

Schrödinger's hydrogen atom

The H atom

Some basic properties of the hydrogen atom:

- Lightest of all the atoms (*listed in the periodic table*)
- Nucleus of charge $+e$
- Delocalized electron of charge $-e$
- Absorbs and emits quanta of electromagnetic energy



Rutherford-Bohr atom

In 1912 Ernest Rutherford proposed a planetary model of the hydrogen atom. He based this model on the results of Geiger and Marsden for scattered α particles, which showed that most of the mass of an atom was concentrated at the nucleus. (*heavy protons, light electrons*)

Classical planetary motion was solved by Newton. A net radial force causes the particle to accelerate inward

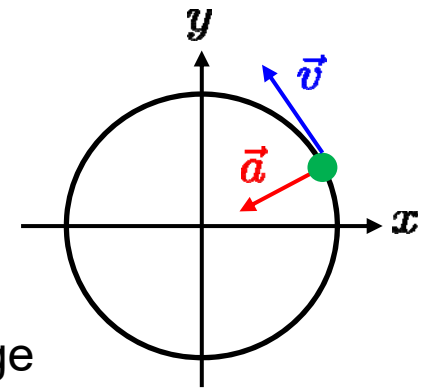
$$m_e a_r = -m_e \omega^2 r$$

In the hydrogen atom, the charge of the proton is e and the charge of an electron is $-e$. Using the Coulomb force between point charges and applying Newton's second law gives

$$m_e \omega^2 r = \frac{e^2}{4\pi\epsilon_0 r^2} \quad \Longrightarrow \quad \omega^2 = \frac{e^2}{4\pi\epsilon_0 m_e r^3}$$

The classical angular momentum, J , and rotational kinetic energy, T , follow as

$$\begin{aligned} J &= I\omega = (m_e r^2) \omega \\ &= \sqrt{\frac{m_e r e^2}{4\pi\epsilon_0}} \end{aligned} \quad \text{and} \quad \begin{aligned} T &= \frac{1}{2} I \omega^2 = \frac{1}{2} (m_e r^2) \omega^2 \\ &= \frac{e^2}{8\pi\epsilon_0 r} \end{aligned}$$



Rutherford-Bohr atom (cont.)

The attractive Coulomb potential for the electron in a hydrogen atom is

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

Thus, the total energy of the circularly orbiting system is $E = \frac{1}{2}V = -T$

Orbits do not need to be circular, and therefore we can instead look at the relationship between the average potential energy and average kinetic energy

$$E = \frac{1}{2}\langle V \rangle = -\langle T \rangle$$

where the average angular momentum is constant in non-circular orbits.

First problem: charged particles that are accelerating lose energy through electromagnetic radiation!!!

Second problem: experiments show that the hydrogen atom's spectrum is NOT continuous and follows the relationship

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ where } n_i = 1, 2, 3, \dots$$

$R = \text{Rydberg const.} \approx 1.097 \times 10^5 \text{ cm}^{-1}$

Rutherford-Bohr atom (cont.)

In 1913, Neils Bohr suggested that these difficulties can be solved by only allowing the angular momentum to have the values

$$J = n\hbar \quad \text{where} \quad n = 1, 2, 3, \dots$$

Therefore, the radius must be $r = \frac{4\pi\epsilon_0 n^2 \hbar^2}{m_e e^2}$

and the allowed energies are $E_n = \frac{-m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$

For $n = 1$, we have the well known Bohr radius $a_B = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \approx 0.529 \text{ \AA}$

Many developments followed, and they are collectively referred to as the *old quantum theory*.

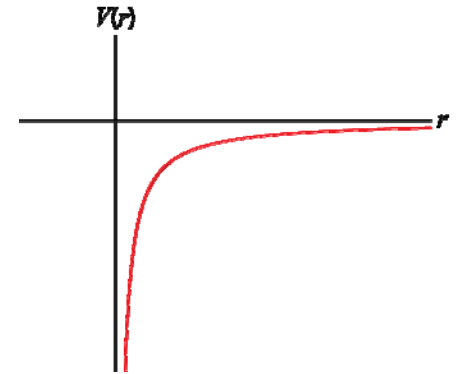
Schrodinger's hydrogen atom

The time-independent Schrodinger equation in three-dimensions may be written as

$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi + V(\vec{r}) \psi = E\psi$$

We know the static Coulomb potential for an electron near a proton at $r = 0$ is given by

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



The hydrogen atom may be represented by the Schrodinger equation with this centrosymmetric Coulomb potential.

