

8.3: Hydrogen Atom

A hydrogen atom consists of an electron, of charge $-e$ and mass m_e , and a proton, of charge $+e$ and mass m_p , moving in the Coulomb potential

$$V(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}|}, \quad (8.3.1)$$

where \mathbf{r} is the position vector of the electron with respect to the proton. Now, according to the analysis in Section [stwo], this two-body problem can be converted into an equivalent one-body problem. In the latter problem, a particle of mass

$$\mu = \frac{m_e m_p}{m_e + m_p} \quad (8.3.2)$$

moves in the central potential

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}. \quad (8.3.3)$$

Note, however, that because $m_e/m_p \simeq 1/1836$ the difference between m_e and μ is very small. Hence, in the following, we shall write neglect this difference entirely.

Writing the wavefunction in the usual form,

$$\psi(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\theta, \phi), \quad (8.3.4)$$

it follows from Section 1.2 that the radial function $R_{n,l}(r)$ satisfies

$$-\frac{\hbar^2}{2m_e} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right] R_{n,l} - \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) R_{n,l} = 0. \quad (8.3.5)$$

Let $r = az$, with

$$a = \sqrt{\frac{\hbar^2}{2m_e(-E)}} = \sqrt{\frac{E_0}{E}} a_0, \quad (8.3.6)$$

where E_0 and a_0 are defined in Equations ([e9.56]) and ([e9.57]), respectively. Here, it is assumed that $E < 0$, because we are only interested in bound-states of the hydrogen atom. The previous differential equation transforms to

$$\left[\frac{d^2}{dz^2} + \frac{2}{z} \frac{d}{dz} - \frac{l(l+1)}{z^2} + \frac{\zeta}{z} - 1 \right] R_{n,l} = 0, \quad (8.3.7)$$

where

$$\zeta = \frac{2m_e a e^2}{4\pi\epsilon_0 \hbar^2} = 2\sqrt{\frac{E_0}{E}}. \quad (8.3.8)$$

Suppose that $R_{n,l}(r) = Z(r/a) \exp(-r/a)/(r/a)$. It follows that

$$\left[\frac{d^2}{dz^2} - 2 \frac{d}{dz} - \frac{l(l+1)}{z^2} + \frac{\zeta}{z} \right] Z = 0. \quad (8.3.9)$$

We now need to solve the previous differential equation in the domain $z = 0$ to $z = \infty$, subject to the constraint that $R_{n,l}(r)$ be square-integrable.

Let us look for a power-law solution of the form

$$Z(z) = \sum_k c_k z^k. \quad (8.3.10)$$

Substituting this solution into Equation ([e9.48]), we obtain

$$\sum_k c_k \{ k(k-1) z^{k-2} - 2k z^{k-1} - l(l+1) z^{k-2} + \zeta z^{k-1} \} = 0. \quad (8.3.11)$$

Equating the coefficients of z^{k-2} gives the recursion relation

$$c_k [k(k-1) - l(l+1)] = c_{k-1} [2(k-1) - \zeta]. \quad (8.3.12)$$

Now, the power series ([e9.49]) must terminate at small k , at some positive value of k , otherwise $Z(z)$ behaves unphysically as $z \rightarrow 0$ [i.e., it yields an $R_{n,l}(r)$ that is not square integrable as $r \rightarrow 0$]. From the previous recursion relation, this is only possible if $[k_{\min}(k_{\min}-1) - l(l+1)] = 0$, where the first term in the series is $c_{k_{\min}} z^{k_{\min}}$. There are two possibilities: $k_{\min} = -l$ or $k_{\min} = l+1$. However, the former possibility predicts unphysical behavior of $Z(z)$ at $z=0$. Thus, we conclude that $k_{\min} = l+1$. Note that, because $R_{n,l}(r) \simeq Z(r/a)/(r/a) \simeq (r/a)^l$ at small r , there is a finite probability of finding the electron at the nucleus for an $l=0$ state, whereas there is zero probability of finding the electron at the nucleus for an $l>0$ state [i.e., $|\psi|^2 = 0$ at $r=0$, except when $l=0$].

