

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

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

$= 197 \text{ (MeV)} \cdot \text{(fm)}$
 $\hookrightarrow (10^6 \text{ eV}) \cdot (10^{-15} \text{ m})$

Hydrogen Atom

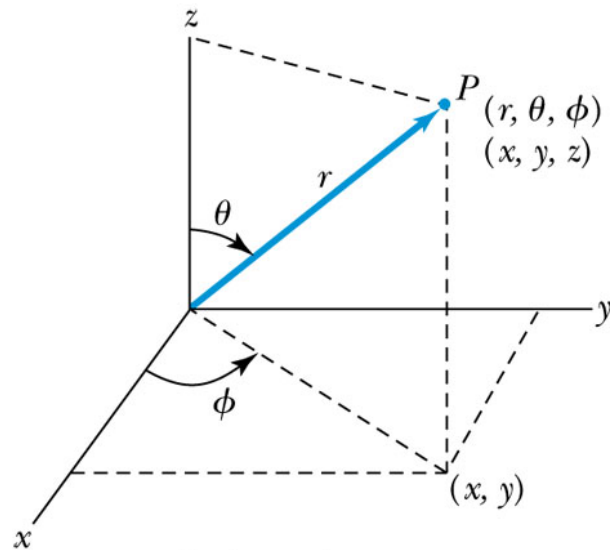
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Since the potential depends only on r , it is convenient to use spherical polar coordinates r , θ and ϕ to solve the Schrodinger equation.



$$\begin{aligned}x &= r \sin \theta \cos \phi \\y &= r \sin \theta \sin \phi \\z &= r \cos \theta\end{aligned}$$

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

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

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

The important point here is that the potential energy that enters the Schrodinger 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

$$\frac{d^2 \Phi}{d\phi^2} + m^2 \Phi = 0,$$

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left[\ell(\ell + 1) - \frac{m^2}{\sin^2 \theta} \right] \Theta = 0,$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{\ell(\ell + 1)}{r^2} R + \frac{2m}{\hbar^2} (E - V) R = 0.$$

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

$Y_\ell^m(\theta, \phi)$ with $\ell = 0, 1, 2, \dots$, $m = -\ell, -\ell + 1, \dots, \ell - 1, \ell$.

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

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

and the z-component is

$$L_z = m\hbar.$$

Building functions on the surface of a sphere:

$$f(\theta, \varphi) = \sum_{\ell, m} c_{\ell m} Y_{\ell m}(\theta, \varphi)$$

$$c_{\ell m} = \langle f, Y_{\ell m} \rangle = \int_0^{2\pi} \int_0^\pi f(\theta, \varphi) Y_{\ell m}^*(\theta, \varphi) \sin \theta \, d\theta \, d\varphi$$

Orthonormality:

$$\langle Y_{\ell m}, Y_{\ell' m'} \rangle = \delta_{\ell \ell'} \delta_{m m'}$$

Completeness:

$$\sum_{\ell, m} Y_{\ell m}(\theta, \varphi) Y_{\ell m}^*(\theta', \varphi') = \frac{\delta(\theta - \theta') \delta(\varphi - \varphi')}{\sin \theta'}$$

Periodicity:

$$Y_{\ell m}(\theta, \varphi) = Y_{\ell m}(\theta, \varphi + 2\pi)$$

Well-behaved:

no singularities, no discontinuities, etc.

