Lecture 3, the hydrogen atom, radial states

The hydrogen atom is the first system that gave detailed quantitative agreement between quantum mechanics and experiments, in this case, measurements of the wavelengths of the spectral lines of hydrogen gas. The exact explicit solution of the hydrogen atom eigenvalue problem and the resulting "shell structure" hints at the physical origin of Mendeleev's periodic table of elements. It also leads to a discovery of the mathematical formulation of the last piece of physics governing "nonrelativistic" electrons, spin. In this lecture, look for the following highlights:

(i) The role of invariance under the rotation group and representations of the rotation group.

(ii) The role of commuting operators, angular momentum operators in this case, and the corresponding extra "quantum numbers" of angular momentum. This is closely related to (i).

(iii) The energy spectrum consisting of localized "bound states" with negative energy and extended "continuous spectrum" of positive energy states.

(iv) The "accidental degeneracy" of levels that is broken under almost any perturbation.

What characterizes the hydrogen atom is that it has a single electron. The same mathematical treatment covers helium (which normally has two electrions) with one electron missing. This is called the He^+ ion because the total charge is $+1$. Other one electron systems include doubly ionized lithium, "positronium" (an "atom" consisting of a positively charged positron and negatively charged electron), and an atom with a negatively charged pion in place of the electron. There is even interest in "heavily stripped uranium", the uranium atom with 91 of 92 electrons missing. We work with the standard model of the atom: all positive charges bound together in a tiny nucleus and the electron (or electrons) interacting with the nucleus (and each other) through the classical coloumb energy of static electric fields. It is amazing that most chemical, electrical, and mechanical properties of ordinary matter can be understood using this model, not that all have been, however.

1 Formulation, scaling, and scales.

As with the quantum harmonic oscillator, we can there is much to learn about the quantum hydrogen atom simply by formulating the Schrödinger equation and nondimensionalizing it. The potential energy between two particles with charge $Z_1 e$ and $Z_2 e$ is

$$\frac{(Z_1 e)\,(Z_2 e)}{r}\ .$$

Here Z_1 and Z_2 are integers, e is the charge of a proton[1] and r is the distance between the particles. For the atomic nucleus and single electron system, Z_1 is the number of protons in the nucleus, and $Z_2 = -1$, corresponding to a single negatively charged electron. The potential is negative and goes to zero as $r \to \infty$. It represents the minimum work needed to increase the distance from r to infinity. The force on the electron has magnitude $Z_1 e^2/r^2$ and points toward the nucleus.

The Schrödinger equation for the one electron atom is

$$i\hbar\partial_t\psi = \frac{p_e^2}{2m_e}\psi + \frac{p_n^2}{2m_n}\psi + V(x,y)\psi = \frac{-\hbar^2}{2m_e}\triangle_x\psi + \frac{-\hbar^2}{2m_n}\triangle_y\psi - \frac{Ze^2}{|x-y|}\psi \ , \quad (1)$$

where m_e and m_n are respectively the masses of the electron and nucleus[2], and $x \in R^3$ and $y \in R^3$ are the respective positions. The nuclear mass is much larger than the electron mass[3], so it is common to regard the nucleus as fixed (at $y = 0$, say) and simply seek a one particle wave function

$$i\hbar\partial_t\psi = \frac{-\hbar^2}{2m_e}\triangle_x\psi - \frac{Ze^2}{|x|}\psi \ . \quad (2)$$

The eigenvalues, or energy levels, are found from the corresponding eigenvalue problem

$$E\psi = \frac{-\hbar^2}{2m_e}\triangle_x\psi - \frac{Ze^2}{|x|}\psi \ . \quad (3)$$

It will turn out that solutions with $E < 0$ have exponential decay for large x (localized bound states) while solutions for $E > 0$ do not decay as $x \to \infty$.

As with the harmonic oscillator, we first nondimensionalize, putting the problem into a cannonical form in terms of suitable length and energy scales, L_0 and E_0:

$$x = L_0 \cdot \xi \ , \qquad E = E_0 \cdot \lambda \ . \quad (4)$$

Substituting the scales into the eigenvalue problem (3) gives

$$E_0 \cdot \lambda\psi = \frac{\hbar^2}{m_e L_0^2}\frac{-1}{2}\triangle\psi - \frac{Ze^2}{L_0}\frac{1}{|\xi|}\psi \ .$$

[1] You might expect a dimensional constant, z, would be needed to make ze^2/r have units of energy. This would definitely be needed if we were to measure e in Coloumbs. The convention in quantum mechanics is to measure e in "electrostatic units", or *esu*. These units have the property that if you take for e the number of esu's and for r the distance in centimeters, then e^2/r is the energy in ergs. The erg is the unit of energy in "cgs" units, i.e., gram $\cdot$ cm^2/sec^2.