For large values of z , the ratio of successive coefficients in the power series ([e9.49]) is

$$\frac{c_k}{c_{k-1}} = \frac{2}{k}, \quad (8.3.13)$$

according to Equation ([e9.51]). This is the same as the ratio of successive coefficients in the power series

$$\sum_k \frac{(2z)^k}{k!}, \quad (8.3.14)$$

which converges to $\exp(2z)$. We conclude that $Z(z) \rightarrow \exp(2z)$ as $z \rightarrow \infty$. It thus follows that $R_{n,l}(r) \sim Z(r/a) \exp(-r/a)/(r/a) \rightarrow \exp(r/a)/(r/a)$ as $r \rightarrow \infty$. This does not correspond to physically acceptable behavior of the wavefunction, because $\int |\psi|^2 dV$ must be finite. The only way in which we can avoid this unphysical behavior is if the power series ([e9.49]) terminates at some maximum value of k . According to the recursion relation ([e9.51]), this is only possible if

$$\frac{\zeta}{2} = n, \quad (8.3.15)$$

where n is an integer, and the last term in the series is $c_n z^n$. Because the first term in the series is $c_{l+1} z^{l+1}$, it follows that n must be greater than l , otherwise there are no terms in the series at all. Finally, it is clear from Equations ([e9.45]), ([e9.47]), and ([e9.54]) that

$$E = \frac{E_0}{n^2} \quad (8.3.16)$$

and

$$a = n a_0, \quad (8.3.17)$$

where

$$E_0 = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} = -\frac{e^2}{8\pi\epsilon_0 a_0} = -13.6 \text{ eV}, \quad (8.3.18)$$

and

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = 5.3 \times 10^{-11} \text{ m}. \quad (8.3.19)$$

Here, E_0 is the energy of so-called *ground-state* (or lowest energy state) of the hydrogen atom, and the length a_0 is known as the *Bohr radius*. Note that $|E_0| \sim \alpha^2 m_e c^2$, where $\alpha = e^2/(4\pi\epsilon_0 \hbar c) \simeq 1/137$ is the dimensionless *fine-structure constant*. The fact that $|E_0| \ll m_e c^2$ is the ultimate justification for our non-relativistic treatment of the hydrogen atom.

We conclude that the wavefunction of a hydrogen atom takes the form

$$\psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\theta, \phi). \quad (8.3.20)$$

Here, the $Y_{l,m}(\theta, \phi)$ are the spherical harmonics (see Section [sharm]), and $R_{n,l}(z = r/a)$ is the solution of

$$\left[\frac{1}{z^2} \frac{d}{dz} z^2 \frac{d}{dz} - \frac{l(l+1)}{z^2} + \frac{2n}{z} - 1 \right] R_{n,l} = 0 \quad (8.3.21)$$

which varies as z^l at small z . Furthermore, the quantum numbers n , l , and m can only take values that satisfy the inequality

$$|m| \leq l < n, \quad (8.3.22)$$

where n is a positive integer, l a non-negative integer, and m an integer.

We expect the stationary states of the hydrogen atom to be orthonormal: that is,

$$\int \psi_{n',l',m'}^* \psi_{n,l,m} dV = \delta_{nn'} \delta_{ll'} \delta_{mm'}, \quad (8.3.23)$$

where dV is a volume element, and the integral is over all space. Of course, $dV = r^2 dr d\Omega$, where $d\Omega$ is an element of solid angle. Moreover, we already know that the spherical harmonics are orthonormal [see Equation ([\[spho\]](#))]: that is,

$$\oint Y_{l',m'}^* Y_{l,m} d\Omega = \delta_{ll'} \delta_{mm'}. \quad (8.3.24)$$

