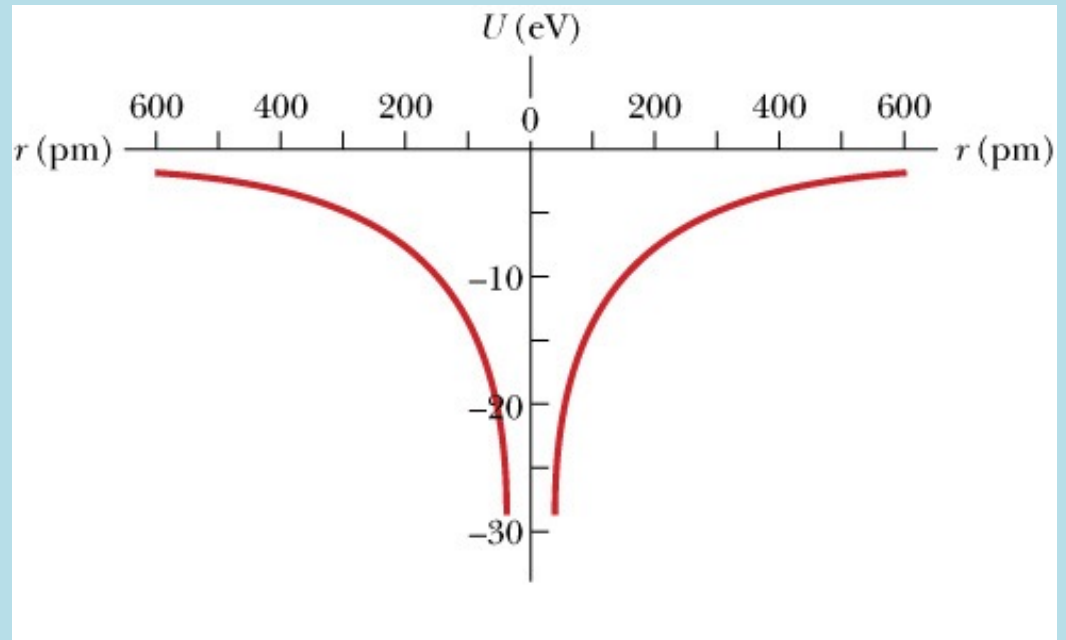
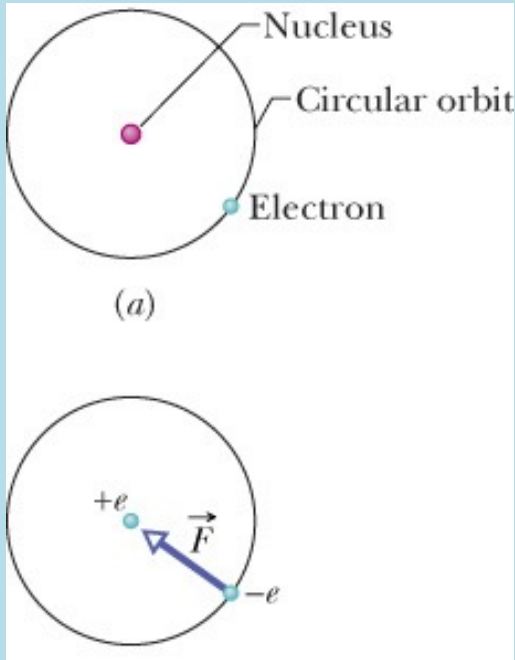


## 氫原子中的電子定態

電子受到來自原子核的庫倫位能： $V(r) = \frac{-e^2}{r}$



這是二體問題，電子繞質心以 reduced mass,  $\mu$ 運動：

$$\mu = \frac{m_e m_p}{m_e + m_p}$$

氫原子核比電子重的多，可假設： $\mu = m_e = m$ 。

以下推導有許多也適用於其他中心力位能。

## Quantization as an Eigenvalue Problem 1926

能量的量子化作為（不過就是）一個本徵值問題

### 3. *Quantisierung als Eigenwertproblem;* *von E. Schrödinger.*

(Erste Mitteilung.)

§ 1. In dieser Mitteilung möchte ich den einfachsten Fall des (nichtrelativistischen) Wasserstoffatoms zeigen, daß die übliche Quantisierung durch eine andere Forderung ersetzt werden kann, die von „ganzen Zahlen“ mehr vorkommt. Die Ganzzahligkeit auf dieselbe Weise zu erklären, ist eine neue Auffassung ist verallgemeinerbar. Ich glaube, sehr tief an das wahre Wesen der Sache zu rühren.

Die übliche Form der letzten Gleichung ist die partielle Differentialgleichung

$$(1) \quad H\left(q, \frac{\partial S}{\partial q}\right) = E$$

Es wird von dieser Gleichung verlangt, daß sie sich darstellen läßt als Summe von Funktionen der unabhängigen Variablen  $q$ .

Wir führen nun für  $S$  eine neue Forderung ein, daß  $\psi$  als ein Produkt von eingriffen Koordinaten erscheinen würde.

$$(2) \quad S = K \ln \psi$$

Die Konstante  $K$  muß aus dem Kontext bestimmt werden, sie hat die Dimension einer Energie.

$$(1') \quad H\left(q, \frac{K}{\psi} \frac{\partial \psi}{\partial q}\right) = E$$

Wir suchen nun *nicht* eine Lösung

### 3. Quantisation as an eigenvalue problem; by E. Schrödinger\*

(first communication.)

§ 1. In this communication I would like first to show, in the simplest case of the (non-relativistic and unperturbed) hydrogen atom, that the usual prescription for quantisation can be substituted by another requirement in which no word about “integer numbers” occurs anymore. Rather, the integerness<sup>1</sup> emerges in the same natural way as, for example, the integerness of the *number of knots* of a vibrating string. The new interpretation is generalisable and touches, as I believe, very deeply the true essence of the quantisation prescription.

The usual form of the latter is tied to the Hamiltonian partial differential equation:

$$(1) \quad H\left(q, \frac{\partial S}{\partial q}\right) = E .$$

Wir werden für  $H$  zunächst die Hamiltonsche Funktion der Keplerbewegung nehmen und zeigen, daß die aufgestellte Forderung für *alle positiven*, aber nur für eine *diskrete Schar von negativen  $E$ -Werten* erfüllbar ist. D. h. das genannte Variationsproblem hat ein diskretes und ein kontinuierliches Eigenwertspektrum. Das diskrete Spektrum entspricht den Balmerischen Termen, das kontinuierliche den Energien der Hyperbelbahnen. Damit numerische Übereinstimmung bestehe, muß  $K$  den Wert  $h/2\pi$  erhalten.

Da für die Aufstellung der Variationsgleichungen die Koordinatenwahl belanglos ist, wählen wir rechtwinkelige kartesische. Dann lautet (1') in unserem Fall ( $e, m$  sind Ladung und Masse des Elektrons):

$$(1'') \quad \left( \frac{\partial \psi}{\partial x} \right)^2 + \left( \frac{\partial \psi}{\partial y} \right)^2 + \left( \frac{\partial \psi}{\partial z} \right)^2 - \frac{2m}{K^2} \left( E + \frac{e^2}{r} \right) \psi^2 = 0 .$$

$$r = \sqrt{x^2 + y^2 + z^2} .$$

Und unser Variationsproblem lautet

$$(3) \quad \left\{ \begin{array}{l} \delta J = \delta \iiint dx dy dz \left[ \left( \frac{\partial \psi}{\partial x} \right)^2 + \frac{\partial^2 \psi_E}{\partial x^2} + \frac{\partial^2 \psi_E}{\partial y^2} + \frac{\partial^2 \psi_E}{\partial z^2} = \nabla^2 \psi_E = \frac{2m}{\hbar^2} [V(r) - E] \psi_E \right. \\ \left. - \frac{2m}{K^2} \left( E + \frac{e^2}{r} \right) \psi^2 \right] = 0 , \end{array} \right.$$

das Integral erstreckt über den ganzen Raum. Man findet daraus in gewohnter Weise

$$(4) \quad \left\{ \begin{array}{l} \frac{1}{2} \delta J = \int df \delta \psi \frac{\partial \psi}{\partial n} - \iiint dx dy dz \delta \psi \left[ \Delta \psi + \right. \\ \left. + \frac{2m}{K^2} \left( E + \frac{e^2}{r} \right) \psi \right] = 0 . \end{array} \right.$$

Es muß also erstens

$$(5) \quad \Delta \psi + \frac{2m}{K^2} \left( E + \frac{e^2}{r} \right) \psi = 0$$

此方程式只有對某些能量值 $E$ 才有解！數學的本徵值問題。

Quantisierung als Eigenwertproblem.

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§ 2. Die Bedingung (15) ergibt

(19) 
$$-E_l = \frac{m e^4}{2 K^2 l^2}.$$

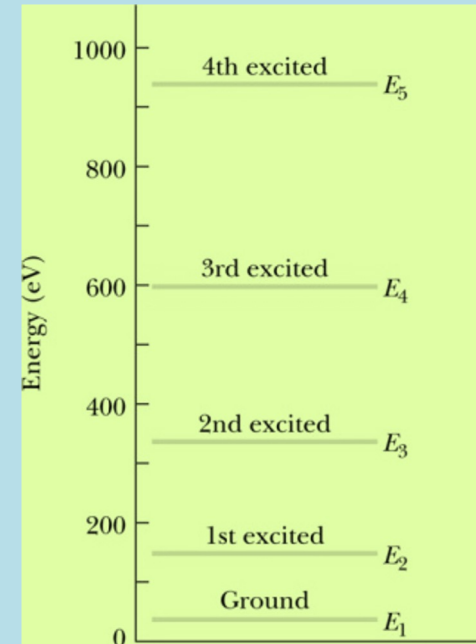
Es ergeben sich also die wohlbekanntes Bohrschen Energieniveaus, die den Balmertermen entsprechen, wenn man der Konstante  $K$ , die wir in (2) aus dimensionellen Gründen einführen mußten, den Wert erteilt

(20) 
$$K = \frac{h}{2\pi}.$$

Dann wird ja

(19') 
$$-E_l = \frac{2\pi^2 m e^4}{h^2 l^2}.$$

Unser  $l$  ist die Hauptquantenzahl.  $n + 1$  hat Analogie mit der Azimutalquantenzahl, die weitere Aufspaltung dieser Zahl bei der näheren Bestimmung der Kugelflächenfunktionen kann mit der Aufspaltung des Azimutalquants in ein „äquatoriales“ und ein „polares“ Quant in Analogie gesetzt werden. Diese Zahlen bestimmen hier das System der Knotenlinien auf der Kugel. Auch die „radiale Quantenzahl“,  $l - n - 1$  bestimmt genau die Zahl der „Knotenkugeln“, denn man kann sich leicht überzeugen, daß die Funktion  $f(x)$  in (18) genau  $l - n - 1$



氫原子能階

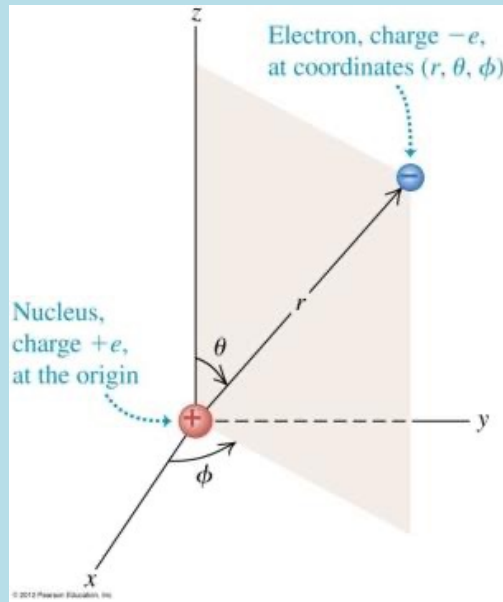
薛丁格能嚴格地得到正確的氫原子能階是天大的成就！

而且完全只用大家所熟悉的波的概念！

這個方法到現在都是解氫原子能階最簡單的方法。

能量的量子化原來是電子的波性的表現！





能量只與n有關。一般會先選定n：

$$R_{nl}(r) = e^{-\frac{Z}{na_0}r} \cdot r^l \cdot (r \text{ 的 } n-l-1 \text{ 次的多項式})$$

$n-l \geq 1$  才有解

$l \leq n-1$  l會有最大值

$$l = 0, 1, 2 \dots n-1$$

$$\psi_{nlm} = R_{nl}(r) \cdot P_l^m(\theta) \cdot \Phi_m(\phi)$$

與m無關。

與n無關。

$$P_l^m(\theta) = \sin^{|m|}\theta \cdot (\cos \theta, l-|m| \text{ 次的多項式})$$

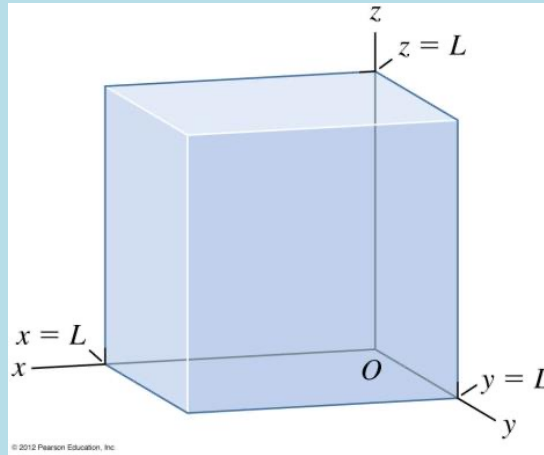
$l-|m| \geq 0$  才有解

$|m| \leq l$  |m|會有最大值

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

$$E_n = -\frac{m}{2} \left( \frac{e^2}{4\pi\epsilon_0\hbar} \right)^2 \frac{1}{n^2}$$

$$\Phi_m(\phi) \sim e^{im\phi}$$



3維空間能量本徵態的定態方程式：

3維空間與時間無關的薛丁格方程式：

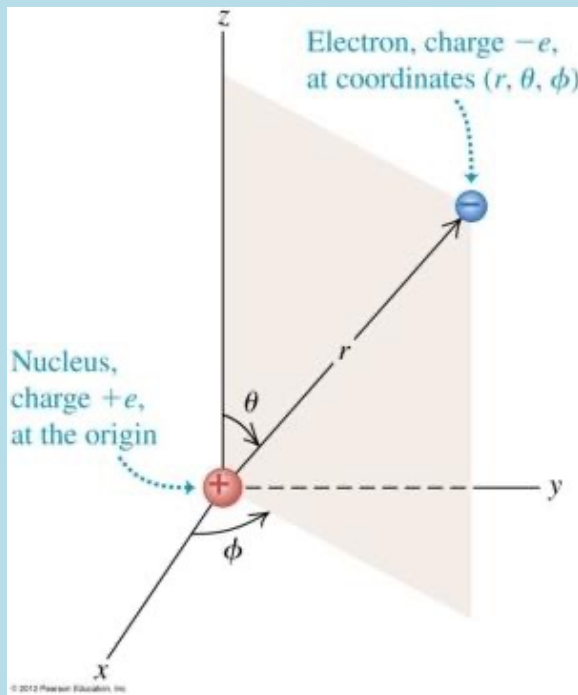
$$H\psi_E(\vec{r}) = \left[ \frac{p^2}{2m} + V(\vec{r}) \right] \psi_E(\vec{r}) = E\psi_E(\vec{r})$$

$$\vec{p} = (p_x, p_y, p_z) = \left( -i\hbar \frac{\partial}{\partial x}, -i\hbar \frac{\partial}{\partial y}, -i\hbar \frac{\partial}{\partial z} \right)$$

$$p^2 = -\hbar^2 \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] = -\hbar^2 \nabla^2$$