[2] Even though the nucleus has an integer number of protons and neutrons, it's mass is not the sum of the proton and neutron masses. This (and $e = mc^2$) is why it is possible to get energy by nuclear fission (splitting) and fusion (combining). If we need to know a nuclear mass, we look it up.

[3] The electron mass is $9.11 \cdot 10^{-28}$ grams, while the proton mass is $1.67 \cdot 10^{-24}$ grams. The ratio is $m_p/m_e = 1838$

As for the harmonic oscilator, we first find a length scale by setting the coefficients of the kinetic and potential energy terms equal:

$$\frac{\hbar^2}{m_e L_0^2} = \frac{Ze^2}{L_0} \ ,$$

which leads to

$$L_0 = \frac{\hbar^2}{m_e e Z} \ . \tag{5}$$

The L_0 for hydrogen is called the "Bohr radius" and is written a_0, or sometimes r_0. Plugging values for $\hbar$, e, m_e, and $Z = 1$ (for hydrogen) gives

$$a_0 = .528 \cdot 10^{-10} m = .528 \text{Å} \ .$$

Note that making the nucleus or the electron more massive makes the single electron atom smaller. For example, He^+ is half the size of H. Using (5), we find the energy scale to be

$$E_0 = \frac{m_e e^4 Z^2}{\hbar^2} \ . \tag{6}$$

Note that the energy scales with Z^2; the energy to remove the remaining electron from He^+ is four times the energy to remove the electron from H. For hydrogen, we have

$$E_0 = 27.2 \text{ ev} \ .$$

Warning: the ground state energy for hydrogen is $E_0/2 = 13.6$ ev, which some people take as the definition of E_0. Our $E_0 = 27.2$ ev is the unit of energy in "atomic units". It is sometimes called the "Hartree". The ground state energy for hydrogen, $E_0/2$ is sometimes called the "Rydberg energy". Be careful: "Rydberg's constant" is ($2\pi\times$) the electromagnetic vibrational frequency corresponding to $E_0/2$. The final nondimensional form of the eigenvalue problem is (writing x for ξ, which is customary):

$$\lambda\psi = \frac{-1}{2} \triangle \psi - \frac{1}{|x|}\psi \ . \tag{7}$$

2 The ground state.

Several general facts about Schrödinger operators will help us find the ground state energy and wave function. We will prove these properties a few lectures hence using variational arguments.

(i) The ground state is simple. The multiplicity of the ground state eigenvalue is one.

(ii) The ground state wave function has constant phase: $\arg(\psi) = const.$ We may choose ψ to be nonnegative.

(*iii*) The ground state wave function never vanishes[4]. We may suppose $\psi(x) > 0$ for every x. No other eigenfunction may have this property, or it could not be orthogonal to the ground state. This also implies (i).

(*iv*) The ground state wave function has as much symmetry as possible. Here $\psi(x) = f(|x|) = f(r)$. Such a state is called "radial". In particular, the ground state is radial.

In view of these facts, we seek a radial wave function, $\psi = f(r)$. We will recognize the ground state by the absense of nodes (places where $\psi = 0$). To translate the differential equation (7) into a differential equation for f, we need to compute $\triangle f(r)$ in terms of derivatives of f with respect to r. Since both f and $\triangle f$ are radially symmetric, we may evaluate $\triangle f$ at any x with $|x| = r$. I choose $x = (r, 0, 0)$. I have to evaluate the three second partials, the first being $\partial^2_{x_1} f(r) = f''(r)$. The other two, $\partial^2_{x_2} f$, and $\partial^2_{x_3} f$ are equal, again by symmetry. Now write[5]

$$r = \left(x_1^2 + x_2^2 + x_3^2\right)^{1/2} \;,$$

so that $\partial_{x_2} r = x_2/r$, which vanishes when $x_2 = 0$. Similarly, when $x_2 = 0$, $\partial^2_{x_2} r = 1/r$ since the other term vanishes. Now we have

$$\partial_{x_2} f(r) = f'(r)\frac{x_2}{r} \;,$$

and then

$$\partial^2_{x_2} f(r) = f'\frac{1}{r}$$

with all other terms vanishing when $x_0 = 0$. This gives

$$\triangle f(r) = f''(r) + \frac{2}{r} f'(r) \;. \tag{8}$$

In general, the coefficient of $\frac{1}{r} f'$ is the number of "transverse" directions, which is oen less than the total dimension. Using (8), the eigenvalue problem (7) translates to