$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi - \frac{e^2}{4\pi\epsilon_0 r} \psi = E\psi$$

Due to the centrosymmetric nature of the potential, we wish to use spherical coordinates. The Laplace operator in spherical coordinates is

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

Schrodinger's hydrogen atom (cont.)

Using spherical coordinates centered at the nucleus, the Schrodinger equation for electron in a hydrogen atom becomes

$$-\frac{\hbar^2}{2m_e} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} \psi = E\psi$$

Because the potential is only a function of the radial coordinate, we should be able to find a solution using separation of variables

$$\psi(\vec{r}) = R(r) Y(\theta, \phi)$$

Substituting the separable solutions in the Schrodinger equation for an electron in the hydrogen atom gives

$$\frac{-\hbar^2}{2m_e} \left[\frac{Y}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{R}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{R}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} RY = E RY$$

Multiplying both sides of the equation by $\frac{-2m_e r^2}{\hbar^2 RY}$ gives

$$\begin{array}{l} \text{Constant} \left(\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2m_e r^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) \right) \\ \text{Constant} \left(+ \frac{1}{Y} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{Y} \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right) = 0 \end{array}$$

Schrodinger's hydrogen atom (cont.)

Setting the constants to $\pm l(l+1)$, we may write down the equations

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = l(l+1) \quad (\text{radial equation})$$

$$\frac{1}{Y \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{Y \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} = -l(l+1) \quad (\text{angular equation})$$

Note that the energy appears only in the radial equation. Thus, the eigen energy will only depend on the radial quantum number for Schrodinger's solution.

Angular equation

Lets first consider the angular equation. Multiplying both sides of the angular equation by $Y \sin^2 \theta$ gives

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -l(l+1) \sin^2 \theta Y$$

Angular equation (cont.)

We can also separate the θ and ϕ variables in angular equation,

$$\text{Constant} \left[\frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + l(l+1) \sin^2 \theta \right] + \left[\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} \right] \text{Constant} = 0$$

where $Y(\theta, \phi) = \Theta(\theta) \Phi(\phi)$

Setting the constant to $\pm m^2$, we can write the two equations as

$$\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + l(l+1) \sin^2 \theta \Theta = m^2 \Theta \quad \text{and} \quad \frac{d^2 \Phi}{d\phi^2} = -m^2 \Phi$$

The second equation has the solution $\Phi = Ae^{im\phi} + Be^{-im\phi}$
where A and B are constants.

We can set m to be both positive or negative to remove a term. Thus we set to $B = 0$ and $A = 1$ to get

$$\Phi = e^{im\phi} \quad \text{where} \quad m = 0, \pm 1, \pm 2, \dots$$

Angular equation (cont.)

The θ dependent equation can be rewritten in the form

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

This equation has solutions represented by the associated Legendre function, where

$$\Theta(\theta) = A P_l^m(\cos \theta)$$

The associated Legendre functions can be determined using the formula

$$P_l^m(\cos \theta) = (1 - \cos^2 \theta)^{|m|/2} \left(\frac{d}{d \cos \theta} \right)^{|m|} P_l(\cos \theta)$$

where $P_l(\cos \theta)$ are the Legendre polynomials. The polynomials can be calculated using the Rodrigues formula

$$P_l(x) = \frac{1}{2^l} \frac{1}{l!} \frac{d^l}{dx^l} (x^2 - 1)^l$$

Combining the θ and ϕ dependent solutions gives the angular solution.

Angular equation (cont.)

The angular solution, $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$, can be normalized via

$$1 = \int_0^{2\pi} \int_0^\pi d\phi d\theta \sin\theta Y^*(\theta, \phi) Y(\theta, \phi)$$

The normalized angular wave functions are called spherical harmonics, Y_l^m .

