January 23

Energy Spectrum: Hydrogen Atom

In the previous lecture, I gave you a general analysis of the eigenfunctions of the Schrödinger equation for a rotationally invariant potential in three dimensions. The time-independent Schrödinger equation for this problem is

$$E\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\psi$$

I showed that the eigenfunctions can be written in the form

$$\psi(r,\theta,\phi) = \psi_{j\ell}(r)\, Y_{\ell m}(\theta,\phi)$$

where $Y_{\ell m}(\theta,\phi)$ is a *spherical harmonic*, defined in the previous lecture, and $\psi_{j\ell}(r)$ is an eigenfunction of the problem

$$E_{j\ell}\,\psi_{j\ell}(r) = \left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + V(r) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}\right)\psi_{j\ell}(r)$$

In this lecture, I will study the solutions to this radial equation.

There is a useful trick to make an intuitive survey of the solutions to this equation. Introduce a new function $\eta(r)$ by writing

$$\psi(r) = \frac{\eta(r)}{r}$$

Since

$$\frac{d}{dr}\psi = \frac{\eta'}{r} - \frac{\eta}{r^2}$$

$$r^2 \frac{d}{dr}\psi = r\eta' - \eta$$

we find

$$\frac{1}{dr} r^2 \frac{d}{dr}\psi = r\eta'' + \eta' - \eta' = r\eta'' = r^2 \frac{\eta''}{r}$$

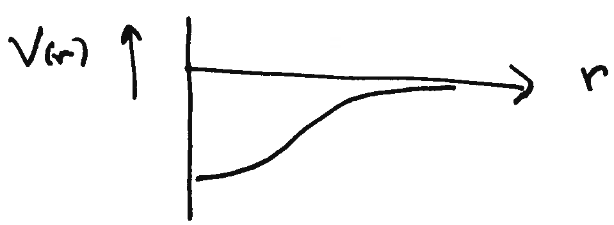
Then, if $\psi(r)$ obeys the original radial equation, $\eta(r)$ obeys

$$E\,\eta(r) = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} \right)\eta$$

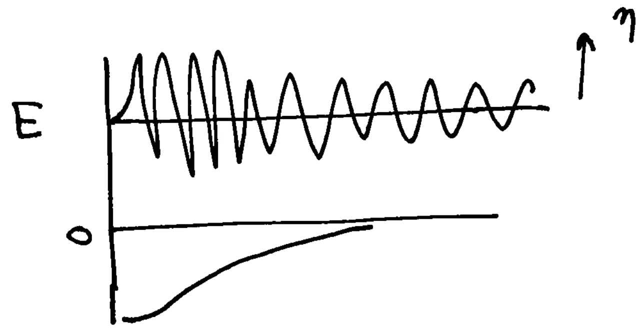
Then is, $\eta(r)$ obeys a one-dimensional Schrödinger equation with the original potential plus the angular momentum barrier. To give a regular solution, $\eta(r)$ must obey the boundary condition

$$\eta(r) = 0 \quad \text{at} \quad r = 0$$

We can now use our intuition from one dimension to visualize the form of the radial wavefunctions and their energy spectrum in the three-dimensional problem. Consider an attractive potential that goes to zero at infinity, of the form



For $\ell = 0$, this problem will have a continuous spectrum for $E > 0$



with the solution behaving asymptotically as

$$\eta_E(r) \sim \sin(kr + \phi)$$

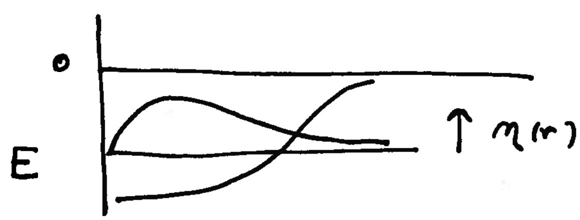
where

$$k = \left(\frac{2mE}{\hbar}\right)^{\frac{1}{2}}$$

Then

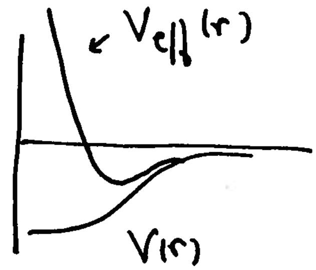
$$\psi_E(r) \sim \frac{\sin(kr + \phi)}{r}$$

For $E < 0$, there may also be discrete eigenfunctions



called *bound states* of the potential. For $\ell > 0$, the potential to be used in this analysis is

$$V_{eff} = V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}$$



but the general conclusions still hold. We find a continuous spectrum for $E > 0$ with, still,

$$\psi_E(r) \sim \frac{\sin(kr + \phi)}{r}$$

and, possibly, bound states at discrete energies $E < 0$.

