Hydrogen Atom

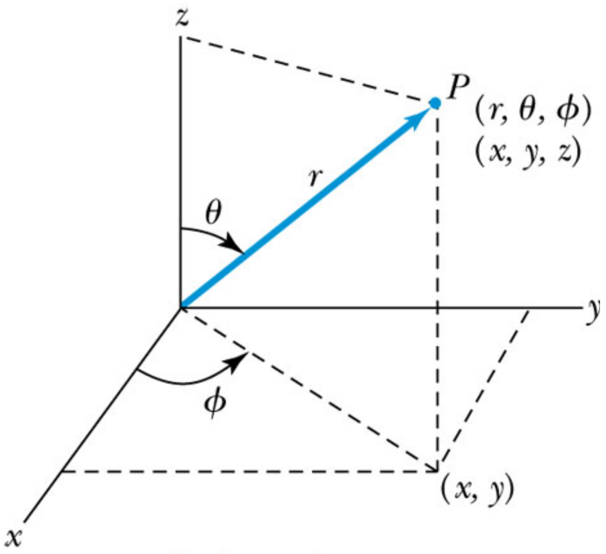
In quantum mechanics, the hydrogen atom is described as an electron moving in response to its Coulomb attraction to the (much heavier) proton. The potential is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} = -\frac{\alpha\hbar c}{r},$$

where

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137.036}, \qquad \hbar c = 1.973 \times 10^{-7}\,\mathrm{eV\,m}.$$

Since the potential depends only on r, it is convenient to use spherical polar coordinates r, θ and ϕ to solve the Schroedinger equation.



$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = \cos^{-1}\frac{z}{r} \quad \text{(Polar angle)}$$

$$\phi = \tan^{-1}\frac{y}{x} \quad \text{(Azimuthal angle)}$$

The important point here is that the potential energy that enters the Schroedinger equation, V(r), is independent of the angular variables. The θ, ϕ solution can thus be calculated once and for all using separation of variables.

The Schroedinger equation is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\,\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\,\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2m}{\hbar^2}(E-V)\psi=0.$$

Tackling this looks rather formidable, but if we put

$$\psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi),$$

we get three separate equations

$$\begin{aligned}\frac{d^2\Phi}{d\phi^2}+m^2\Phi &= 0,\\ \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left[\ell(\ell+1)-\frac{m^2}{\sin^2\theta}\right]\Theta &= 0,\\ \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{\ell(\ell+1)}{r^2}R+\frac{2m}{\hbar^2}\left(E-V\right)R &= 0.\end{aligned}$$

The solutions to the angular equations, while not easy to obtain, results in an infinite collection of functions

$$Y_\ell^m(\theta,\phi) \text{ with } \ell = 0, 1, 2, \ldots, \; m = -\ell, -\ell+1, \ldots, \ell-1, \ell.$$

For every l there are (2l+1) m's. The interpretation of these quantum numbers is that the square of the angular momentum L is

$$\vec{L}^2 = \ell(\ell+1)\hbar^2,$$

and the z-component is

$$L_z = m\hbar.$$

Explicit Y_l^m's are shown in the Table.

Note that the pattern of angular momentum quantization is very different from Bohr's model. In particular, $l = 0$ is allowed.