The normalized spherical harmonics are given by

$$Y_l^m = (-1)^m \sqrt{\frac{2l+1}{4\pi}} \sqrt{\frac{(l-m)!}{(l+m)!}} e^{im\phi} P_l^m(\cos\theta) \quad \text{for } m \geq 0$$

$$Y_l^m = \sqrt{\frac{2l+1}{4\pi}} \sqrt{\frac{(l-m)!}{(l+m)!}} e^{im\phi} P_l^m(\cos\theta) \quad \text{for } m < 0$$

where $m = -l, \dots, 0, \dots, l$

Properties of spherical harmonics

Orthonormal relationship

$$\int_0^{2\pi} \int_0^\pi d\phi d\theta \sin \theta Y_l^{m*}(\theta, \phi) Y_{l'}^{m'}(\theta, \phi) = \delta_{ll'} \delta_{mm'}$$

Any square-integrable function of θ and ϕ can be expanded in terms of spherical harmonics by one way only,

$$f(\theta, \phi) = \sum_l \sum_m c_{lm} Y_l^m(\theta, \phi)$$

where
$$c_{lm} = \int_0^{2\pi} \int_0^\pi d\phi d\theta \sin \theta Y_l^{m*}(\theta, \phi) f(\theta, \phi)$$

Spherical harmonic addition theorem

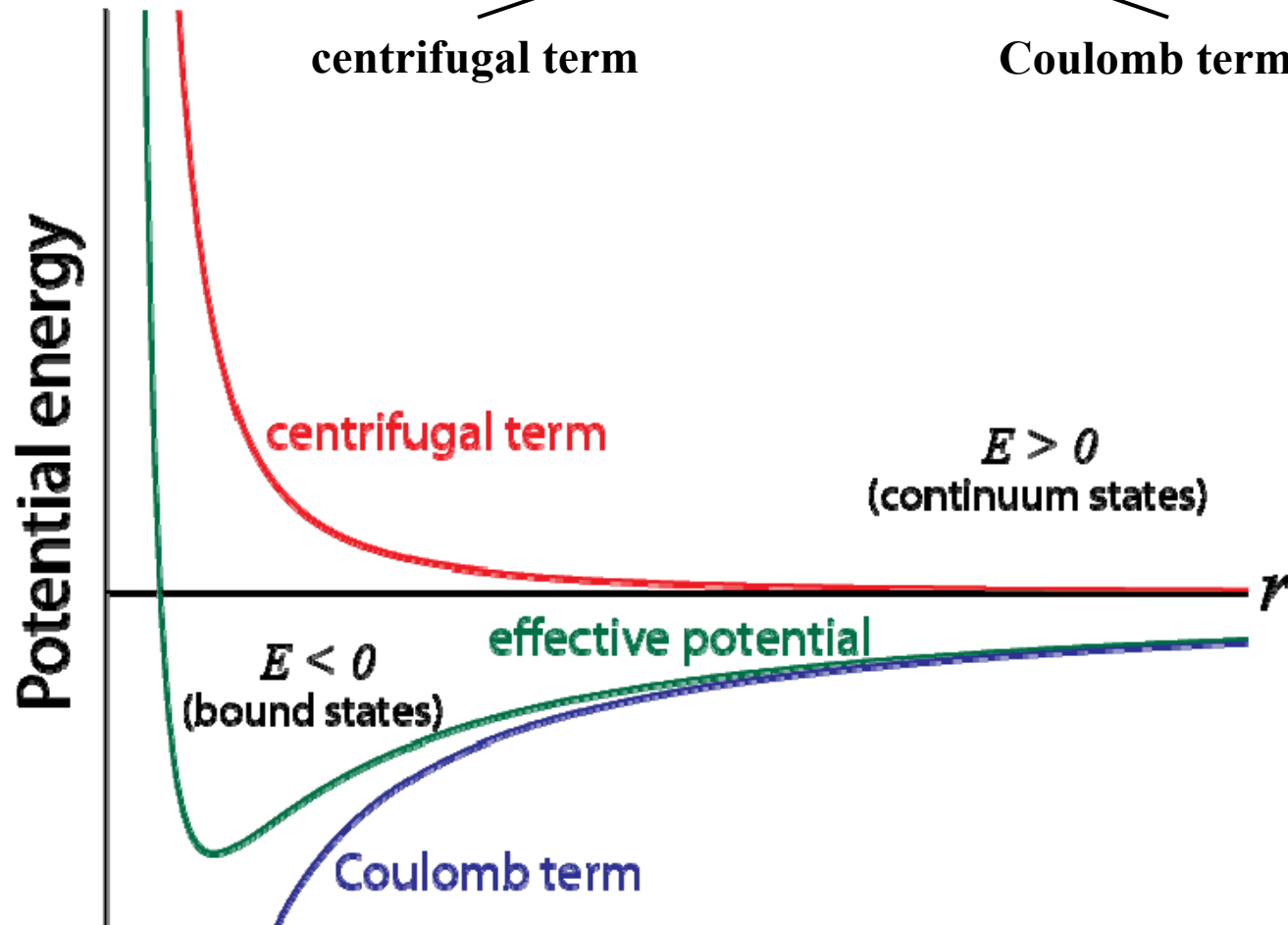
Consider two arbitrary directions in space defined by the angles (θ, ϕ) and (θ', ϕ') . The angle between the directions is α . The spherical harmonic addition theorem follows as