An important reference case is that of zero potential

$$V(r) = 0$$

Then the radial eigenfunction equation is

$$\frac{2m}{\hbar^2} E_{j\ell} \psi_{j\ell} = \left[-\frac{1}{r^2}\frac{d}{dr} r^2 \frac{d}{dr} + \frac{\ell(\ell+1)}{r^2} \right] \psi_{j\ell}$$

If we define

$$k_{j\ell} = \left(\frac{2mE_{j\ell}}{\hbar^2}\right)^{1/2} \qquad z = k_{j\ell} r$$

as we did for the corresponding problem in two dimensions, this equation becomes independent of E_{jm} and takes a standard form

$$\left[z^2 \frac{d^2}{dz^2} + 2z \frac{d}{dz} + z^2 - \ell(\ell+1) \right] \psi_{j\ell}(z) = 0$$

This equation is very close but not identical to Bessel's equation. The solutions are called *spherical Bessel functions*. The solution regular at $z = 0$ is called $j_\ell(z)$; the second, independent, solution is $y_\ell(z)$. As $z \to 0$, these functions have the asymptotic behavior

$$j_\ell(z) \approx \frac{z^\ell}{(2\ell+1)!!} + \cdots \qquad y_\ell(z) = -\frac{(2\ell-1)!!}{z^{\ell+1}} + \cdots$$

where

$$(2\ell+1)!! = 1 \cdot 3 \cdot 5 \cdots (2\ell+1)$$

These spherical Bessel functions are closely related to ordinary Bessel functions of half-integer degree; explicitly,

$$j_\ell(z) = \sqrt{\frac{\pi}{2z}}\, J_{\ell+\frac{1}{2}}(z)$$

In principle, we could go to our handbooks of special functions to learn more properties of the spherical Bessel functions, but, in fact, it is not necessary. Consider first the case $\ell = 0$. Let

$$\psi(z) = \frac{\eta(z)}{z}$$

Then, following the steps above, the equation for $\eta(z)$ is

$$\left(\frac{d^2}{dz^2} + 1 \right) \eta = 0$$

so

$$\eta = \sin z \quad \text{or} \quad \cos z$$

This gives for the spherical Bessel functions of degree 0

$$j_0(z) = \frac{\sin z}{z} \qquad y_0(z) = -\frac{\cos z}{z}$$

We can look for further solutions of this type. For example, if

$$\eta = -z \frac{d}{dz}\left(\frac{\sin z}{z} \right) = \frac{\sin z}{z} - \cos z$$

then

$$\eta' = -\frac{\sin z}{z^2} + \frac{\cos z}{z} - \sin z$$

$$\eta'' = 2\frac{\sin z}{z^3} - \frac{\cos z}{z^2} - \frac{\cos z}{z^2} - \frac{\sin z}{z} + \cos z$$
$$= \left(-1 + \frac{2}{z^2} \right) \eta$$

So this is a solution to the problem with a repulsive barrier with coefficient

$$\ell = 1 \qquad \ell(\ell+1) = 2$$

Rayleigh showed that this trick works quite generally. He found the ℓth spherical Bessel function to be given explicitly by

$$j_\ell(z) = z^\ell \left(-\frac{1}{z}\frac{d}{dz}\right)^\ell \frac{\sin z}{z}$$

This special function is then, surprisingly, given in explicit form as a combination of elementary functions.

