1. The wave function of a particle subjected to a spherically symmetrical potential $V(r)$ is given by

$$\psi(x, y, z) = (x - y + 2z)f(r).$$

(a) Is ψ an eigenfunction of L^2?

(b) What are the possibilities for the particle to be found in various m state?

2. If the wave function for a rigid rotator with moment of inertia I at time $t = 0$ is in the state

$$\psi(0) = \frac{1}{\sqrt{6}}(Y_1^1 + 2Y_1^0 + Y_1^{-1}).$$

What is the probability if the measurement on L_y yields $-\hbar$?

3. The eigenvalue equation for the radial part of the wave function of the hydrogeon atom is given by

$$\frac{1}{r^2}\frac{d}{dr}(r^2\frac{d}{dr})R(r) + \frac{2m}{\hbar^2}[E - V - \frac{\hbar^2}{2mr^2}l(l+1)]R(r) = 0.$$

Consider a wave function for a hydrogeon atom

$$\psi(r, \theta, \phi) = \frac{1}{4\sqrt{2\pi}}re^{-r/2}cos\theta,$$

where r is expressed in terms of the Bohr radius a.

(a) Find the corresponding values of the quantum numbers n, l and m by introducing the wave function $\psi(r, \theta, \phi)$ into the eigenvalue equation . (10%)

(b) Calculate the most probable value of r for an electron in this state. (20%)

4. A hydrogen atom is at the following state

$$\psi(r) = \frac{1}{(2a)^{3/2}}[\sqrt{\frac{2}{\pi}}e^{-r/a} + A\frac{r}{a}e^{-r/2a}Y_1^{-1}]$$

(a) What is the value of the normalization constant A? (10%)

(b) What is the probability density that the electron is found between the radius r and $r + dr$ from the proton? (15%)

(c) Where is the most probable position that the electron locates? (15%)

5. Find the value of r where the radial probability density of the hydrogen atom at $n = 2,\ l = 0,\ m = 0$ reaches its maximum. (30%)

Spectroscopic Notation	Normalized Time-Independent Eigenstates
$1S$	$\varphi_{100} = \frac{2}{a_0^{3/2}} e^{-r/a_0} Y_0{}^0(\theta, \phi)$
$2S$	$\varphi_{200} = \frac{2}{(2a_0)^{3/2}} (1 - r/2a_0) e^{-r/2a_0} Y_0{}^0(\theta, \phi)$
$2P$	$\begin{pmatrix} \varphi_{211} \\ \varphi_{210} \\ \varphi_{21-1} \end{pmatrix} = \frac{1}{\sqrt{3}\,(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \begin{pmatrix} Y_1{}^1(\theta, \phi) \\ Y_1{}^0(\theta, \phi) \\ Y_1{}^{-1}(\theta, \phi) \end{pmatrix}$
$3S$	$\varphi_{300} = \frac{2}{3(3a_0)^{3/2}} [3 - 2r/a_0 + 2(r/3a_0)^2] e^{-r/3a_0} Y_0{}^0(\theta, \phi)$
$3P$	$\begin{pmatrix} \varphi_{311} \\ \varphi_{310} \\ \varphi_{31-1} \end{pmatrix} = \frac{4\sqrt{2}}{9(3a_0)^{3/2}} \frac{r}{a_0} (1 - r/6a_0) e^{-r/3a_0} \begin{pmatrix} Y_1{}^1(\theta, \phi) \\ Y_1{}^0(\theta, \phi) \\ Y_1{}^{-1}(\theta, \phi) \end{pmatrix}$
$3D$	$\begin{pmatrix} \varphi_{322} \\ \varphi_{321} \\ \varphi_{320} \\ \varphi_{32-1} \\ \varphi_{32-2} \end{pmatrix} = \frac{2\sqrt{2}}{27\sqrt{5}\,(3a_0)^{3/2}} \left(\frac{r}{a_0}\right)^2 e^{-r/3a_0} \begin{pmatrix} Y_2{}^2(\theta, \phi) \\ Y_2{}^1(\theta, \phi) \\ Y_2{}^0(\theta, \phi) \\ Y_2{}^{-1}(\theta, \phi) \\ Y_2{}^{-2}(\theta, \phi) \end{pmatrix}$

