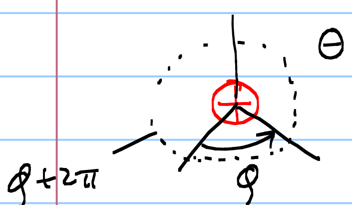
Summary of Sep. of variables of

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

spherically symm potential

Azimuthal equation

$$\Phi(\varphi) + m^2\Phi = 0$$



$$\boxed{\Phi = A e^{im\varphi}}$$

$m = 0, \pm 1, \pm 2 \ldots$

m = magnetic quantum number

Colatitude equation

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

ℓ = orbital quantum number
azimuthal

$$\boxed{\Theta(\theta) = A P_\ell^m(\cos\theta)}$$

$\ell(\ell+1)$ $\ell = 0, 1, 2, \ldots$

$L^2 = \ell(\ell+1)\hbar^2$ = orbital angular momentum

The z-component of the angular momentum is

$$L_z = m\hbar$$

Radial equation

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \underbrace{\left[V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]}_{\text{called the effective potential}} u = Eu$$

$$u(r) \equiv r\,R(r)$$

$$V_{eff} = V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

Need to specify $V(r)$ to go further.

E.g. $$V(r) = \begin{cases} 0 & \text{if } r \le a \\ \infty & \text{if } r > a \end{cases}$$

for $r \le a$ $\quad V(r) = 0$ $\quad$ so

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}u = Eu$$

$$u'' + \left(\frac{2m}{\hbar^2}E - \frac{l(l+1)}{r^2}\right)u = 0$$

simplest case $\ell = 0$

$$u'' + k^2 u = 0 \qquad k^2 = \frac{2mE}{\hbar^2}$$

$$u(r) = A\sin(kr) + B\cos(kr)$$

$$\Rightarrow R(r) = \frac{A\sin(kr)}{r} + \frac{B\cos(kr)}{r}$$

$$\lim_{r \to 0} \frac{\cos(kr)}{r} = \infty \qquad \text{So } B \text{ must } = 0$$

$$R(r) = \frac{A\sin(kr)}{r}$$

B.C. $\qquad \dfrac{A\sin(ka)}{a} = 0$

$$\Rightarrow ka = n\pi$$

$$\frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{a^2}$$

$$\Rightarrow \boxed{E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2}}$$

$n = 1, 2, 3.$
Same as ∞ square well

<u>NB</u> Normalization of ψ is over volume:

$$1 = \int |\psi|^2 r^2 dr \sin\theta \, d\theta \, d\varphi$$

in the present case this means

$$\int_0^a |R|^2 r^2 \, dr = 1 = \int_0^a |u|^2 \, dr$$

$$\Rightarrow A^2 \frac{a}{2} = 1$$

$$\Rightarrow A = \sqrt{2/a}$$

The angular part of the solution is

$$Y(\theta,\varphi) = \sum A_\ell^m Y_\ell^m(\theta,\varphi)$$

but since $V = V(r)$ the solution must be sph. symm.

$$Y_0^0 = \sqrt{\frac{1}{4\pi}} \qquad Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm i\varphi} \quad \ldots$$

only Y_0^0 has no angular dep.

So for $\ell = 0$

$$\psi(r,\theta,\phi) = \frac{1}{\sqrt{4\pi}} \sqrt{\frac{2}{a}} \; \frac{\sin(kr)}{r}$$

$$\underbrace{\psi_{n00}}_{\text{3 quantum numbers}} = \sqrt{\frac{1}{2\pi a}} \; \frac{\sin(n\pi r)}{r}$$

Now the more general case.

mass not magnetic Q.N.

$$u'' + \left(\frac{2m}{\hbar^2} E - \frac{\ell(\ell+1)}{r^2} \right) u = 0$$

$$u'' + \left(k^2 - \frac{\ell(\ell+1)}{r^2} \right) u = 0$$

$$u(r) = A\, r\, j_\ell(kr) + B\, r\, n_\ell(r)$$

$$j_\ell(x) = (-x)^\ell \left(\frac{1}{x} \frac{d}{dx} \right)^\ell \frac{\sin x}{x}$$ spherical bessel

$$n_\ell(x) = -(-x)^\ell \left(\frac{1}{x} \frac{d}{dx} \right)^\ell \frac{\cos x}{x}$$ spherical Neumann

