# Schrödinger Equation for Spherically Symmetric Potentials

11/29/99

The Laplacian in spherical coordinates is (11/25/99),

$$\nabla^2 = \frac{1}{r^2\sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{1}$$

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

The Schrödinger equation for a wave function, $\psi(r,\theta,\varphi)$, in a spherically symmetric potential, $V(r)$, is

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(r,\theta,\varphi)$$

$$+ V(r)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{3}$$

Let's expand the wave function in the spherical-harmonics basis set (6/12/99),

$$\begin{cases} Y_\ell^m(\theta,\varphi) = (-1)^m\sqrt{\dfrac{(2\ell+1)}{4\pi}\dfrac{(\ell-m)!}{(\ell+m)!}}\,P_\ell^m(\cos\theta)\,e^{im\varphi} & (4) \\ P_\ell^m(x) = (1-x^2)^{m/2}\left(\dfrac{d}{dx}\right)^m P_\ell(x) \qquad (-\ell\le m\le\ell) & (5) \end{cases}$$

The Legendre polynomial, $P_\ell(x)$, is defined through a generating function,

$$\frac{1}{\sqrt{1-2tx+t^2}} = \sum_{\ell=0}^{\infty} P_\ell(x)\,t^\ell \quad (|t|<1) \tag{6}$$

and the Rodrigues' formula states that

$$P_\ell(x) = \frac{1}{2^\ell\ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell \tag{7}$$

(Orthonormality)

$$\int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\varphi\, Y_{l_1}^{m_1}(\theta,\varphi)\, Y_{l_2}^{m_2}(\theta,\varphi) = \delta_{l_1 m_1}\, \delta_{l_2 m_2} \tag{8}$$

(Differential Equation)

$$(1-x^2)\, P_l^{m\,''}(x) - 2x\, P_l^{m\,'}(x) + \left[ l(l+1) - \frac{m^2}{1-x^2} \right] P_l^m(x) = 0 \tag{9}$$

(see 6/12/92). For $x = \cos\theta$, note that $\frac{d}{dx} = \frac{d\theta}{dx}\frac{d}{d\theta} = \frac{1}{-\sin\theta}\frac{d}{d\theta}$,

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

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

$$\frac{d^2}{d\theta^2} - \cancel{\sin\theta}\frac{\cos\theta}{\sin^{\cancel{2}}\theta}\frac{d}{d\theta} + \frac{2\cos\theta}{\sin\theta}\frac{d}{d\theta}$$

$$= \frac{d^2}{d\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{d}{d\theta} = \frac{1}{\sin\theta}\frac{d}{d\theta}\left( \sin\theta \frac{d}{d\theta} \right)$$

$$\therefore \left\{ \frac{1}{\sin\theta}\frac{d}{d\theta}\left( \sin\theta \frac{d}{d\theta} \right) + \left[ l(l+1) - \frac{m^2}{\sin^2\theta} \right] \right\} P_l^m(\cos\theta) = 0 \tag{10}$$

From the definition, Eq. (4),

$$\left\{ \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left( \sin\theta \frac{\partial}{\partial\theta} \right) + \left[ l(l+1) - \frac{m^2}{\sin^2\theta} \right] \right\} Y_l^m(\theta,\varphi) = 0 \tag{11}$$

Also from Eq. (4),

$$\frac{d^2}{d\varphi^2} Y_l^m(\theta,\varphi) = -m^2 Y_l^m(\theta,\varphi) \tag{12}$$

Combining Eqs (11) and (12),

$$\left[ \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \right] Y_l^m(\theta,\varphi) = -l(l+1) Y_l^m(\theta,\varphi) \tag{13}$$

A general wave function can thus be expressed as,

$$\psi(r,\theta,\varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{\chi_{lm}(r)}{r} Y_l^m(\theta,\varphi) \tag{14}$$

Substituting Eq. (14) in Eq. (3)

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\sum_{lm}\frac{\chi_{lm}(r)}{r}\right] Y_l^m(\theta,\varphi)$$