$$\sum_{m=-l}^l Y_l^m(\theta', \phi') Y_l^m(\theta, \phi) = \frac{2l+1}{4\pi} P_l(\cos \alpha)$$

The radial equation

The radial equation is given by

$$\frac{-\hbar^2}{2mr^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left(\frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) R = E R$$



The radial equation (cont.)

We can simplify the notation from the previous slide's radial equation by making the following substitutions:

$$\left\{ \begin{array}{l} k^2 = -\frac{2m_e E}{\hbar^2} \quad (\text{where } k \text{ is real for bound states, } E < 0) \\ \Gamma = r R \quad \left(\text{where } \frac{dR}{dr} = \frac{r \frac{d\Gamma}{dr} - \Gamma}{r^2} \text{ and } \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) = r \frac{d^2\Gamma}{dr^2} \right) \\ \xi = \frac{m_e e^2}{2\pi\epsilon_0 \hbar^2 k} \quad (\text{which is a dimensionless constant}) \end{array} \right.$$

We can now rewrite the radial equation in the form

$$\frac{d^2\Gamma}{d(kr)^2} - \left[1 - \frac{\xi}{kr} + \frac{l(l+1)}{(kr)^2} \right] \Gamma = 0$$

Immediately we see that as $r \rightarrow \infty$, the constant is the only surviving term. Therefore,

$$\frac{d^2\Gamma}{d(kr)^2} - \Gamma = 0 \quad \text{with the general solution} \quad \Gamma = Ae^{-kr} + Be^{kr}$$

The radial equation (cont.)

The general solution when $r \rightarrow \infty$ is physical if it approaches zero in the limit,

$$\Gamma \propto e^{-kr}$$

When $r \rightarrow 0$, we have the inverse square term dominating,

$$\frac{d^2\Gamma}{d(kr)^2} - \frac{l(l+1)}{(kr)^2}\Gamma = 0 \quad \text{with a solution of the form } A(kr)^{l+1} + B(kr)^{-l}$$

This solution is unphysical when $r \rightarrow 0$ unless $B = 0$. Thus, in the limit of small r we have

$$\Gamma \propto (kr)^{l+1}$$

We still have to look for the intermediate dependence, and so we are looking for a solution of the form

$$\Gamma(r) = (kr)^{l+1} e^{-kr} g(r)$$

The radial equation (cont.)

Taking the first derivative of Γ gives

$$\frac{d\Gamma}{d(kr)} = (kr)^l e^{-kr} \left[(l+1 - kr) g(r) + kr \frac{dg}{d(kr)} \right]$$

The second derivative follows as

$$\begin{aligned} \frac{d^2\Gamma}{d(kr)^2} = & (kr)^l e^{-kr} \left[\left(kr - 2l - 2 - \frac{l(l+1)}{kr} \right) g(r) \right. \\ & \left. + (l+1 - kr) \frac{dg}{d(kr)} + kr \frac{d^2g}{d(kr)^2} \right] \end{aligned}$$

The radial equation in terms of the function $g(r)$ can now be written as

$$kr \frac{d^2g}{d(kr)^2} + 2(l+1 - kr) \frac{dg}{d(kr)} + (\xi - 2l - 2) g = 0$$

A power series solution is assumed to satisfy this equation, $g(r) = \sum_{j=0}^{j_{\max}} a_j (kr)^j$

Note that the series solution has unphysical characteristics for the radial solution, R , when the maximum index $j_{\max} = n - (l + 1)$ is surpassed.

The radial equation (cont.)