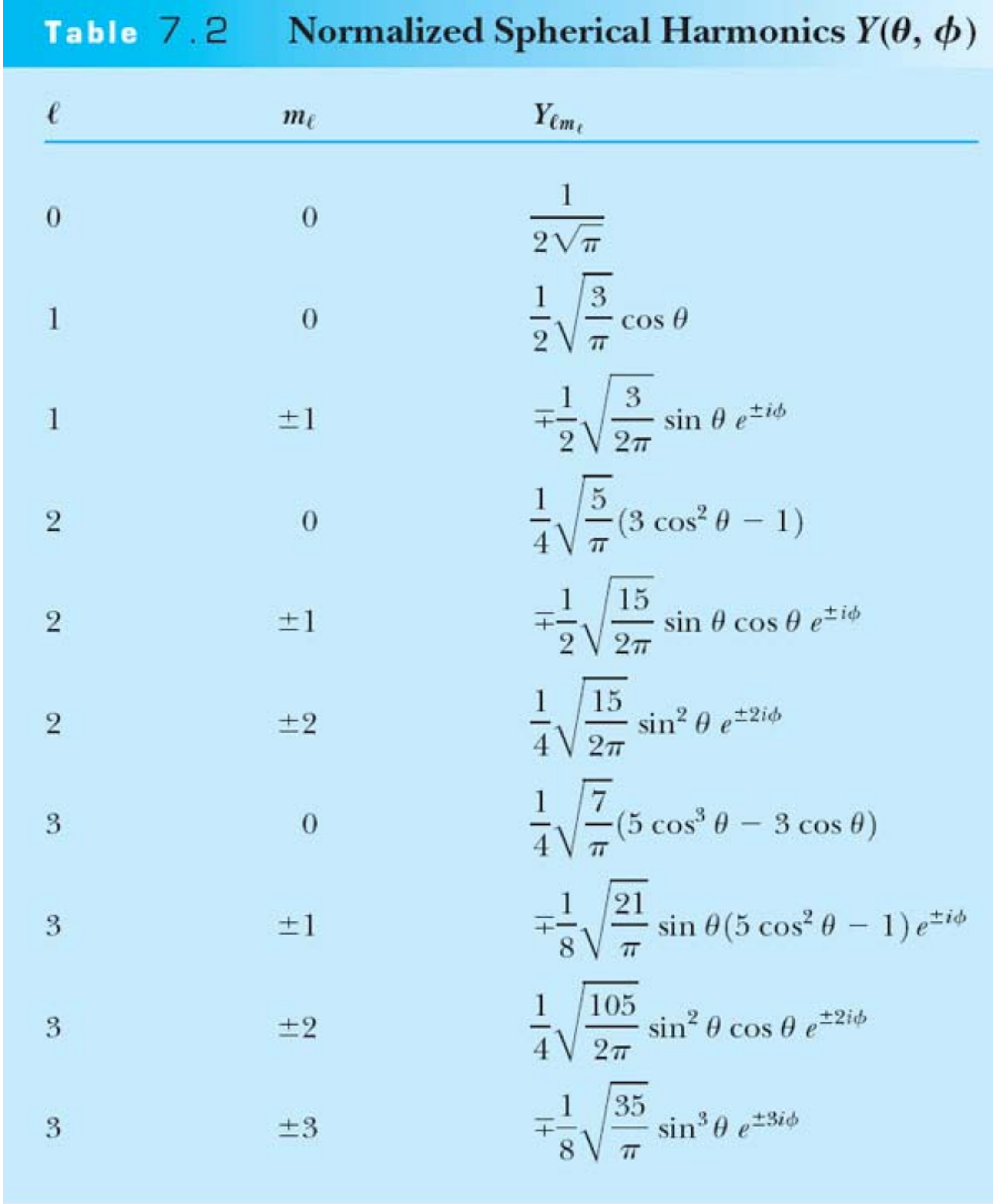


Table 7.2 Normalized Spherical Harmonics $Y(\theta, \phi)$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	±1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	±1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
2	±2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$
3	±1	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)\, e^{\pm i\phi}$
3	±2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
3	±3	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

Just like the energy eigenfunctions in one dimension, the $Y_l^m(\theta,\phi)$ satisfy orthogonality relations. Since $dxdydz = r^2 dr \underline{\sin\theta d\theta d\phi}$, the angular integrals are

$$\begin{aligned}\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \, Y_{\ell'}^{m'\,*}(\theta,\phi) Y_\ell^m(\theta,\phi) &= 0 \text{ for } \ell' \neq \ell \; m' \neq m, \\ \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \, |Y_\ell^m(\theta,\phi)|^2 &= 1.\end{aligned}$$

These functions serve as the angular part of any system with a potential V(r), and

$$\psi(r,\theta,\phi) = R_{n\ell}(r) \, Y_\ell^m(\theta,\phi).$$

The Coulomb Potential

The remaining equation for R(r), the radial equation, determines the actual energy levels E. In general, E will depend on l. Note that, for different l's, the wave functions $\psi(r,\theta,\phi)$ are orthogonal because their angular factors $Y_l^m(\theta,\phi)$ are orthogonal.

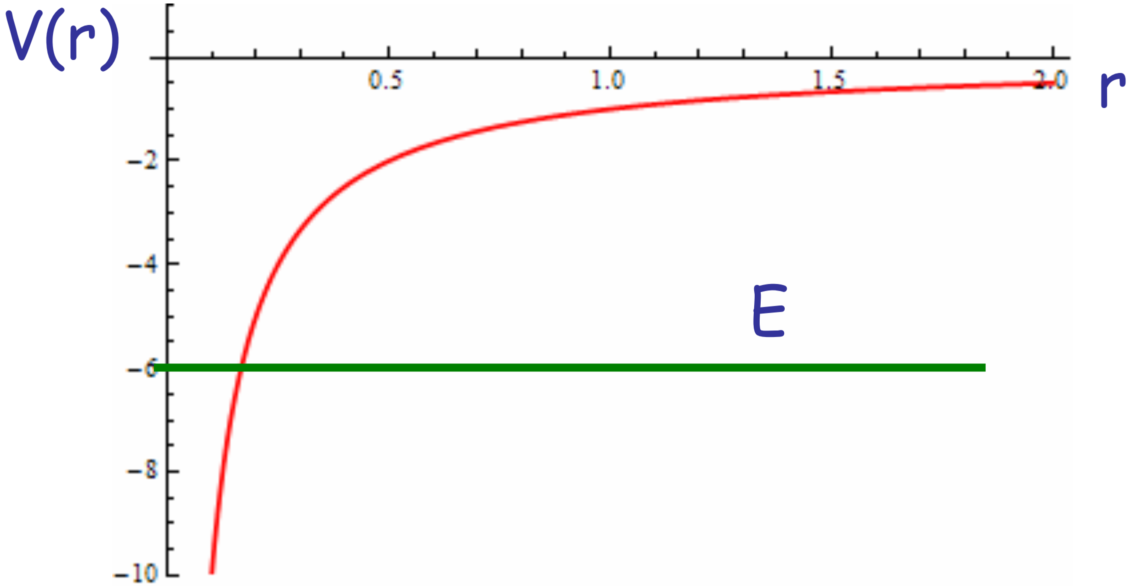
For a fixed l, the orthogonality of $\psi(r,\theta,\phi)$ is determined by the radial integral

$$\int_0^\infty dr r^2 R_{n'\ell}(r) R_{n\ell}(r) = 0 \text{ for } n' \neq n.$$

For hydrogen, the radial equation is

$$
\begin{aligned}
\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{\ell(\ell+1)}{r^2}R+\frac{2m}{\hbar^2}\left(E+\frac{\alpha\hbar c}{r}\right)R &= 0\\
\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}-\frac{\ell(\ell+1)}{r^2}R+\frac{2m}{\hbar^2}\left(E+\frac{\alpha\hbar c}{r}\right)R &= 0.
\end{aligned}
$$

From the form of the potential, the bound states are those with E < 0.