Laplace's equation $\vec{\nabla} \cdot \vec{\nabla} f(\vec{r}) = 0$

$$f(\vec{r}) = \Theta(\theta) \Phi(\varphi)$$

Angular part of Laplace's equation:

$$\frac{1}{\Theta(\theta)} \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) \Theta(\theta) + C \sin^2 \theta = -\frac{1}{\Phi(\varphi)} \frac{d^2}{d\varphi^2} \Phi(\varphi)$$



$$\frac{d^2}{d\varphi^2} \Phi(\varphi) = -m^2 \Phi(\varphi) \Rightarrow \Phi(\varphi) = Ae^{im\varphi} + Be^{-im\varphi}$$

$$\Phi(\varphi) = \Phi(\varphi + 2\pi) \Rightarrow m = 0, \pm 1, \pm 2, \dots$$

$$\frac{1}{\Theta(\theta)} \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) \Theta(\theta) + \ell(\ell + 1) \sin^2 \theta = m^2 \Rightarrow \Theta(\theta) = D P_\ell^m(\cos \theta) + E Q_\ell^m(\cos \theta)$$

$$\Theta(\theta) \text{ should be well-behaved: } \Rightarrow \ell = 0, 1, 2, \dots, \quad |m| \leq \ell, \quad E = 0$$

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 $dx dy dz = r^2 dr \sin\theta d\theta d\phi$, the angular integrals are

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

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

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

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

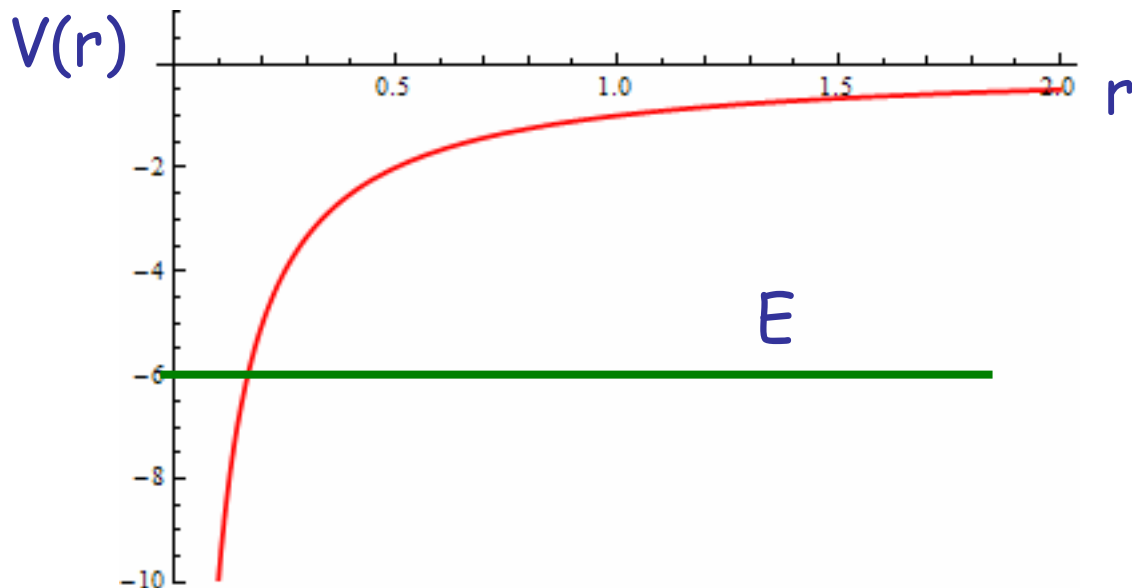
$$\int_0^{\infty} dr r^2 R_{n'l}(r) R_{nl}(r) = 0 \text{ for } n' \neq n.$$

For hydrogen, the radial equation is

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

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

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

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

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

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

gives

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

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

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

These polynomials are Laguerre polynomials.

The means that the s-state energies are

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

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

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

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

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

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

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

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

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

that satisfies

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

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 $dx dy dz = \underline{r^2 dr \sin\theta d\theta d\phi}$.