Taking the first and second derivative of the assumed power series solution gives

$$\frac{dg}{d(kr)} = \sum_{j=1}^{j_{\max}} j a_j (kr)^{j-1} \quad \text{and} \quad \frac{d^2g}{d(kr)^2} = \sum_{j=2}^{j_{\max}} j(j-1) a_j (kr)^{j-2}$$

The summations can be re-indexed such that

$$\frac{dg}{d(kr)} = \sum_{j=0}^{j_{\max}} (j+1) a_{j+1} (kr)^j \quad \text{and} \quad \frac{d^2g}{d(kr)^2} = \sum_{j=1}^{j_{\max}} j(j+1) a_j (kr)^{j-1}$$

Inserting this series back into the radial equation [still in terms of $g(r)$] gives

$$\begin{aligned} & \sum_{j=1}^{j_{\max}} j(j+1) a_{j+1} (kr)^j + 2(l+1) \sum_{j=0}^{j_{\max}} (j+1) a_{j+1} (kr)^j \\ & - 2 \sum_{j=1}^{j_{\max}} j a_j (kr)^j + (\xi - 2l - 2) \sum_{j=0}^{j_{\max}} a_j (kr)^j = 0 \end{aligned}$$

For like powers, the coefficients are related by

$$j(j+1) a_{j+1} + 2(l+1)(j+1) a_{j+1} = 2j a_j (2l+2-\xi) a_j$$

The radial equation (cont.)

Solving for a_{j+1} in terms of a_j , we can write down the recursion relation

$$a_{j+1} = \frac{2(j+l+1) - \xi}{(j+1)(j+2l+2)} a_j$$

The maximum index can be found by setting $a_{j_{\max}+1} = 0$, where all coefficients beyond this maximum index are zero. The above equation gives the relationship

$$a_{j_{\max}+1} = \frac{2(j_{\max} + l + 1) - \xi}{(j_{\max} + 1)(j_{\max} + 2l + 2)} a_{j_{\max}} = 0$$

Remembering that $j_{\max} = n - (l + 1)$, the above equation gives the relationship between the principal quantum number n and the constant ξ ,

$$\xi = 2n$$

Using the earlier substitutions $k^2 = -\frac{2m_e E}{\hbar^2}$ and $\xi = \frac{m_e e^2}{2\pi\epsilon_0 \hbar^2 k}$ gives the energy for the n^{th} level,

$$E_n = \frac{-m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$$

The radial equation (cont.)

The energy level can be written in terms of the Bohr radius a_B ,

$$\begin{aligned} E_n &= \frac{-\hbar^2}{2m_e n^2} \left(\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2} \right)^2 \\ &= \frac{-\hbar^2}{2m_e n^2} \frac{1}{a_B^2} \quad \text{where} \quad a_B = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \end{aligned}$$

Solving the recurrence relationships for the power function $g(r)$ will result in the formula (with A_0 being the constant determined by normalization)

$$g(r) = A_0 L_{n-l-1}^{2l+1}(2kr)$$

given in terms of the associated Laguerre polynomials,

$$L_{q-p}^p(x) = (-1)^p \frac{d^p}{dx^p} L_q(x)$$

The Laguerre polynomials are defined by

$$L_q(x) = e^x \frac{d^q}{dx^q} (x^q e^{-x})$$

Solution to the radial equation

The radial equation can now be given in terms of the associated Laguerre polynomials,

$$\begin{aligned} R_{nl}(r) &= \frac{1}{r} (kr)^{l+1} e^{-kr} g(r) \\ &= \frac{A_0}{r} (kr)^{l+1} e^{-kr} L_{n-l-1}^{2l+1}(2kr) \end{aligned}$$