$$\lambda f = \frac{-1}{2} f'' - \frac{1}{r} f' - \frac{1}{r} f \;. \tag{9}$$

Finding all the radial eigenfunctions f is a bit messy, but the ground state has the form[6] $f = e^{-\alpha r}$. Substituting this and dividing through by f gives

$$-\lambda = -\frac{1}{2}\alpha^2 + \frac{1}{r}\alpha - \frac{1}{r} \;.$$

[4] This is not true of ground states for systems of more than one fermion. For example, if $\psi(x_1, x_2)$ is any wave function of a two electron problem, then $\psi(x_2, x_1) = -\psi(x_1, x_2)$.

[5] In two dimensions you can visualize this calculation when $f(r) = r$ so that the graph of ψ is a cone. We want to differentiate the height function with respect to x_2 keeping $x_1 = r$ fixed. The intersection of the plane in three dimensions given by $x_1 = r$ with the cone is a conic section.

[6] We know this from Schrödinger's paper. There are several somewhat systematic ways to find it.

We get a solution if $\alpha = 1$, which implies that $\lambda = \frac{1}{2}$. Since the eigenfunction $f(r) = e^{-r}$ has no nodes, it must be the ground state, and $\lambda = -1/2$ the ground state eigenvalue. Going back to the dimensional form, this shows that the ground state energy for the hydrogen atom is $\frac{1}{2}E_0 = 13.6$ em.

3 Other radial states.

Besides the ground state there are many other radially symmetric bound states. These satisfy the radial eigenvalue equation (9). The spectral for this equation follows the general theory of second order ODE spectral problems. The general structure is that, for any λ, there are two linearly independent solutions defined for $0 \leq r \leq \infty$. A general solution probably blows up as $r \to 0$ or $r \to \infty$ in a way that makes f irrelevent for the spectral problem. For one thing, $\psi(x) = f(|x|)$ needs to be defined at $x = 0$, not just $x \neq 0$ (i.e. $r > 0$. Only for special values of $\lambda < 0$ will there be a solution bounded both near 0 and infinity.

We will soon see that for any $\lambda < 0$ there is a one dimensional subspace of solutions (We often say "one solution".) that remains bounded as $r \to 0$, while any linearly independent solution behaves like $1/r$. Let $f_1(r) \to 1$ as $r \to 0$. If f is bounded as $r \to 0$ then $f(r) = const \cdot f_1(r)$. Similarly, as $r \to \infty$ there is one solution (actually a one dimensional subspace of solutions) that decays to zero as $r \to \infty$, while any linearly independent solution grown exponentially. Let $f_-(r)$ be any non–zero exponentially decaying solution. To be an eigenfunction, $f(r)$ must be proportional to $f_1(r)$ to have good behavior as $r \to 0$ and $f(r)$ must be proportional to $f_-(r)$ to have good behavior as $r \to \infty$. This means that $f_1(r) = const \cdot f_-(r)$. The values of λ for which this is possible are the radial eigenvalues.

We can construct $f_1(r)$, the solution regular near zero, using Taylor series:

$$f_1(r) = 1 + a_1 r + a_2 r^2 + \cdots \ . \tag{10}$$

Substituting this into (9) and equating powers of r starting with the lowest leads to

$$\begin{array}{rlll} O\left(\dfrac{1}{r}\right) & : & -a_1 - 1 = 0 \ , & a_1 = -1 \\ O\left(1\right) & : & \lambda a_0 = -3a_2 - a_1 \ , & a_2 = -\frac{\lambda}{3} + 1 \\ & & \vdots & \\ O\left(r^n\right) & : & & a_{n+2} = -\dfrac{-2}{(n+2)(n+3)}\left(\lambda a_n + a_{n+1}\right) \end{array}$$

From this we can see that the Taylor series (10) has at least a finite radius of convergence: if $|\lambda| \leq 1$ and $n \geq 1$ then $|a_{n+2}| \leq \max(|a_n|, |a_{n+1}|)$. This shows that there is a smooth solution, $f_1(r)$, that is bounded and analytic up to $r = 0$.