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

3維空間量子動能為Laplacian微分算子。



三度空間中氫原子內電子能量本徵態的定態方程式：

$$\frac{\partial^2 \psi_E}{\partial x^2} + \frac{\partial^2 \psi_E}{\partial y^2} + \frac{\partial^2 \psi_E}{\partial z^2} = \frac{2m}{\hbar^2} [V(r) - E] \psi_E$$



$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

$$\nabla^2 \psi_E + \frac{2m}{\hbar^2} \left[ \frac{e^2}{4\pi\epsilon_0 r} + E \right] \psi_E = 0$$

位能只與距離有關，有球對稱性質，以極座標表示最方便：

$$x = r \sin \theta \cos \phi, y = r \sin \theta \sin \phi, z = r \cos \theta$$

$\nabla^2 \psi_E \rightarrow ?$  Laplacian在極座標如何寫？ Laplacian是梯度的散度！

極座標的變化 $dr, d\theta, d\phi$ 所對應的位移，方向 $\hat{r}, \hat{\theta}, \hat{\phi}$ 在每一點都彼此垂直，  
位移大小與極座標的變化成正比：

$$ds_r = dr$$

$$ds_\theta = r d\theta$$

$$ds_\phi = r \sin \theta d\phi$$

我們可以用一組普遍的符號來描述：

$$ds_i = h_i dq_i \quad i = 1, 2, 3 \text{ or } r, \theta, \phi$$

$$h_r = 1$$

$$h_\theta = r$$

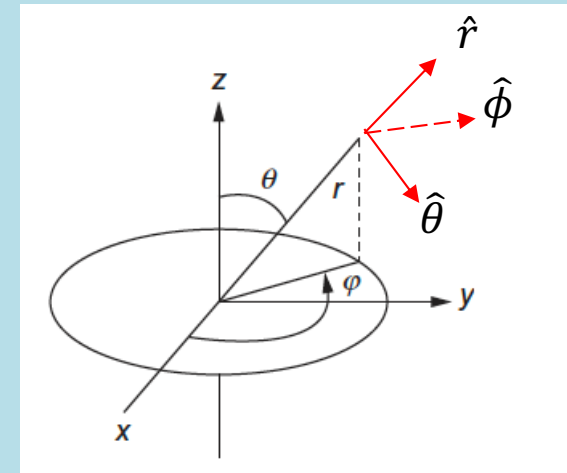
$$h_\phi = r \sin \theta$$

梯度向量便可定義於這個垂直基底之上，分量就是沿各個方向的變化率：

$$\vec{\nabla}\psi \equiv \hat{r} \cdot \frac{\partial\psi}{\partial r} + \hat{\theta} \cdot \frac{1}{r} \frac{\partial\psi}{\partial\theta} + \hat{\phi} \cdot \frac{1}{r \sin\theta} \frac{\partial\psi}{\partial\phi}$$

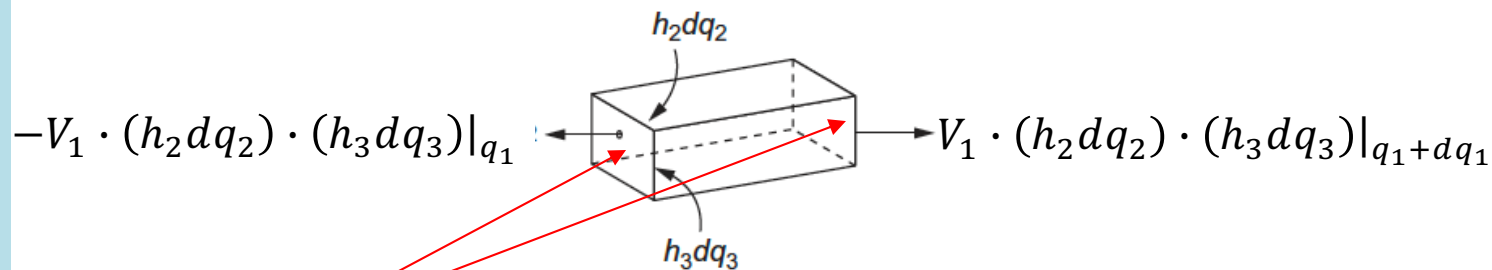
用分量來表示：

$$\vec{\nabla}\psi = \left( \frac{\partial\psi}{\partial r_1}, \frac{\partial\psi}{\partial r_2}, \frac{\partial\psi}{\partial r_3} \right) = \left( \frac{\partial\psi}{h_1 \partial q_1}, \frac{\partial\psi}{h_2 \partial q_2}, \frac{\partial\psi}{h_3 \partial q_3} \right)$$





散度：考慮由 $h_i dq_i$ 組成的小體積，某向量場 $\vec{V}$ 的通量等於散度 $\vec{\nabla} \cdot \vec{V}$ 乘體積！



如圖這兩面的通量等於：

$$-V_1(q_1, q_2, q_3) \cdot (h_2 dq_2) \cdot (h_3 dq_3) \Big|_{q_1} + V_1(q_1 + dq_1, q_2, q_3) \cdot (h_2 dq_2) \cdot (h_3 dq_3) \Big|_{q_1 + dq_1}$$

$$= dq_1 \frac{\partial}{\partial q_1} [V_1 \cdot (h_2 dq_2) \cdot (h_3 dq_3)]$$

$$h_r = 1$$

$$h_\theta = r$$

$$h_\phi = r \sin \theta$$

注意 $h_{2,3}$ 與 $q_1$ 有關

$$= dq_1 dq_2 dq_3 \frac{\partial}{\partial q_1} (V_1 h_2 h_3)$$

其他四個面的通量也可以以類似方法處理，可以得：

$$dq_1 dq_2 dq_3 \frac{\partial}{\partial q_2} (V_2 h_3 h_1) + dq_1 dq_2 dq_3 \frac{\partial}{\partial q_3} (V_3 h_1 h_2)$$

散度 $\vec{\nabla} \cdot \vec{V}$ 等於 $\vec{V}$ 的通量除以體積 $h_1 h_2 h_3 dq_1 dq_2 dq_3$ ！

$$\vec{\nabla} \cdot \vec{V} = \frac{1}{h_1 h_2 h_3} \left[ \frac{\partial}{\partial q_1} (V_1 h_2 h_3) + \frac{\partial}{\partial q_2} (V_2 h_3 h_1) + \frac{\partial}{\partial q_3} (V_3 h_1 h_2) \right]$$

$$\vec{\nabla} \cdot \vec{V} = \frac{1}{h_1 h_2 h_3} \left[ \frac{\partial}{\partial q_1} (V_1 h_2 h_3) + \frac{\partial}{\partial q_2} (V_2 h_3 h_1) + \frac{\partial}{\partial q_3} (V_3 h_1 h_2) \right]$$

代入梯度就可以得到Laplacian： $\vec{\nabla}\psi = \left( \frac{\partial\psi}{h_1\partial q_1}, \frac{\partial\psi}{h_2\partial q_2}, \frac{\partial\psi}{h_3\partial q_3} \right)$

$$\nabla^2\psi = \vec{\nabla} \cdot \vec{\nabla}\psi = \frac{1}{h_1 h_2 h_3} \left[ \frac{\partial}{\partial q_1} \left( \frac{h_2 h_3}{h_1} \frac{\partial\psi}{\partial q_1} \right) + \frac{\partial}{\partial q_2} \left( \frac{h_3 h_1}{h_2} \frac{\partial\psi}{\partial q_2} \right) + \frac{\partial}{\partial q_3} \left( \frac{h_1 h_2}{h_3} \frac{\partial\psi}{\partial q_3} \right) \right]$$

極座標： $h_r = 1$      $h_\theta = r$      $h_\phi = r \sin \theta$

$$\nabla^2\psi = \vec{\nabla} \cdot \vec{\nabla}\psi = \frac{1}{r^2 \sin \theta} \left[ \frac{\partial}{\partial r} \left( r^2 \sin \theta \frac{\partial\psi}{\partial r} \right) + \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial\psi}{\partial \theta} \right) + \frac{\partial}{\partial \phi} \left( \frac{1}{\sin \theta} \frac{\partial\psi}{\partial \phi} \right) \right]$$

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

Laplacian可以寫成極座標兩次微分，沒有交差項。

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

這看起來很複雜，但第二項及第三項就是角動量大小！

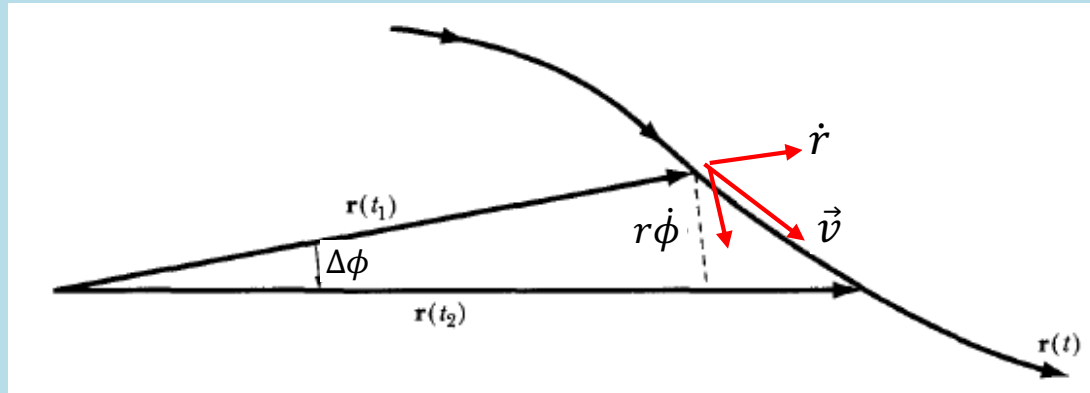
$$= \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{L^2}{\hbar^2 r^2}$$

因此能量算子也能大幅簡化：

$$H = \left[ -\hbar^2 \frac{\nabla^2}{2m} + V(r) \right]$$

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

$$= \frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \right] + \frac{L^2}{2mr^2} + V(r)$$



動能中的角動量項在古典中心力運動就有！

$$E = \frac{1}{2} m v^2 + V(r) = \frac{1}{2} m \left[ \left( \frac{dr}{dt} \right)^2 + r^2 \left( \frac{d\phi}{dt} \right)^2 \right] + V(r)$$

$\frac{d\phi}{dt} = l/mr^2$  角度變化率  $\frac{d\phi}{dt}$  由距離決定！轉動動能如同位能一樣！

$$E = \frac{1}{2} m \left( \frac{dr}{dt} \right)^2 + \frac{l^2}{2mr^2} + V(r)$$

$$H = \frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \right] + \frac{L^2}{2mr^2} + V(r)$$

有了 $H$ 的表示式，很容易可以導出 $H$ 與 $L_z$ 對易： $[H, L_z] = 0$

$$[V(r), L_z] = \left[ V(r), -i\hbar \frac{\partial}{\partial \phi} \right] = 0 \quad V(r) \text{ 沒有 } \phi \text{ 座標，自然與 } L_z = -i\hbar \frac{\partial}{\partial \phi} \text{ 對易！}$$

同理：

$$\left[ \frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \right] - i\hbar \frac{\partial}{\partial \phi} \right] = 0$$

$L^2$ 與 $L_z$ 本來就對易： $[L^2, L_z] = 0$

因此 $H$ 與 $L_z$ 對易：

$$[H, L_z] = \left[ \frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \right] + \frac{L^2}{2mr^2} + V(r), L_z \right] = 0$$

不意外： $H$ 算子中完全沒有 $\phi$ 座標，自然與 $L_z = -i\hbar \frac{\partial}{\partial \phi}$ 對易！

因為旋轉對稱，三個角動量分量的性質應該沒有區別，因此 $H$ 也與 $L_{x,y}$ 對易。

$$[H, L_z] = [H, L_x] = [H, L_y] = 0$$

$L^2$ 由 $L_{x,y}$ 組成，自然也 $H$ 對易。 $[H, L^2] = 0$

$$[H, L_z] = [H, L_x] = [H, L_y] = 0$$

$$[H, L^2] = 0$$

因此可以選擇能量的本徵態，同時也是 $L^2, L_z$ 的本徵態，也就是： $R \cdot Y_{lm}(\theta, \phi)$ ：  
與 $\theta, \phi$ 無關的 $R$ ，可以是 $r$ 的函數：

$$\psi_E(r, \theta, \phi) = R(r) \cdot Y_{lm}(\theta, \phi)$$

$$L^2 \cdot Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi)$$

$$L_z \cdot Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi)$$

以上推導的關鍵是  $[V(r), L_z] = [V(r), L^2]$

這個結果適用於任何的中心力位能 $V(r)$ ，不限於氫原子中的庫倫位能。

有了以上簡化，就可求解定態波函數的與時間無關薛定格方程式：

$$-\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi_E}{\partial r} \right) - \frac{1}{\hbar^2 r^2} (L^2 \psi_E) = -\frac{2m}{\hbar^2} [V(r) - E] \psi_E$$

