

HYDROGEN ATOM

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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.

The Schrödinger equation for the hydrogen atom 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 potential energy term, $-e^2/r$, which is a function of the radial distance, naturally suggests the use of the spherical coordinate system. 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. Although m is used in the text through out it could actually be replaced with μ .

We proceed to solve this differential equation in the usual way, that is by the separation of variables method. 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 $l(l+1)\hbar^2$, for reasons that are not obvious now.

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.

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.

There is a classical analog to what we have done above. 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 $p_L r$, a fictitious centrifugal force.

Rather than pull the solution to the radial Schrödinger equation out of a hat we will make an attempt to provide some insight as to why the solutions are what they are.

The effective well depth and the location of the minimum of the effective potential 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, which is pulling the electron to the nucleus. As a result the number of bound states would depend on the value of l and so also would the classical turning point (the point where $E = V_{eff}$). For small r the effective potential tends to $-\infty$ for states with $l = 0$ and to $+\infty$ 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 $r \rightarrow 0$. Because the square of the solution to the radial Schrödinger equation gives the probability distribution for the position of the electron with respect to the nucleus, the $l = 0$ states 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. This suggests that the wave function should have a large amplitude at small r and should decrease rapidly as r increases. In addition, 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 . For all states irrespective of l the wave function goes to zero as $r \rightarrow \infty$ since $V > E$ in this region.

After this discussion on some of the expected features of the solution to the radial Schrödinger equation, we attempt now to obtain it. 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 diverge 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.

Let us look at the solution to this differential equation in two limiting cases. At large distances the differential equation becomes

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

because all terms involving r can be neglected. 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.

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} . You could verify this by substituting it back in the differential equation. The latter of these is not an acceptable wavefunction because it goes to ∞ as $r \rightarrow 0$.

We have the two limiting solutions from which we can write the general solution to the radial Schrödinger equation to be

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

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

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

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 and become finite 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. Physically admissible solutions to this differential equation are defined when $n = l+1$ or $l = 0, 1, \dots, (n-1)$ and is a polynomial in r of order $n-l-1$. These polynomials are the associated Laguerre polynomials, L_q^p . 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.

$$R_{1s} = 2 \left(\frac{1}{a_0}\right)^{3/2} \exp(-r/a_0)$$

$$R_{2s} = \frac{1}{2\sqrt{2}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) \exp(-r/2a_0)$$

$$R_{2p} = \frac{1}{2\sqrt{6}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} \exp(-r/2a_0)$$

$$R_{3s} = \frac{2}{81\sqrt{3}} \left(\frac{1}{a_0}\right)^{3/2} \left(27 - 18\frac{r}{a_0} + 2\left(\frac{r}{a_0}\right)^2\right) \exp(-r/3a_0)$$

$$R_{3p} = \frac{4}{81\sqrt{6}} \left(\frac{1}{a_0}\right)^{3/2} \left(6\frac{r}{a_0} - \left(\frac{r}{a_0}\right)^2\right) \exp(-r/3a_0)$$

$$R_{3d} = \frac{4}{81\sqrt{30}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{r}{a_0}\right)^2 \exp(-r/3a_0)$$