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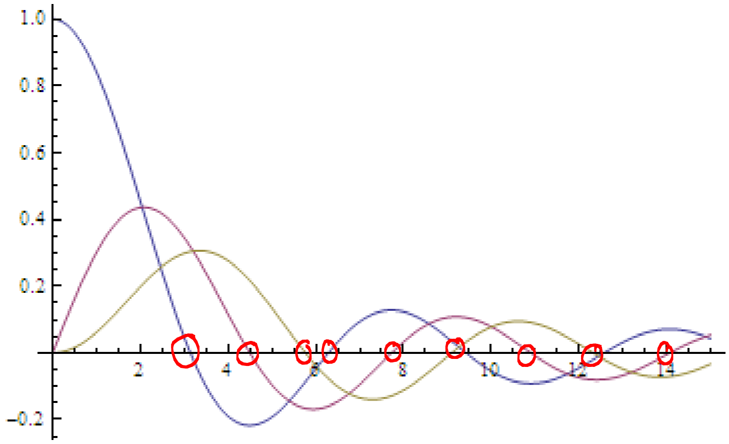
In[1]:= Plot[{SphericalBesselJ[0, x], SphericalBesselJ[1, x],
   SphericalBesselJ[2, x]}, {x, 0, 15}, PlotRange → All]
```

Out[1]=



o zeros.

These are the Neumann fcns. A.K.A.
sphericaL Bessel Y in Mathematica

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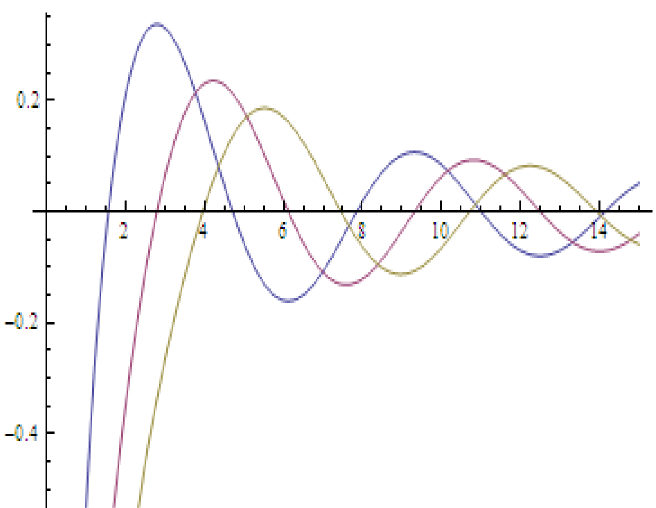
In[4]:= Plot[{SphericalBesselY[0, x], SphericalBesselY[1, x],
   SphericalBesselY[2, x]}, {x, 0, 15}]
```

Out[4]=

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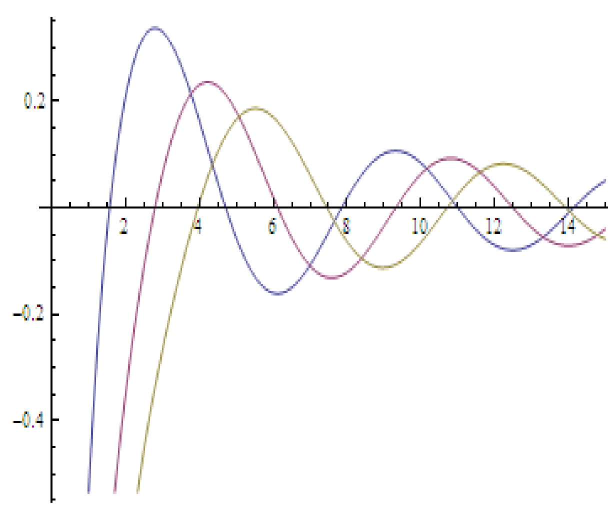
In[6]:= Plot[{-Cos[x] / x, -Cos[x] / x^2 - Sin[x] / x,
   - (3 / x^3 - 1 / x) Cos[x] - 3 / x^2 Sin[x]}, {x, 0, 15}]
```

Out[6]=



Notice that the $N_\ell(kr)$ blow up at the origin, so again (as with $\ell=0$) B_ℓ must $=0$.

$$R(r) = A\, j_\ell(kr)$$

<u>BC</u> $\quad j_\ell(ka)=0$

So for each ℓ, $k_{N\ell}\,a$ is to be one of the zeros of j_ℓ.

Call these zeros $\beta_{N\ell}$

Then $$E_{N\ell} = \frac{\hbar^2}{2ma^2}\beta_{N\ell}^2$$

$$\psi_{N\ell m}(r,\theta,\varphi) = A_{N\ell}\, j_\ell(\beta_{N\ell}\, r/a)\, Y_\ell^m(\theta,\varphi)$$

$A_{N\ell}$ normalization.

<u>NB</u> E does not depend on m!

For each ℓ there are $2\ell+1$ values of m $\underbrace{[m=-\ell, -\ell+1 \ldots 0, 1, \ell-1, \ell]}_{2\ell+1}$

So each energy level is $2\ell+1$

fold degenerate.

Goal: to become comfortable recognizing the basic pieces of the solution to the $V(r)$ schrodinger equation

$$\psi_{n\ell m}(r,\theta,\varphi) = A_{n\ell}\, \underbrace{j_\ell(kr)}_{\text{regular at } r=0}\, Y_\ell^m(\theta,\varphi) + B_{n\ell}\, \underbrace{N_\ell(kr)}_{\text{Blows up at } r=0}\, Y_\ell^m(\theta,\varphi)$$

The specific form of the radial solution depends on the potential.

Hydrogen: $V(r) = \dfrac{-e^2}{4\pi\epsilon_0}\dfrac{1}{r}$

charge on e^-

permitivity of vacuum

So radial part of Schrödinger:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{-e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu$$

$u = rR$

Let $k^2 = \dfrac{-2mE}{\hbar}$

k is real for bound states

$$\left[\frac{-e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} \right] u$$

attractive coulomb potential

repulsive "centrifugal" potential

first nonzero term $\ell = 1$

balance of 2 terms:

$$\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} = \frac{\hbar^2}{2m} \frac{2}{r^2}$$

$$\Rightarrow \quad r = \boxed{4\pi\epsilon_0 \frac{\hbar^2}{me^2} \equiv a_0}$$

Bohr radius $\approx .53$ Å $= .053$ nm
$= 53$ pm

Angstrom

nano meter

picometer