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\sum_{lm}\frac{\chi_{lm}(r)}{r}\underbrace{\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y_l^m(\theta,\varphi)}_{-l(l+1)Y_l^m(\theta,\varphi) \quad (\because \text{Eq. } (13))}$$

$$+\sum_{lm}\left[V(r)\frac{\chi_{lm}(r)}{r}\right] Y_m^l(\theta,\varphi) = E\sum_{lm}\frac{\chi_{lm}(r)}{r} Y_l^m(\theta,\varphi)$$

Note that all $(l,m)$ equations are decoupled.

$$\int_0^{\pi}\sin\theta\, d\theta \int_0^{2\pi} d\varphi\, Y_{lm}^*(\theta,\varphi) \times \text{ above}((l,m)\to(l',m'))$$

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)\frac{\chi_{lm}(r)}{r} + \frac{\hbar^2 l(l+1)}{2mr^2}\frac{\chi_{lm}(r)}{r} + V(r)\frac{\chi_{lm}(r)}{r}$$

$$= E\frac{\chi_{lm}(r)}{r} \tag{15}$$

Note that this equation does not depend on $m$. We can thus conclude that for spherically symmetric potentials a general wave function can be expanded as

$$\boxed{\psi(r,\theta,\varphi) = \sum_{l=0}^{\infty}\frac{\chi_l(r)}{r} Y_l^m(\theta,\varphi)} \tag{16}$$

and each $\chi_l(r)$ satisfies

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{\hbar^2 l(l+1)}{2mr^2}+V(r)\right]\frac{\chi_l(r)}{r} = E\frac{\chi_l(r)}{r} \tag{17}$$

Let's rewrite

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\, r^2 \underbrace{\frac{d}{dr}\frac{\chi_\ell(r)}{r}}_{\frac{\chi_\ell'}{r}-\frac{\chi_\ell}{r^2}}$$

$$= -\frac{\hbar^2}{2m}\frac{1}{r^2}\underbrace{\frac{d}{dr}(r\chi_\ell' - \chi_\ell)}_{\cancel{\chi_\ell'} + r\chi_\ell'' - \cancel{\chi_\ell'}}$$

$$= -\frac{\hbar^2}{2m}\frac{1}{r}\chi_\ell''$$

$$\therefore\ -\frac{\hbar^2}{2m}\frac{1}{\cancel{r}}\chi_\ell'' + \left[V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}\right]\frac{\chi_\ell}{\cancel{r}} = E\frac{\chi_\ell}{r}$$

$$\boxed{\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \left[V(r) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}\right]\right\}\chi_\ell(r) = E\chi_\ell(r)} \qquad (18)$$

① Eigen values do not depend on $m$, i.e., for each $\ell$, there is $(2\ell+1)$-fold degeneracy.

② For each $\ell$, a series of eigenvalues are obtained by solving the radial wave equation, Eq. (18).

③ The radial motion is equivalent to the one-dimensional motion in an additional centrifugal potential,

$$V(r) + \underbrace{\frac{\hbar^2\ell(\ell+1)}{2mr^2}}$$

# Schrödinger Equation for Spherically Symmetric Potentials – II

11/30/99

For $\psi(r,\theta,\varphi) = [\chi_\ell(r)/r]\, Y_\ell^m(\theta,\varphi)$,

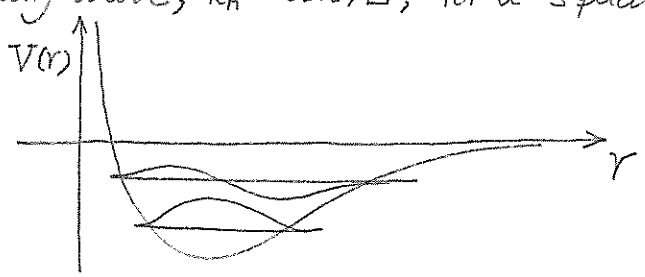
$$\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \left[V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} - E\right]\right\}\chi_\ell(r) = 0 \tag{1}$$