能量的本徵態，同時也是 $L^2, L_z$ 的本徵態：

$$\psi_E(r, \theta, \phi) = R(r) \cdot Y_{lm}(\theta, \phi)$$

將上式代入定態方程式：

$$-Y \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) - \frac{1}{r^2} R \cdot L^2 Y + \frac{2m}{\hbar^2} [V(r) - E] R Y = 0$$

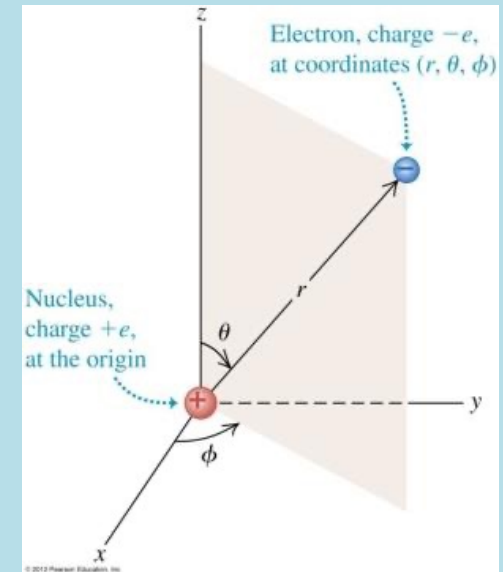
整個方程式除 $Y$ ：

$$-\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) - \frac{R}{r^2 Y} L^2 Y + \frac{2m}{\hbar^2} [V(r) - E] R = 0$$

代入 $L^2$ 的本徵值， $R(r)$ 滿足：

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

這是求解 $R(r)$ 的方程式。



有一種看法可以很快判斷出能量 $E$ 是量子化的：

$$-\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \frac{1}{r^2} l(l+1)R + \frac{2m}{\hbar^2} V(r)R = \frac{2mE}{\hbar^2} R$$

可把第一項改寫為二次微分，利用

$$\frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) = 2r \frac{dR}{dr} + r^2 \frac{d^2 R}{dr^2} = r \frac{d^2 (rR)}{dr^2}$$

$$-\frac{1}{r} \frac{d^2 (rR)}{dr^2} + \frac{1}{r^3} l(l+1)(rR) + \frac{1}{r} \frac{2m}{\hbar^2} V(r)(rR) = \frac{1}{r} \frac{2mE}{\hbar^2} (rR)$$

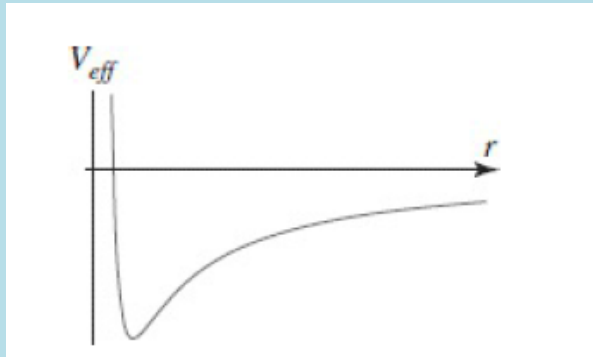
$$-\frac{d^2 u}{dr^2} + \frac{1}{r^2} l(l+1)u + \frac{2m}{\hbar^2} V(r)u = \frac{2mE}{\hbar^2} u \quad u \equiv rR(r)$$

這是一個一維 $0 \leq r \leq \infty$ 的位能本徵值問題。

有效位能為：

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

原點 $r = 0$ 會如一個無限大位能的固定點！



與古典的有效位能幾乎完全一致！

$V(r)$ 的具體細節會決定 $R(r)$ 。

能量若小於零，電子會被束縛，因此我們已經可以預期能量是量子化的。



解 $R(r)$ ：Radial Equation是一個Sturm-Liouville Problem。

$$-\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \frac{1}{r^2} l(l+1)R + \frac{2m}{\hbar^2} V(r)R = \frac{2mE}{\hbar^2} R$$

可以把它展開，代入庫倫位能：

$$-\frac{d^2R}{dr^2} - \frac{2}{r} \frac{dR}{dr} + \frac{l(l+1)}{r^2} R - \frac{2m}{\hbar^2} \frac{e^2}{4\pi\epsilon_0 r} R - \frac{2mE}{\hbar^2} R = 0$$

找負能量的解： $E < 0, |E| = -E$ 。

前三項都正比於長度平方，可以選一長度單位，使第五項的係數簡化為 $1/4$ ，

$$\rho = \sqrt{\frac{8m|E|}{\hbar^2}} r$$

化簡得：

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2} R - \frac{1}{4} R + \frac{\lambda}{\rho} R = 0$$

這樣的選擇，使量子化的 $\lambda$ 會剛好是自然數。

$$\lambda = \frac{e^2}{4\pi\epsilon_0 \hbar} \sqrt{\frac{m}{2|E|}}$$

此數 $\lambda$ 就含能量本徵值 $E$ 。

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2} R - \frac{1}{4} R + \frac{\lambda}{\rho} R = 0$$

此式並沒有有限次多項式解，

趨近原點時第三項獨大，趨近無限遠處時第四項獨大。沒有其他項可以抵消。

讓我們先找出 $R$ 在原點及無限遠處的極端行為，極端情況下方程式可以簡化：

$$\rho \rightarrow \infty \quad \frac{d^2 R}{d\rho^2} - \frac{1}{4} R \sim 0 \quad \text{第四項dominates。}$$

$$R \sim e^{-\frac{\rho}{2}} \quad \text{無限遠處是指數遞減。}$$

$$\rho \rightarrow 0 \quad \frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2} R \sim 0$$

$$R \sim \rho^l \quad \text{第三項dominates。}$$

因此 $R(r)$ 在原點的行為，由量子數 $l$ 決定。

現在已知 $R$ 在原點及無限遠處的極端行為：

$$\rho \rightarrow \infty \quad R \sim e^{-\frac{\rho}{2}}$$

$$\rho \rightarrow 0 \quad R \sim \rho^l$$

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2} R - \frac{1}{4} R + \frac{\lambda}{\rho} R = 0$$

此式並沒有有限次多項式解，

若把這兩個極端情況提出，剩餘的部分將可能是有限次多項式。

這與SHO非常類似！

$R(\rho) \sim e^{-\frac{\rho}{2}} \rho^l H(\rho)$  期待 $H(\rho)$ 為有限 $N$ 次多項式。代入前式：可得：

$$\frac{d^2 H}{d\rho^2} + \left( \frac{2l+2}{\rho} - 1 \right) \frac{dH}{d\rho} + \frac{\lambda - l - 1}{\rho} H = 0$$

原來有問題的第三項及第四項都消失了。各冪次都有兩個以上的項。

$\rho^l$ 的  $\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho}$  消掉了第三項， $e^{-\frac{\rho}{2}}$  的兩次微分消掉了第四項。

$$\frac{d^2 H}{d\rho^2} + \left( \frac{2l+2}{\rho} - 1 \right) \frac{dH}{d\rho} + \frac{\lambda - l - 1}{\rho} H = 0$$

設 $H(\rho)$ 為有限 $N$ 次多項式。

$$H(\rho) = \sum_{i=0}^N a_i \rho^i$$

代入並先取最高次項試一下：

$$N(N-1)a_N \rho^{N-2} + N \left( \frac{2l+2}{\rho} - 1 \right) a_N \rho^{N-1} + (\lambda - l - 1) a_N \rho^{N-1} = 0$$

$$-N a_N \rho^{N-1} + (\lambda - l - 1) a_N \rho^{N-1} = 0$$

$$-N + (\lambda - l - 1) = 0$$

$\lambda = N + l + 1$  包含能量 $E$ 的 $\lambda$ 必須是自然數！

因此可知能量是量子化的。

$$\lambda = \frac{e^2}{4\pi\epsilon_0 \hbar} \sqrt{\frac{m}{2|E|}}$$

包含能量 $E$ 的常數 $\lambda$ 必須是自然數，方程式才有解！

$$\lambda = N + l + 1$$

重新命名 $\lambda$ 為自然數主量子數 $n$ ： $n = \lambda = N + l + 1$

$H(\rho)$ 是 $N$ 次的多項式  $N = n - l - 1$ 。

多項式冪次 $N$ 必須大於等於零，因此對特定的 $l$ ， $n$ 有最小值：

$$n \geq l + 1$$

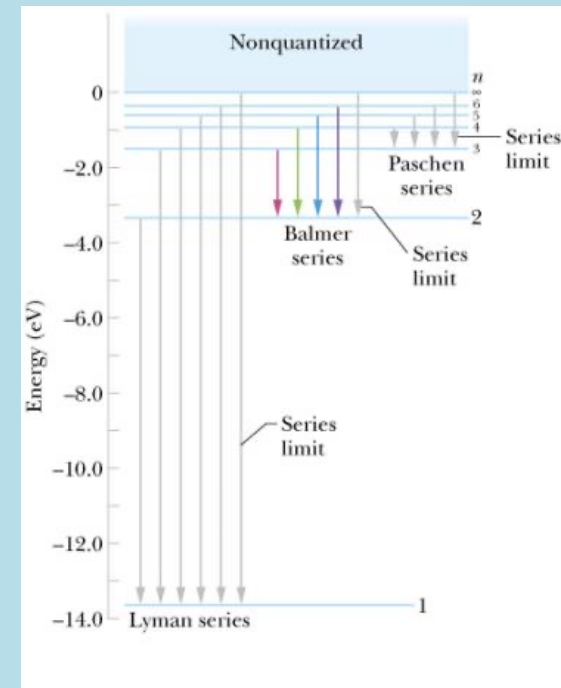
$$\lambda = \frac{e^2}{4\pi\epsilon_0\hbar} \sqrt{\frac{m}{2|E|}} = n$$

$$E_n = -\frac{m}{2} \left( \frac{e^2}{4\pi\epsilon_0\hbar} \right)^2 \frac{1}{n^2}$$

$$E_n = (-13.6\text{eV}) \left( \frac{1}{n^2} \right)$$

因此能量是量子化的。能量只與 $n$ 有關。

所以一般會倒過來，先固定 $n$ ， $l$ 會有最大值



$$l \leq n - 1$$

$$l = 0, 1, 2 \dots n - 1$$

有限 $N$ 次多項式 $H(\rho)$ 可以以遞迴關係解出： $\lambda$ 重新命名為 $n$ ：

$$\frac{d^2 H}{d\rho^2} + \left( \frac{2l+2}{\rho} - 1 \right) \frac{dH}{d\rho} + \frac{n-l-1}{\rho^2} H = 0$$

$$H(\rho) = \sum_{i=0}^N a_i \rho^i$$

代入得到：

$$\sum_{i=0}^N [i(i-1)a_i \rho^{i-2} + i(2l+2)a_i \rho^{i-2} - i a_i \rho^{i-1} + (n-l-1)a_i \rho^{i-1}] = 0$$

取 $\rho^{k-1}$ 的係數必須為零：

$$[(k+1)(k+2l+2)a_{k+1} + (n-l-1-k)a_k] = 0$$

$$\frac{a_{k+1}}{a_k} = \frac{k+l+1-n}{(k+1)(k+2l+2)}$$

$$\frac{a_{k+1}}{a_k} = \frac{k + l + 1 - n}{(k + 1)(k + 2l + 2)}$$

當 $k$ 很大時， $\frac{a_{k+1}}{a_k} \rightarrow \frac{1}{k}$ ， $a_{k+1} \rightarrow \frac{1}{k!}$

$$H(\rho) \leftrightarrow \sum_{k=0}^{\infty} \frac{1}{k!} \rho^k = e^\rho$$

$e^\rho$ 在 $\rho \rightarrow \infty$ 發散。

因此如果 $H(\rho)$ 是無限次多項式，將會無法歸一化。

如前所示，若 $H(\rho)$ 是有限 $N$ 次多項式， $n$ 是自然數。  $n = N + l + 1$

$k = N = n - l - 1$ 時上式分子為零。  $a_{N+1} = 0$  遞迴就會中止。

$H(\rho) \equiv H_{nl}(\rho)$ 有兩個量子數 $n, l$ ，它是 $N = n - l - 1$ 次的多項式。

$$H_{nl}(\rho) = \sum_{m=0}^{n-l-1} \binom{n+l}{n-m} \frac{(-\rho)^m}{m!}$$

$H(\rho)$  are Associate Laguerre Polynomials.

$$\frac{d^2 H_{nl}(\rho)}{d\rho^2} + \left( \frac{2l+2}{\rho} - 1 \right) \frac{dH_{nl}(\rho)}{d\rho} + \frac{n-l-1}{\rho^2} H_{nl}(\rho) = 0$$

$$\left[ \rho \frac{d^2}{d\rho^2} + (q+1-\rho) \frac{d}{d\rho} + p \right] L_p^q(\rho) = 0 \quad \text{如下表：}$$

$$H_{nl}(\rho) = L_{n-l-1}^{2l+1}(\rho)$$

**TABLE 10.3** Eigenfunctions of hydrogen in terms of associated Laguerre polynomials

*The Normalized Eigenfunctions of Hydrogen ( $Z = 1$ )*

$$\varphi_{nlm}(r, \theta, \phi) = (2\kappa)^{3/2} A_{nl} \rho^l e^{-\rho/2} F_{nl}(\rho) Y_l^m(\theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$

$$\rho = 2\kappa r = \frac{2Z}{a_0 n} r \quad \int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1$$

$$A_{nl} = \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}}$$

$$\varphi_{100} = \frac{1}{\sqrt{8\pi}} \left( \frac{2Z}{a_0} \right)^{3/2} e^{-(Z/a_0)r}$$

$$F_{nl}(\rho) = L_{n-l-1}^{2l+1}(\rho) = L_{i_{\max}}^{2l+1}(\rho) = \sum_{i=0}^{n-l-1} \frac{(-1)^i [(n+l)!]^2 \rho^i}{i!(n-l-1-i)!(2l+1+i)!}$$