To solve for R(r), note that for r large, the radial equation reduces to

$$\frac{d^2R(r)}{dr^2} - \kappa^2 R(r) = 0, \ \text{with } \kappa = \sqrt{-\frac{2mE}{\hbar^2}}.$$

Hence, at large r,

$$R(r) \sim Ae^{-\kappa r}.$$

For r near 0, it can be shown that

$$R(r) \rightarrow Br^{\ell}.$$

So, we know the behavior at the boundaries.

Let's focus on $l = 0$. We anticipate that the ground state has no nodes between 0 and infinity, the first excited state has one node, etc. Since the solutions vanish exponentially fast as r approaches ∞, a solution of the form

$$R(r) = L(r)e^{-\kappa r},$$

where L(r) is a polynomial could work. Putting this into the $l = 0$ radial equation

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2m}{\hbar^2}\left(E + \frac{\alpha\hbar c}{r}\right)R = 0$$

gives

$$rL''(r) + 2(1 - \kappa r)L'(r) + 2(mc\alpha/\hbar - \kappa)L(r) = 0.$$

If we try the polynomial

$$L_{n'}(r) = \sum_{k=0}^{n'} b_k r^k,$$

the coefficient of $r^{n'}$ can only vanish if

$$\begin{aligned} \left(-2n'\kappa + 2(mc\alpha/\hbar - \kappa)\right) b_{n'} &= 0 \\ \kappa &= \frac{mc\alpha}{(n'+1)\hbar}. \end{aligned}$$

These polynomials are Laguerre polynomials.

The means that the s-state energies are

$$E = -\frac{\hbar^2}{2m}\kappa^2 = -\frac{mc^2\alpha^2}{2(n'+1)^2}, \quad n' = 0, 1, \ldots$$

These are the Bohr levels with n = n′ + 1. This is clearly not the whole story because there are infinitely more levels for

$$\ell = 1, 2, 3, \ldots$$

Taking the other angular momentum states into account gives a very similar formula

$$E_n = -\frac{mc^2\alpha^2}{2n^2} = -\frac{mc^2\alpha^2}{2(n'+\ell+1)^2}, \quad \ell = 0, 1, \ldots, n-1.$$

For a given n there are many equal values of E_n corresponding to a variety of quantum numbers. For example, if $n = 2$, the single s-state with $n' = 1$ and $l = 0$ and the three p-states with $n' = 0$ and $l = 1$ have the same energy.

The energies E_n are said to be degenerate. For any n the degeneracy is n^2. This is a new feature of this more complete description of quantum mechanics.

Our expression for the radial solution for s-states takes the form

$$R_{n0}(r) = L_{n-1}(r)e^{-r/(na)}, \quad a = \frac{\hbar}{mc\alpha},$$

where $L_{n-1}(r)$ is the polynomial

$$L_{n-1}(r) = \sum_{k=0}^{n-1} b_k r^k,$$

that satisfies

$$rL''(r) + 2(1 - \kappa r)L'(r) + 2(mc\alpha/\hbar - \kappa)L(r) = 0.$$

The ground state corresponds to $n = 1$, and the polynomial $L_0(r)$ is just a constant. Our solution is

$$R_{10}(r) = b_0 e^{-r/a}.$$

b_0 is determined by normalization,

$$\int_0^\infty dr\, r^2 \, |R_{10}(r)|^2 = 1.$$

Note that the r^2 appears because the volume element is $dxdydz = \underline{r^2dr}\sin\theta d\theta d\phi$.

Normalizing hydrogen wave functions is relatively easy because of this simple result

$$\int_0^\infty dr r^n e^{-\lambda r} = \frac{1}{\lambda^{n+1}} \int_0^\infty du u^n e^{-u} = \frac{n!}{\lambda^{n+1}}.$$