The general eigenfunction of the Schrödinger equation in three dimensions with $V(r) = 0$ is then

$$\psi_{j\ell m}(r,\theta,\phi) = N_{j\ell}\, j_\ell(k_{j\ell} r)\, Y_{\ell m}(\theta,\phi)$$

The solutions exists only for $E > 0$ and, in that domain, can be found for every value of the energy

$$E_{j\ell} = \frac{\hbar^2 k_{j\ell}^2}{2m}$$

Now we turn to the simplest example of a realistic atom, the Hydrogen atom. For simplicity, I will consider the problem of an electron of mass m and charge $(-e)$ in the electrostatic field of a nucleus approximated as a very heavy point charge with charge $(+Ze)$ The potential is

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}$$

The radial Schrödinger equation is

$$E_{jl}\psi_{jl}(r) = \left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2 l(l+1)}{2mr^2}\right]\psi_{jl}(r)$$

The problem is obviously one of practical importance. We will see in the next lecture that the solution provides the paradigm for the structure of atoms and the implications of this structure for chemistry. It is quite a miracle that the problem can be solved exactly. The solution carries with it a certain amount of romance. Schrödinger was, by this time in his life, a middle-aged professor in a marriage carried out, in the Viennese style, with affairs on both sides. At Christmas, 1925, Schrödinger wrote to "an old girlfriend in Vienna" to meet him at an Alpine hideaway, the Villa Herwig in Arosa. Schrödinger's biographer writes: "Like the dark lady who inspired Shakespeare's sonnets, the lady of Arosa may remain forever mysterious ... Whoever might have been his inspiration, the increase in Erwin's powers was dramatic, and he began a twelve-month period of sustained creative activity that is without parallel in the history of science."

Now let's look into that solution. It is very useful to begin by making the equation dimensionless. We are interested in bound state solutions, $E < 0$, so write

$$\varkappa = \left(-\frac{2mE}{\hbar^2}\right)^{1/2}$$

Then

$$-\varkappa^2\psi_{jl} = \left[-\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - 2\left(\frac{mZe^2}{4\pi\epsilon_0\hbar^2}\right)\frac{1}{r} + \frac{l(l+1)}{r^2}\right]\psi_{jl}$$

or

$$\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + 2\left(\frac{Zme^2}{4\pi\epsilon_0\hbar^2}\right)\frac{1}{r} - \varkappa^2 - \frac{l(l+1)}{r^2}\right]\psi_{jl} = 0$$

It is useful to define the quantity

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{e^2 m}$$

called the *Bohr radius*. It has the dimensions of m and the value

$$a_0 = 0.529 \times 10^{-10}\,\mathrm{m} \simeq \frac{1}{2}\,\mathring{A}$$

This will turn out to be the natural size scale of atoms. A way to represent the Bohr radius is to begin from the dimensionless representation of the electric charge

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} = [137.036]^{-1}$$

called the *fine structure constant*, and the length

$$\lambda_e = \frac{\hbar}{mc} = 3.862 \times 10^{-13}\,\mathrm{m}$$

called the *electron Compton wavelength*. Here c is the speed of light. The Compton wavelength is defined as the de Broglie wavelength/2π for a particle whose momentum is mc. These combine to form

$$a_0 = \frac{1}{\alpha} \lambda_e$$

We might also guess that the scale of energies of the Hydrogen atom problem is

$$\frac{e^2}{4\pi\epsilon_0}\frac{1}{a_0} = \left(\frac{e^2}{4\pi\epsilon_0 \hbar c}\right)\hbar c \cdot \alpha \frac{mc}{\hbar} = \alpha^2 mc^2$$

Indeed, we will see in a moment that the energy of the lowest discrete energy of the Hydrogen atom problem is (for $Z=1$)

$$E_1 = -Ry$$

where

$$Ry = \frac{1}{2}\alpha^2 mc^2 = \frac{e^2}{8\pi\epsilon_0 a_0}$$

Ry is called the Rydberg energy; its value is

$$Ry = 13.6\ eV$$

Now set

$$\rho = r/a_0 \qquad \kappa^2 = \frac{k^2}{a_0^2} \qquad \left(\begin{array}{l} \text{for } Z>1 \\ \text{use } \quad a_Z = \dfrac{a_0}{Z} \end{array}\right)$$

In this notation, the $\psi_{j\ell}$ equation reads

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} + \frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2} - k^2\right]\psi_{j\ell}(\rho) = 0$$

Asymptotically as $\rho \to \infty$, this equation becomes

$$\left[\frac{d^2}{d\rho^2} - k^2 \right] \psi_{jl}(\rho) = 0$$

so

$$\psi_{jl} \sim e^{-k\rho} \quad \text{or} \quad e^{+k\rho}$$

For a solution with correct boundary conditions at infinity, only the decreasing exponential solution is acceptable.

