(量三版 chapter 7. 8)

Chapter 10-12. The Schrödinger eq. in 3D (II), Angular Momentum 及 H-atom.

此章節討論 二体力中 $V(\vec{r}) = V(r)$ (the central potential) 之例.

討論之 系統為 two-particle system:

$$\hat{H} = \frac{\vec{p}_1^{\,2}}{2m_1} + \frac{\vec{p}_2^{\,2}}{2m_2} + V(|\vec{r}_1 - \vec{r}_2|)$$

與 1D 之情形一樣: $\vec{R} \equiv \dfrac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1+m_2}$

$$\vec{r} = \vec{r}_1 - \vec{r}_2$$

$$\vec{P} = \vec{p}_1 + \vec{p}_2, \quad \vec{p} = \frac{m_2\vec{p}_1 - m_1\vec{p}_2}{m_1+m_2}$$

$$H = \frac{P^2}{2M} + \frac{\vec{p}^{\,2}}{2\mu} + V(|\vec{r}|) \qquad M = m_1+m_2, \quad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

Q.M. $\vec{P} = \frac{\hbar}{i}\vec{\nabla}_R, \quad \vec{p} = \frac{\hbar}{i}\vec{\nabla}_r$

$$\therefore [P_n, R_m] = \frac{\hbar}{i}\delta_{nm} \qquad [p_n, r_m] = \frac{\hbar}{i}\delta_{nm}$$

$[\vec{P}, H] = 0$ ∴ 可以找 $\vec{P}$ 與 H 之共同 eigenstate

$$\therefore \Psi(\vec{R}, \vec{r}) = u(\vec{P}, \vec{R})\,\phi_E(\vec{r})$$

$$u(\vec{P}, \vec{R}) = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i\vec{P}\cdot\vec{R}}{\hbar}}$$

$$\left(\frac{\vec{p}^2}{2\mu} + V(r)\right)\phi_E(\vec{r}) = E\,\phi_E(\vec{r}), \quad E = E_{total} - \frac{P^2}{2M}$$

即 $\left(\frac{-\hbar^2}{2\mu}\nabla^2 + V(r)\right)\phi_E(\vec{r}) = E\,\phi_E(\vec{r})$ — ①

* Consequences of rotational invariance

Classical: $\vec{L} = \vec{r}\times\vec{p}$ = 角動量

$\because \vec{F} = -\nabla V(r) \parallel \hat{r}$, $\therefore \underbrace{\vec{\tau} = \vec{r}\times\vec{F} = 0}$

$\therefore \frac{d\vec{L}}{dt} = 0$. $\vec{L}$ = conserved!

與旋轉不變之關係:

$|\delta\vec{r}| = r\sin\theta\,\delta\phi$

$\delta\vec{r} = \delta\vec{\phi}\times\vec{r}$

$V(\vec{r}) = V(\vec{r}+\delta\vec{r}) \quad \because |\vec{r}| = |\vec{r}+\delta\vec{r}|$

$\parallel$

$V(\vec{r}) + \underbrace{\delta\vec{r}\cdot\nabla V(\vec{r})}$

$\parallel$

$\delta\vec{\phi}\cdot\underbrace{\vec{r}\times\nabla V(r)}_{-\vec{\tau}}$.

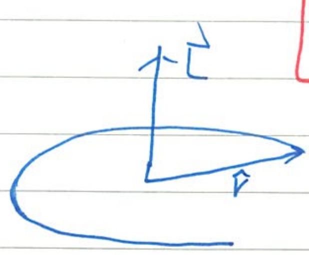
$\therefore \vec{\tau} = 0$

此時, $\because L^2 = (\vec{r}\times\vec{p})\cdot(\vec{r}\times\vec{p})$

$= r^2p^2 - (\vec{r}\cdot\vec{p})^2$

$\therefore p^2 = \frac{L^2}{r^2} + (\hat{r}\cdot\vec{p})^2 = P_r^2 + \frac{L^2}{r^2}$