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

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

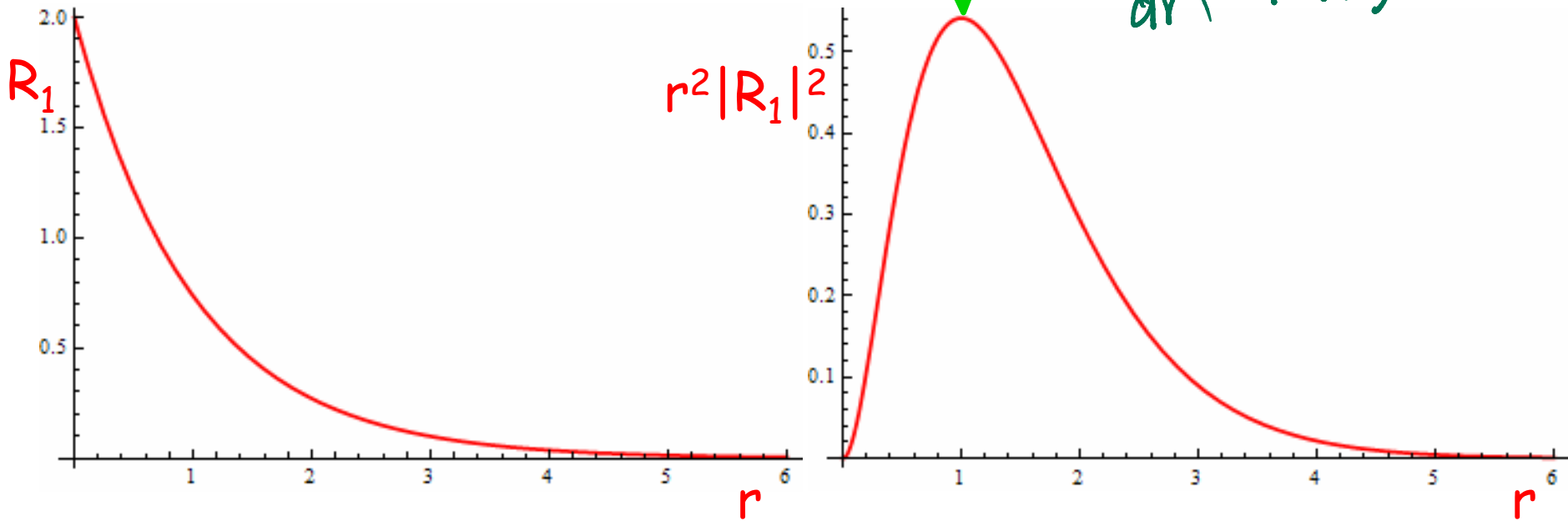
Using this formula, the normalized ground state radial wave function is

