Lecture 14 QM

18. 12. 2020

Schröedinger equation:

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}, \quad \hat{H} = \hat{T} + \hat{V}$$

$$\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{1}{2m}\frac{\partial^2}{\partial x^2} \xrightarrow{3D} \hat{T} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2)$$

$$\hat{p}_x \to -i\hbar\frac{\partial}{\partial x} \qquad \hat{p}_y \to -i\hbar\frac{\partial}{\partial y} \qquad \hat{p}_z \to -i\hbar\frac{\partial}{\partial z}$$

$$\boxed{\hat{p} \to -i\hbar \bar{\nabla}}$$

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial \Psi}{\partial t}}$$

where $V(\vec{r}, t)$

$\vec{r}(x, y, z)$

$$\nabla^2 \equiv \bar{\nabla}\bar{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$ – Laplacian

$$\underbrace{\int d^3r\, |\Psi(\bar{r}, t)|^2}= 1$$ – normalization

$V(\vec{r}, t) = V(\bar{r})$ if the potential is time independent

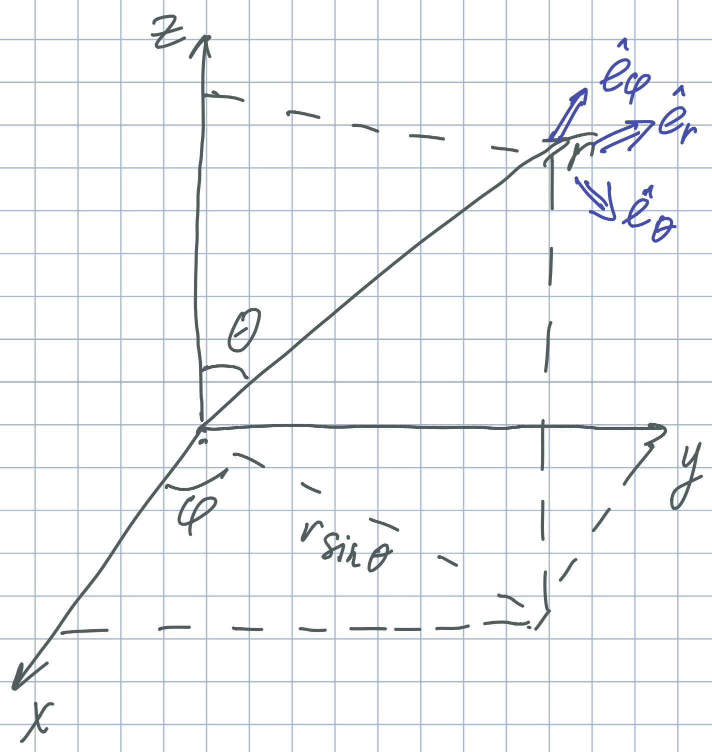
$\Psi_n(\bar{r}, t) = \Psi_n(\bar{r})\, e^{-\frac{i}{\hbar}E_n t}$ a complete set of stationary states

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\Psi_n(\bar{r}) + V\Psi_n = E_n\Psi_n}$$

general solution: $\Psi(\bar{r}, t) = \sum_n C_n \Psi_n(\bar{r})\, e^{-\frac{i}{\hbar}E_n t}$

Central potential

$V(\bar r) \equiv V(r), \quad r = |\bar r|$



$$\begin{cases} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi \\ z = r\cos\theta \end{cases}$$

$$\begin{cases} \hat e_r = \sin\theta\cos\varphi\,\hat i + \sin\theta\sin\varphi\,\hat j + \cos\theta\,\hat k \\ \hat e_\theta = \cos\theta\cos\varphi\,\hat i + \cos\theta\sin\varphi\,\hat j - \sin\theta\,\hat k \\ \hat e_\varphi = -\sin\varphi\,\hat i + \cos\varphi\,\hat j \end{cases}$$

$$\bar\nabla f = \left(\frac{\partial f}{\partial x}\right)\hat i + \left(\frac{\partial f}{\partial y}\right)\hat j + \left(\frac{\partial f}{\partial z}\right)\hat k =$$

$$= (\bar\nabla_r f)\hat e_r + (\bar\nabla_\theta f)\hat e_\theta + (\bar\nabla_\varphi f)\hat e_\varphi$$

$$(\bar\nabla_r f) = \hat e_r \bar\nabla f = \left(\frac{\partial f}{\partial x}\right)\underbrace{\sin\theta\cos\varphi}_{\frac{\partial x}{\partial r}} + \left(\frac{\partial f}{\partial y}\right)\underbrace{\sin\theta\sin\varphi}_{\frac{\partial y}{\partial r}} + \frac{\partial f}{\partial r}\underbrace{\cos\theta}_{\frac{\partial z}{\partial r}} = \frac{\partial f}{\partial r}$$