Associated Laguerre Polynomials  $L_p^q(\rho)$  and Laguerre Polynomials  $L_p(\rho)$

Differential equation

$$\left[ \rho \frac{d^2}{d\rho^2} + (q+1-\rho) \frac{d}{d\rho} + p \right] L_p^q(\rho) = 0$$



$$\frac{a_{k+1}}{a_k} = \frac{k + l + 1 - n}{(k + 1)(k + 2l + 2)}$$

$$H_{10}(\rho) \sim a_0 \quad H_{20}(\rho) \sim a_0 \left(1 - \frac{\rho}{2}\right) \quad H_{21}(\rho) \sim a_0$$

$n - l$  決定了幕次  $H_{nl}(\rho)$  是  $n - l - 1$  次的多項式。

$H_{nl}(\rho)$  are Associate Laguerre Polynomials.  $H_{nl}(\rho) = L_{n-l-1}^{2l+1}(\rho)$

$$R_{nl}(r) \sim e^{-\frac{\rho}{2}} \cdot \rho^l \cdot H_{nl}(\rho)$$

$$R_{nl}(r) \sim e^{-\frac{r}{na_0}} \cdot r^l \cdot H_{nl}\left(\frac{2}{na_0} r\right)$$

$$\rho = \sqrt{\frac{8m|E|}{\hbar^2}} r = \frac{2m}{n\hbar} \left(\frac{e^2}{4\pi\epsilon_0\hbar}\right) r \equiv \frac{2}{na_0} r$$

$$a_0 \equiv \frac{\hbar}{m} \left(\frac{e^2}{4\pi\epsilon_0\hbar}\right)^{-1} \text{ called Bohr radius.}$$

$$R_{10}(r) = 2 \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$R_{20}(r) = 2 \left(\frac{Z}{2a_0}\right)^{3/2} \left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0}$$

**TABLE 10.3** Eigenfunctions of hydrogen in terms of associated Laguerre polynomials

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$$\varphi_{nlm}(r, \theta, \phi) = (2\kappa)^{3/2} A_{nl} \rho^l e^{-\rho/2} F_{nl}(\rho) Y_l^m(\theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$

$$\rho = 2\kappa r = \frac{2Z}{a_0 n} r \quad \int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1$$

$$A_{nl} = \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}}$$

$$\varphi_{100} = \frac{1}{\sqrt{8\pi}} \left(\frac{2Z}{a_0}\right)^{3/2} e^{-(Z/a_0)r}$$

$$F_{nl}(\rho) = L_{n-l-1}^{2l+1}(\rho) = L_{i_{\max}}^{2l+1}(\rho) = \sum_{i=0}^{n-l-1} \frac{(-1)^i [(n+l)!]^2 \rho^i}{i!(n-l-1-i)!(2l+1+i)!}$$

*Associated Laguerre Polynomials  $L_p^q(\rho)$  and Laguerre Polynomials  $L_p(\rho)$*

*Differential equation*

$$\left[ \rho \frac{d^2}{d\rho^2} + (q+1-\rho) \frac{d}{d\rho} + p \right] L_p^q(\rho) = 0$$

*Generating function*

$$\frac{e^{-\rho s/(1-s)}}{(1-s)^{q+1}} = \sum_{p=0}^{\infty} \frac{s^p}{(p+q)!} L_p^q(\rho) \quad L_0^p(0) = p!$$

*Orthonormality*

$$\int_0^\infty e^{-\rho} \rho^q L_p^q L_{p'}^q d\rho = \frac{[(p+q)!]^3}{p!} \delta_{pp'}$$

*Rodrigues's formula*

$$L_p(\rho) \equiv L_p^0(\rho) = e^\rho \frac{d^p}{d\rho^p} (\rho^p e^{-\rho}), \quad L_1(\rho) = 1 - \rho, \quad L_2(\rho) = 2! \left( 1 - 2\rho + \frac{\rho^2}{2} \right)$$

$$L_p^q(\rho) \equiv (-1)^q \frac{d^q}{d\rho^q} [L_{q+p}(\rho)]$$

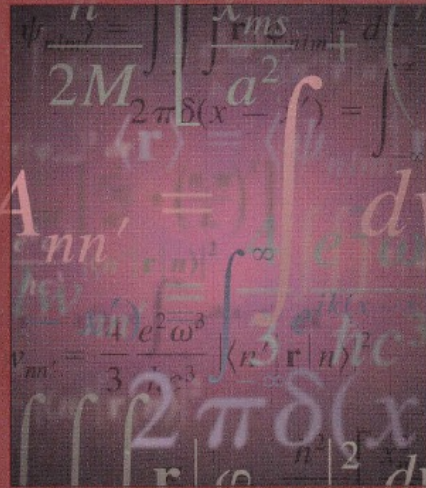
*Recurrence relations*

$$\rho L_p^q(\rho) = (2p+q+1)L_p^q(\rho) - [(p+1)/(p+q+1)]L_{p+1}^q(\rho) - (p+q)^2 L_{p-1}^q(\rho)$$

$$\left( \rho \frac{d}{d\rho} + q - \rho \right) L_p^q(\rho) = (p+1)L_{p+1}^{q-1}(\rho)$$

$$\frac{d}{d\rho} L_p^q(\rho) = -L_{p-1}^{q+1}(\rho)$$

INTRODUCTORY  
QUANTUM  
MECHANICS  
FOURTH EDITION



Richard L. Liboff

# Normalization

The associated Laguerre equation, Eq. (18.69), is not self-adjoint, but the weighting function needed to bring it to self-adjoint form (for upper index  $k$ ) can be found in the usual way:

$$w_k(x) = \frac{1}{x} \exp \left[ \int \frac{k+1-x}{x} dx \right] = x^k e^{-x}. \quad (18.70)$$

When we also note that Sturm-Liouville boundary conditions are satisfied at  $x = 0$  and  $x = \infty$ , we see that the associated Laguerre polynomials are orthogonal according to the equation

$$\int_0^\infty e^{-x} x^k L_n^k(x) L_m^k(x) dx = \frac{(n+k)!}{n!} \delta_{mn}. \quad (18.71)$$

The value of the integral in Eq. (18.71) for  $m = n$  can be established using the generating function, Eq. (18.58). Doing so is left as an exercise.

Equation (18.71) shows the same orthogonality interval  $(0, \infty)$  as that for the Laguerre polynomials, but with a different weighting function for each  $k$ . We see that for each  $k$  the associated Laguerre polynomials define a new set of orthogonal polynomials.

A Rodrigues representation of the associated Laguerre polynomials is useful and can be found in various ways. A fairly direct approach is simply to use Eq. (12.9) with  $p(x) = x$ , the coefficient of the second-derivative term in Eq. (18.69) and the value of  $w_k(x)$  given in Eq. (18.70). The result is

$$L_n^k(x) = \frac{e^x x^{-k}}{n!} \frac{d^n}{dx^n} (e^{-x} x^{n+k}). \quad (18.72)$$

Note that this and all our earlier formulas involving the  $L_n^k(x)$  reduce properly to corresponding expressions involving  $L_n(x)$  when  $k = 0$ .

By letting  $\psi_n^k(x) = e^{-x/2} x^{k/2} L_n^k(x)$ , we find that  $\psi_n^k(x)$  satisfies the self-adjoint ODE,

$$x \frac{d^2 \psi_n^k(x)}{dx^2} + \frac{d \psi_n^k(x)}{dx} + \left( -\frac{x}{4} + \frac{2n+k+1}{2} - \frac{k^2}{4x} \right) \psi_n^k(x) = 0. \quad (18.73)$$

The  $\psi_n^k(x)$  are sometimes called **Laguerre functions**. Equation (18.57) is the special case  $k = 0$  of Eq. (18.73).

A further useful form is given by defining<sup>6</sup>

$$\Phi_n^k(x) = e^{-x/2} x^{(k+1)/2} L_n^k(x). \quad (18.74)$$

Substitution into the associated Laguerre equation yields

$$\frac{d^2 \Phi_n^k(x)}{dx^2} + \left( -\frac{1}{4} + \frac{2n+k+1}{2x} - \frac{k^2-1}{4x^2} \right) \Phi_n^k(x) = 0. \quad (18.75)$$

The  $\Phi_n^k(x)$  are orthogonal with weighting function  $x^{-1}$ .

The associated Laguerre ODE, Eq. (18.69), has solutions even if  $n$  is not an integer, but they are then not polynomials and diverge proportionally to  $xke^x$  as  $x \rightarrow \infty$ . This fact is useful in the following example.

<sup>6</sup>This corresponds to modifying the function  $\psi$  in Eq. (18.73) to eliminate the first derivative.

It is sometimes convenient to define orthogonalized Laguerre functions (with unit weighting factor) by

$$\varphi_n(x) = e^{-x/2} L_n(x). \quad (18.56)$$

Our new orthonormal functions,  $\varphi_n(x)$ , satisfy the self-adjoint ODE

$$x\varphi_n''(x) + \varphi_n'(x) + \left(n + \frac{1}{2} - \frac{x}{4}\right)\varphi_n(x) = 0, \quad (18.57)$$

and are eigenfunctions of a Sturm-Liouville system on the range  $(0 \leq x < \infty)$ .

## Associated Laguerre Polynomials

In many applications, particularly in quantum mechanics, we need the associated Laguerre polynomials defined by<sup>4</sup>

$$L_n^k(x) = (-1)^k \frac{d^k}{dx^k} L_{n+k}(x). \quad (18.58)$$

By differentiating the power series for  $L_n(x)$  given in Eq. (18.53) (compare Table 18.2), we can get the explicit forms shown in Table 18.3. In general,

$$L_n^k(x) = \sum_{m=0}^n (-1)^m \frac{(n+k)!}{(n-m)!(k+m)!m!} x^m, \quad k \geq 0. \quad (18.59)$$

One of the present authors<sup>5</sup> has recently found a new generating function for the associated Laguerre polynomials with the remarkably simple form

$$g_l(x, t) = e^{-tx} (1+t)^l = \sum_{n=0}^{\infty} L_n^{l-n}(x) t^n. \quad (18.60)$$

<sup>4</sup>Some authors use  $\mathfrak{L}_{n+k}^k(x) = (d^k/dx^k)[L_{n+k}(x)]$ . Hence our  $L_n^k(x) = (-1)^k \mathfrak{L}_{n+k}^k(x)$ .

<sup>5</sup>H. J. Weber, Connections between real polynomial solutions of hypergeometric-type differential equations with Rodrigues formula, *Cent. Eur. J. Math.* 5: 415–427 (2007).

Table 18.3 Associated Laguerre Polynomials

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$L_0^k = 1$
$1! L_1^k = -x + (k+1)$
$2! L_2^k = x^2 - 2(k+2)x + (k+1)_2$
$3! L_3^k = -x^3 + 3(k+3)x^2 - 3(k+2)_2x + (k+1)_3$
$4! L_4^k = x^4 - 4(k+4)x^3 + 6(k+3)_2 - 4(k+2)_3 + (k+1)_4$
$5! L_5^k = -x^5 + 5(k+5)x^4 - 10(k+4)_2x^3 + 10(k+3)_3x^2 - 5(k+2)_4x + (k+1)_5$
$6! L_6^k = x^6 - 6(k+6)x^5 + 15(k+5)_2x^4 - 20(k+4)_3x^3 + 15(k+3)_4x^2$
$\quad - 6(k+2)_5x + (k+1)_6$
$7! L_7^k = -x^7 + 7(k+7)x^6 - 21(k+6)_2x^5 + 35(k+5)_3x^4 - 35(k+4)_4x^3$
$\quad + 21(k+3)_5x^2 - 7(k+2)_6x + (k+1)_7$

---

*Exercise.* Evaluate  $I_l$  by a method of your choice. (One such method is to establish the relation  $I_l = -[2l/(2l+1)]I_{l-1}$ , using integration by parts. Can you suggest any others?)

The normalization integral can also be derived from the generating function. Write

$$\frac{1}{\sqrt{1-2xt+t^2}} = \sum_{l=0}^{\infty} t^l P_l(x)$$

and square both sides:

$$\frac{1}{1-2xt+t^2} = \sum_{m=0}^{\infty} \sum_{l=0}^{\infty} t^{l+m} P_l(x) P_m(x).$$

Integrate both sides with respect to  $x$  from  $-1$  to  $+1$ . Because of the orthogonality of Legendre polynomials only the terms with  $m = l$  on the right-hand side of the equation will survive, reducing the double series to a simple one:

$$\int_{-1}^{+1} \frac{1}{1-2xt+t^2} = \sum_{l=0}^{\infty} t^{2l} \int_{-1}^{+1} [P_l(x)]^2 dx.$$

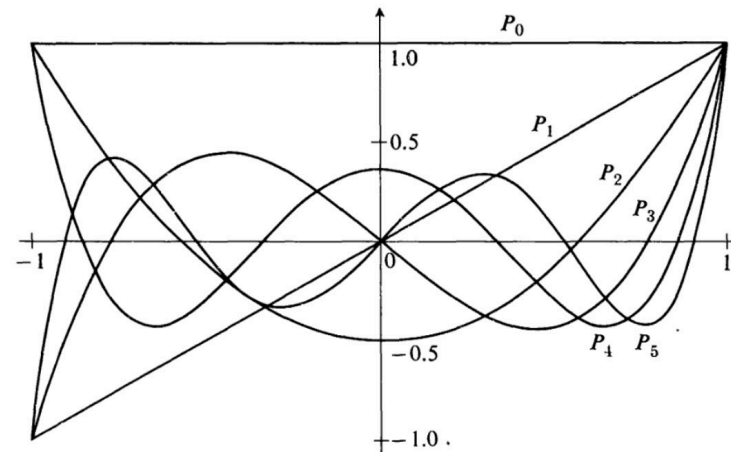
Now evaluate the left-hand side of the equation:

$$\int_{-1}^{+1} \frac{1}{1-2xt+t^2} = \frac{1}{t} \log \frac{1+t}{1-t} \quad (t < 1).$$

Expand this function in powers of  $t$  by utilizing the Maclaurin series for  $\log(1+t)$ , and obtain

$$\frac{1}{t} \log \frac{1+t}{1-t} = 2 \sum_{n=0}^{\infty} \frac{1}{(2n+1)} t^{2n},$$

and the normalization integral  $N_l = 2/(2l+1)$  follows.