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

and the ground state probability density is

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

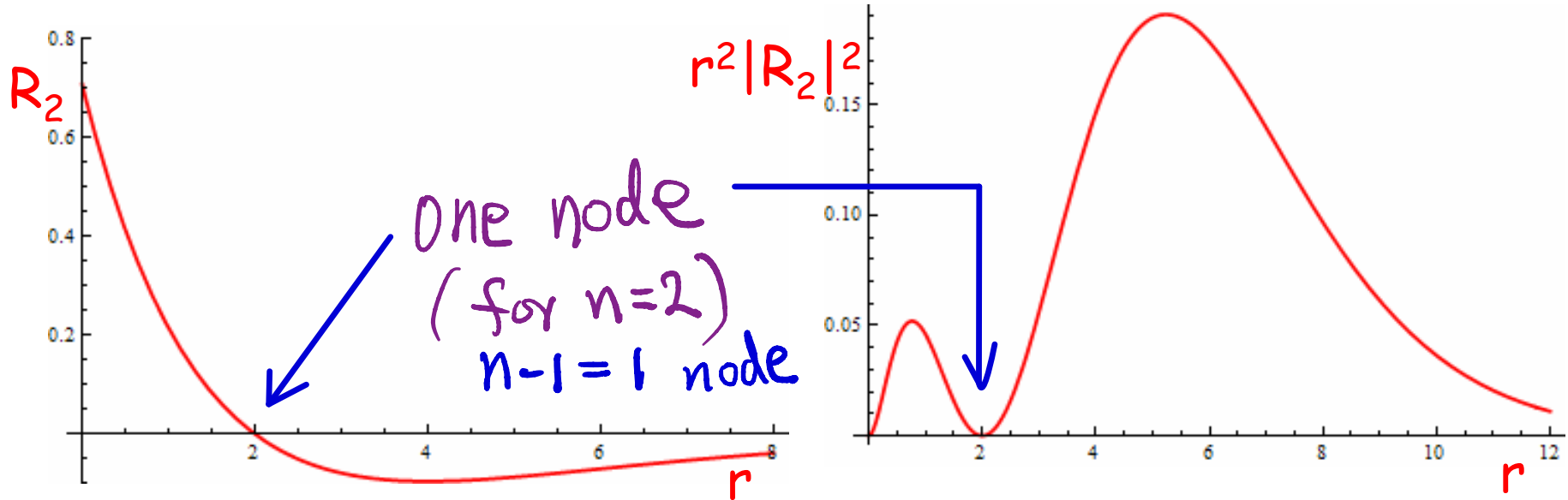
These look like



These graphs illustrate

- The radial wave function is finite at $r = 0$.
- The electron is not located at $r = a$.
- The **most probable value** of r is $r = a$.

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



Here, the circumstances are

- The radial wave function is finite at $r = 0$.
- There are two peaks in the probability density, neither at $r = 4a$, the Bohr value.
- The ψ is one node in the radial wavefunction⁶.