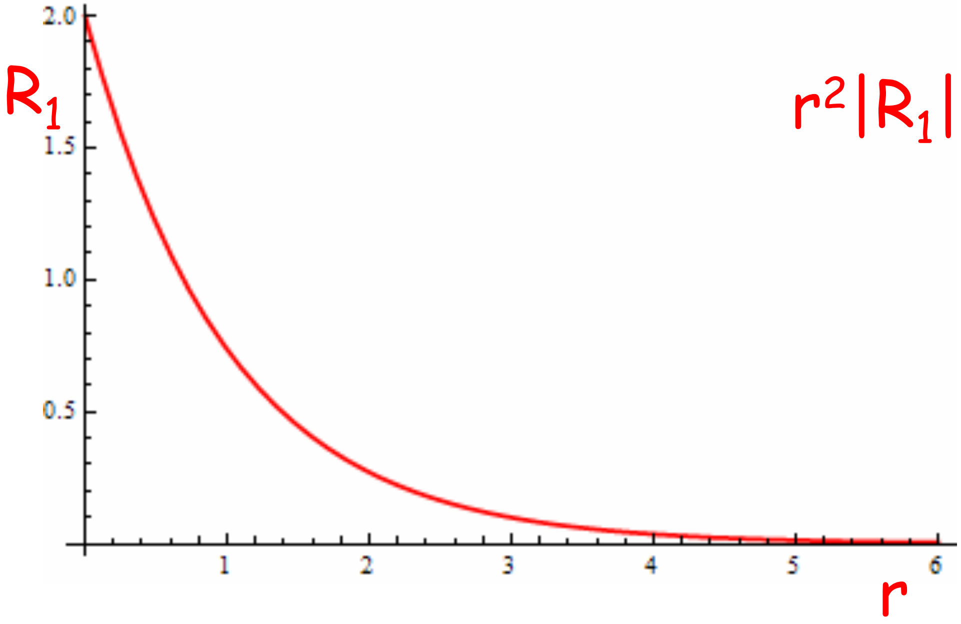
Using this formula, the normalized ground state radial wave function is

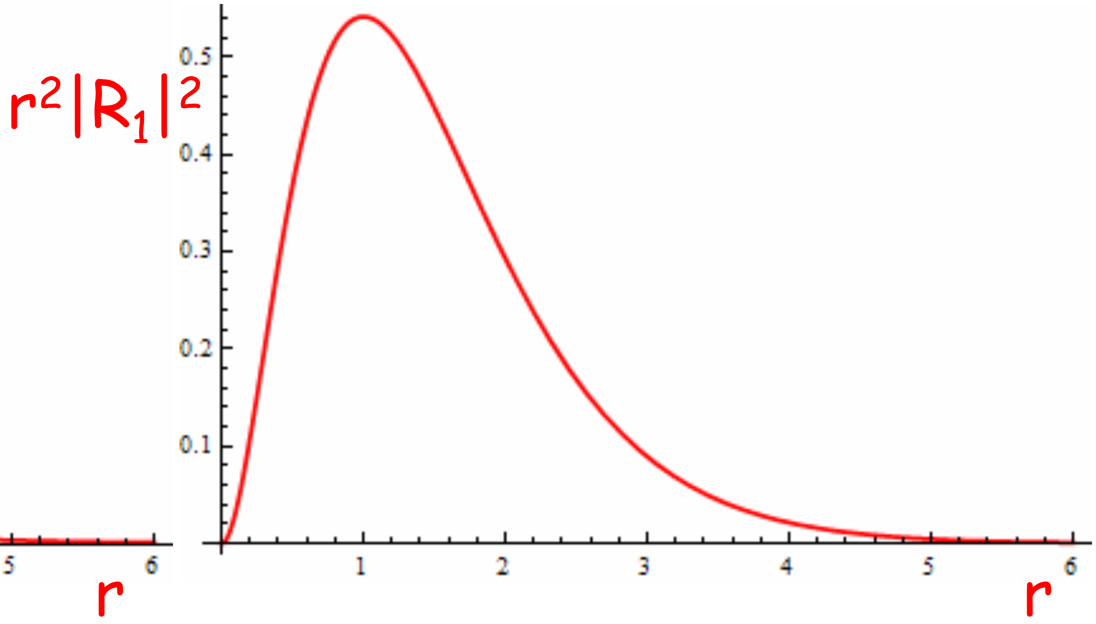
$$R_{10}(r) = \frac{2}{\sqrt{a^3}} e^{-r/a},$$