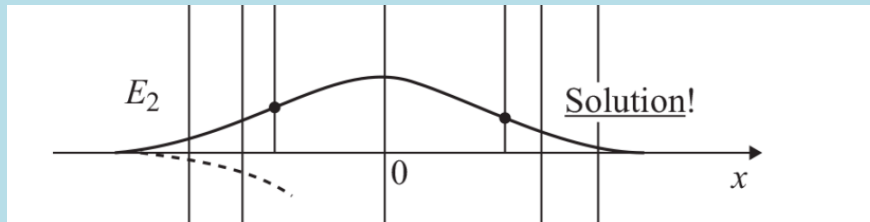
Legendre polynomials

Figure 9.1

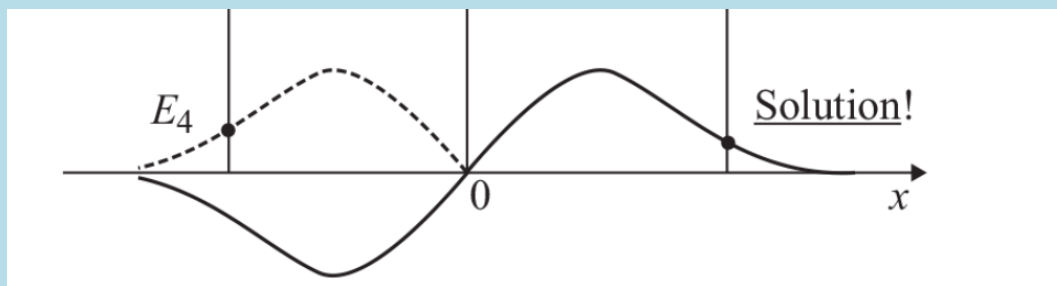
簡諧運動的定態函數 $u(y)$ 的特性：

$$u(y) = e^{-\frac{y^2}{2}} \times (\text{一個特別的多項式})$$

若式中(特別的多項式)是常數，此函數就是一個單純的高斯分佈：  
在 $\infty$ 趨近指數遞減，在原點附近維持緩慢變化：

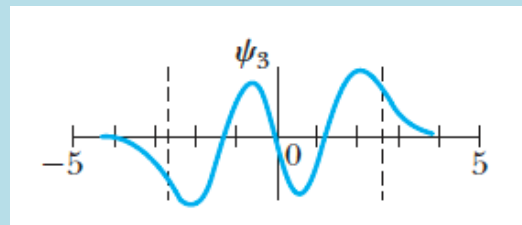
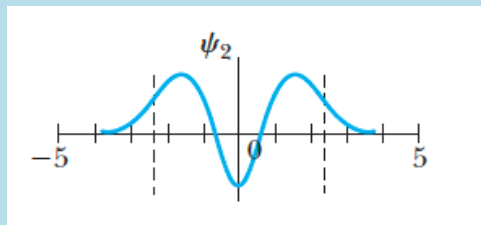


若(特別的多項式)是一次方 $x$ ，此函數在遠處是高斯分佈：  
在 $\infty$ 趨近指數遞減，在原點附近穿過 $x$ 軸，在此函數需為零：



**大膽猜想：在趨近 $\infty$ 處此解由高斯分佈控制，在原點附近則由多項式控制！**

該多項式若是 $n$ 次，則會穿過 $x$ 軸 $n$ 次， $n$ 越大能量越大。



氫原子定態的徑向波函數 $R_{nl}(r)$ 也非常類似，現在端點是 $0 < r < \infty$ 。

$$R_{nl}(r) \sim e^{-\frac{r}{na_0}} \cdot r^l \cdot H_{nl}\left(\frac{2}{na_0}r\right)$$

在趨近 $\infty$ 處此解由遞減指數函數控制： $e^{-\frac{r}{na_0}}$

在原點附近則由角動量的量子數 $l$ 決定函數的行為： $r^l$

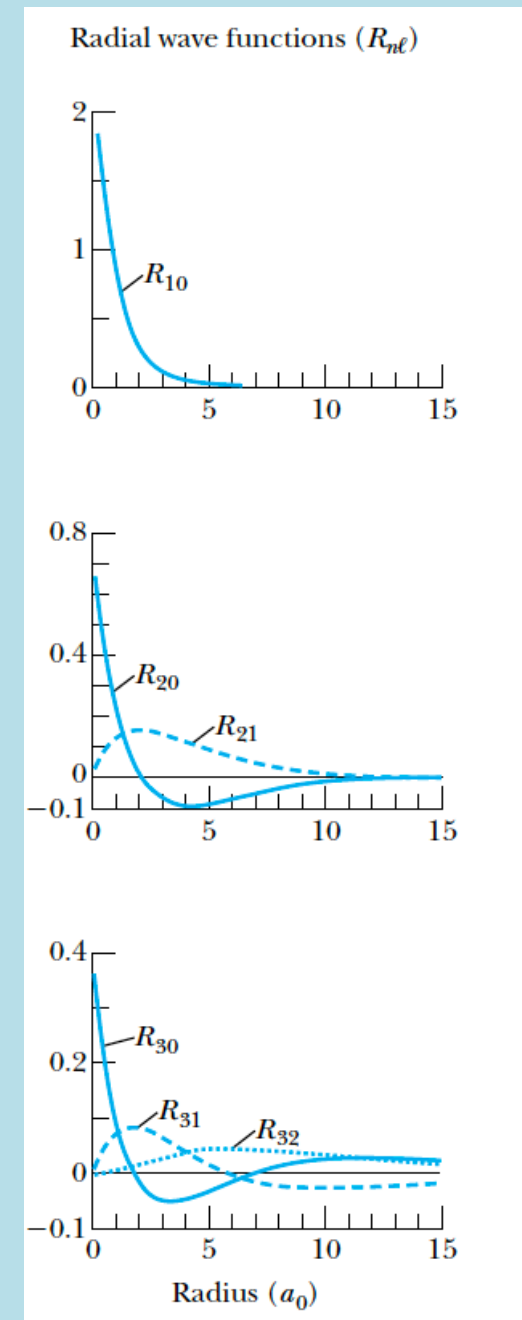
特別是 $l = 0$ 時， $R$ 趨近一常數。 $l \neq 0$ 時， $R$ 趨近零。

乘上多項式 $H_{nl}$ ！

它是 $n - l - 1$ 次的多項式， $H_{nl}(r) = 0$ 有 $n - l - 1$ 個解。

$R_{nl}(r)$ 會通過 $r$ 軸 $n - l - 1$ 次，有 $n - l - 1$ 個節點。

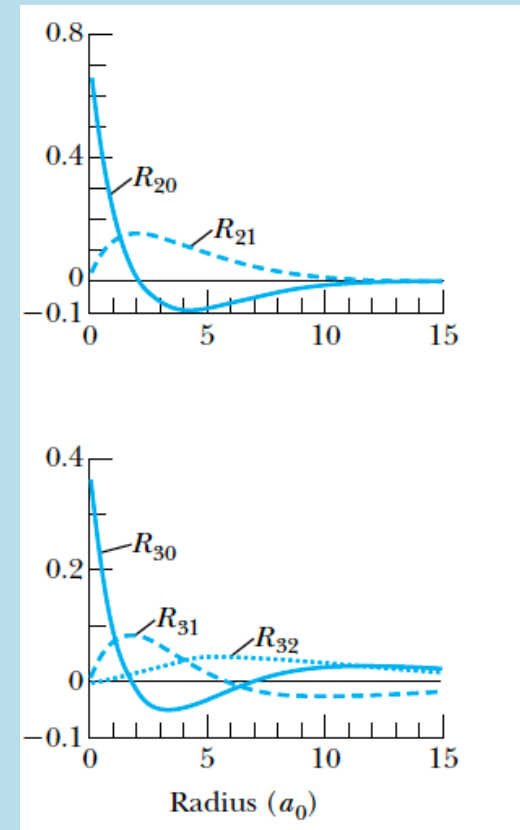
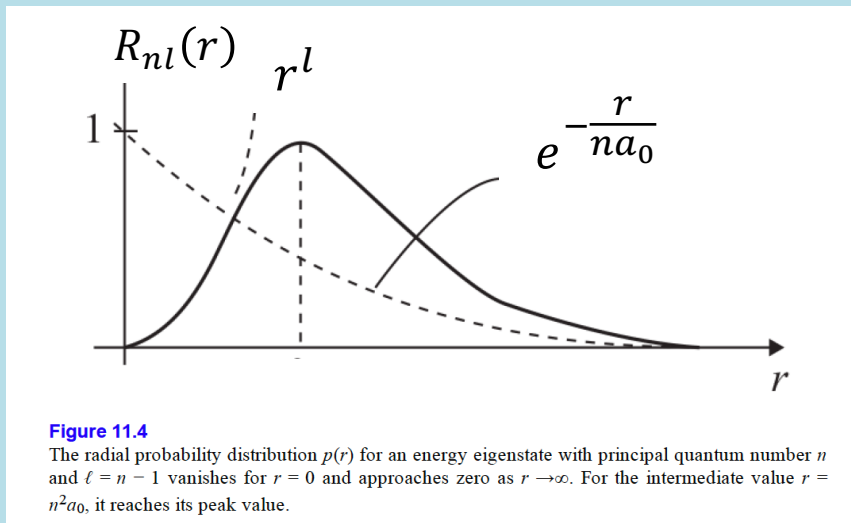
例如： $R_{20}$ 有一個節點， $R_{30}$ 有2個節點。





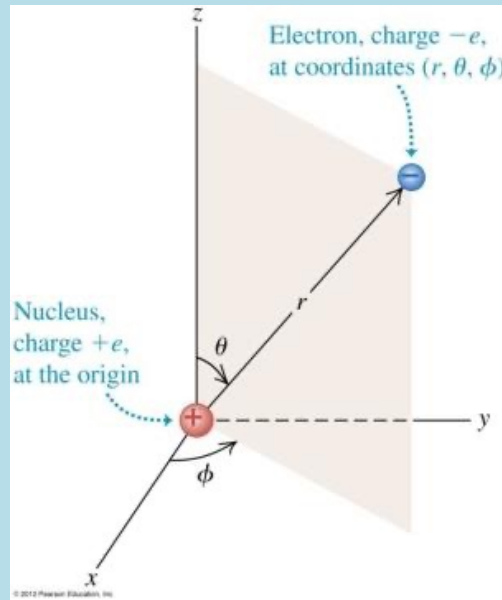
$$R_{nl}(r) \sim e^{-\frac{r}{na_0}} \cdot r^l \cdot H_{nl}\left(\frac{2}{na_0}r\right)$$

若  $l = n - 1$ ， $H_{nn-1}$  是  $n - l - 1 = 0$  次，即是常數：



$$R_{nn-1}(r) \sim e^{-\frac{r}{na_0}} \cdot r^{n-1} \quad \text{例如：} R_{21}, R_{32}$$

乘上Spherical Harmonics，就得到完整定態波函數。



$$\psi_{nlm} = R_{nl}(r) \cdot P_l^m(\theta) \cdot \Phi_m(\phi)$$

與m無關。      與n無關。

$$P_l^m(\theta) = \sin^{|m|} \theta \cdot (\cos \theta, l - m \text{ 次的多項式})$$

$$\Phi_m(\phi) \sim e^{im\phi}$$

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

Table of Spherical Harmonics

$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$
$Y_{1,1} = -\sqrt{\frac{3}{8\pi}} e^{i\varphi} \sin \theta$
$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta$
$Y_{2,2} = \sqrt{\frac{15}{32\pi}} e^{2i\varphi} \sin^2 \theta$
$Y_{2,1} = -\sqrt{\frac{15}{8\pi}} e^{i\varphi} \sin \theta \cos \theta$
$Y_{2,0} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$
$Y_{3,3} = -\sqrt{\frac{35}{64\pi}} e^{3i\varphi} \sin^3 \theta$
$Y_{3,2} = \sqrt{\frac{105}{64\pi}} e^{2i\varphi} \sin^2 \theta \cos \theta$
$Y_{3,1} = -\sqrt{\frac{21}{64\pi}} e^{i\varphi} \sin \theta (5 \cos^2 \theta - 1)$
$Y_{3,0} = \sqrt{\frac{7}{16\pi}} (5 \cos^3 \theta - 3 \cos \theta)$