7.2 單一質點在中心力位能作用下的穩定態

一質點在中心力位能 $V(\vec{r}) = V(r,\theta,\varphi) = V(r)$ 下運動，代表此質點所受之位能，只與質點到原點或力心的距離大小有關，而與方向角度無關。由於此時質點角動量 $\vec{L}$ 之變率為

$$\frac{d\vec{L}}{dt} = \frac{d}{dt}(\vec{r} \times \vec{p}) = \frac{d\vec{r}}{dt} \times \vec{p} + \vec{r} \times \frac{d\vec{p}}{dt}$$

$$= \underbrace{\vec{v} \times \vec{p}}_{0} + \vec{r} \times \frac{d\vec{p}}{dt} = \vec{r} \times \vec{F} = -\vec{r} \times \nabla V(r) = -\vec{r} \times \frac{\partial V}{\partial r}\vec{e}_r = 0 \qquad (7.19)$$

故角動量 $\vec{L} =$ 常數，亦即質點之 $\vec{r}$ 和 $\vec{P}$ 永遠在同一平面上，因為此平面之法線，即為角動量 $\vec{L}$ ，維持恆常不變。所以，一質點若受中心力場作用，必有角動量守恆，以及運動軌跡為一平面運動。

在中心力場作用下，此質點之能量固有值方程式，由式(7.18)得

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V(r)\right]\Psi(\vec{r}) = E\Psi(\vec{r}) \qquad (7.20)$$

其中

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2}(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}) \qquad (7.21)$$

又由角動量運算子 $\hat{L}^2$ 之定義式(6.62)，故

$$[\frac{-\hbar^2}{2mr^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{2mr^2}\hat{L}^2 + V(r)]\Psi(r,\theta,\varphi) = E\Psi(r,\theta,\varphi) \qquad (7.22)$$

因 $\hat{L}^2$ 和 $\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$ 僅為 θ 和 φ 的函數，所以任何僅與 r 有關，而與 θ,φ 無關的運算子，皆可與它們交換，即

$$[\hat{H},\hat{L}^2] = [\frac{-\hbar^2}{2mr^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{2mr^2}\hat{L}^2 + V(r),\ \hat{L}^2] = 0 \qquad (7.23)$$

同理，$[\hat{H},\hat{L}_z] = 0$。

由數學基本定理 II，當

$$[\hat{H},\hat{L}^2]=[\hat{H},\hat{L}_z]=[\hat{L}^2,\hat{L}_z]=0 \qquad (7.24)$$

$\hat{H}$ 、$\hat{L}^2$ **和** $\hat{L}_z$ **分享有共同的固有向量** $\Psi_{n\ell m}(r,\theta,\varphi)$，並具有對應的固有值，即

$$\hat{H}\,\Psi_{n\ell m}(r,\theta,\varphi)=E_n\,\Psi_{n\ell m}(r,\theta,\varphi) \qquad (7.25)$$

$$\hat{L}^2\,\Psi_{n\ell m}(r,\theta,\varphi)=\ell(\ell+1)\hbar^2\,\Psi_{n\ell m}(r,\theta,\varphi) \qquad (7.26)$$

$$\hat{L}_z\,\Psi_{n\ell m}(r,\theta,\varphi)=m\hbar\,\Psi_{n\ell m}(r,\theta,\varphi) \qquad (7.27)$$

由式 (6.69) 與 (6.70)，已知 $\hat{L}^2$ 和 $\hat{L}_z$ 之固有值方程式之解為 $Y_\ell^m(\theta,\varphi)$，故**質點在中心力位能下的穩定態函數，可分為徑向距離部分與角度部分**，

$$\Psi_{n\ell m}(r,\theta,\varphi)=R(r)\,Y_\ell^m(\theta,\varphi) \qquad (7.28)$$

其中**徑向部分** $R(r)$ **須滿足**

$$\left[\frac{-\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{1}{2mr^2}\ell(\ell+1)+V(r)\right]R(r)=ER(r) \qquad (7.29)$$

而**角度部分，永遠為球面調和函數** $Y_\ell^m(\theta,\varphi)$，不須重新再去解它。

7.3 似氫原子（$H, L_i^+, B_e^{2+}, B^{3+}, \cdots$）

利用二體問題之處理方法與中心力場之特性，現在我們可探討氫原子系統之能量與行為。氫原子或似氫原子(核外僅有單一電子)，包含兩個部分，一個是帶有 Zq 正電荷之原子核，另一個是核外之單一電子。其交互作用的庫倫力為

$$\vec{F} = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r^2}\vec{e}_r = -\nabla V(r) \tag{7.30}$$

對應的交互作用庫倫位能則為

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{(Zq)(-q)}{r} = \frac{-Ze^2}{r} \tag{7.31}$$