$$(\bar\nabla_\theta f) = \hat e_\theta \bar\nabla f = \left(\frac{\partial f}{\partial x}\right)\underbrace{\cos\theta\cos\varphi}_{\frac{1}{r}\frac{\partial x}{\partial \theta}} + \left(\frac{\partial f}{\partial y}\right)\underbrace{\cos\theta\sin\theta}_{\frac{1}{r}\frac{\partial y}{\partial \theta}} + \left(\frac{\partial f}{\partial z}\right)\underbrace{(-\sin\theta)}_{\frac{1}{r}\frac{\partial z}{\partial \theta}} = \frac{1}{r}\frac{\partial f}{\partial \theta}$$

$$(\bar\nabla_\varphi f) = \hat e_\varphi \bar\nabla f = \left(\frac{\partial f}{\partial x}\right)\underbrace{(-\sin\varphi)}_{\frac{1}{r\sin\theta}\frac{\partial x}{\partial \varphi}} + \left(\frac{\partial f}{\partial y}\right)\underbrace{(\cos\varphi)}_{\frac{1}{r\sin\theta}\frac{\partial y}{\partial \varphi}} = \frac{1}{r\sin\theta}\frac{\partial f}{\partial \varphi}$$

$$\boxed{\nabla = \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta} + \hat{e}_\varphi \frac{1}{r\sin\theta}\frac{\partial}{\partial \varphi}}$$

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

Time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\varphi^2}\right] +$$
$$+ V(r)\Psi = E\Psi$$

$$\Psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$$

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)\right.$$
$$\left. + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right] + V(r)\underline{\underline{RY}} = E\underline{\underline{RY}} \quad \Big| : RY \quad \times\left(\frac{-2mr^2}{\hbar}\right)$$

$$\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left[V(r)-E\right]\right\} +$$

$$+ \underbrace{\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right\}}_{\theta,\varphi} = 0$$

depends only on r

$l(l+1)$ - constant

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left[V(r)-E\right] = l(l+1)$$ radial equation

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

Angular equation

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

$$Y(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi)$$

$$\underbrace{\left\{\frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + l(l+1)\sin^2\theta\right\}}_{\text{depends only on }\Theta} + \underbrace{\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}}_{\varphi} = 0$$

$$\boxed{\begin{aligned} &\frac{1}{\Theta}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + l(l+1)\sin^2\theta = m^2 \\ &\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = -m^2 \end{aligned}}$$

$$\underline{\Phi(\varphi) = e^{im\varphi}}$$

$$\Phi(\varphi + 2\pi) = \Phi(\varphi) \qquad e^{im2\pi} = 1$$

$\Rightarrow m = 0, \pm 1, \pm 2 \ldots$ integer.

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

$$x = \cos\theta \qquad \frac{d}{d\theta} = -\sin\theta\frac{d}{dx}$$

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

$$\sin^2\theta = 1 - x^2$$

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

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

$$\Big| : (1-x^2)$$

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

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

$\hookrightarrow$ associated Legendre functions

$$P_l^m(x) \equiv (1-x^2)^{m/2}\frac{d^m}{dx^m}P_l(x)$$

$\hookrightarrow$ Legendre polynomials

$$P_l^0(x) = P_l(x)$$

Rodrigues formula

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

Special cases:

$$P_0(x) = 1$$

$$P_1(x) = \frac{1}{2}\frac{d}{dx}(x^2-1) = x$$

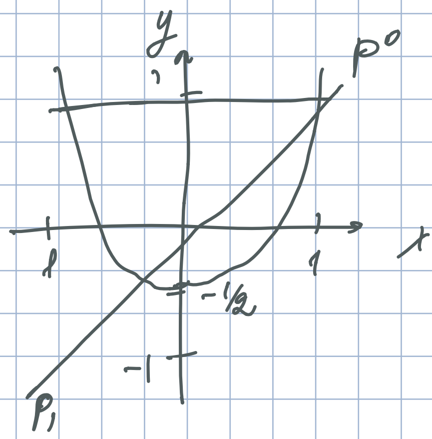
$$P_2(x) = \frac{1}{4\cdot 2}\frac{d^2}{dx^2}(x^2-1)^2 = \frac{1}{2}\frac{d}{dx}((x^2-1)x) = \frac{1}{2}(3x^2-1)$$

$\vdots$

$P_l(x)$ - polynomial of degree l in x

l even $\rightarrow$ P_l is even in x

l odd $\rightarrow$ P_l is odd in x



P_ℓ^m special cases:

$\ell \Rightarrow (2\ell+1)$ possible values of m

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

$P_0^0 = 1$

$P_1^m = (\sqrt{1-x^2})^m \frac{d^m}{dx^m} P_1(x) = (\sqrt{1-x^2}) \frac{d^m}{dx^m} x$