or

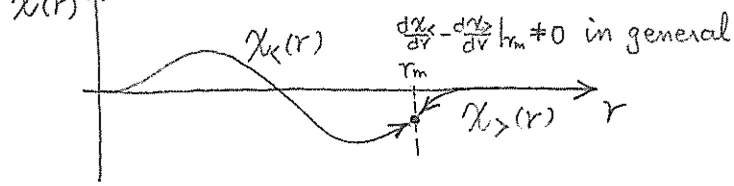
$$\left\{\frac{d^2}{dr^2} + \left[\frac{2m}{\hbar^2}(E - V(r)) - \frac{\ell(\ell+1)}{r^2}\right]\right\}\chi_\ell(r) = 0 \tag{2}$$

$$\therefore \begin{cases} \left[\dfrac{d^2}{dr^2} + k^2(r)\right]\chi_\ell(r) = 0 & (3) \\[2ex] k^2(r) = \dfrac{2m}{\hbar^2}\left(E - V(r)\right) - \dfrac{\ell(\ell+1)}{r^2} & (4) \end{cases}$$

① For negative energies, the eigen values $\underbrace{\text{are}}_{\text{for the finite-ranged wave functions}}$ discrete.
(cf. Standing wave, $k_n = \pi n/L$, for a square well.)




∵ If we integrate Eq. (3) starting from both $r=0$ power expansion and $r\to\infty$ evanscent mode, $\chi_\ell(r) = \exp\left(-\sqrt{-\frac{2mE}{\hbar^2}}\, r\right)$, we can always match the outward, $\chi_<(r)$, and inward, $\chi_>(r)$, solutions at a meeting point, $r_m$, by linear scaling (since Eq. (3) is a homogeneous equation). To make the derivative continuous, however, E must take special values.



② The eigenstates corresponding for different energies are orthogonal,

$$\int_0^\infty dr\, \chi_{n_1 l}(r)\, \chi_{n_2 l}(r) = 0 \qquad (n_1 \neq n_2)$$

∵

$\chi_{n_2 l}(r) \times$

$$\frac{d^2}{dr^2}\chi_{n_1 l}(r) + \left[\frac{2m}{\hbar^2}(E_{n_1 l} - V(r)) - \frac{l(l+1)}{r^2}\right]\chi_{n_1 l}(r) = 0$$

$\chi_{n_1 l}(r) \times$

$$-)\quad \frac{d^2}{dr^2}\chi_{n_2 l}(r) + \left[\frac{2m}{\hbar^2}(E_{n_2 l} - V(r)) - \frac{l(l+1)}{r^2}\right]\chi_{n_2 l}(r) = 0$$

$$\underbrace{\chi_2 \chi_1'' - \chi_1 \chi_2''}_{\frac{d}{dr}(\chi_2\chi_1' - \chi_1\chi_2')} + \frac{2m}{\hbar^2}(E_1 - E_2)\chi_1\chi_2 = 0$$

$\int_0^\infty dr \times$ (above)

$$\chi_2\chi_1' - \chi_1\chi_2'\Big|_0^\infty + \frac{2m}{\hbar^2}(E_1 - E_2)\int_0^\infty \chi_1\chi_2\, dr = 0$$

↳ 0 (∵ same boundary condition)

$$\therefore\ (E_1 - E_2)\int_0^\infty \chi_1\chi_2\, dr = 0 \qquad //$$

③ If we order the eigen values in ascending order starting from $n' = 0, 1, 2, \ldots$, the $n'$-th eigen function has $n'$ nodes (or zero points).

(Plausible argument)

In classically admissible regions, $k^2(r) > 0$, the larger E, hence the larger $k(r)$ causes more oscillatory function, accordingly to more nodes. In order to satisfy the orthogonality, higher eigenstates must have more positive and negative regions.

④ We introduce the principal quantum number,

$$n = n' + l + 1 \qquad (n = l+1,\ l+2, \ldots) \tag{5}$$

so that $n \geq l+1$ and the $n$-th state has $n' = n-l-1$ nodes. This is to make a continuity to noninteracting case, where $V(r) = -Ze^2/r$ and all $E_{nl} = E_n$ are degenerate.