and the ground state probability density is

$$r^2 R_{10}^2(r) = \frac{4}{a^3} r^2 e^{-2r/a}.$$

These look like





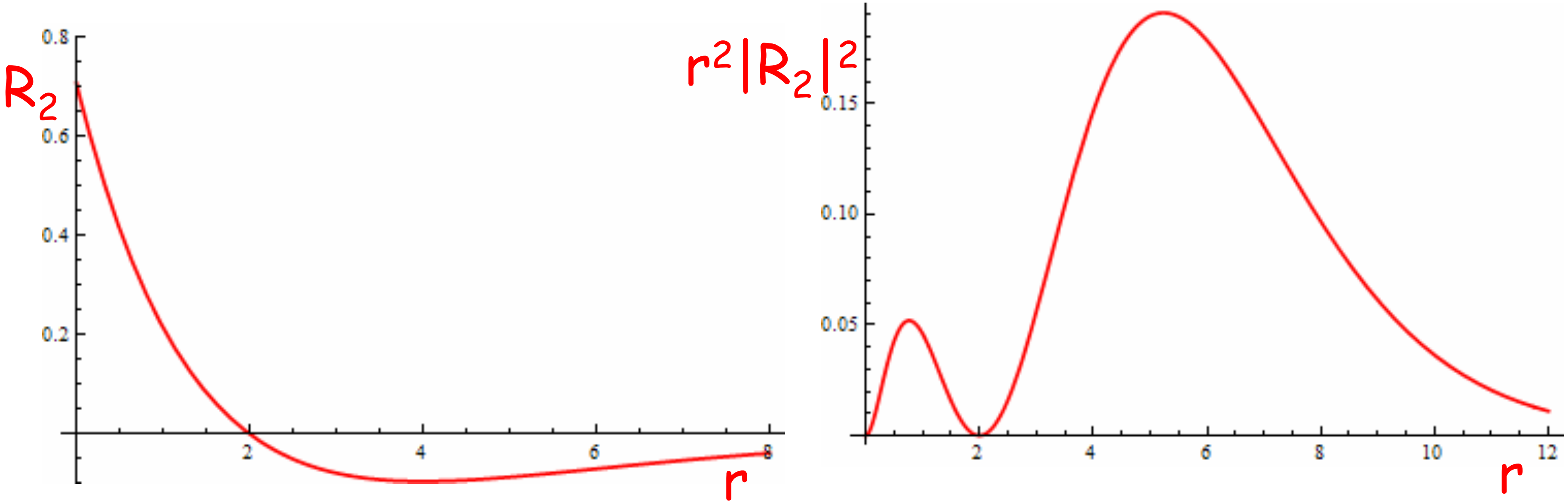
These graphs illustrate

a. The radial wave function is finite at $r = 0$.

b. The electron is not located at $r = a$.

c. The most probable value of r is $r = a$.

For the n = 2 s-state, the graphs are



Here, the circumstances are

a. The radial wave function is finite at $r = 0$.

b. There are two peaks in the probability density, neither at $r = 4a$, the Bohr value.

c. The is one node in the radial wavefunction.

Table 7.1 Hydrogen Atom Radial Wave Functions

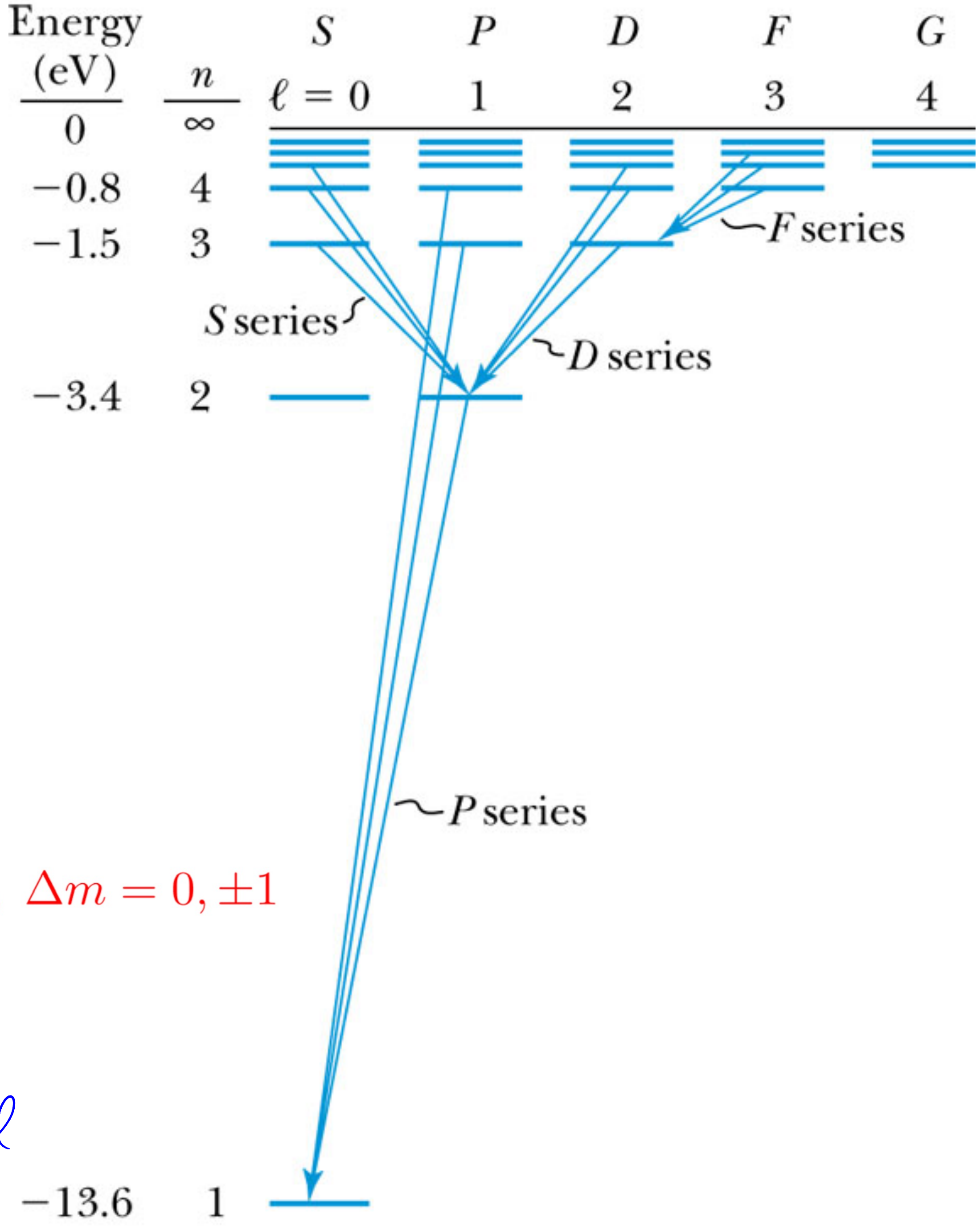
n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0^2} e^{-r/3a_0}$

The complete hydrogen spectrum is made up of many lines. The S levels start at n = 1. The P levels start at n = 2, are degenerate with the S levels for n = 2,3,…. The D levels begin at n = 3 and are degenerate with the S and P levels for n = 3,4,… .

