

HYDROGEN ATOM

CYL100 2013–14

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We will now obtain the eigenfunctions and eigenvalues of the Schrödinger equation for the hydrogen atom or more generally one-electron atoms or ions. Many of the things we discuss are, in principle, applicable to any central-field potential but for concreteness we will only consider the coulombic potential.

The Schrödinger equation for the system under consideration is

$$\hat{H}\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

with the Hamiltonian given by

$$\hat{H} = \left[-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \phi^2} \right) - \frac{e^2}{r} \right]$$

In terms of the angular momentum operator the Hamiltonian can be written as

$$\left[-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\hat{L}^2}{\hbar^2 r^2} \right) - \frac{e^2}{r} \right] \psi(r, \theta, \phi) = E\psi(r, \theta, \phi).$$

There are a number of things to note in this equation. First, you will notice that we have written the Laplacian in spherical coordinates. The reason for this is not hard to understand. The symmetry of the problem, dictated by the spherically symmetric (independent of the angular coordinates) potential energy term $-e^2/r$, is such that the spherical coordinate system is the natural choice. Secondly, we are working in gaussian units, which means that a factor of $1/(4\pi\epsilon_0)$ is missing from the potential energy. Thirdly, we are considering the nucleus to be of infinite mass, or in other words, the nucleus is assumed to be stationary and the m that occurs is that of the electron. If we remove this approximation then we would still be able to reduce the two-body problem by using the reduced mass in place of the electron mass, as has been done previously in the case of the harmonic oscillator and the rigid rotor. Note that the potential is only a function of the electron-nuclear distance. This results in the total Hamiltonian separating out into one for the COM and another for the reduced mass. We are not interested in the COM because it only represents the hydrogen atom moving as a whole in a field-free region or in other words it behaves like a free particle, the energies and wavefunctions for which have been obtained many times. So we will from now on only consider the reduced mass Hamiltonian. In short, realize that although m is used in the text through out it should actually read μ .

We proceed to solve this differential equation in the usual way, that is by the separation of variables method. You will notice that the angular part of the Schrödinger equation is identical to that in the rigid rotor, which we now know to be the \hat{L}^2 operator and whose solutions we have worked out in great detail earlier. Thus we need to be concerned only with solving the radial Schrödinger equation, which is

$$\left[-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2}{r} \right] R(r) = ER(r).$$

In this equation the term containing $l(l + 1)$, which is the eigenvalue of the L^2 operator, is the constant obtained on separating out the angular part from the three-dimensional Schrödinger equation. I will sketch the steps (it is for you to explicitly carry this out and convince yourself) involved in arriving at this radial Schrödinger equation. We conjecture that the solution $\psi(r, \theta, \phi)$ can be written as $R(r)Y(\theta, \phi)$.

1. Substitute $\psi = RY$ in the Schrödinger equation and perform the required operations.
2. Divide through by RY and separate the functions of r (say LHS) from those involving θ and ϕ (RHS). The separation constant that appears we call $l(l + 1)\hbar^2$.

If you stare at the radial equation for a little bit you will notice that the separation of variables leads to an effective potential energy

$$V_{eff} = -e^2/r + l(l + 1)\hbar^2/(2mr^2).$$

The second term, called the centrifugal barrier, arises as a result of the orbital motion of the electron around the nucleus and is non-zero for all electrons other than those with $l = 0$ (s states). You will also notice that the $-e^2/r$ term is attractive ($V < 0$ for all r) while the centrifugal barrier is repulsive (> 0 for all r). The effect of the centrifugal barrier is to reduce the effective depth of the potential well, an effect which increases as l increases.

The kinetic energy of a particle of mass m can be written in terms of two components of momentum; p_r along the radius, and p_l at right angles to it. The radial part of the kinetic energy is $p_r^2/2m$, whereas the angular part is $p_l^2/2m$. We can rewrite this latter term in the form $(p_l r)^2/2mr^2$, where the quantity $p_l r$ is the angular momentum. Then the classical conservation of energy can be written in the form

$$\frac{p_r^2}{2m} + \frac{(p_l r)^2}{2mr^2} - \frac{e^2}{r} = E.$$

By the law of conservation of angular momentum, the quantity $p_l r$ remains constant provided there is no torque acting on the particle. Thus the equation given above is like the law of conservation of energy for a particle in one-dimensional motion along r , subject to a potential energy which consists, not merely of the Coulomb energy but also the term containing $p_l r$, which may be interpreted as the fictitious centrifugal force.