Table 7.1

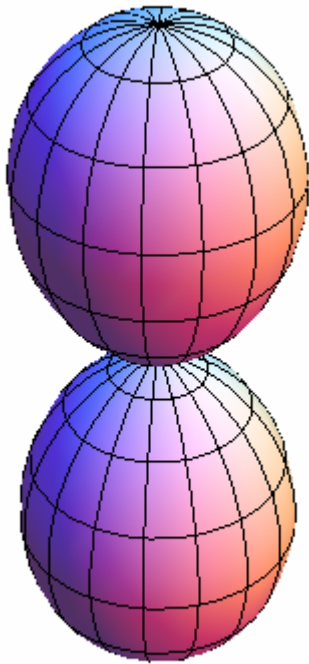
Hydrogen Atom Radial Wave Functions

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

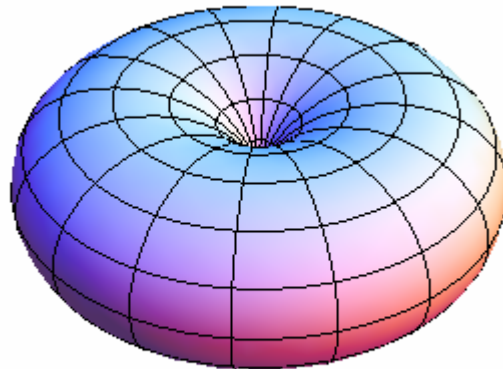
$R_{n0}(r) \neq 0$

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

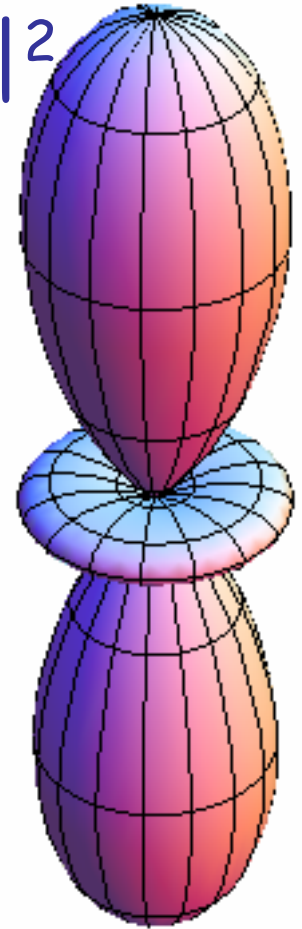
$$|Y_1^0|^2$$



$$|Y_1^1|^2$$



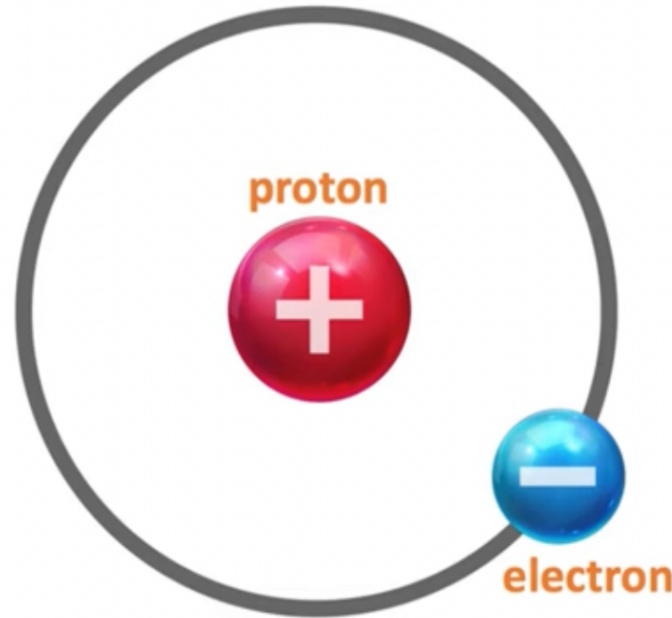
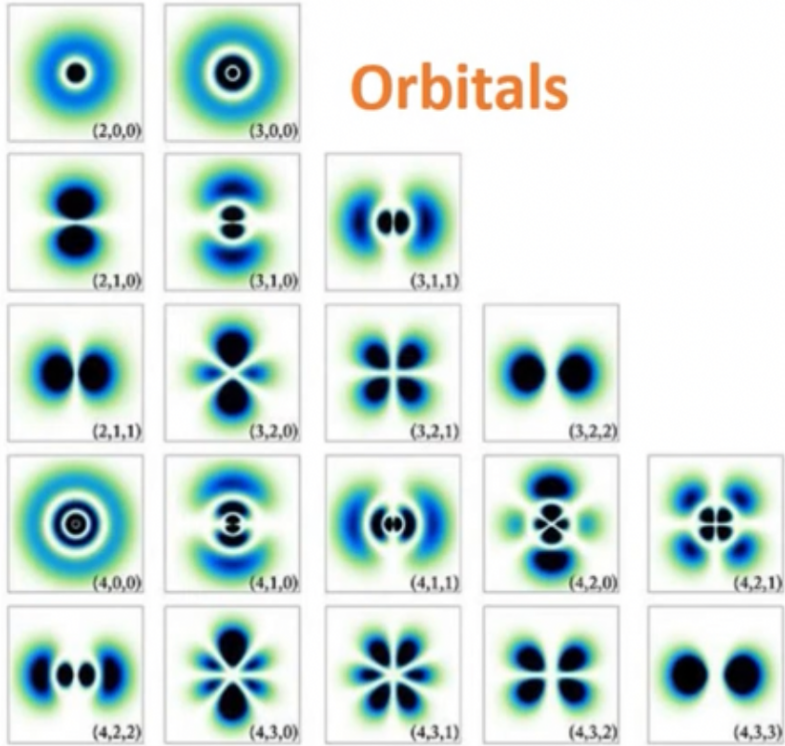
$$|Y_2^0|^2$$



The Hydrogen atom

Atomic Wavefunctions

$$\psi_{n,l,m}(r, \theta, \varphi) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-r/na} \left(\frac{2r}{na}\right)^l [L_{n-l-1}^{2l+1}(2r/na)] Y_l^m(\theta, \varphi)$$



Bohr formula

$$E_n = -\frac{\hbar^2}{2m} \left(\frac{1}{an}\right)^2$$

Rydberg formula

$$\frac{1}{\lambda} = \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) R$$

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 $n = 2, 3, \dots$. The D levels begin at $n = 3$ and are degenerate with the S and P levels for $n = 3, 4, \dots$.