Various photon transitions can occur between these levels. The dominant among these satisfy

$$\begin{aligned} \Delta n &= \text{anything},\ \Delta\ell = \pm 1,\ \Delta m = 0, \pm 1 \\ E_\gamma &= E_{n'} - E_n = \hbar\omega. \end{aligned}$$

The photon decay patterns are outline in this figure. Note that the situation is more complex than the Bohr model.



© 2006 Brooks/Cole - Thomson

$$\Delta n = \text{anything},\ \Delta\ell = \pm 1,\ \Delta m = 0, \pm 1$$

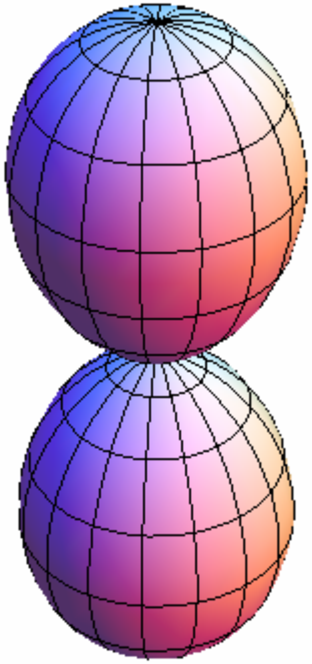
$$E_\gamma = E_{n'} - E_n = \hbar\omega.$$

$\ell = 0, 1, 2, \cdots n$

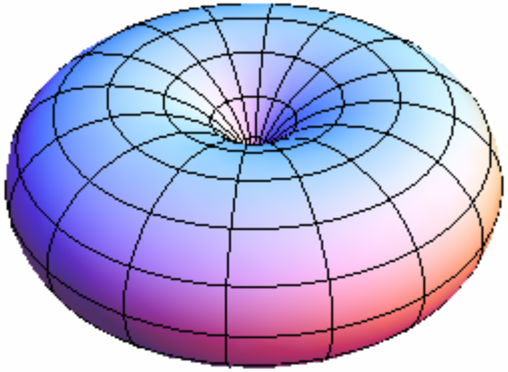
$m = -\ell, -\ell+1, \cdots 0, \cdots \ell-1, +\ell$

The angular distributions for the $l = 1,2$ probabilities and very directional.

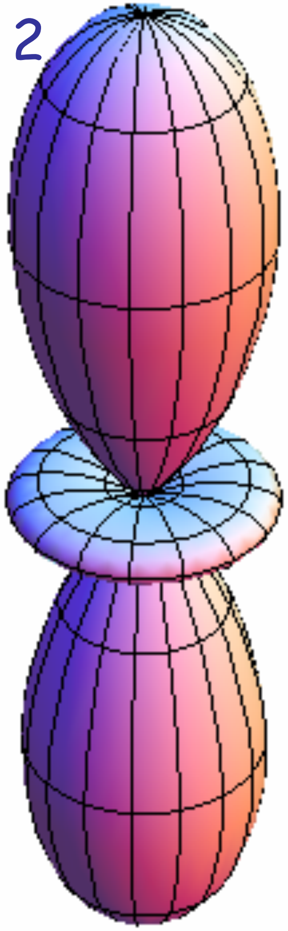
$|Y_1^0|^2$



$|Y_1^1|^2$



$|Y_2^0|^2$



We know that the electron in a hydrogen atom is characterized by an principle quantum number $n = 1,2,3,\ldots,$ and an angular momentum quantum number $l = 0,1,2,\ldots,$ where, for a given n, $\boxed{l = 0,1,\ldots,n-1.}$ The angular wave functions a $(2l+1)$ fold degenerate and are labeled by m, with

$$\boxed{m = 0, \pm 1, \pm 2, \ldots, \pm(\ell - 1), \pm \ell.}$$

For all this complicated structure, the hydrogen energy is simply

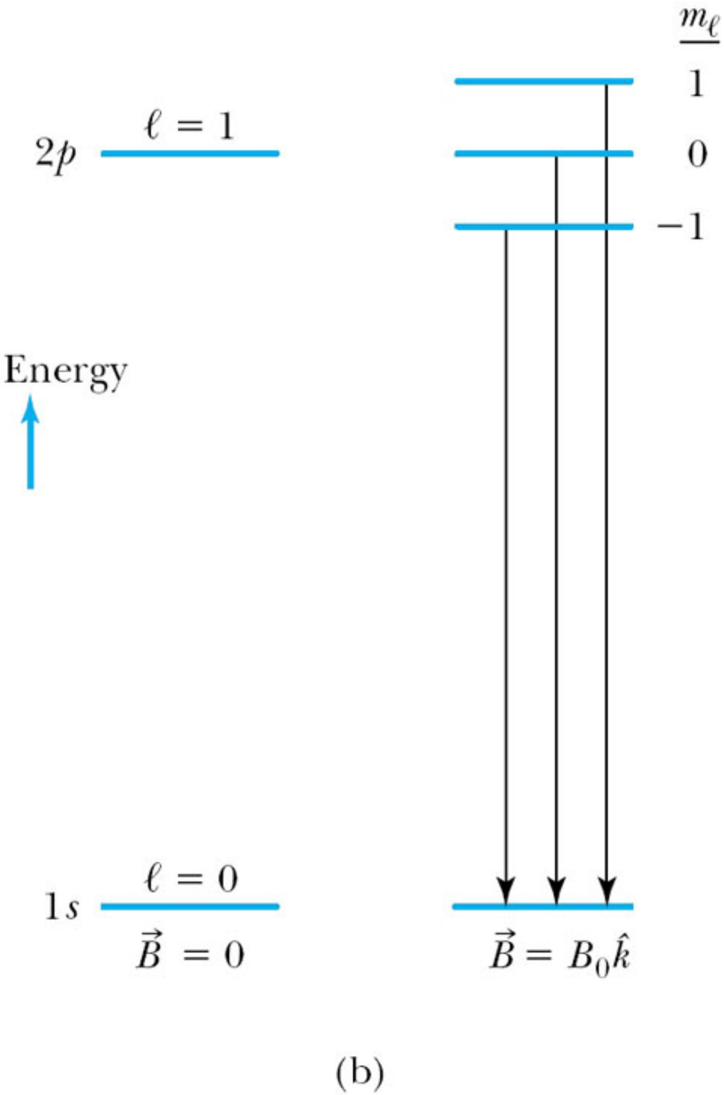
$$E_n = -\frac{mc^2\alpha^2}{2n^2} = -\frac{13.6\,\mathrm{eV}}{n^2}.$$