For the harmonic oscillator, we saw that the simple asymptotic exponential actually gave an exact solution. Let's try that here. Plugging

$$\psi = e^{-k\rho}$$

into the radial equation, we find

$$k^2 - 2\frac{k}{\rho} + \frac{2}{\rho} - \frac{l(l+1)}{\rho^2} - k^2 = 0$$

There is one solution

$$k = 1 \qquad l = 0$$

The corresponding energy is

$$E = -\frac{\hbar^2 \cdot 1}{2ma_0^2} = -\frac{\hbar^2}{2m}\alpha^2\left(\frac{mc}{\hbar}\right)^2$$

which is just

$$E = -\frac{1}{2}\alpha^2 mc^2 = -R_y = -13.6\,eV$$

as I quoted above.

A more general set of solutions might be of the form

$$\psi = \rho^{n-1} e^{-k\rho}$$

Plugging this expression into the radial equation gives

$$k^2\rho^{n-1} - 2(n-1)k\rho^{n-2} + (n-1)(n-2)\rho^{n-3}$$
$$- 2k\rho^{n-2} + 2(n-1)\rho^{n-3} + 2\rho^{n-2} - l(l+1)\rho^{n-3} - k^2\rho^{n-1} = 0$$

The term with ρ^{n-2} is

$$(-2nk + 2)\rho^{n-2} = 0$$

which implies

$$k = \frac{1}{n}$$

The term with ρ^{n-3} is

$$\left[(n-1)(n-2) + 2(n-1) - \ell(\ell+1) \right] \rho^{n-3} = 0$$

or

$$(n-1)\cdot n - \ell(\ell+1) = 0$$

so this expression is a solution for

$$\ell = (n-1) \qquad n = 1, 2, 3, \cdots$$

The explicit form of the solution is

$$\psi(r,\theta,\phi) = N \cdot r^{n-1} e^{-r/na_0} Y_{\ell m}(\theta,\phi)$$

with energy

$$E = -\frac{\hbar^2}{2m\, n^2 a_0^2} = -R_y \cdot \frac{1}{n^2}$$

We are now getting close to the complete picture. The general bound state eigenfunction will be of the form

$$\psi_{n\ell}(\rho) = F_n^{\ell}(\rho)\, e^{-k\rho}$$

If we are lucky, $F_n^\ell(\rho)$ will be a polynomial. This idea turns out to be correct. If the highest degree of the polynomial is $(n-1)$,

$$F_n^\ell(\rho) = \rho^{n-1} + a\rho^{n-2} + \cdots$$

then the above analysis implies

$$k = \frac{1}{n} \qquad E = -R_y \cdot \frac{1}{n^2}$$

Similarly, if the lowest power of ρ is ρ^k, the terms of lowest power in the radial equation will be

$$k(k-1)\rho^{k-2} + 2k\rho^{k-2} - \ell(\ell+1)\rho^{k-2} = 0$$

that is

$$k(k+1) - \ell(\ell+1) = 0$$

Since $k > 0$, we find

$$k = \ell$$

Finally, we have

$$\psi_{n\ell}(\rho) = \rho^{\ell} f_n^{\ell}(\rho)\, e^{-\rho/n}$$

where $f_n^\ell(\rho)$ is a polynomial of degree $(n-\ell-1)$.