We could take the straightforward and mathematically instructive approach of solving the Schrödinger equation by the Frobenius series method but this is characterized by a lack of physical insight. We forsake rigor in an attempt at insight - the proof of the pudding will lie in the eating.

We know, from the properties of wave functions, that the states corresponding to $E > 0$ are not bound states (Why?). Such states are important in collisional processes and in what follows we will not pay any attention to them except to note that there is no restriction on the energy (it is continuous) of such states. The wave function is, of course, a function of three variables: x, y , and z , or r, θ , and ϕ , or some other set. It must be normalizable; that is, the integral $\int |\psi|^2 r^2 \sin \theta dr d\theta d\phi$ must converge. For unbound states this is not the case, and the integral must be made finite by imposing suitable boundary conditions. For bound states there is no difficulty as $r \rightarrow \infty$, since ψ normally vanishes exponentially. For small r , suppose that ψ varies as r^α . Then the indefinite integral varies as $r^{2\alpha+3}$, and it will converge at the origin provided that

$$\alpha \geq -\frac{3}{2}$$

But normalizability is not the only requirement to be imposed in this respect, and it turns out that hermiticity of \hat{H} is more stringent. Suppose that $f(r)$ is a member of the class of admissible functions that has the most early singular behavior at the origin permitted to any admissible function. We write f in the neighborhood of the origin as

$$f(r) = (a + br + \dots)r^\alpha$$

where a and b depend in general on the angles θ and ϕ but not on r and a is not zero. The Hermiticity of \hat{H} requires that

$$\langle H \rangle = \int f^* \hat{H} f d\tau$$

exists and is real. Operating with the Laplacian on f yields

$$\nabla^2 f = (a' + b'r + \dots)r^{\alpha-2}$$

where a' and b' are again generally functions of θ and ψ . Writing the volume element $d\tau$ as $r^2 dr d\Omega$, where $d\Omega$ is an element of solid angle, we have

$$\begin{aligned} \langle H \rangle &= -\frac{\hbar^2}{2m} \int [a^* a' + (a^* b' + b^* a')r + \dots] r^{2\alpha} \\ &\quad - \frac{2m}{\hbar^2} V(r) [|a|^2 + (a^* b + b^* a)r + \dots] r^{2\alpha+2} dr d\Omega \end{aligned}$$

If $V(r)$ is no more singular than r^{-2} , the integral's convergence at the origin is determined by $r^{2\alpha}$, so that $\langle H \rangle$ exists if

$$\alpha > -\frac{1}{2}.$$

This is a more restrictive condition than that imposed by normalizability.

As already remarked, the effective well depth and the location of the minimum are an interplay between the centrifugal barrier arising from the orbital motion, which is trying to push the electron out and the Coulombic attractive term (What are you waiting for? Go ahead and determine where the minimum is and what is the minimum potential). As a result the number of bound states would depend on the value of l and so also the classical turning point. For small r the effective potential tends to $-\infty$ for the s states and ∞ for the other states. We know that when the potential is infinite the wave function is 0, which implies that for the $l \neq 0$ states the wave function goes to 0 as $r \rightarrow 0$. For all states irrespective of l the wave function goes to zero as $r \rightarrow \infty$ since $V > E$ in this region. For the s states, as one approaches inward at constant energy the kinetic energy increases since the potential is negative resulting in more oscillations in the wave functions at smaller r .

It is convenient to introduce a function

$$u = rR,$$

which allows us to establish a correspondence with the problem of one-dimensional motion. Because

$$\left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) \frac{u}{r} = \frac{1}{r} \frac{d^2}{dr^2} u$$

it follows that

$$\frac{d^2 u}{dr^2} + \frac{2m}{\hbar^2} \left[E + \frac{e^2}{r} - \frac{l(l+1)\hbar^2}{2mr^2} \right] u = 0.$$

It is this differential equation whose solution we will determine. Bear in mind that $R(r) = u(r)/r$ is the solution of the radial Schrödinger equation. The boundary condition to be satisfied by the function u at the point $r = 0$ is that it should vanish; otherwise, the radial function R would be divergent at the origin. The boundary condition that u should vanish for $r = 0$ is equivalent to the assumption that the potential energy should be infinite there.