$\therefore E = \frac{P^2}{2\mu} + V(r) = \frac{P_r^2}{2\mu} + \underbrace{\frac{L^2}{2\mu r^2} + V(r)}_{V_{eff}(r)}$



$\because L^2$ = 常數, $P_r = \hat{r}\cdot\vec{P}$

$= m\vec{v}\cdot\hat{r} = \mu\dot{r}$

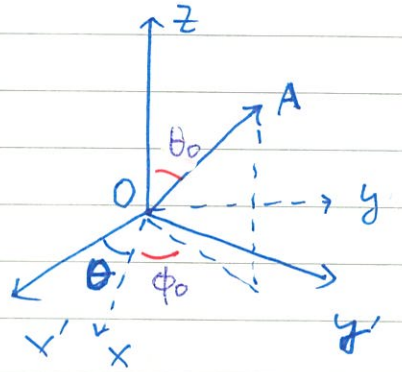
$\therefore E = \frac{1}{2}\mu\dot{r}^2 + V_{eff}(r)$

整個運動變成一維運動! 其中等效一維位能 $V_{eff}(r) = V(r) + \frac{L^2}{2\mu r^2}$

(事實上是一半 Eδ 1維, $\because r \geq 0$)

Quantum：我們將看到，$V(\vec{r})=V(r)$ 時，整個運動也會 reduce 到 1D 之運動！(但此時：$\vec{L} = \vec{r}\times\vec{p}$)
所以整個推導不同
$[L]=\hbar$

首先，先檢視对 z軸之旋轉不變：



$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

$$z' = z$$

$$|\overline{OA}|^2 = x^2+y^2+z^2 = x'^2+y'^2+z'^2 \text{ 不變}$$

$$\begin{pmatrix} x \\ y \end{pmatrix} = \overline{OA} \begin{pmatrix} \sin\theta_0 \cos\phi_0 \\ \sin\theta_0 \sin\phi_0 \end{pmatrix}$$

$$\therefore \begin{pmatrix} x' \\ y' \end{pmatrix} = \overline{OA} \begin{pmatrix} \sin\theta_0 \cos(\phi_0+\theta) \\ \sin\theta_0 \sin(\phi_0+\theta) \end{pmatrix}$$

注意：$\frac{\partial}{\partial x'} = \cos\theta \frac{\partial}{\partial x} - \sin\theta \frac{\partial}{\partial y}$，$\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} x' \\ y' \end{pmatrix}$

$\frac{\partial}{\partial y'} = \sin\theta \frac{\partial}{\partial x} + \cos\theta \frac{\partial}{\partial y}$

$\therefore \left(\frac{\partial}{\partial x'}\right)^2 + \left(\frac{\partial}{\partial y'}\right)^2 = \left(\frac{\partial}{\partial x}\right)^2 + \left(\frac{\partial}{\partial y}\right)^2$，$D^2 = D'^2$，又 $V(r) = V(r')$

$\therefore$ 对 z軸旋轉 θ 度，$\hat{H}$ 不變！

$\theta \to 0$ 時　$x' = x - \theta y$
$y' = \theta x + y$

$\because \underbrace{H(x',y',z')}_{= H(x,y,z)} \phi_E(x',y',z') = E\phi_E(x',y',z')$ ← ②

由 $\phi_E(x',y',z') = \phi_E(x-\theta y,\ y+\theta x,\ z)$

$$= \phi_E(x,y,z) - \theta y \frac{\partial}{\partial x}\phi_E(x,y,z) + \theta x \frac{\partial}{\partial y}\phi_E(x,y,z)$$

∴ ②式

$$\Rightarrow \quad H(x,y,z)\left[\phi_E(x,y,z) + \theta\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\phi_E\right] = E\left(\phi_E(x,y,z) + \theta\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\phi_E\right) \quad \text{--- ③}$$