Magnetic Fields and the Quantum Number m

The spherical symmetry of the Coulomb potential implies that the 2l+1 values of m in the angular functions $Y_l^m(\theta,\phi)$ all have the same energy. If a hydrogen atom is placed in a magnetic field B, this degeneracy is removed. The potential is modified by an additional term

$$V_{L\ \mathrm{Mag}} = \boxed{\frac{e}{2m_e}} L_z B = \mu_B m_\ell B, \quad \mu_B = \frac{e\hbar}{2m_e} = 5.79 \times 10^{-5}\,\mathrm{eV/T}.$$

For the 2p state, the effect is to split the level into three different energies.

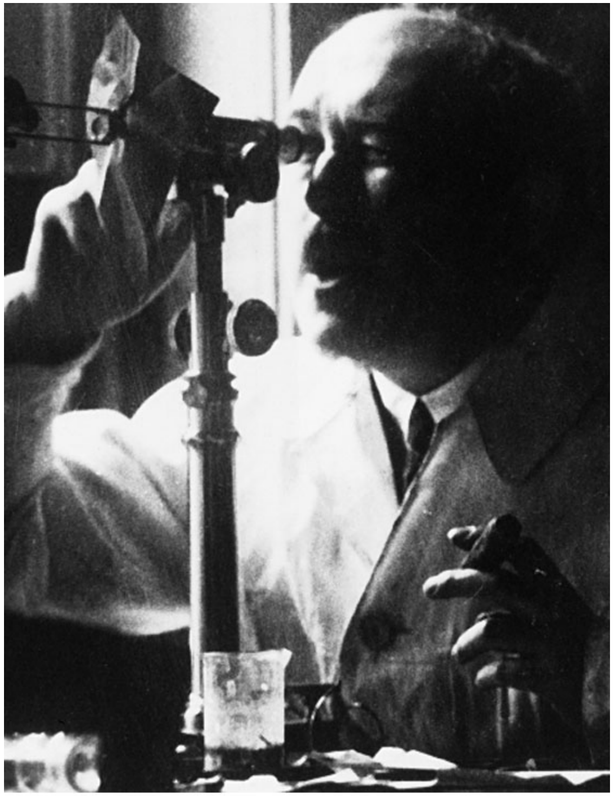


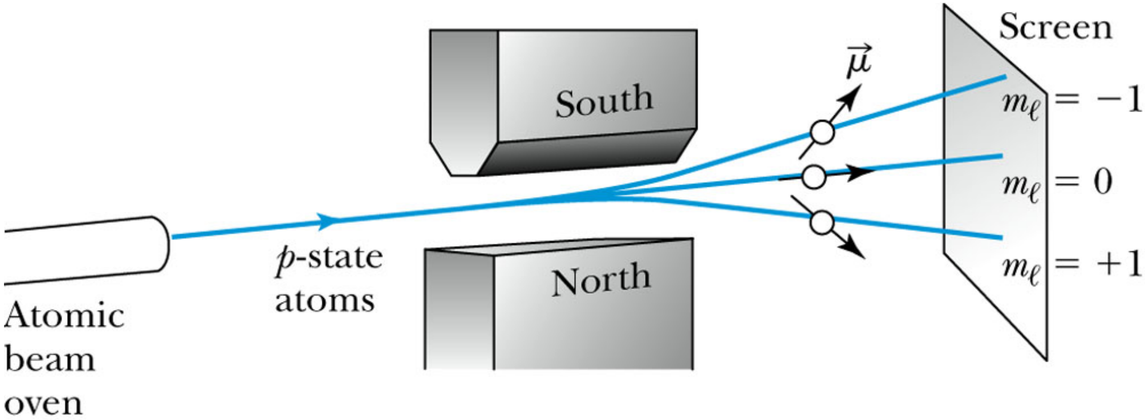
In a 2 Tesla field, the splitting is small

$$\Delta E_{Mag} = 1.16 \times 10^{-4}\,\mathrm{eV}.$$

Pieter Zeeman
Nobel Prize
1902

The observation of magnetic splitting in the spectrum motivated Otto Stern and Walter Gerlach to search for evidence of spatial splitting using a atomic beam and an inhomogeneous magnet.