1 Ground and other s states

First consider the case of zero angular momentum, $l = 0$:

$$\frac{d^2 u_0}{dr^2} + \frac{2m}{\hbar^2} \left[E + \frac{e^2}{r} \right] u_0 = 0.$$

Because the squares of the solution to the radial Schrödinger equation give probability distribution for the position of the electron with respect to the nucleus, the state of lowest total energy should have a wavefunction that is large in regions where the potential energy is large and negative. However, the distribution of the electron cannot be confined to too small a volume, because this would require a high energy, in accordance with the uncertainty principle. The region of lowest potential energy is near the origin, which suggests that the ground state wave function should have a large amplitude at small r and should decrease rapidly as r increases. At the origin, u should start out with the value zero. When r is less than the classical turning point (a), $E - V$ is positive; hence if u is positive, the wave function has a negative curvature. If $E - V$ is sufficiently large, the solution may curve enough to make the slope of u negative at $r = a$. Beyond $r = a$ the curvature is positive. In general u will ultimately approach an increasing exponential as $r \rightarrow \infty$, but for a certain value of $|E|$, it will fit a decaying exponential exactly. The wave function so obtained has no nodes, except the unavoidable one at the origin. It must be the lowest energy state, because a wave function which oscillates has a higher kinetic energy than one which does not.

Let us look at the solutions in two limiting cases. At large distances we expect the function to fall off exponentially with distance. The solution in this region is

$$u \sim A \exp\left(-\sqrt{\frac{2m|E|}{\hbar^2}} r\right) + B \exp\left(\sqrt{\frac{2m|E|}{\hbar^2}} r\right).$$

In order that the wavefunction remain finite as $r \rightarrow \infty$ the coefficient B must vanish. Near $r = 0$ the term $1/r$ tends to infinity and is dominant. We anticipate that u will then be proportional to r , in order to counter this so that the wavefunction remains finite at $r = 0$. Having obtained the solutions in the two limiting cases it is natural to wonder if

$$u_0 = C \frac{r}{a} \exp(-r/a),$$

where a and C are constants could be a solution over all r . Now

$$\frac{d^2 u_0}{dr^2} = \frac{C}{a} \left(\frac{r}{a^2} - \frac{2}{a} \right) \exp(-r/a)$$

so on substituting u_0 into the radial Schrödinger equation we find that it is a solution over all r provided

$$\frac{r}{a^2} - \frac{2}{a} + \frac{2me^2}{\hbar^2} + \frac{2mE}{\hbar^2} r = 0.$$

Written slight differently this condition implies that

$$r \left(a^2 + \frac{2mE}{\hbar^2} \right) + \left(\frac{2me^2}{\hbar^2} - \frac{2}{a} \right) = 0.$$

For u_0 to be a solution each of the terms in parenthesis should be separately zero. This may be seen as follows: if either term is zero, the equation itself states that the other is zero; on the other hand, if neither is zero, then the equation may be solved for r . Suppose the solution is $r = r_1$; then for $r \neq r_1$

the equation does not hold, and we cannot assert that it holds for all r . This may also be arrived at slightly differently. As r approaches zero, the first and last terms become negligible, and we find that

$$a = \frac{\hbar^2}{me^2} = a_0.$$

We recognize a_0 as the Bohr radius. As r becomes large, the first and last terms dominate, giving

$$E_0 = -\frac{me^4}{2\hbar^2}$$

the ionization energy for an infinitely massive hydrogen atom. The normalization constant of u_0 may be determined from

$$\int_0^\infty (u_0)^2 dr = 1$$

or

$$\int_0^\infty (R_0)^2 r^2 dr = 1$$

if you work with $R_0 = u_0/r$. Note the extra r^2 factor in the second normalization integral, which is a result of the conversion into spherical coordinates. You will note that this approach for the $l = 0$ states resembles closely the method we used to obtain the spherically symmetric solutions from the SE of the H-atom.

2 First excited state and other $l > 0$ states

The first excited state fits a decaying exponential after it goes through a node. Because E is greater, the wavelength inside the potential, $\lambda = h/p = h/\sqrt{2m(E - V)}$ is less, so that this function oscillates more rapidly than does the lower energy solution. There is, furthermore, more room to oscillate, because the turning point occurs at a larger radius when $|E|$ is smaller. Still higher energy states would involve wave functions with still more nodes. The Coulomb force has an indefinitely large number of bound states. This is because it dies out comparatively slowly as a function of the distance.