Various photon transitions can occur between these levels. The dominant among these satisfy *(electric dipole transition)*

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

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

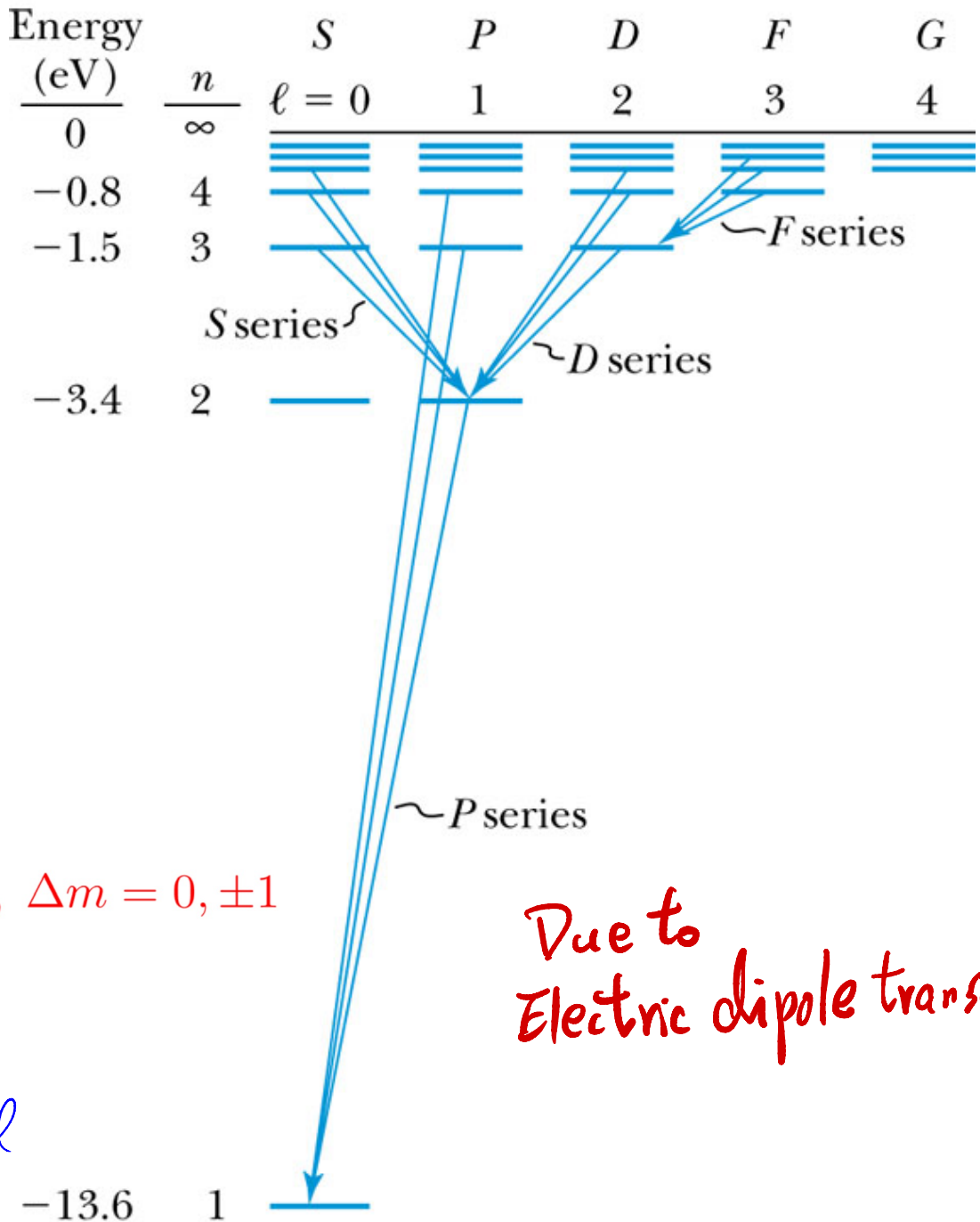
The photon decay patterns are outline in this figure. Note that the situation is more complex than the Bohr model.