All that remains is to find these polynomials explicitly, and to bring them into a form that gives them in terms of standard special functions. I will begin with the case $\ell = 0$. The radial equation for $f_n^0(\rho)$ is

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} - \frac{2}{\rho} - \frac{1}{n^2}\right] f_n^{\ell=0} e^{-\rho/n} = 0$$

where I have put

$$k = \frac{1}{n}$$

already. Differentiating, we find

$$\frac{d^2}{d\rho^2} f_n^0 - \frac{2}{n}\frac{d}{d\rho} f_n^0 + \cancel{\frac{1}{n^2} f_n^0} + \frac{2}{\rho}\frac{d}{d\rho} f_n^0 - \frac{2}{n\rho} f_n^0$$
$$+ \frac{2}{\rho} f_n^0 - \cancel{\frac{1}{n^2} f_n^0} = 0$$

or

$$\frac{d^2}{d\rho^2} f_n^0 + \left(\frac{2}{\rho} - \frac{2}{n}\right)\frac{d}{d\rho} f_n^0 + \frac{2}{\rho}\left(1 - \frac{1}{n}\right) f_n^0 = 0$$

It is convenient to set

$$z = \frac{2\rho}{n} \qquad \frac{d}{d\rho} = \frac{2}{n}\frac{d}{dz}$$

and let $f_n' = (d/dz)f_n$. Then

$$\left(\frac{2}{n}\right)^2 f_n^{0\,\prime\prime} + \left(\frac{2}{n}\right)^2\left(\frac{2}{z} - 1\right) f_n^{0\,\prime} + \left(\frac{2}{n}\right)^2 (n-1) f_n^0 = 0$$

or, finally,

$$z f_n^{0\,\prime\prime} + (2-z) f_n^{0\,\prime} + (n-1) f_n^0 = 0$$

If we try a solution

$$f_n^0 = z^{n-1} + a z^{n-2} + \cdots$$

then the term with z^{n-1} is

$$-(n-1)z^{n-1} + (n-1)z^{n-1} = 0$$

so the ansatz is consistent. We can then solve the equation systematically for the coefficients of the lower-order terms, as we did in the case of the harmonic oscillator. The first few polynomial solutions are

$$n=1 \qquad f_n^{0} = 1$$

$$n=2 \qquad f_n^{0} = z-2$$

$$n=3 \qquad f_n^{0} = z^2-6z+6$$

This problem is related to a standard problem in the classical theory of orthogonal polynomials. The Laguerre equation is

$$z\, L_m''(z) + (1-z)\, L_m'(z) + m\, L_m(z) = 0$$

You can check that this equation has polynomial solutions, called *Laguerre polynomials*. For example,

$$m=0 \qquad L_0(z) = 1 \quad ; \qquad m=1 \qquad L_1(z) = z-1$$

If we differentiate this equation, we find

$$z\left(L_m'\right)'' + (2-z)\left(L_m'\right)' + (m-1)\left(L_m'\right) = 0$$

which is identical to the equation derived above for $\ell = 0$. Differentiating again,

$$z\left(L_m''\right)'' + (3-z)\left(L_m''\right)' + (m-2)\left(L_m''\right) = 0$$

After p steps,

$$z\left(L_m^{(p)}\right)'' + (p+1-z)\left(L_m^{(p)}\right)' + (m-p)\,L_m^{(p)} = 0$$

Now return to the radial equation with the $\ell(\ell+1)$ term restored. The suggested form of the solution above gives

$$\left(\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} + \frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2} - \frac{1}{n^2}\right)\rho^\ell f_n^\ell(\rho)\, e^{-\rho/n} = 0$$

that is,

$$\frac{d^2}{d\rho^2} f_n^\ell + 2\frac{df_n^\ell}{d\rho}\left(\frac{\ell}{\rho}-\frac{1}{n}\right) + \left(\cancel{\frac{\ell(\ell-1)}{\rho^2}} - \frac{2\ell}{n\rho} + \cancel{\frac{1}{n^2}}\right) f_n^\ell$$

$$+ \frac{2}{\rho}\frac{df_n^\ell}{d\rho} + \left(\cancel{\frac{2\ell}{\rho^2}} - \frac{2}{n\rho}\right)f_n^\ell + \left(\frac{2}{\rho} - \cancel{\frac{\ell(\ell+1)}{\rho^2}} - \cancel{\frac{1}{n^2}}\right)f_n^\ell = 0$$