加上 ϕ_E 本來就滿足

$$H(x,y,z)\,\phi_E(x,y,z) = E\,\phi_E(x,y,z) \quad \text{— ④}$$

∴ ③, ④式 $\Rightarrow$ $H\underbrace{\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)}\phi_E = E\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\phi_E$

$$\propto L_z = (\vec{r}\times\vec{p})_z = xp_y - yp_x$$

$$= \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

∴ $H L_z \phi_E = E L_z \phi_E$ — ⑤

⑤ − L_z · ④ $\Rightarrow$ $(HL_z - L_zH)\phi_E = 0$ ∴ $[H, L_z] = 0$

$\frac{d\langle L_z\rangle}{dt} = 0$ L_z is conserved!

同理, $[H, L_x] = 0$, $[H, L_y] = 0$

∴ H可以与 L_z, L_x $\boxed{\text{或}}$ L_y 同時被"对角化", 即找共同之 eigenstate

注意: 這不表示, 可以找到 L_x, L_y, L_z 及 H 之共同 eigenstate, 因為 $[L_x, L_y]$, $[L_y, L_z]$.. 不一定 $= 0$!

* The angular momentum commutation relation.

正如上所述，雖然 $[H, L_x]=0$, $[H, L_y]=0$, $[H, L_z]=0$

但 $[L_x, L_y] \neq 0$, $[L_y, L_z] \neq 0$, $[L_x, L_z] \neq 0$

因此，無法找到 H, L_x, L_y 及 L_z 之共同 eigenfunction：

$$[L_x, L_y] = [yP_z - zP_y, zP_x - xP_z]$$

$$= [yP_z, zP_x] - \cancel{[zP_y, zP_x]}^{\,0} - \cancel{[yP_z, xP_z]}^{\,0} + [zP_y, xP_z]$$

$$= y\underbrace{[P_z, z]}_{\hbar/i}P_x + x\underbrace{[z, P_z]}_{-\hbar/i}P_y$$

$$= \frac{\hbar}{i}(yP_x - xP_y) = i\hbar L_z \quad \text{—⑥}$$

同理 $[L_y, L_z] = i\hbar L_x$ —⑦

$[L_z, L_x] = i\hbar L_y$ —⑧

以上可以以 $\underbrace{\vec{L}\times\vec{L}} = i\hbar\vec{L}$ 統合之

z: $L_xL_y - L_yL_x = i\hbar L_z$

⑥-⑧式表示，L_x, L_y 及 L_z 在 $\hbar \neq 0$ 時，找不到共同之 eigenfunction (其根本來源為 x 與 p 之測不準原理)：

設 u 為 L_x 及 L_y 之共同 eigenfunction，即

$$L_x u = l_x u$$

$$L_y u = l_y u$$

$$\therefore (L_xL_y - L_yL_x)u = (l_xl_y - l_yl_x)u = 0 = i\hbar L_z u$$

$\therefore L_z u = 0$. 但 $\underbrace{(L_zL_x - L_xL_z)u}_{= l_x L_z u = 0} = i\hbar L_y u$ $\therefore L_y u = 0$ $\therefore l_y = 0$

同理 $\ell_x=0$, ∴只有 $\vec{L}=0$ 才可能!

但雖然 $[L_x,L_y]\neq 0$, $[L_x,L_z]\neq 0\ldots$, $[L_i,L_j]=i\hbar\epsilon_{ijk}L_k$

$[L^2,L_i]=0$ (L^2 = 所謂的 Casimir operator)

check. $[L_z,L^2]=[L_z,L_x^2+L_y^2]$

$$=\cancel{\underbrace{[L_z,L_x]}_{i\hbar L_y}L_x}+L_x\underbrace{[L_z,L_x]}_{i\hbar L_y}+\underbrace{[L_z,L_y]}_{-i\hbar L_x}L_y+\cancel{L_y\underbrace{[L_z,L_y]}_{-i\hbar L_x}}$$

$$=0$$

∴ 如此 L_z, L^2 及 H 可以 找到共同之 eigenfunction!