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

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

$$l = 0, 1, 2, \dots, n-1$$

$$m = -l, -l+1, \dots, 0, \dots, l-1, +l$$



Due to Electric dipole transition

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

$$m = 0, \pm 1, \pm 2, \dots, \pm(l - 1), \pm l.$$

For all this complicated structure, the hydrogen energy is simply

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

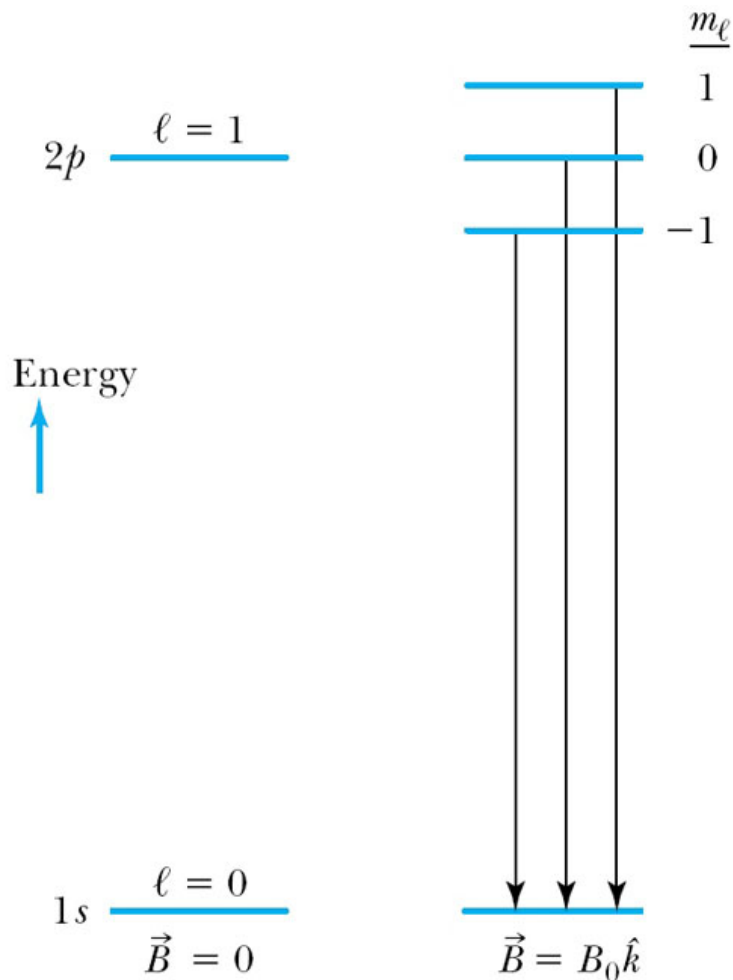
Magnetic Fields and the Quantum Number m

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

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

\uparrow
Bohr magneton

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



(b)