We can find the behavior of the other linearly independent solution near zero using the Wronskian, a method restricted to one dimensional problems. Let g

be another solution of the eigenvalue ODE (9), then the Wronskian is

$$\begin{aligned} W(r) &= \det \begin{pmatrix} f & g \\ f' & g' \end{pmatrix} \\ &= fg' - f'g \ . \end{aligned}$$

Differentiating gives $W'(r) = fg'' - f''g$. Substituting (9) for f'' and g'' gives

$$W' - \frac{-2}{r} W \ ,$$

which implies that

$$W(r) = \frac{c}{r^2} \ .$$

The point is that once we know one solution, f, we may find a complementary linearly independent solution, g by solving the first order ODE given by the known functional form of the Wronskian:

$$\begin{aligned} fg' - f'g &= \frac{c}{r^2} \\ g' - \frac{f'}{f} g &= \frac{c}{r^2 f} \ . \end{aligned}$$

If $f = f_1(r)$ is the solution bounded and analytic near zero, we may expand everything in at least locally convergent power series to get

$$g' - (b_0 + b_1 r + \cdots) \, g = \frac{c_{-2}}{r^2} + \frac{c_{-1}}{r} + c_0 + c_1 r + \cdots \ .$$

Integrating near zero then gives

$$g(r) = \frac{d_{-2}}{r} + d_{-1} \log(r) + d_0 + d_1 r + \cdots \ .$$

Again, this series converges at least locally. This shows that any solution linearly independent of f_1 has a $1/r$ singularity as $r \to 0$.

Such a singular solution does not correspond to a eigenfunction, ψ. The function $\psi(x) = g(|x|)$ deos not satisfy the eigenvalue equation (7). Even though the equation is satisfied algebraically at any point $x \neq 0$, the 3D Laplacian of $1/r$ has a delta function at $x = 0$ that is not matched by anything on the left side. Remember that the Green's function, G, for $\triangle$ has a $1/r$ singularity at $x = 0$ in 3D. Even though $\triangle G(x) = 0$ when $x \neq 0$, still, it is not true that $\triangle G = 0$ as a function. Altogether, we have shown that if $\psi(x) = f(|x|)$ is an eigenfunction, then $\psi(x) = const \cdot f_1(|x|)$.

I have not been able to treat the behavior as $r \to \infty$ as quickly, so I will be sketchier. For large r we might hope that the $1/r$ terms in (9) are small perturbations. If we drop them, we get

$$\lambda h = \frac{-1}{2} h'' \ .$$

For $\lambda < 0$ this has exponential solutions

$$h(r) = \exp(\pm\sqrt{-2\lambda}r) \ .$$

With some work (left out here), one can show that there is a solution

$$f_-(r) = A(r)e^{-\sqrt{-2\lambda}r} \ ,$$

where $|A(r)| \leq C{\cdot}r^p$ for some $p > 0$ as $r \to \infty$. Then, using the Wronskian to get a first order ODE, it can be shown that any linearly independent solution grown like $e^{+\sqrt{-2\lambda}r}$ as $r \to \infty$, up to a polynomially bounded factor. An eigenvalue, then, is a λ value for which $f_1(r) \sim const \cdot r^p e^{-\sqrt{-2\lambda}r}$ as $r \to \infty$. Since the alternative to exponential decay is exponential growth, any $\lambda < 0$ for which $f_1(r)$ is bounded as $r \to \infty$ is an eigenvalue.

To examine the large r behavior of $f_1(r)$, we again write $\alpha = \sqrt{-2\lambda}$ and write

$$f_1(r) = A(r)e^{-\alpha r} \ . \tag{11}$$

Since $e^{-\alpha r}$ has the right behavior at 0, never vanishes, and has something like the right behavior at infinity, $A(r)$ should be regular as $r \to 0$ and $r \to \infty$. Therefore, we assume a power series

$$A(r) = A_0 + A_1 r + A_2 r^2 + \cdots = \sum_{n=0}^{\infty} A_n r^n \ .$$

First we substitute into (11) to get

$$0 = \alpha A' - \frac{1}{2}A'' + \frac{\alpha}{r}A - \frac{1}{r}A' - \frac{1}{r}A \ .$$

Then we substitute the power series for A, calculate, and equate powers of r to get

$$A_{n+1} = 2\left(\frac{\alpha n - 1}{n^2 + 3n + 2}\right) A_n \ . \tag{12}$$

We know we are doing something right because (12) is a two term relation while we had a three term relation for f before.