After this interlude let us now consider the $l \neq 0$ states. Once again the approach we adopt is to look at the two limiting cases of r close to zero and r tending to ∞ . In the latter case we see that terms in the radial Schrödinger equation that have r in the denominator drop out and we get the following differential equation with constant coefficients

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2}Eu = 0,$$

which we are experts at solving. On the other hand, when r tends to 0 we find the differential equation that u satisfies to be

$$\frac{d^2u}{dr^2} - \frac{l(l+1)}{r^2}u = 0.$$

The two independent solutions to this differential equation can be readily verified to be r^{l+1} and r^{-l} . (How would you verify this?) The latter of these is not an acceptable wavefunction (Why?) because it goes to ∞ as $r \rightarrow 0$ (I hope you guessed that). Once we have the two limiting solution we can write the general solution (the steps are identical to the Hermite and Legendre case) to the radial Schrödinger equation to be

$$Cr^{l+1} \exp(-\alpha r)G(r)$$

where $G(r)$ is of the form $A_0 + A_1r + A_2r^2 + \dots$. Substituting this guess solution in the differential equation satisfied by u yields a recurrence relation for the coefficients A_k ,

$$A_k = -2A_{k-1} \frac{\frac{me^2}{\hbar^2} - (l+k)\sqrt{-\frac{2mE}{\hbar^2}}}{(l+k)(l+k+1) - l(l+1)}.$$

Like in the case of the harmonic oscillator, the series $G(r)$ represents a function going infinite as r becomes infinite, unless it breaks off to form a polynomial. In fact we can show that the series becomes infinite like $\exp(\alpha 2r)$ so that u becomes infinite like $\exp(\alpha r)$. The series can however break off if $A_k = 0$. This would happen when the numerator in the expression for A_k is zero,

$$\frac{me^2}{\hbar^2} = (l + k) \sqrt{-\frac{2mE}{\hbar^2}}.$$

Defining $n = (l + k)$ we can now solve for the energy from this expression and it turns out to be

$$E = -\frac{me^4}{2n^2\hbar^2}.$$

Note the dependence of the energy on mass and n , the principal quantum number. It turns out the polynomial $G(r)$ satisfies a differential equation that is well-known in mathematics, called the Kummer-Laplace differential equation. The physically admissible solutions to this differential equation are the associated Laguerre polynomials, L_q^p . The Laguerre polynomials are defined when $n = l + 1$ or $l = 0, 1, \dots, (n - 1)$ and is a polynomial in r of order $n - l - 1$. Putting all this together we can write the radial functions as

$$R_{nl}(r) = N_{nl} \exp(-r/na_0) (2r/na_0)^l L_{n-l}^{2l+1}(2r/na_0),$$

where N_{nl} is the normalization constant. The normalization constant is

$$N_{nl} = -\sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}.$$

For small r , u goes as r^{l+1} . That is, the greater l is, the more rapidly the function approaches zero as r approaches zero. This is natural for we see that the larger l is, the greater is the effective potential energy near the origin, and hence the greater the negative kinetic energy. This corresponds to the classical situation. For large values of r , the limit to the classical motion is set mostly by the total energy, or by n , the principal quantum number. The greater n is, the larger the classical orbit. Corresponding to this, the wave function has large values further out, for large n values. For large values the most important term is the function of r is that in the highest power of r . The highest power of r is n , so that for large values of r the function u approaches $r^n \exp(-r/na_0)$. The largest power of r in $u_{nl}(r)$ is $r^{l+1}r^{n-l-1} = r^n$. The nodes in the radial function are determined by the nodes in the Laguerre polynomial which has $n - l - 1$ nodes.

Here, for completeness, I give you the first few radial functions of the hydrogen atom.

$$\begin{aligned} R_{1s} &= 2 \left(\frac{1}{a_0}\right)^{3/2} \exp(-r/a_0) \\ R_{2s} &= \frac{1}{2\sqrt{2}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) \exp(-r/2a_0) \\ R_{2p} &= \frac{1}{2\sqrt{6}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} \exp(-r/2a_0) \\ R_{3s} &= \frac{2}{81\sqrt{3}} \left(\frac{1}{a_0}\right)^{3/2} \left(27 - 18\frac{r}{a_0} + 2\left(\frac{r}{a_0}\right)^2\right) \exp(-r/3a_0) \\ R_{3p} &= \frac{4}{81\sqrt{6}} \left(\frac{1}{a_0}\right)^{3/2} \left(6\frac{r}{a_0} - \left(\frac{r}{a_0}\right)^2\right) \exp(-r/3a_0) \\ R_{3d} &= \frac{4}{81\sqrt{30}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{r}{a_0}\right)^2 \exp(-r/3a_0) \end{aligned}$$