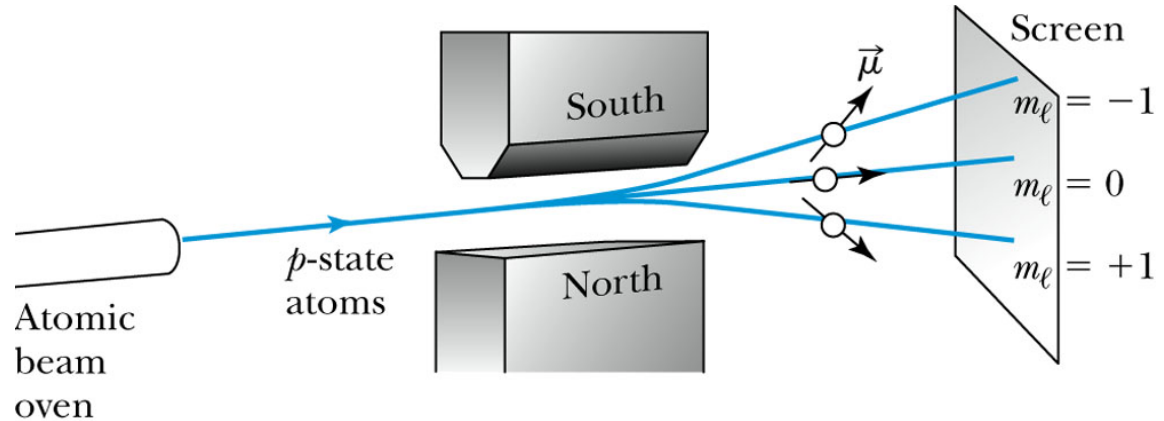
In a 2 Tesla field, the splitting is small

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



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 an atomic beam and an inhomogeneous magnet.

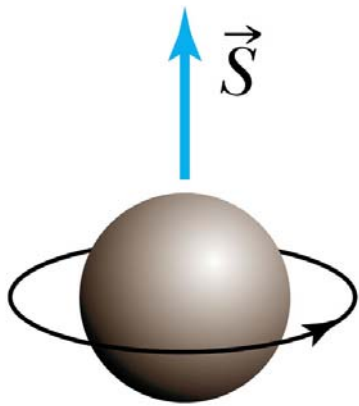


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1922

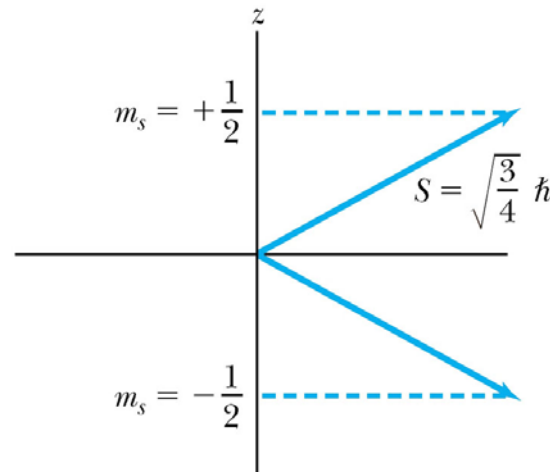
The Stern-Gerlach experiment used a silver atomic beam that passed through the magnet and produced two spots on the screen.

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)

$$\begin{aligned}
 S &= \sqrt{s(s+1)} \hbar \\
 &= \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} \hbar \\
 &= \sqrt{\frac{3}{4}} \hbar
 \end{aligned}$$



(b)

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

$$\left(S_z = m_s \hbar \right)$$

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

$$\uparrow \quad m_s = \pm \frac{1}{2}$$

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

← (Quantum Mechanics)
Special Relativity⁶

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

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

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

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

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 .

$$S_z \chi^+ = \frac{\hbar}{2} \chi^+,$$
$$S_z \chi^- = -\frac{\hbar}{2} \chi^-.$$

orbitals are labelled by (n, l, m_l) .
The complete picture of a hydrogen eigenstate is

$$H\psi_{nlm_l m_s}(\vec{r}) = \boxed{-\frac{mc^2\alpha^2}{2n^2}} \psi_{nlm_l m_s}(\vec{r}) = E_n$$

$$\vec{L}^2\psi_{nlm_l m_s}(\vec{r}) = l(l+1)\hbar^2\psi_{nlm_l m_s}(\vec{r})$$

$$L_z\psi_{nlm_l m_s}(\vec{r}) = m_l\hbar\psi_{nlm_l m_s}(\vec{r})$$

$$S_z\psi_{nlm_l m_s}(\vec{r}) = m_s\hbar\psi_{nlm_l m_s}(\vec{r})$$

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

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

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

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

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