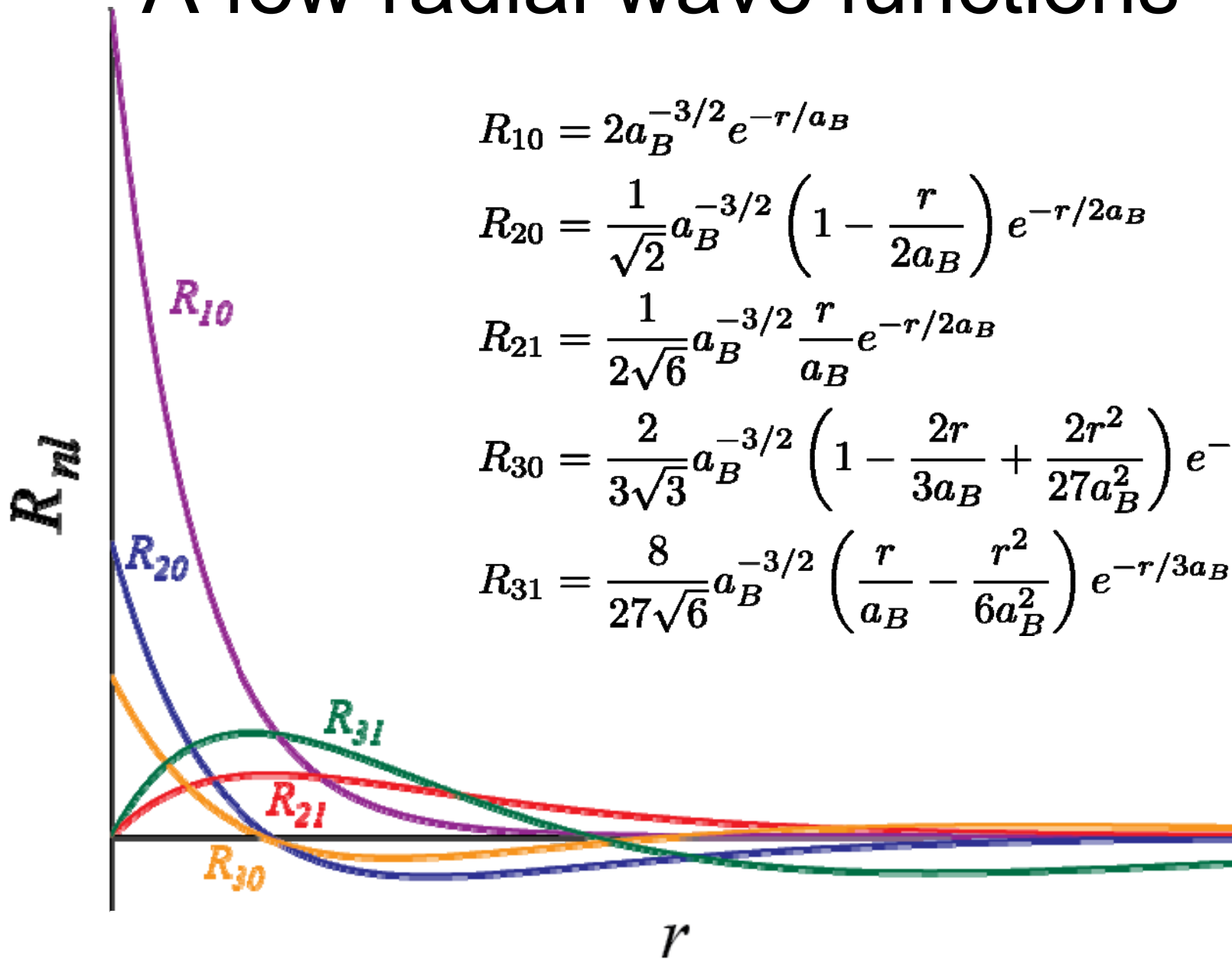
The radial wavefunction can be normalized via

$$1 = \int_0^{\infty} dr r^2 |R_{nl}|^2$$

The normalized radial wave functions follow as

$$R_{nl}(r) = \sqrt{\left(\frac{2}{na_B(n+l)!}\right)^3 \frac{(n-l-1)!}{2n^4}} e^{-r/na_B} \left(\frac{2r}{na_B}\right)^l L_{2l+1}^{n-l-1}\left(\frac{2r}{na_B}\right)$$

A few radial wave functions



Hydrogen atom wave function

The full wave function for the Schrodinger equation is given by

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na_B(n+l)!}\right)^3 \frac{(n-l-1)!}{2n^4}} e^{-r/na_B} \left(\frac{2r}{na_B}\right)^l L_{2l+1}^{n-l-1} \left(\frac{2r}{na_B}\right) Y_l^m(\theta, \phi)$$