* 等效一維問題

古典: $p^2=\frac{L^2}{r^2}+(\hat{r}\cdot\vec{p})^2$

即 $r^2p^2=L^2+(\vec{r}\cdot\vec{p})^2$, $L^2=r^2p^2-(\vec{r}\cdot\vec{p})^2$ — (4a)

↑可利用 $(\vec{A}\times\vec{B})\cdot(\vec{C}\times\vec{D})=(\vec{A}\cdot\vec{C})(\vec{B}\cdot\vec{D})-(\vec{A}\cdot\vec{D})(\vec{B}\cdot\vec{C})$

量子:

$L^2=(\vec{r}\times\vec{p})\cdot(\vec{r}\times\vec{p})$, $\vec{p}=\frac{\hbar}{i}\nabla$ 為 operator

∴ 此 $\vec{p}$ 也作用在上!

$$(\vec{r}\times\vec{p})_x\cdot(\vec{r}\times\vec{p})_x=-\hbar^2\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$$

← 此二項為得 $\vec{r}$ 及 $\vec{p}$ 當作可交換之形式的結果

$$=-\hbar^2\left[\left(y^2\frac{\partial^2}{\partial z^2}+z^2\frac{\partial^2}{\partial y^2}\right)-2yz\frac{\partial^2}{\partial y\partial z}\right]$$

$$+\underbrace{\hbar^2\left(z\frac{\partial}{\partial z}+y\frac{\partial}{\partial y}\right)}$$ ← 由 $\vec{p}$ 與 $\vec{r}$ 不可交換產生的

(4b) ~~結合 x, y, z 分量~~ → $2\hbar^2\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right)$

另外，古典 $(\vec{r}\cdot\vec{p})^2$ 之表示，在量子中，也要小心！

$\because$ $(\vec{r}\cdot\vec{p})(\vec{r}\cdot\vec{p})$ 中包括了 $\vec{p}$ 作用在 $\vec{r}$ 之結果：

也 $(\vec{r}\cdot\vec{p})(\vec{r}\cdot\vec{p})$

$$= (x p_x + y p_y + z p_z)\cdot(x p_x + y p_y + z p_z)$$

$$= x^2 p_x^2 + x\left(\frac{\hbar}{i}\frac{\partial}{\partial x}x\right)p_x + \cdots$$

$$= (\vec{r}\cdot\vec{p})^2_{古典} + \underbrace{\frac{\hbar}{i}x p_x + \cdots}_{-\hbar^2\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right)} \quad \text{— (Pc)}$$

綜合 (Pb) 及 (Pc)，除了古典 (Pa) 之結果外，量子：

$$L^2 = r^2p^2 - (\vec{r}\cdot\vec{p})^2_{古典} + 2\hbar^2\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right)$$

$$= r^2p^2 - \left[(\vec{r}\cdot\vec{p})^2 + \hbar^2\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right)\right] + 2\hbar^2\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right)$$

$$= r^2p^2 - (\vec{r}\cdot\vec{p})^2 + \hbar^2\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right)$$

$$= r^2p^2 - (\vec{r}\cdot\vec{p})^2 + i\hbar\,\vec{r}\cdot\vec{p}$$

$$p^2 = \frac{L^2}{r^2} + \frac{1}{r^2}(\vec{r}\cdot\vec{p})^2 - \frac{i\hbar}{r}\hat{r}\cdot\vec{p}$$

$$\nabla = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi} \qquad \frac{1}{r^2}(\vec{r}\cdot\vec{p})^2 = \frac{-\hbar^2}{r^2}\left(r\frac{\partial}{\partial r}\right)^2 = \frac{-\hbar^2}{r^2}r\frac{\partial}{\partial r}r\frac{\partial}{\partial r}$$

$$= -\hbar^2\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{r}\frac{\partial}{\partial r} \qquad \frac{-i\hbar}{r}\hat{r}\cdot\vec{p} = \frac{-\hbar^2}{r}\frac{\partial}{\partial r}$$

$$\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} = \frac{1}{r}\frac{\partial^2}{\partial r^2}r \quad \left(= \frac{1}{r}\frac{\partial}{\partial r}\left(1 + r\frac{\partial}{\partial r}\right) = \frac{2}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2}\right)$$