其中 $$e^2 = \frac{q^2}{4\pi\varepsilon_0} \quad , \quad q = 1.6\times 10^{-19} C$$

若不考慮總質量為 M（原子核質量與電子之質量和 ＝ $m_n + m_e$），之直線運動所攜帶的動能，則在此質心坐標下，能量固有值方程式，由式(7.20) (為方便起見底下均設 Z=1, 對似氫原子僅需以 Ze^2 取代 e^2 即可)

$$[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}]\,\Psi(\vec{r}) = E\,\Psi(\vec{r}) \tag{7.32}$$

其中

$$\vec{r} = \vec{r}_1 - \vec{r}_2 \quad , \quad m = \frac{m_e m_N}{m_e + m_N} \tag{7.33}$$

$\vec{r}_1$ 、$\vec{r}_2$ 分別為電子、與原子核之位置向量。則似氫原子之二體問題（原子核與電子）簡化為攜帶縮減質量 m（既不是原子核，也不是電子）之一體問題。又因庫倫位能為一中心力位能，故由式(7.28)，其解含有徑向與角度部分。而角度部分必為球面調和函數 $Y_\ell^m(\theta,\varphi)$，而徑向部分 $R(r)$ 則滿足

$$[\frac{-\hbar^2}{2mr^2}\frac{d}{dr}(r^2\frac{d}{dr}) + \frac{1}{2mr^2}\ell(\ell+1) - \frac{e^2}{r}]R(r) = ER(r) \tag{7.34}$$

且因在無限遠處找到質點 m 之機率為 0，故在 $r\to\infty$ 時，**徑向部分需滿足邊界條件**

$$\boxed{R(r\to\infty) = 0} \tag{7.35}$$

若令

$$u(r) \equiv rR(r) \tag{7.36}$$

則**函數** $u(r)$ **有兩邊界條件**

$$u(r=0)=0\ ,\quad u(r\to\infty)=rR(r\to\infty)=0 \tag{7.37}$$

而

$$\frac{d}{dr}(r^2\frac{d}{dr})R(r)=\frac{d}{dr}r^2\frac{d}{dr}\frac{u(r)}{r}=\frac{d}{dr}[\,ru'(r)-u(r)\,]=ru''(r) \tag{7.38}$$

故式(7.34)乘上 $2m/\hbar^2$ 後得

$$-\frac{1}{r^2}\cdot ru''(r)+\frac{\ell(\ell+1)}{r^2}R(r)-\frac{2m}{\hbar^2}\cdot\frac{e^2}{r}R(r)-\frac{2mE}{\hbar^2}R(r)=0 \tag{7.39}$$

乘上 r 後得

$$(-\frac{d^2}{dr^2}-\frac{\ell(\ell+1)}{r^2}-\frac{2m}{\hbar^2}\frac{e^2}{r}+\frac{2m|E|}{\hbar^2})u(r)=0 \tag{7.40}$$

若電子之總能量$E>0$，則電子將游離成為自由粒子，若僅討論侷限在氫原子內之電子，則其總能量$E<0$，故此處設 $E=-|E|$ 。令 $k^2=\dfrac{2m|E|}{\hbar^2}$

並將 $-1/4k^2$ 乘上式(7.40)，得

$$(\frac{d^2}{d(2kr)^2}-\frac{\ell(\ell+1)}{(2kr)^2}+\frac{me^2}{k\hbar^2}\frac{1}{2kr}-\frac{1}{4k^2}\frac{2m|E|}{\hbar^2})u(r)=0 \tag{7.41}$$

現引進無因次的參數 ρ與τ ，設

$$\rho\equiv 2kr \tag{7.42}$$

$$\tau^2=\frac{1}{(ka_0)^2}=(\frac{me^2}{k\hbar^2})^2=\frac{2m}{\hbar^2k^2}\cdot\frac{me^4}{2\hbar^2}=\frac{1}{|E|}\cdot\frac{me^4}{2\hbar^2}=\frac{|E_0|}{|E|} \tag{7.43}$$

其中 $a_0=\hbar^2/me^2=0.53\mathring{A}=$ 波爾半徑，$|E_0|=me^4/2\hbar^2$ 。對氫原子而言，$|E_0|=13.6\ eV$ 。而 E，k 或 τ 均**為待決定值**。式(7.41)則可化簡為

$$\frac{d^2}{d\rho^2}u(\rho)-\frac{\ell(\ell+1)}{\rho^2}u(\rho)+(\frac{\tau}{\rho}-\frac{1}{4})u(\rho)=0 \tag{7.44}$$