Schrodinger equation in 3D central force

\[ \left(-\frac{\hbar^2}{2m} \nabla^2 + V(r)\right)\psi(r) = E\psi(r) \]

in spherical coordinates

\[ \frac{d^2}{dr^2} \left( r^2 \frac{d}{dr} \right) \psi(r) = \frac{\hbar^2}{2m} \left( \frac{\sin \theta \frac{d}{d \theta} \sin \theta \frac{d}{d \theta} + \frac{1}{\sin^2 \theta} \frac{d^2}{d \phi^2} \right) \psi(r) = \frac{E}{\hbar^2} \]

separate coordinates

\[ \psi(r) = R(r) Y_{\ell m}^\ell(\theta, \phi) \]

Radial equation with \( \ell^2 \) eigenvalue inserted.

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

\( \ell = 0 \) square well \( V = -V_0 \) \( r < r_0 \) \( V = 0 \) outside

\[ \frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2m}{\hbar^2} \left( V_0 + E \right) R = 0 \quad r < r_0 \]

\[ \frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} - \frac{2m |E|}{\hbar^2} R = 0 \quad r > r_0 \]

To eliminate the first derivative, let \( U(r) = \frac{1}{r} R(r) \)

Then \( U(0) = 0 \) since \( R(r) \) is finite at the origin

\[ R(r) = \frac{U(r)}{r} \quad R' = \frac{U'}{r} - \frac{U}{r^2} \]

\[ R'' = \frac{U'' - 2U'}{r^2} + \frac{2U}{r^3} \]
wave eqn \[ \frac{\partial^2 u}{\partial t^2} - \frac{2m}{\hbar^2} \left( V_0 - 1E_1 \right) u = 0 \]
gives \[ \frac{\partial^2 u}{\partial t^2} + \frac{2m}{\hbar^2} \left( V_0 - 1E_1 \right) u = 0 \quad r < r_0 \]
and \[ \frac{\partial^2 u}{\partial t^2} - \frac{2m}{\hbar^2} \left( 1E_1 \right) u = 0 \quad r > r_0 \]

This looks just like the one dimensional equation, except that \( u(0) = 0 \) and there is nothing for \( r < 0 \) (negative x).

The ground state is the first odd parity solution to the 1-D problem.

\[ \frac{mV_0 a^2}{2\hbar^2} > \frac{1}{4} \]

\[ \frac{a}{2} + \frac{aV_0}{2} = r_0 \]

for a bound state.

So it is possible in 3-D to have a well so weak that there are no bound states. Not true in 1-D.

Coulomb problem \[ V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \]
\[ \frac{\partial^2 R}{\partial t^2} + \frac{2}{r} \frac{\partial R}{\partial t} + \frac{2m}{\hbar^2} \left( E + \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r} \right) R = 0 \]

\[ E = -|E_1| \] is negative for a bound state.

Asymptotic form \[ E = -|E_1| \]
\[ \frac{\partial^2 R}{\partial t^2} - \frac{2m}{\hbar^2} |E_1| R = 0 \]
\[ R(r) \to \left( \frac{2m|E_1|}{\hbar^2} \right)^{1/2} \rho \quad \text{as } r \to \infty \]
effective potential: \( U(r) = -\frac{2e^2}{4\pi\varepsilon_0 r} + \frac{r^2 \mu}{2m r^2} \)

As you increase \( l \), the centrifugal repulsion term dominates as \( r \to 0 \). But the energy level \(-|E_l|\) stays constant.

Turning points of the classical ellipse are shown for \( l \neq 0 \).

Classically \( E \) can be increased until \( |E_l| \) is just tangent, giving a circular orbit with radius \( r_0 \).

\[ |E_l| = \frac{2e^2}{4\pi\varepsilon_0} \frac{1}{2} \frac{m^2 c^2 \hbar^2}{2r_0} \]

Classically, \( E \) can be increased until \( |E_l| \) is just tangent, giving a circular orbit with radius \( r_0 \).

\[ |E_l| \text{ for a circular orbit is } \frac{\alpha^2 mc^2 \hbar^2}{2} \]

which gives the Bohr formula for \( \alpha^2 = \frac{e^2}{\hbar^2} \) (Bohr's hypothesis) but doesn't quite work for \( \alpha^2 = \frac{e^2}{\hbar^2} x (x+1) \)
anticipating the Bohr formula \( 1E_1 = \frac{Z^2 e^2}{4\pi \hbar^2} \frac{I}{L} \frac{1}{a_0 M^2} \)

\( a_0 = \text{Bohr radius} = \frac{4\pi e^2}{m_e c^2} \)

So \( 2m_1E_1 = \frac{Z^2 m_e c^2}{\hbar^2} \frac{I}{L} \frac{1}{a_0 M^2} = \frac{Z^2}{a_0 \hbar^2} \left( \frac{2m_1E_1}{\hbar^2} \right) = \frac{Z}{a_0 M} \)

and the asymptotic form

\( R(r) \to e^{-\frac{r}{a_0}} \)

Note that unlike the harmonic oscillator, where

\( \psi(x) \to e^{-\frac{1}{2}x^2} \) is independent of the energy level,

here the asymptotic form depends on \( \frac{1}{n} \). Higher quantum numbers have less damping.

Also, the damping is exponential rather than Gaussian.