It, thus, follows that the radial wavefunction satisfies the orthonormality constraint

$$\int_0^\infty R_{n',l}^* R_{n,l} r^2 dr = \delta_{nn'}. \quad (8.3.25)$$

The first few radial wavefunctions for the hydrogen atom are listed below:

$$\begin{aligned} R_{1,0}(r) &= \frac{2}{a_0^{3/2}} \exp\left(-\frac{r}{a_0}\right), \\ R_{2,0}(r) &= \frac{2}{(2a_0)^{3/2}} \left(1 - \frac{r}{2a_0}\right) \exp\left(-\frac{r}{2a_0}\right), \\ R_{2,1}(r) &= \frac{1}{\sqrt{3} (2a_0)^{3/2}} \frac{r}{a_0} \exp\left(-\frac{r}{2a_0}\right), \\ R_{3,0}(r) &= \frac{2}{(3a_0)^{3/2}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) \exp\left(-\frac{r}{3a_0}\right), \\ R_{3,1}(r) &= \frac{4\sqrt{2}}{9 (3a_0)^{3/2}} \frac{r}{a_0} \left(1 - \frac{r}{6a_0}\right) \exp\left(-\frac{r}{3a_0}\right), \\ R_{3,2}(r) &= \frac{2\sqrt{2}}{27\sqrt{5} (3a_0)^{3/2}} \left(\frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{3a_0}\right). \end{aligned}$$

These functions are illustrated in Figures [\[coul1\]](#) and [\[coul2\]](#).

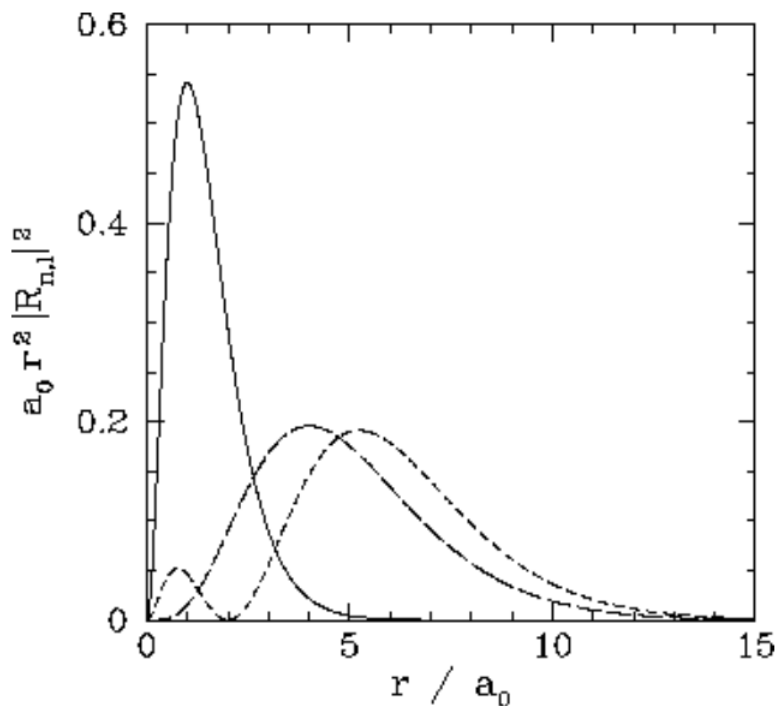


Figure 21: The $a_0 r^2 |R_{n,l}(r)|^2$ plotted as a functions of r/a_0 . The solid, short-dashed, and long-dashed curves correspond to $n, l = 1, 0$, and $2, 0$, and $2, 1$, respectively.