基態 Ground State 1S  $n = 1, l = 0, m = 0$

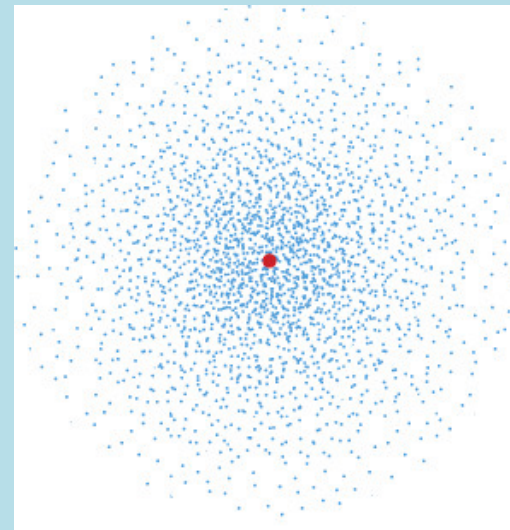
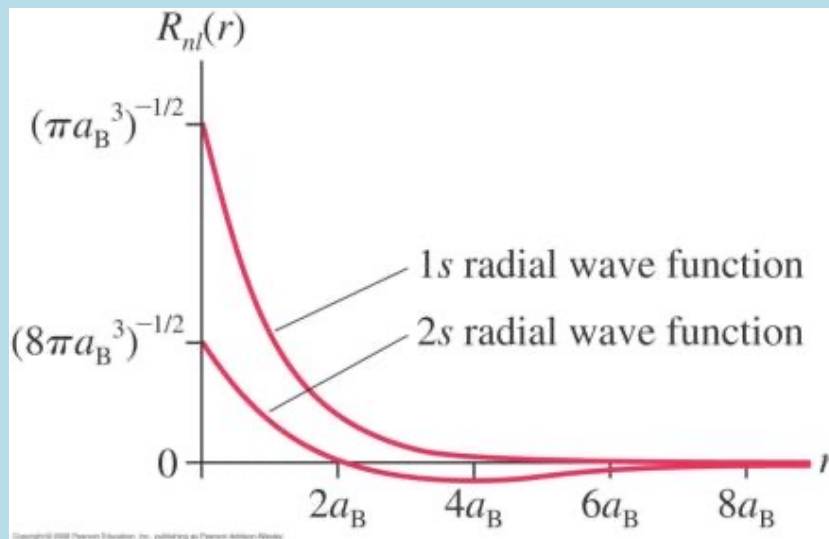
$$R_{nl}(r) \sim e^{-\frac{r}{a_0}} \cdot r^l \cdot H\left(\frac{2}{na_0} r\right) \quad H(\rho) \text{ 為一常數：}$$

$$R_{10}(r) \sim e^{-\frac{r}{a_0}}$$

這是一個單純指數遞減函數。

$$\psi_{1s} = R_{10}(r) \cdot P_0^0(\theta) \cdot \Phi_0(\phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$$

$P_0^0(\theta), \Phi_0(\phi)$  都是常數，這是與角度無關，球對稱的波函數

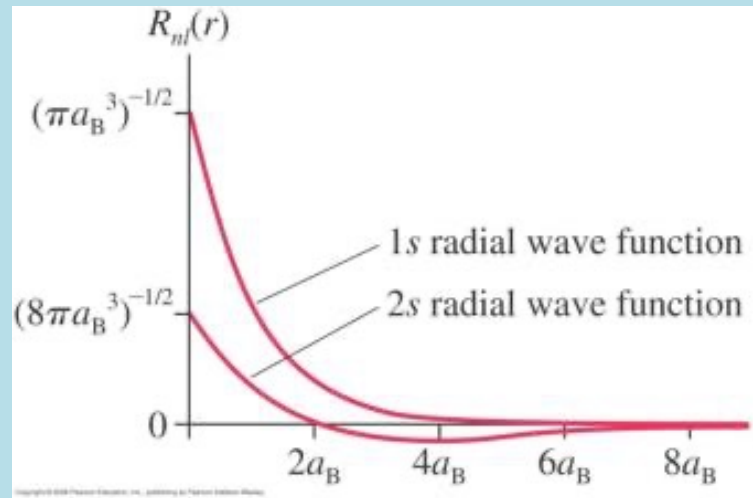
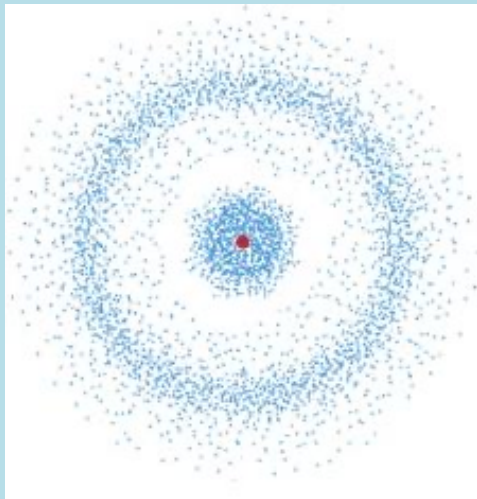


波函數在原點最大！

激發態2s

$$n = 2, l = 0, m = 0$$

$$R_{20}(r) = e^{-\frac{\rho}{2}} \cdot \rho^l \cdot H(\rho) \sim e^{-\frac{r}{2a_0}} \left(1 - \frac{r}{2a_0}\right)$$



$H(\rho)$ 為一次多項式，因此有1個節點。

$$\psi_{2s} = \frac{1}{\sqrt{8\pi a_0^3}} \left(1 - \frac{r}{2a_0}\right) \cdot e^{-\frac{r}{2a_0}}$$

依然是與角度無關，球對稱的波函數

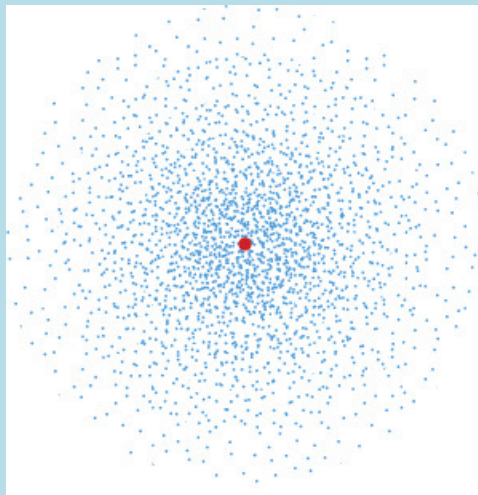
定態波函數可以計算發現電子的機率密度。

機率密度： $P(r, \theta, \phi) \sim |R(r)P_m^l(\theta)e^{im\phi}|^2$

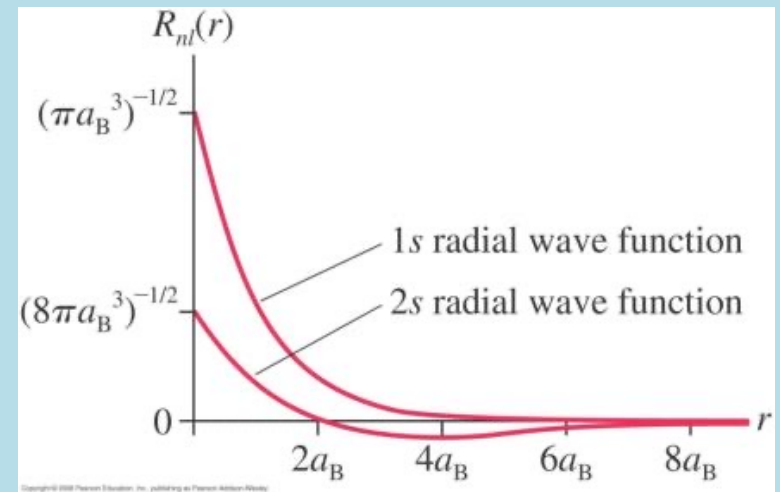
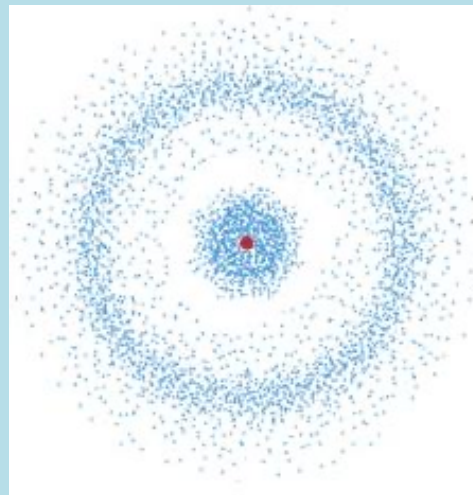
與 $\phi$ 無關！這是因為選 $L_z$ 本徵態。

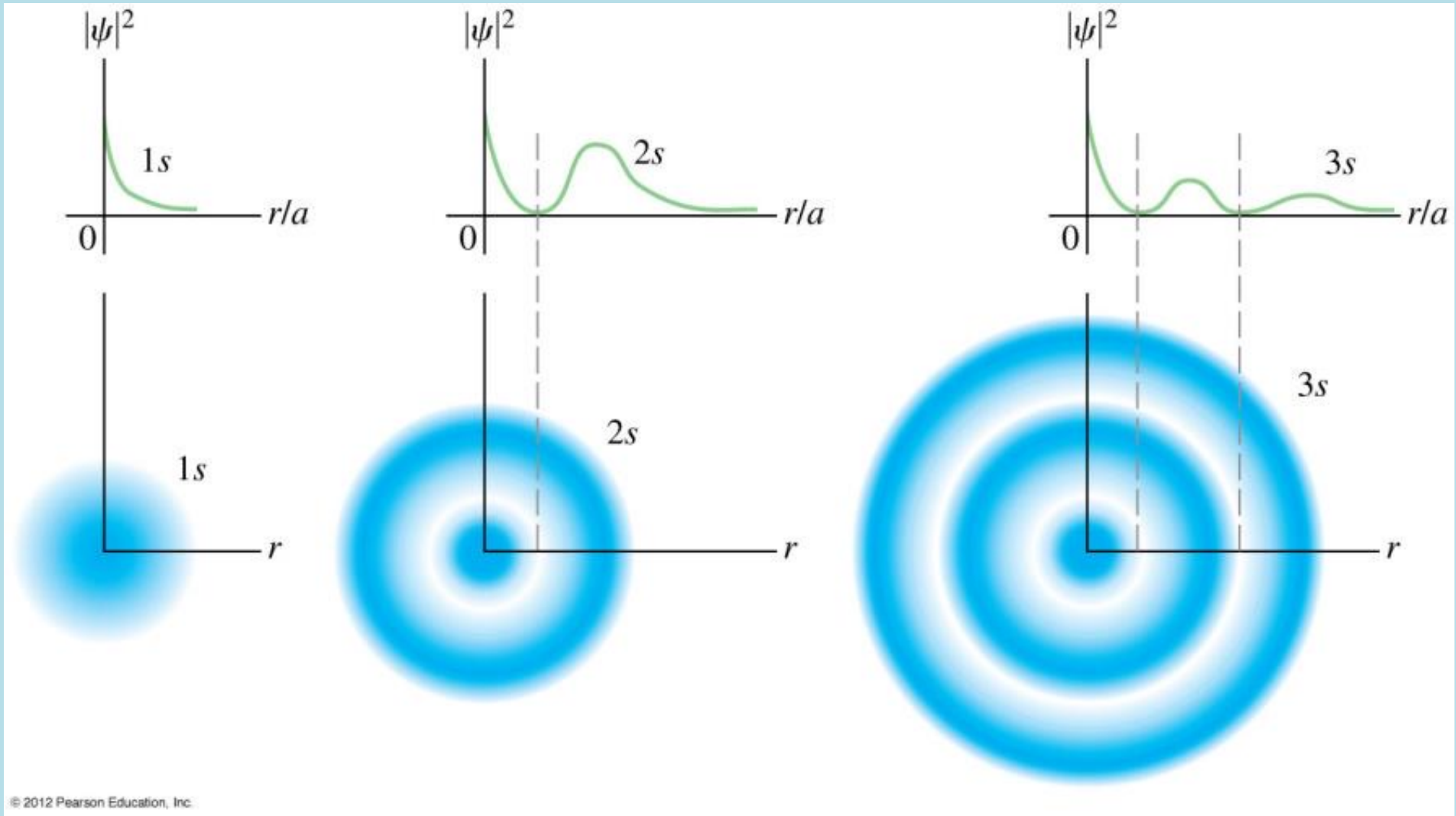
可以以點的密度來代表機率密度的大小：

基態 1s



激發態 2s





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$$R_{nl}(r) = e^{-\frac{Z}{na_0}r} \cdot r^l \cdot (r \text{ 的 } n - l - 1 \text{ 次的多項式})$$

注意  $R$  有  $n - l - 1$  個節點。

激發態2p

$$n = 2, l = 1, m = 0, \pm 1$$

$$R_{21}(r) = e^{-\frac{\rho}{2}} \cdot \rho^1 \cdot H(\rho) \sim e^{-\frac{r}{2a_0}} \cdot r$$

