}{4}(1 + 2En^2)\rho)h(\rho) = 0.$$

We see that the equation simplifies when $n = \frac{1}{\sqrt{-2E}}$, i.e., $E = -\frac{1}{2n^2}$, so let us make this choice. Then we have

$$\rho h''(\rho) + (2\ell + 2 - \rho)h'(\rho) + (n - \ell - 1)h(\rho) = 0,$$

which is the **generalized Laguerre equation**. Moreover, we have $||\psi||^2 < \infty$, which translates to

$$\int_0^\infty \rho^{2\ell+2} e^{-\rho} |h(\rho)|^2 d\rho < \infty \tag{38.4}$$

(the factor ρ^2 comes from the Jacobian of the spherical coordinates).

How do solutions of the generalized Laguerre equation behave at $\rho = 0$? Let us look for a solution of the form $\rho^s(1 + o(1))$. The characteristic equation for s then has the form

$$s(s + 2\ell + 1) = 0,$$

which gives $s = 0$ or $s = -2\ell - 1$. Thus, for $\ell \geq 1$ the solution $\rho^{-2\ell-1}(1 + o(1))$ does not satisfy (38.4), so we are left with a unique solution $h_n(\rho)$ which is regular at $\rho = 0$ and $h_n(0) = 1$. On the other hand, if $\ell = 0$, the solution $\rho^{-1}(1+o(1))$, even though it satisfies (38.4), gives rise to a rotationally invariant function $\psi \sim \frac{1}{r}$ as $r \to 0$, so we don't get $H\psi = E\psi$, but rather get $H\psi = E\psi + C\delta_0$, where δ_0 is the delta function concentrated at zero. So ψ does not really satisfy the stationary Schrödinger equation as a distribution and has to be discarded, leaving us, as before, with the unique solution $h_n(\rho)$ such that $h_n(0) = 1$.

Using the power series method, we obtain

$$h_n(\rho) = \sum_{k=0}^\infty \frac{(1 + \ell - n)...(k + \ell - n)}{(2\ell + 2)...(2\ell + 1 + k)} \frac{\rho^k}{k!}.$$

It is easy to see that this series converges for all ρ and

$$\lim_{\rho \to +\infty} \frac{\log h_n(\rho)}{\rho} = 1$$

unless the series terminates, which happens iff $n - \ell - 1$ is a non-negative integer. (To check the latter, show that the Taylor coefficients a_k of h_n are bounded below by $\frac{1}{(k+N)!}$ for some N). So it fails (38.4) unless $n-\ell-1 \in \mathbb{Z}_{\geq 0}$. In this case,

$$h_n(\rho) = \sum_{k=0}^{n-\ell-1} \frac{(1+\ell-n)...(k+\ell-n)}{(2\ell+2)...(2\ell+1+k)} \frac{\rho^k}{k!} = L_{n-\ell-1}^{2\ell+1}(\rho),$$

the $n-\ell-1$-th **generalized Laguerre polynomial** with parameter $\alpha = 2\ell+1$, a polynomial of degree $n-\ell-1$. Namely, the generalized Laguerre polynomials L_N^α are defined by the formula

$$L_N^\alpha(\rho) := \sum_{k=0}^{N} (-1)^N \frac{N...(N-k+1)}{(\alpha+1)...(\alpha+k)} \frac{\rho^k}{k!}.$$

Thus we obtain the following theorem.

Theorem 38.2. *The bound states of the hydrogen atom, up to scaling, are*

$$\psi_{n\ell m}(r,\phi,\theta) = r^\ell e^{-\frac{r}{n}} L_{n-\ell-1}^{2\ell+1}(\tfrac{2r}{n}) Y_\ell^m(\theta,\phi),$$

where $Y_\ell^m(\theta,\phi) = e^{im\theta} P_\ell^m(\phi)$ are spherical harmonics, where $n \in \mathbb{Z}_{>0}$, ℓ an integer between 0 and $n-1$, and m is an integer between ℓ and $-\ell$. The energy of the state $\psi_{n\ell m}$ is $E_n = -\frac{1}{2n^2}$.

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