If we combine terms, we find

$$\frac{d^2}{d\rho^2}f_n^\ell + \left(\frac{2}{\rho}+\frac{2\ell}{\rho}-\frac{1}{n}\right)\frac{df_n^\ell}{d\rho} + \frac{2}{\rho}\left(1-\frac{1}{n}-\frac{\ell}{n}\right)f_n^\ell = 0$$

Converting from ρ to $z = 2\rho/n$ as before, this becomes

$$z\left(f_n^\ell\right)'' + \left(2(\ell+1)-z\right)\left(f_n^\ell\right)' + (n-1-\ell)\,f_n^\ell$$

which is exactly the equation for $L_m^{(p)}(z)$ with

$$p = 2\ell+1 \qquad m = n+\ell$$

Now we have an set of explicit formulae for the bound state eigenfunctions of the Hydrogen atom. The Laguerre polynomials have a representation

$$L_m = e^{z} \frac{d^m}{dz^m} \left(z^m e^{-z} \right)$$

(My notation here follows Griffiths and differs from that of MathWorld.) The *associated Laguerre polynomials* are defined as

$$L_m^p = (-1)^p \frac{d^p}{dz^p} L_m$$

This is a polynomial of degree $(m-p)$. Then bound state eigenfunctions of the Hydrogen atom then take the form

$$\psi_{n\ell m}(r,\theta,\phi) = N_{n\ell m} \left(\frac{r}{a_0} \right)^{\ell} L_{n-\ell-1}^{2\ell+1} \left(\frac{2r}{a_0} \right) e^{-r/na_0} \cdot Y_{\ell m}(\theta,\phi)$$

The eigenfunction for fixed n have energy

$$E = -Ry \cdot \frac{1}{n^2}$$

For given ℓ, the prefactors of the exponential are polynomials of degree

$$\ell, \ \ell+1, \ \ell+2, \ \cdots$$

with, respectively, 0, 1, 2, 3, ... zeros for $r > 0$. These exhaust the eigenfunctions in each ℓ channel.

For given n, we have one radial eigenfunction for each ℓ such that $\ell < n$. Each radial eigenfunction can be multiplied by any of the $(2\ell + 1)$ spherical harmonics with different values of m from $(-\ell$ to ℓ. Thus, each gives $(2\ell + 1)$ independent eigenfunctions. In all, the number of eigenfunctions at each n level is

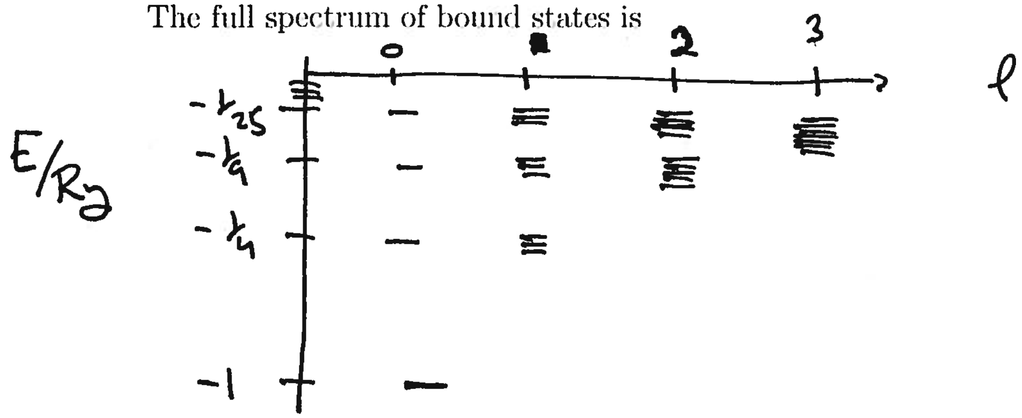
$$1 + 3 + 5 + \cdots + (2\ell+1)$$

which sums to

$$1, 4, 9, 25, \ldots$$

that is n^2 states in all.

The full spectrum of bound states is



For each ℓ, the problem also has a continuous spectrum for $E > 0$.

I will discuss the relation of this solution to the structure of atoms in the next lecture.