$P_1^0 = 0$

$P_1^1 = \sqrt{1-x^2}$

$P_2^0 = P_2 = \frac{1}{2}(3x^2-1)$

$m \neq 0 \quad P_2^m = (1-x^2)^{m/2} \frac{d^m}{dx^m} \frac{1}{2}(3x^2-1)$

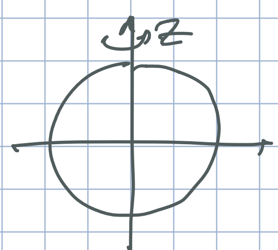
$P_2^1(x) = \sqrt{1-x^2}\, 3x$

$P_2^2(x) = 3(1-x^2)$

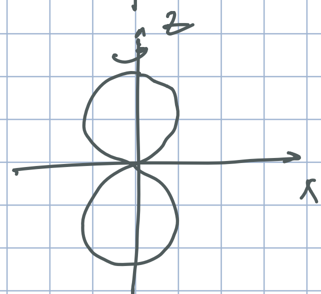
m odd $\rightarrow P_\ell^m$ is polynomial $\times \sqrt{1-x^2}$

m even $\rightarrow P_\ell^m$ is polynomial

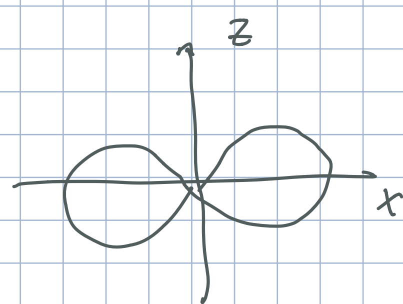
$P_0^0 = 1$



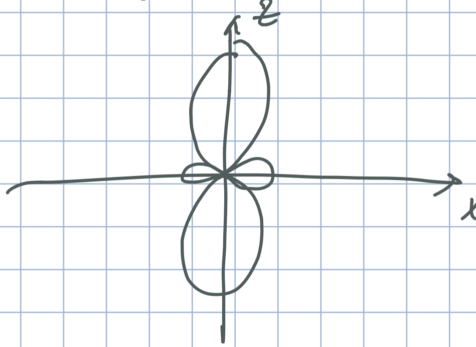
$P_1^0 = \cos\theta$



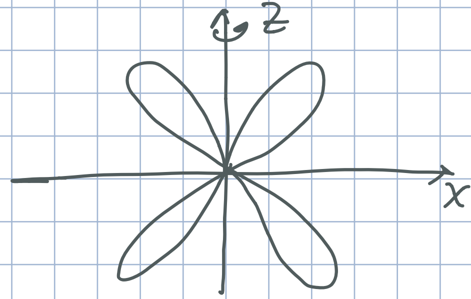
$P_1^1 = \sin\theta$



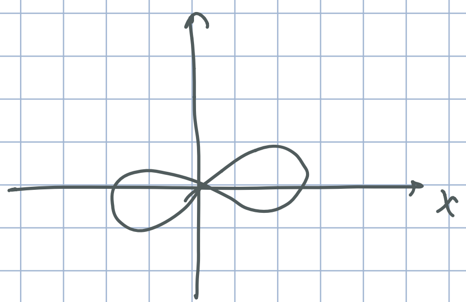
$$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$$



$$P_2^1 = 3\sin\theta\cos\theta$$



$$P_2^2 = 3\sin^2\theta$$



$$\int d^3\bar{r}\,|\Psi|^2 = 1$$

$$d^3\bar{r} = r^2\sin\theta\,dr\,d\theta\,d\varphi$$

$$\Psi(\bar{r}) = R(r)\,Y(\theta,\varphi)$$

$$\int dr\,r^2\,|R(r)|^2 \int d\varphi\,d\theta\,\sin\theta\,|Y(\theta,\varphi)|^2 = 1$$

$$\int_0 dr\,r^2\,|R(r)|^2 = 1$$

normalization

$$\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta\,\sin\theta\,\underline{\underline{|Y(\theta,\varphi)|^2}} = 1$$

$$\boxed{Y(\theta,\varphi) = Y_{\ell,m}(\theta,\varphi) = (-1)^m\sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}}\,e^{im\varphi}P_\ell^m(\cos\theta)}$$

spherical harmonics

$$Y_{\ell\,-m}(\theta,\varphi) = (-1)^m\,Y_{\ell m}^*(\theta,\varphi)$$

Radial equation

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

$$U(r) \equiv rR(r)$$

$$R = \frac{U}{r}$$

$$\frac{dR}{dr} = \frac{1}{r^2}\left(r\frac{dU}{dr} - U\right)$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \cancel{\frac{dU}{dr}} + r\frac{d^2U}{dr^2} - \cancel{\frac{dU}{dr}}$$

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2U}{dr^2} + \underbrace{\left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]}_{V_{eff}}U = EU}$$

V_{eff} - effective potential

$\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$ - repulsive centrifugal potential

normalization $\int_0^\infty dr\,|U(r)|^2 = 1$