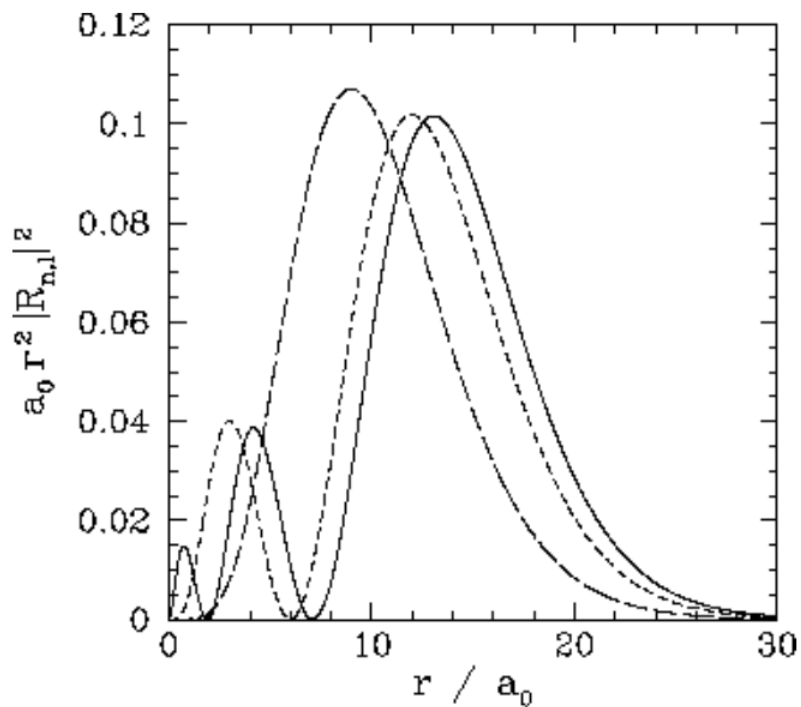


Figure 22: The $a_0 r^2 |R_{n,l}(r)|^2$ plotted as a functions of r/a_0 . The solid, short-dashed, and long-dashed curves correspond to $n, l = 3, 0$, and $3, 1$, and $3, 2$, respectively.

Given the (properly normalized) hydrogen wavefunction ([\[e9.59\]](#)), plus our interpretation of $|\psi|^2$ as a probability density, we can calculate

$$\langle r^k \rangle = \int_0^\infty r^{2+k} |R_{n,l}(r)|^2 dr, \quad (8.3.26)$$

where the angle-brackets denote an expectation value. For instance, it can be demonstrated (after much tedious algebra) that

$$\begin{aligned} \langle r^2 \rangle &= \frac{a_0^2 n^2}{2} [5n^2 + 1 - 3l(l+1)], \\ \langle r \rangle &= \frac{a_0}{2} [3n^2 - l(l+1)], \\ \left\langle \frac{1}{r} \right\rangle &= \frac{1}{n^2 a_0}, \\ \left\langle \frac{1}{r^2} \right\rangle &= \frac{1}{(l+1/2)n^3 a_0^2}, \\ \left\langle \frac{1}{r^3} \right\rangle &= \frac{1}{l(l+1/2)(l+1)n^3 a_0^3}. \end{aligned}$$

According to Equation ([e9.55]), the energy levels of the bound-states of a hydrogen atom only depend on the radial quantum number n . It turns out that this is a special property of a $1/r$ potential. For a general central potential, $V(r)$, the quantized energy levels of a bound-state depend on both n and l . (See Section 1.3.)

The fact that the energy levels of a hydrogen atom only depend on n , and not on l and m , implies that the energy spectrum of a hydrogen atom is highly degenerate: that is, there are many different states which possess the same energy. According to the inequality ([e9.61]) (and the fact that n , l , and m are integers), for a given value of l , there are $2l+1$ different allowed values of m (i.e., $-l, -l+1, \dots, l-1, l$). Likewise, for a given value of n , there are n different allowed values of l (i.e., $0, 1, \dots, n-1$). Now, all states possessing the same value of n have the same energy (i.e., they are degenerate). Hence, the total number of degenerate states corresponding to a given value of n is

$$1 + 3 + 5 + \dots + 2(n-1) + 1 = n^2. \quad (8.3.27)$$

Thus, the ground-state ($n=1$) is not degenerate, the first excited state ($n=2$) is four-fold degenerate, the second excited state ($n=3$) is nine-fold degenerate, et cetera (Actually, when we take into account the two spin states of an electron, the degeneracy of the n th energy level becomes $2n^2$.)

Contributors and Attributions

- [Richard Fitzpatrick](#) (Professor of Physics, The University of Texas at Austin)

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