A few associated Laguerre functions

$$L_0^0(x) = 1$$

$$L_1^0(x) = -x + 1$$

$$L_0^1(x) = 1$$

$$L_1^1(x) = -2x + 4$$

$$L_0^2(x) = 2$$

$$L_2^0(x) = x^2 - 4x + 2$$

$$L_1^2(x) = -6x + 18$$

$$L_2^1(x) = 3x^2 - 18x + 18$$

$$L_2^2(x) = 12x^2 - 96x + 144$$

A few spherical harmonics

$$Y_0^0 = \sqrt{\frac{1}{4\pi}}$$

$$Y_1^0 = \sqrt{\frac{1}{4\pi}} \cos \theta$$

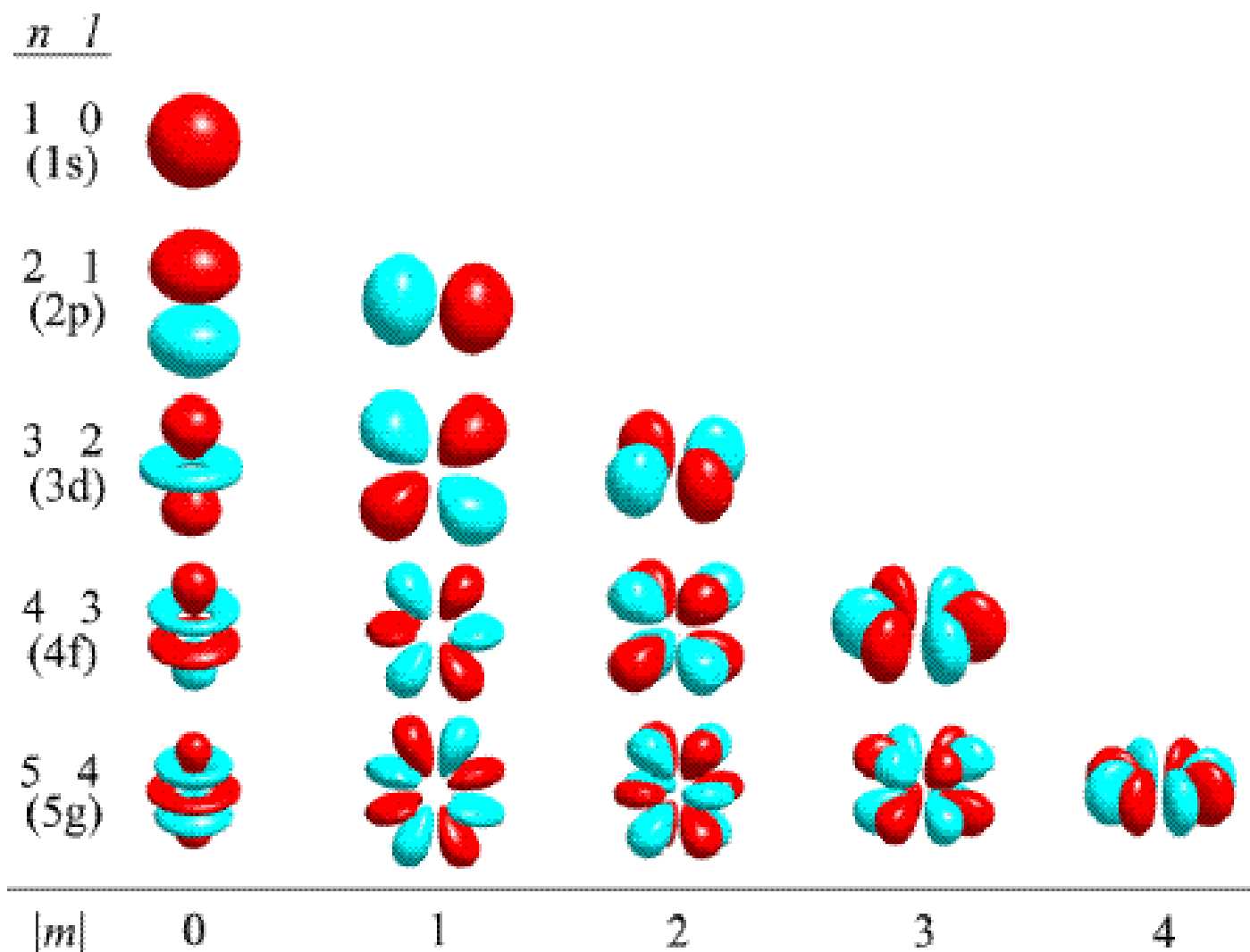
$$Y_1^{\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$$Y_2^{\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \cos \theta \sin \theta e^{\pm i\phi}$$

$$Y_2^{\pm 2} = \mp \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$$

Diagrams of orbitals



How accurate is our solution?