\( R(r) = e^{-\frac{2\pi}{a_0}} \) is the correct wave function

for the ground state, for which \( l=0 \).

\( R' = -\frac{Z}{a_0} R \quad R'' = -\frac{Z^2}{a_0^2} R \) ; then if \( l=0 \)

\( \frac{Z^2}{a_0^2} + \frac{2m_1 (Z^2 e^2}{4\pi \hbar^2} \frac{I}{L} \frac{1}{a_0 M^2} = 0 \)

Matching terms gave \( 1E_1 = \frac{Z^2 e^2}{2a_0^2 M} \) and \( \frac{Z^2 e^2}{4\pi \hbar^2} \frac{I}{L} \frac{1}{a_0 M^2} = \frac{Z}{a_0 M} \) or \( a_0 = \frac{\hbar^2 m_e c^2}{Z e^2} \)

both of which are true.

The ground state energy is \( E_{l=1} = -\frac{Z^2 e^2}{2a_0^2 M^2} \quad a_0 = \frac{\hbar}{mc} \frac{1}{L} \) so \( E_{l=1} = -\frac{Z^2 e^2}{2m (\frac{m e^2 c^2}{\hbar^2})} = \frac{Z}{2} \)
The radial wave function $R_{n\ell}(r)$ depend on the principal quantum number $n$ and the orbital quantum number $\ell$. But the energy eigenvalues depend only on $n$.

The complete solution to the radial equation proceeds like the harmonic oscillator.

1. Make the equation dimensionless $p = \alpha r$

   \[ \frac{\alpha}{2} = \left( \frac{2mE_1}{\hbar^2} \right)^{1/2} \]

   so the asymptotic form

   \[ R(p) \to e^{-p/2} \]

   \[ p \to \infty \]

   Then factor $R(p) = F(p) e^{-p/2}$

   gives a differential equation for $F(p)$.

2. Expand $F(p) = \sum a_\ell p^\ell$ and get a recursion formula. The dimensionless differential equation is

   \[ \frac{1}{p^2} \frac{d}{dp} \left( p^2 \frac{dR}{dp} \right) + \left( \lambda - \frac{1}{4} - \frac{\ell(\ell+1)}{p^2} \right) R = 0 \]

   and

   \[ F'' + \left( \frac{2}{p} - 1 \right) F' + \left( \frac{\lambda - 1}{p} - \frac{\ell(\ell+1)}{p^2} \right) F = 0 \]

   \[ \lambda = \frac{2e^2}{\hbar^2} \frac{1}{M} \left( \frac{M}{2\hbar^2} \right)^{1/2} \]

   The recursion formula is

   \[ a_{\ell+1} = \frac{(k+\ell+1-\lambda)}{(k+1)(k+2\ell+2)} a_k; \quad a_k \to \frac{1}{\ell} \text{ as } k \to \infty \]

   which is like $e^p$, requiring the series to terminate.
a_k \neq 0 \text{ but } a_{k+1} = 0 \Rightarrow \lambda = k+l+1

K is an integer in the power series (which becomes a polynomial), \( \lambda = m \) is the principal quantum number, \( M = k+l+1 \).

Since \( K = 0 \) is the lowest value in the power series, for a given \( M \), the max value of \( L \) is \( L = M-1 \).

Hence given \( M, L = 0, 1, 2 \ldots M-1 \) in integer steps, the polynomials \( F_k(p) \) are called Laguerre polynomials (another French mathematician!)

Spectroscopic notation:
- \( L = 0 \) s-wave
- \( L = 1 \) p-wave
- \( L = 2 \) d-wave
- \( L = 3 \) f-wave

State wave function:
\[
\psi_{100} = \frac{2}{a_0^{3/2}} e^{-\frac{r}{a_0}} Y_0(\theta, \phi)
\]

\[
\psi_{200} = \frac{2}{(2a_0)^{3/2}} (1 - \frac{r}{2a_0}) e^{-\frac{r}{2a_0}} Y_0
\]

\[
\psi_{11} = \frac{1}{\sqrt{3}} (2a_0^{3/2} a_0 - \frac{r}{2a_0}) Y_1^0 - \frac{1}{\sqrt{3}} (2a_0^{3/2} a_0 + \frac{r}{2a_0}) Y_{-1}^0
\]

\[
\psi_{300} = \frac{2}{3(3a_0)^{3/2}} \left( 3 - \frac{2r}{a_0} + 2 \left( \frac{r}{3a_0} \right)^2 \right) e^{-\frac{r}{3a_0}} Y_0
\]
A few notes: For atomic number \( Z = a_0 \rightarrow a_0/2 \)

Only the s wave \((l=0)\) radial wave function are finite at \( r=0 \). In fact \( R_{nl}(r) \sim r^l \)

The constants normalize the radial wave function:

\[
\int_0^{\infty} r^2 dr (R_{nl}(r))^2 = 1
\]

The spherical harmonics are already normalized.

The wave functions are orthogonal. \( Y_m \) takes care of \( m \) and \( R_{nl}(r) \) takes care of \( n \). The radial integrals have the form of factorials \((\Gamma\text{ functions})\)

\[
\int_0^\infty x^2 e^{-x} dx = \Gamma(3) = 2!, \quad \int_0^\infty x^{2-1} e^{-x} dx = \Gamma(2) = 1
\]

shows that \( 0! = 1! = 1 \quad 0 \geq 1 \)