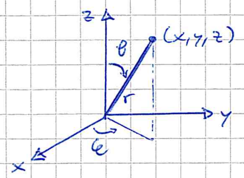
5.3 Spherical coordinates

The hydrogen atom is obviously spherically symmetric and it is natural to use spherical coordinates.



$$x = r \sin\theta \cos\varphi$$
$$y = r \sin\theta \sin\varphi$$
$$z = r \cos\theta$$

The change of coordinates can be viewed as an isometry between $L^2(\mathbb{R}^3)$ and $L^2([0,\infty) \times [0,\pi] \times S^1)$. We use the notation $F(x,y,z)$ or $F(x_1,x_2,x_3)$ for a function in $L^2(\mathbb{R}^3)$, and $f(r,\theta,\varphi)$ for the corresponding function in $L^2([0,\infty) \times [0,\pi] \times S^1)$. The first step is to find the expression for the Laplacian in spherical coordinates.

Exercise 12. Show that

$$\Delta = \Delta_r + \frac{1}{r^2} \Delta_{sph},$$

where the radial Laplacian is

$$\Delta_r = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}$$

and the spherical Laplacian, or Laplace-Beltrami operator, is

$$\Delta_{sph} = \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2}.$$

In other words, all functions (that are smooth enough) satisfy

$$\Delta F(x_1,x_2,x_3) = \left(\Delta_r + \tfrac{1}{r^2} \Delta_{sph}\right) f(r,\theta,\varphi).$$

We describe without proofs the main facts about the Laplace-Beltrami operator in $L^2(S^2)$. Its eigenvectors are the spherical harmonics

$$Y_\ell^k(\theta,\varphi) = c_{\ell k} P_\ell^{|k|}(\cos\theta)\, e^{ik\varphi}$$

where $\ell = 0,1,2,\dots$ and $k \in \{-\ell,\dots,\ell\}$. $c_{k\ell}$ is a normalisation constant and P_ℓ^k are Legendre polynomials,

$$P_\ell^k(u) = \frac{(1-u^2)^{\frac{k}{2}}}{2^\ell\, \ell!} \frac{d^{\ell+k}}{du^{\ell+k}} (u^2-1)^\ell.$$

The functions $\{Y_\ell^k\}$ form an orthonormal basis of $L^2(S^2)$ and they satisfy

$$-\Delta_{sph} Y_\ell^k = \ell(\ell+1) Y_\ell^k.$$

Exercise 13. If you are not afraid of tedious calculations, check that

(a) $(Y_\ell^k, Y_{\ell'}^{k'}) = \delta_{\ell\ell'} \delta_{kk'}$, where $(Y_\ell^k, Y_{\ell'}^{k'}) = \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\varphi\, \overline{Y_\ell^k(\theta,\varphi)}\, Y_{\ell'}^{k'}(\theta,\varphi)$.

(b) $-\Delta_{sph} Y_\ell^k = \ell(\ell+1) Y_\ell^k$.

Remark: Let $L = X \times P$ denote the angular momentum operator. Then $L^2 Y_\ell^k = \ell(\ell+1) Y_\ell^k$ and $L_3 Y_\ell^k = k Y_\ell^k$.

5.4 The radial equation and its solution

The eigenvalue equation in spherical coordinates is given by

$$\left(-\Delta_r - \frac{1}{r^2}\Delta_{sph} - \frac{1}{r}\right) f(r,\theta,\varphi) = E\, f(r,\theta,\varphi).$$

We are looking for functions of the form $f(r,\theta,\varphi) = R(r)\, A(\theta,\varphi)$. (This is the method of "separation of variables"). Then $A(\theta,\varphi)$ must be a spherical harmonic Y_ℓ^m with eigenvalue $\ell(\ell+1)$, and we get the differential equation for the radial coordinate:

$$\left(-\Delta_r + \frac{\ell(\ell+1)}{r^2} - \frac{1}{r}\right) R(r) = E\, R(r).$$

For r very large the equation is approximately $-\frac{\partial^2}{\partial r^2} R(r) = E R(r)$, whose solutions behave like $e^{i\sqrt{E}r}$ if $E>0$ and $e^{\pm\sqrt{-E}r}$ if $E<0$. One can construct a sequence of normalised functions ψ_n that are approximately equal to $e^{i\sqrt{E}r}$ (for $E>0$) and that "escapes to infinity", and such that

$$\| (-\Delta - \tfrac{1}{r} - E)\psi_n \| \longrightarrow 0$$

as $n\to\infty$. Thus any $E>0$ belongs to the spectrum of H. It is possible to show that $\sigma_c(H) = [0,\infty)$.

Eigenvalues are possible for $E<0$ and the eigenvectors should behave as $e^{-\sqrt{-E}r}$ for large r. It is useful to introduce the fct $F(x)$ by

$$R(r) = 2\sqrt{-E}\; x^\ell\, e^{-\frac{1}{2}x} F(x),$$

with $x = 2\sqrt{-E}\,r$.

The equation becomes, with $n = \frac{1}{2\sqrt{-E}}$,

$$\left[x^2 \frac{d^2}{dx^2} + (2\ell+2-x)\frac{d}{dx} - (\ell+1-n) \right] F(x) = 0.$$

It can be checked that only one solution is finite at the origin, the others have singularity $\frac{1}{x^{2\ell+1}}$. Assume that F has the Taylor expansion

$$F(x) = \sum_{k\geq 0} a_k \frac{x^k}{k!}.$$

One can find the coefficients recursively, finding

$$a_k = \frac{(\ell-n+k)(\ell-n+k-1)\dots(\ell-n+1)}{(2\ell+1+k)(2\ell+1+k-1)\dots(2\ell+2)}.$$

If $n\in\{\ell+1, \ell+2, \dots\}$, we have $a_k = 0$ $\forall\, k\geq n-\ell$ and $F(x)$ is a polynomial. Let us denote it $F_{n\ell}(x)$. Otherwise, we have $a_k \sim k^{-n-\ell}$ for large k and $F(x)\sim e^x$. Then $R(r)\sim e^{\frac{1}{2}x}$ and this cannot be eigenvector. It turns out that we have found all eigenvectors.

Exercise 14. Write down the eigenvector with lowest eigenvalue explicitly. Check that it satisfies the eigenvalue equation.