We have obtained a solution to Schrodinger's equation, but is this model predicting the exact physical details of the hydrogen atom?

Sources of error arise from the following:

- The nucleus and the electron rotate together about their center-of-mass.

We can easily fix the error introduced by the finite mass of the nucleus by using the effective mass of the electron,

$$m^* = \frac{m_e m_{\text{nucl}}}{m_e + m_{\text{nucl}}} \approx 0.9995 m_e$$

- The potential is not perfectly a static electric potential.

Aspects not introduced into the current model are the magnetic contributions from moving charges, finite size of the nucleus, quantum nature of the electromagnetic field, and even fluctuating electric and magnetic fields of the vacuum.

- Schrodinger equation is not exact.

Our solution does not incorporate the relativistic properties of the hydrogen atom.

H-like systems without an electron

Muonic atoms

μ^- can be attracted by a positively charged nucleus. When this occurs, the combined system is called a “muonic” atom.

$$\text{muonic Bohr radius: } a_0^\mu \approx \frac{1}{200} a_0$$

$$\text{muonic ionization energy: } E_I^\mu \approx 200 E_I^H$$

Hadronic atoms

Hadrons such as baryons and mesons can also form hydrogen-like systems. These systems are also subject to strong forces unlike those involving leptons.

Examples: nucleus – π^- meson, nucleus – Σ^- particle, and proton – antiproton.

Hamiltonian with a magnetic field

When a magnetic field is uniform, $\vec{B} = \nabla \times \vec{A}$, and the vector potential is

$$\vec{A} = \frac{1}{2} \vec{r} \times \vec{B}$$

From classical mechanics, we know that the kinetic energy term in the Hamiltonian multiplied by twice the mass is

$$\left(\vec{p} - e\vec{A}\right)^2 = p^2 + \frac{e}{2} \left[\vec{p} \cdot \left(\vec{r} \times \vec{B}\right) + \left(\vec{r} \times \vec{B}\right) \cdot \vec{p} \right] + \frac{e^2}{4} \left(\vec{r} \times \vec{B}\right)^2$$

Because we have a constant magnetic field, everything commutes with it. Thus,

$$\left(\vec{p} - e\vec{A}\right)^2 = p^2 + \frac{e}{2} \left[\vec{B} \cdot (\vec{p} \times \vec{r}) + (\vec{r} \times \vec{p}) \cdot \vec{B} \right] + \frac{e^2}{4} \left[r^2 B^2 - \left(\vec{r} \cdot \vec{B}\right)^2 \right]$$

From the classical orbital angular momentum, $\vec{L} = \vec{r} \times \vec{p}$, and we may write

$$H = H_0 + H_{\text{para}} + H_{\text{dia}} \quad \left\{ \begin{array}{l} H_0 = \frac{p^2}{2m_e} + V(r) \\ H_{\text{para}} = -\frac{e}{2m_e} \vec{L} \cdot \vec{B} \\ H_{\text{dia}} = \frac{e^2}{8m_e} r_{\perp}^2 B^2 \end{array} \right.$$

Energy shifts from orbital angular momentum

Let us ignore the diamagnetic term and spin for the moment. The Hamiltonian follows as

$$H \approx H_0 - \frac{e}{2m_e} \vec{L} \cdot \vec{B}$$

By ignoring the diamagnetic term (no radial dependent changes to the Hamiltonian), the eigenvectors remain the same. If we choose the magnetic field to be along the z-axis

$$\left(H_0 - \frac{e}{2m_e} \vec{L} \cdot \vec{B} \right) |n, l, m\rangle = \left(E_n - m \frac{e}{2m_e} \hbar B \right) |n, l, m\rangle$$

Notice that there is no orbital angular momentum for the 1s state. Thus, there is no splitting of the energy due to orbital angular momentum alone.

For the 2p state, the orbital angular momentum has the value $l=1$. For $(n=2, l=1, m=\pm 1)$, we see that the energy is shifted by the quantum number m .