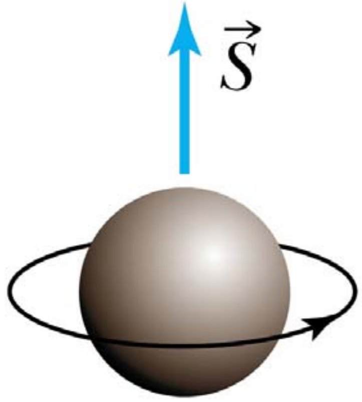




1922

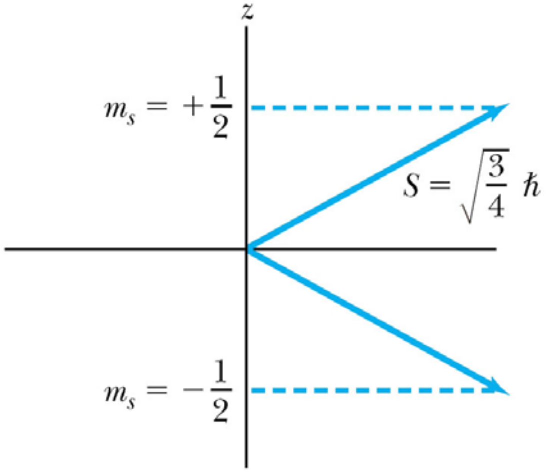
The Stern-Gerlach experiment used a silver atomic beam that passed through the magnet and produced <u>two</u> spots on the screen.

In 1925, Dutch graduate students George Uhlenbeck and Samuel Goudsmit proposed that the electron itself had an intrinsic spin with two m_s values, 1/2 and -1/2.



(a)

© 2006 Brooks/Cole - Thomson



(b)

© 2006 Brooks/Cole - Thomson

Because of its charge, the electron would also have a magnetic moment that interacted with a uniform magnetic field as

$$V_{S\,\mathrm{Mag}} = \frac{e}{m} S_z B = 2\mu_B m_s B.$$

The extra factor of 2, that was determined from experiment, can only be derived by a relativistic treatment. As we shall see, the inclusion of electron spin is crucial in understanding atomic structure.

→ Dirac Equation

With the electron spin, the hydrogen energy eigenstates have the form

$$\psi_{n\ell m_\ell m_s}(\vec{r}) = R_{n\ell}(r)Y_\ell^{m_\ell}(\theta,\phi)\chi^{m_s},$$

where the last factor is the spin wave function and $m_s = 1/2, -1/2$.

The degeneracy of any level is, including the electron spin, $2n^2$. This does not alter the energy levels. They remain

$$E_n = -\frac{mc^2\alpha^2}{2n^2} = -\frac{13.6\,\mathrm{eV}}{n^2}.$$

We have developed explicit forms for the radial and angular wavefunctions. The spin wave function is usually treated as a two-component column vector.

$$\chi^{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi^{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Since there are only two values of m_s, the notation is often shortened to

$$\chi^{+} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi^{-} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

The x, y and z components of the spin are then represented by 2 x 2 matrices introduced by Wolfgang Pauli.

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

In this picture, χ^+ and χ^- are eigenvectors of S_z.

$$\begin{aligned} S_z\chi^+ &= \frac{\hbar}{2}\chi^+, \\ S_z\chi^- &= -\frac{\hbar}{2}\chi^-. \end{aligned}$$

The complete picture of a hydrogen eigenstate is

$$\begin{aligned}
H\psi_{n\ell m_\ell m_s}(\vec{r}) &= -\frac{mc^2\alpha^2}{2n^2}\psi_{n\ell m_\ell m_s}(\vec{r}) \\
\vec{L}^2\psi_{n\ell m_\ell m_s}(\vec{r}) &= \ell(\ell+1)\hbar^2\psi_{n\ell m_\ell m_s}(\vec{r}) \\
L_z\psi_{n\ell m_\ell m_s}(\vec{r}) &= m_\ell\hbar\,\psi_{n\ell m_\ell m_s}(\vec{r}) \\
S_z\psi_{n\ell m_\ell m_s}(\vec{r}) &= m_s\hbar\,\psi_{n\ell m_\ell m_s}(\vec{r})
\end{aligned}$$

that is, it is an eigenstate of four physically measurable quantities, energy, the square of the orbital angular momentum, its z component and the z component of spin.

Although more complicated, the superposition principle works and we can write the complete time-dependent solution as

$$\Psi(\vec{r},t) = \sum_{n=1}^{\infty} \sum_{\ell=0}^{n-1} \sum_{m_\ell=-\ell}^{\ell} \sum_{m_s=-1/2}^{1/2} a_{n\ell m_\ell m_s} \psi_{n\ell m_\ell m_s}(\vec{r}) e^{-iE_n t/\hbar}.$$

The probability interpretation of the coefficients still applies, so, for example, the probability that a measurement of the energy will yield $E = -mc^2\alpha^2/8$ is

$$P(E = -mc^2\alpha^2/8) = \sum_{\ell=0}^{1} \sum_{m_\ell=-\ell}^{\ell} \sum_{m_s=-1/2}^{1/2} |a_{2\ell m_\ell m_s}|^2 .$$