Now there are two possibilities. Either the recurrence stops because

$$\frac{\alpha n - 1}{n^2 + 3n + 2} = 0 \qquad \text{for some } n, \tag{13}$$

or

$$\begin{aligned} & A_{n+1} \sim \frac{2\alpha}{n} A_n \\ \Longrightarrow \quad & A_n \sim \frac{(2\alpha)^n}{n} \\ \Longrightarrow \quad & A(r) \sim e^{2\alpha r} \\ \Longrightarrow \quad & f(r) = A(r)e^{-\alpha r} \sim e^{\alpha r} \to \infty \quad \text{as } r \to \infty. \end{aligned}$$

Clearly, only the first possibility corresponds to an eigenvalue. In that case, (13) implies that $\alpha n = 1$ for some n, or,

$$\alpha = \frac{1}{n} \, . \tag{14}$$

This identifies all the radial bound state eigenfunctions and eigenvalues. The eigenvalues are

$$\lambda_n = -\alpha_n^2 = \frac{-1}{n^2} \, . \tag{15}$$

The corresponding eigenfunctions are

$$\psi_n(x) = A_n(|x|)e^{|x|/n} \, , \tag{16}$$

where $A_n(r)$ is a polynomial of degree n in r. This is the simple structure of radial bound states. Because the answer is so much simpler than the derivation, there must be a better derivation.

We will soon consider the non symmetric eigenfalue problem. For the $1/r$ potential, there are no new eigenvalues. This is "accidental degeneracy". It is broken for (almost) any perturbation of the potential. In real atoms, people often say that the "core electrons" screen the outer, or "valence" electrons from some of the charge in the nucleus. An electron far from the nucleus will feel less force than Ze^2/r^2 because of the $Z-1$ electrons between the outer most electron and the nucleus. For this reason, the accidental degeneracy will be broken and nonradial eigenvalues will in general be larger (closer to zero) than symmetric ones.

When $\lambda > 0$ the behavior as $r \to 0$ is similar, but the beharior as $r \to \infty$ is different. Now both linearly independent solutions seem to be bounded (or at least not exponentially growing). This suggests that any $\lambda > 0$ is in the spectrum. This is true but I won't have time to talk about this much.

4 Exercises.

1. One electron volt is $1.6 \cdot 10^{-12}$ ergs. The charge of a proton is $e = 4.8 \cdot 10^{-10}$ esu. What is the potential energy of an electron separated from a proton by one Ångström? Is this about what you expect given the value of E_0 for the hydrogen atom?

2. Find the wave number k_H and vibrational frequency, ω_H, of a photon (quantum of electromagnetic field vibration) having energy $E_0/2 = 13.6$ ev. This involves knowing the speed of light (see lecture 1, or almost any basic physics book). Convert k_H into a the corresponding wave length. Which energy transitions in hydrogen would produce visible light? (You may have to look up the wavelengths range of visible light.) For example, would the transition $\mid n = 3\rangle \longrightarrow \mid n = 2\rangle$ be visible? Rydberg's constant is $R = 2\pi\omega_H$.

3. Use the recurrence relation (12) to compute the radial eigenfunctions corresponding to $\lambda_1 = -\frac{1}{2}$, $\lambda_2 = -\frac{1}{2}\frac{1}{4}$ and $\lambda_3 = -\frac{1}{2}\frac{1}{9}$. Verify by direct integration that

$$\int_{R^3} \phi_1(x)\phi_2(x)dx = \int_{R^3} \phi_1(x)\phi_2(x)dx = \int_{R^3} \phi_1(x)\phi_2(x)dx \ .$$

Hint: this reduces to easy arithmetic if you first compute $\int_0^\infty r^k e^{-\beta r} dr$ as a function of k and β.

4. Show that the n^{th} radial eigenfunction, $f_n(r) = p_n(r)e^{-r/n}$, has exactly $n-1$ zeros as a function of r. Possible solution: otherwise the necessary orthogonality would be impossible.

5. There is a WKB approximation for eigenfunctions. While hard to make rigorous, it does give physical insight. It is based on the relation

$$E = \frac{p^2}{2m} + V(x) \ . \tag{17}$$

a. If E is the energy of a state (and therefore independent of x) and $\widehat{p} = \frac{\hbar}{i}\nabla$ and $\hbar \to 0$, derive (17) as an eikonal equation corresponding to the ansatz $\psi = A(x)e^{iS(x)/\hbar}$, with the identification $p \sim \nabla S$.

b. The eigenfunction ψ is defined for all x, not only x values for which (17) defined a real p (the "classically allowed" region). For radial eigenfunctions, show that (17) correctly predicts the exponential decay rate as $r \to \infty$ together with the relationship between λ and α. The intuition is that an eigenfunction will be oscillatory in the classically allowed region and exponentially decaying, or "evanescent" in the disallowed region.

c. Derive a transport equation and show that it correctly predicts the power law correction to exponential decay for $n > 1$ radial modes. If you get tired of the algebra, quit.

d. Estimate the size of large n hydrogen atom states (as a function of n) by estimating the size of the classically allowed region. High n states are called "Rydberg states". States with $n > 1000$ have been created in a lab.