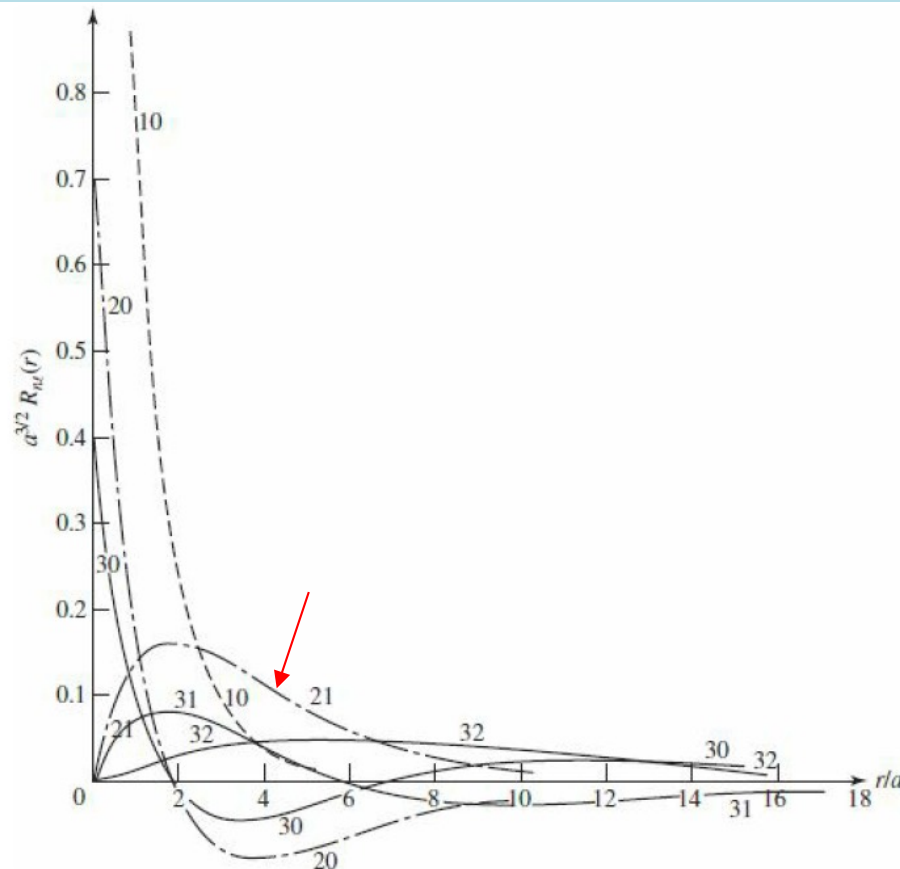
無節點

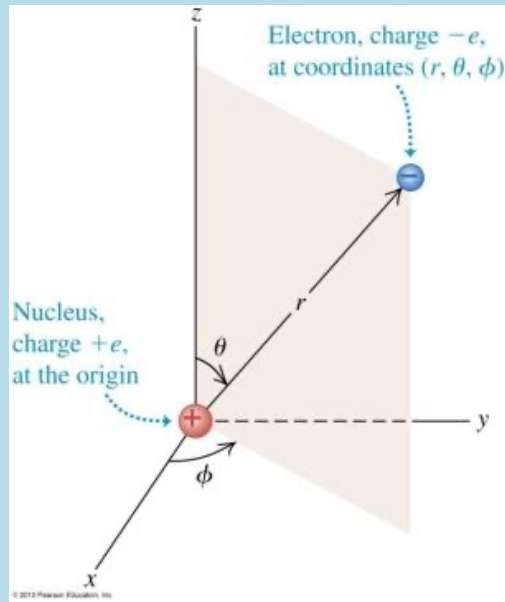
$$\psi_{2p} = \frac{1}{8\sqrt{\pi a_0^3}} \frac{r}{a_0} \cdot e^{-\frac{r}{2a_0}} \cdot \sin \theta \cdot e^{\pm i\phi}$$

$$m = \pm 1$$

$$\psi_{2p} = \frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} \cdot e^{-\frac{r}{2a_0}} \cdot \cos \theta$$

$$m = 0$$





能量只與 $n$ 有關。一般會先選定 $n$ ：

$$R_{nl}(r) = e^{-\frac{Z}{na_0}r} \cdot r^l \cdot (r \text{ 的 } n-l-1 \text{ 次的多項式})$$

$n-l \geq 1$  才有解

$l \leq n-1$   $l$  會有最大值

$$l = 0, 1, 2 \dots n-1$$

$$\psi_{nlm} = R_{nl}(r) \cdot P_l^m(\theta) \cdot \Phi_m(\phi)$$

與 $m$ 無關。

與 $n$ 無關。

$$P_l^m(\theta) = \sin^{|m|}\theta \cdot (\cos \theta, l-|m| \text{ 次的多項式})$$

$l-|m| \geq 0$  才有解

$|m| \leq l$   $|m|$  會有最大值

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

$$E_n = -\frac{m}{2} \left( \frac{e^2}{4\pi\epsilon_0\hbar} \right)^2 \frac{1}{n^2}$$

$$\Phi_m(\phi) \sim e^{im\phi}$$



能量只與 $n$ 有關

$$E_n = (-13.6\text{eV}) \left( \frac{1}{n^2} \right)$$

$$E_n = -\frac{m}{2} \left( \frac{e^2}{4\pi\epsilon_0\hbar} \right)^2 \frac{1}{n^2}$$

$$\psi_{nlm} = R_{nl}(r) \cdot P_{lm}(\theta) \cdot \Phi_m(\phi)$$

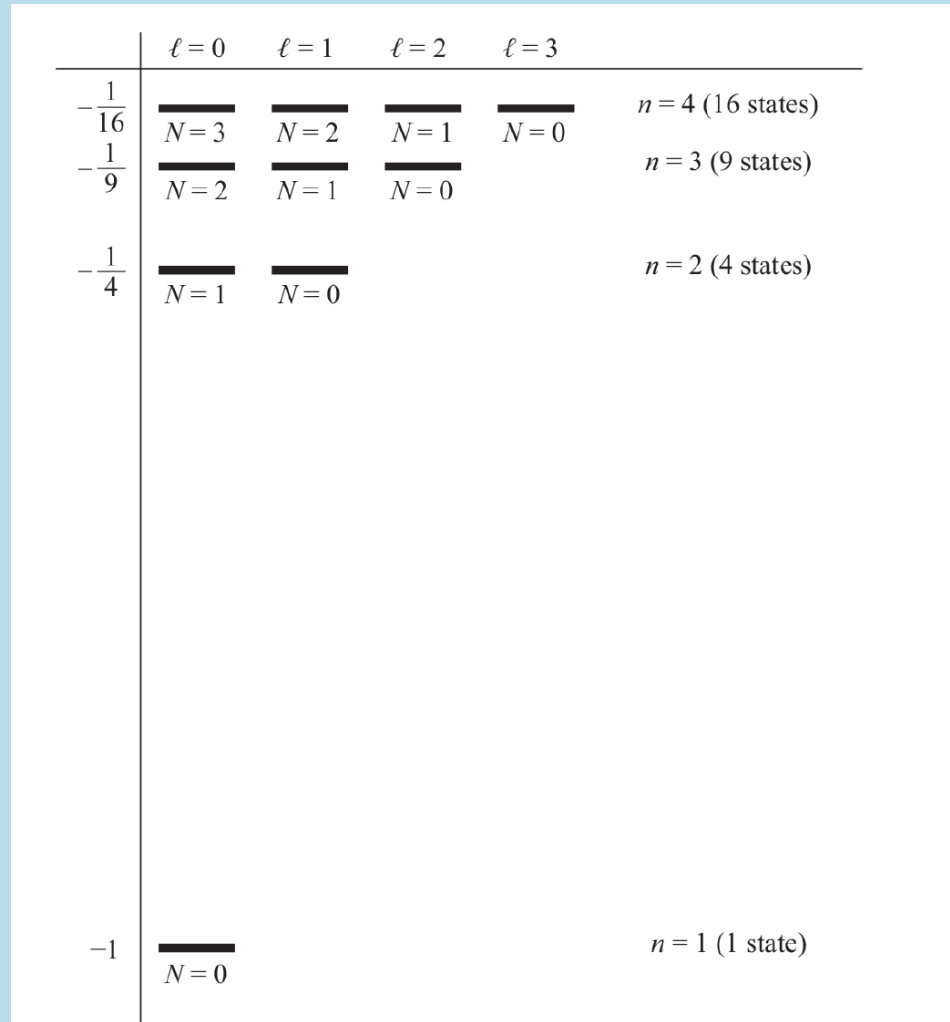
主量子數  $n = \text{positive integer}$



軌道量子數  $l = 0, 1, 2 \dots n - 1$



軌道磁量子數  $m = -l, -l + 1 \dots 0, 1, \dots l - 1, l$



**Table 42.3**

Allowed Quantum States for an Atom up to $n = 3$															
$n$	1	2				3									
$\ell$	0	0	1			0	1			2					
$m$	0	0	1	0	-1	0	1	0	-1	2	1	0	-1	-2	
$m_s$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	

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$$l = 0, 1, 2 \dots n - 1$$

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

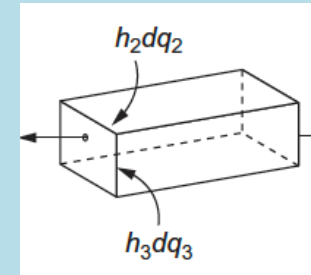
**TABLE 42.1** Symbols used to represent quantum number  $l$

$l$	Symbol
0	$s$
1	$p$
2	$d$
3	$f$

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電子的機率密度就是在一個小的極座標體積內發現電子的機率

$$|R(r)P_m^l(\theta)e^{im\phi}|^2 \cdot dr \cdot r d\theta \cdot r \sin \theta d\phi \quad \text{極座標體積！}$$



$$\sim (R(r))^2 r^2 dr \cdot (P_m^l(\theta))^2 \sin \theta d\theta \cdot d\phi$$

我們也可以問在距離為 $r$ 及 $r + dr$ 間，無論方向發現該電子的機率：

稱為Radial probability density 徑向機率密度： $P(r) \cdot dr$

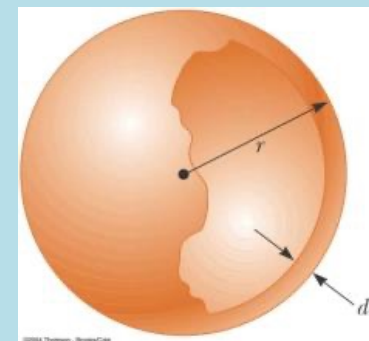
那就要將半徑 $r$ 厚度 $dr$ 的球殼內機率加起來：也就是對 $d\theta \cdot d\phi$ 積分。

已知 $P_m^l(\theta)$ 滿足歸一化：

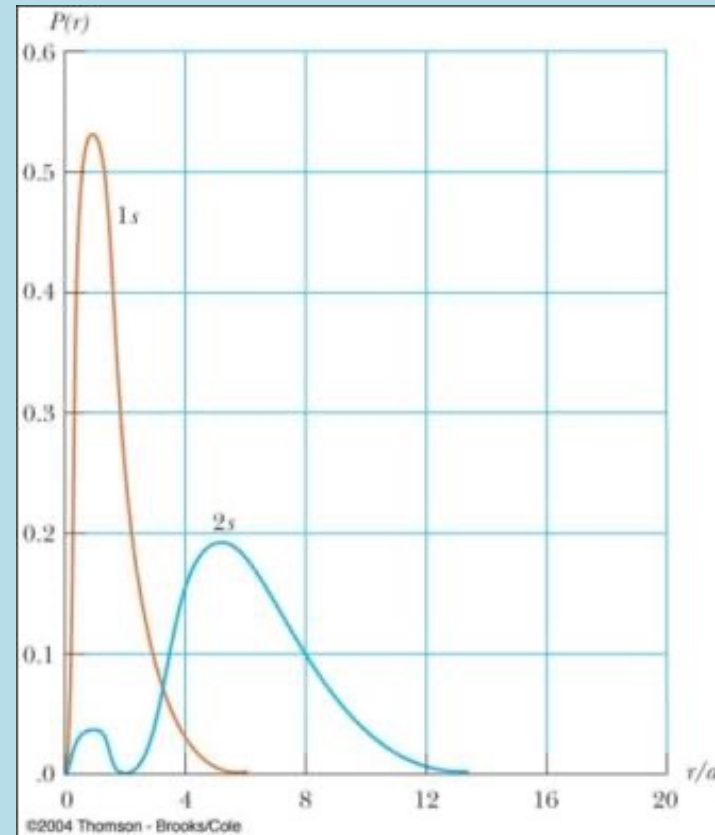
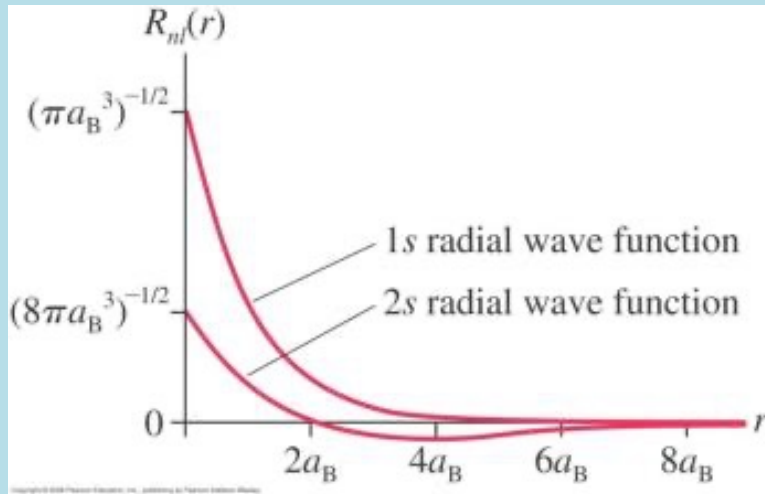
$$\int [P_m^l(\theta)]^2 \sin \theta d\theta \cdot d\phi = 1$$

因此：

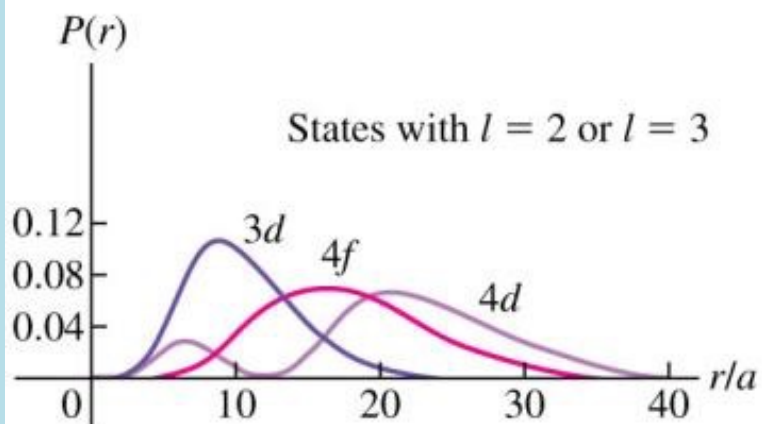
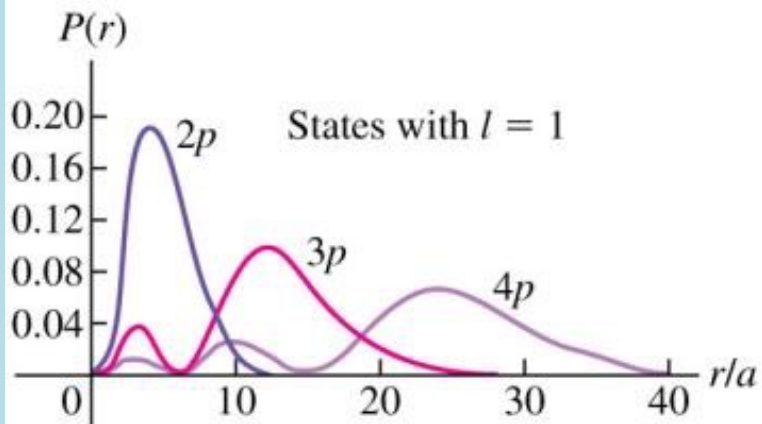
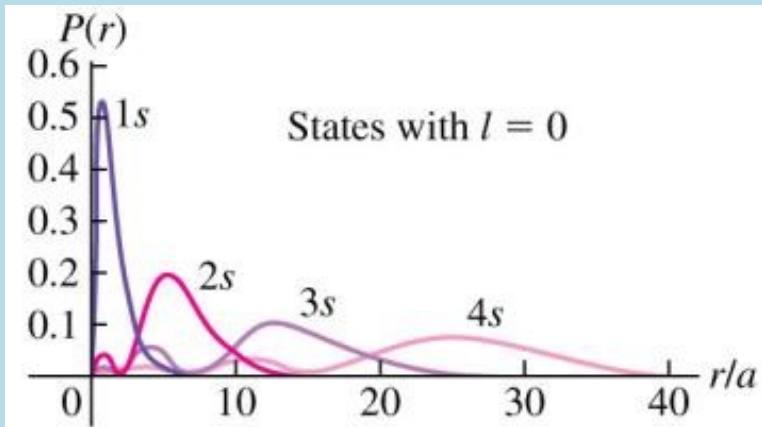
$$P(r) = [R(r)]^2 r^2$$