$\because \quad p^2 = \frac{L^2}{r^2} - \frac{\hbar^2}{r}\frac{d^2}{dr^2}r$

注意：當我們將 x, y, z 放大成 $\lambda x, \lambda y$ 及 λz 時，$r \to \lambda r$

$$\left.\begin{aligned} L_x &= \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ L_y &= \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ L_z &= \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{aligned}\right\} \text{不變}$$

$\therefore L^2$ 與 r 無關，只與 θ, ϕ 有關！

如前所述，對 central potential 而言，我們可以同時找到 $\hat{H}$, $\hat{L}_z$ 及 $\hat{L}^2$ 之共同 eigenstate

若將 $\hat{L}^2$ 之 eigenvalue 記為 $\hbar^2 l(l+1)$

$\hat{L}_z$ 〃 〃 $m\hbar$

(註：$[L_z] = [\hbar]$ （角動量 $= \vec{r} \times \vec{p}$，其單位 $= [mv][L] = [mv^2]\cdot[t]$
$= [\hbar\omega]\cdot[t] = [\hbar]$ ）)

若共同之 eigenstate 記為 $\psi_{E l, m}$

則

$$\hat{H}\psi_{Elm} = E\psi_{Elm} \quad \text{—— (10)}$$

$$\hat{L}^2\psi_{Elm} = \hbar^2 l(l+1)\psi_{Elm}$$

$$\hat{L}_z\psi_{Elm} = \hbar m\psi_{Elm}$$

$\because \quad \hat{H} = \frac{\hat{p}^2}{2m} + V(r) = \frac{-\hbar^2}{2m}\left[\frac{1}{r}\frac{d^2}{dr^2}r\right] + \frac{\hat{L}^2}{2mr^2} + V(r)$ —— (11)

且 $\hat{L}^2$ 只與 θ 及 ϕ 有關 $\therefore$ $\hat{H}\psi_{Elm} = E\psi_{Elm}$ 為

一 separable 問題，可以設

$$\psi_{E\ell m} = R_{E\ell m}(r)\, Y_{\ell m}(\theta,\phi)$$

其中 $\hat{L}^2 Y_{\ell m}(\theta,\phi) = \hbar^2\ell(\ell+1)\, Y_{\ell m}(\theta,\phi)$ — 12

$\hat{L}_z\, Y_{\ell m}(\theta,\phi) = m\hbar\, Y_{\ell m}(\theta,\phi)$ — 13

此時 10 式（即 11 式）

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2} r R_{E\ell m} + \frac{\hbar^2\ell(\ell+1)}{2mr^2} R_{E\ell m} + V(r) R_{E\ell m} = E R_{E\ell m}$$

若設 $u(r) = r R_{E\ell m}(r)$，上式變成

$$\frac{-\hbar^2}{2m}\frac{d^2}{dr^2} u(r) + \underbrace{\left(\frac{\hbar^2\ell(\ell+1)}{2mr^2} + V(r)\right)}_{V_{eff}(r)} u(r) = E\, u(r) \quad \text{— 14}$$

即 $u(r)$ 滿足一個一維 Schrödinger 方程式！

但略有不同，其實這裏的一維只是半個一維，因為 $0 < r < \infty$！

∵ $\psi_{E\ell m}$ 在 $r=0$ 是 well-defined，∴ $R_{E\ell m}(r)$ is finite at $r=0$ 因此，$u(r=0)=0$，換句話說，$V_{eff}(r)=\infty$ for $r<0$！