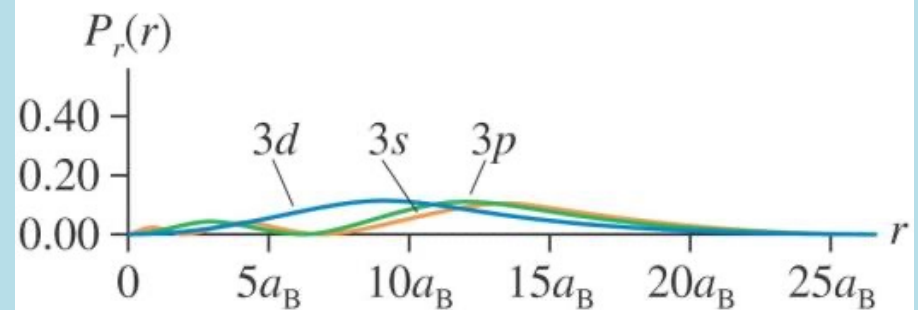
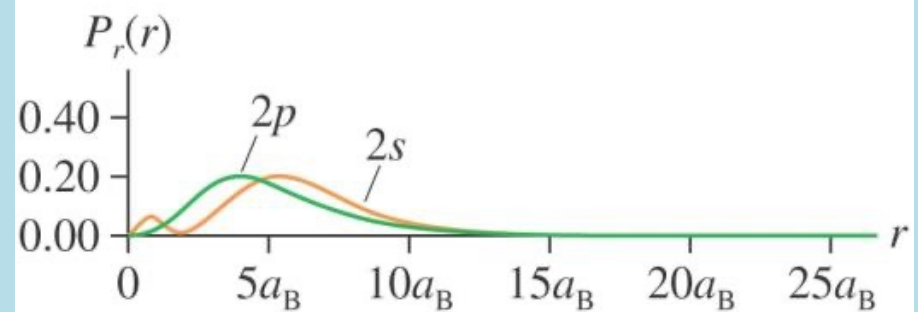
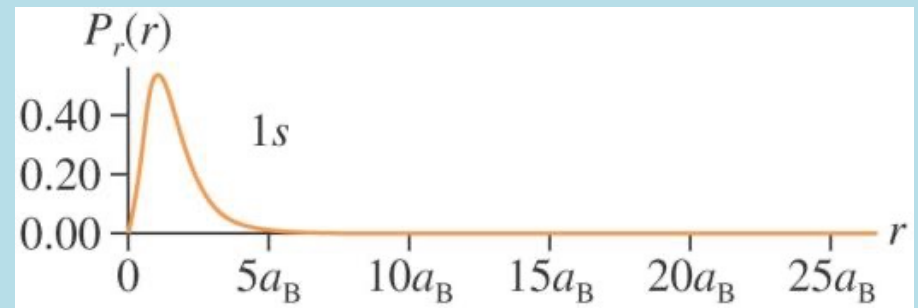
$$P(r) = [R(r)]^2 r^2$$



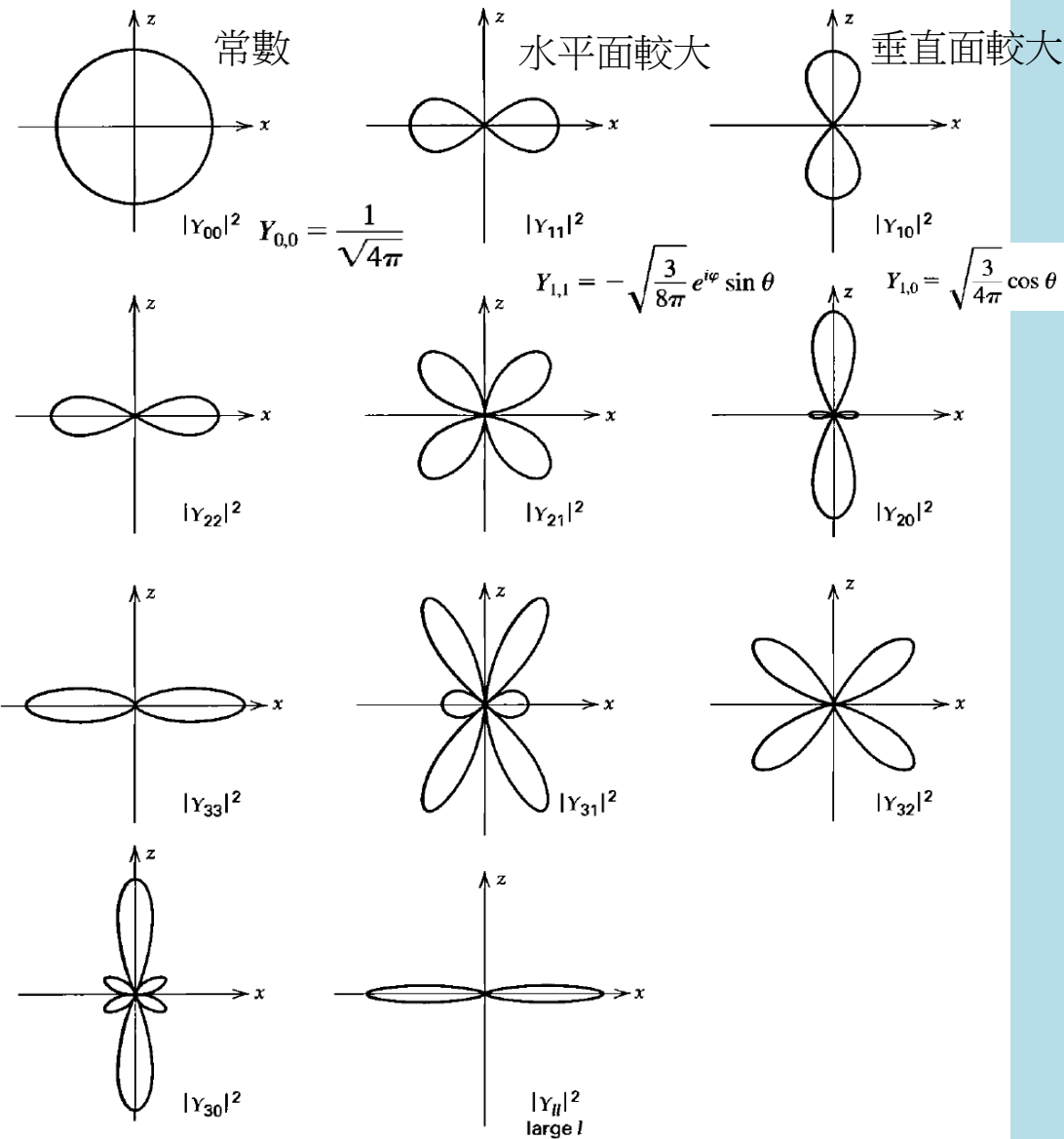
儘管波函數在原點最大，但電子最可能發現的距離並不是在原點。  
對1s電子， $P(r)$ 最大值在距離等於 $a_0$ 。



$P_r(r)$ 有 $n - l - 1$ 個節點。



以下是以  $r$  代表各個方向的機率密度  $(P_m^l(\theta))^2$  :



**Figure 8-4** Distributions of  $|Y_{lm}(\theta, \phi)|^2$ . The sketches represent sections of the distributions made in the  $z$ - $x$  plane. It should be understood that the three-dimensional distributions are obtained by rotating the figures about the  $z$ -axis.

### Table of Spherical Harmonics

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{1,1} = -\sqrt{\frac{3}{8\pi}} e^{i\varphi} \sin \theta$$

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{2,2} = \sqrt{\frac{15}{32\pi}} e^{2i\varphi} \sin^2 \theta$$

$$Y_{2,1} = -\sqrt{\frac{15}{8\pi}} e^{i\varphi} \sin \theta \cos \theta$$

$$Y_{2,0} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$$Y_{3,3} = -\sqrt{\frac{35}{64\pi}} e^{3i\varphi} \sin^3 \theta$$

$$Y_{3,2} = \sqrt{\frac{105}{64\pi}} e^{2i\varphi} \sin^2 \theta \cos \theta$$

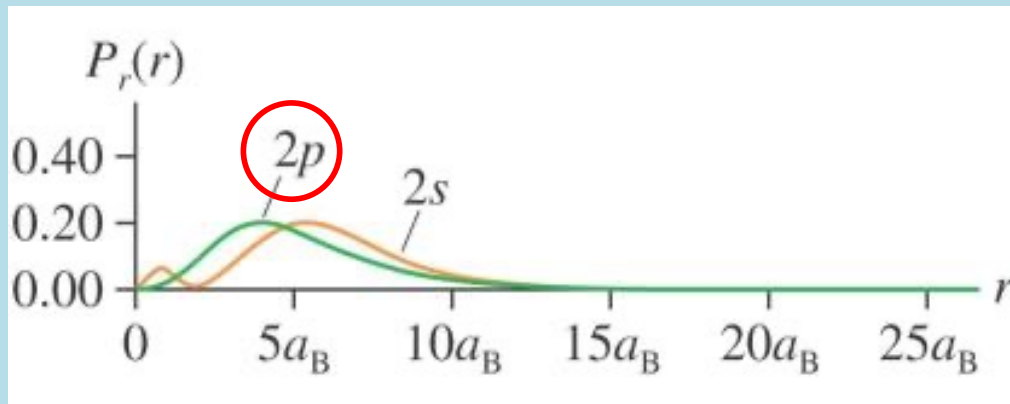
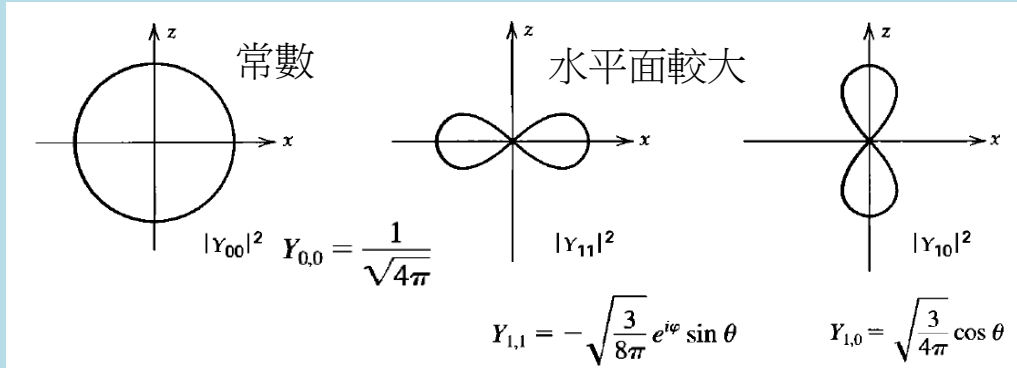
$$Y_{3,1} = -\sqrt{\frac{21}{64\pi}} e^{i\varphi} \sin \theta (5 \cos^2 \theta - 1)$$

$$Y_{3,0} = \sqrt{\frac{7}{16\pi}} (5 \cos^3 \theta - 3 \cos \theta)$$

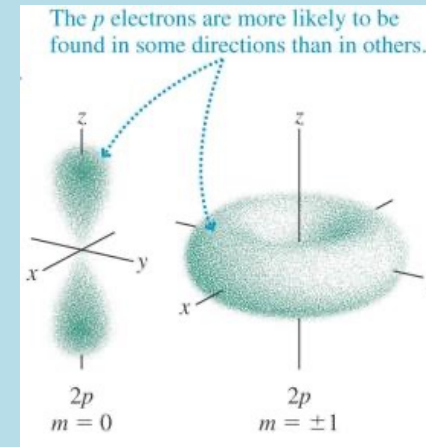
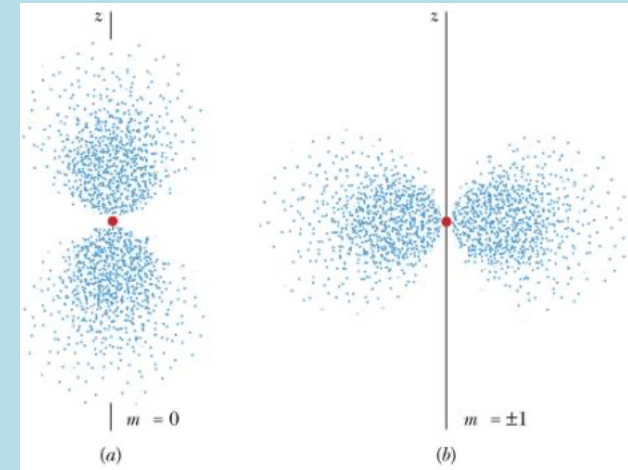
激發態2p

$n = 2, l = 1, m = 0, \pm 1$

波函數與角度 $\theta, \phi$ 有關！但絕對值平方與 $\phi$ 無關。



點密度圖



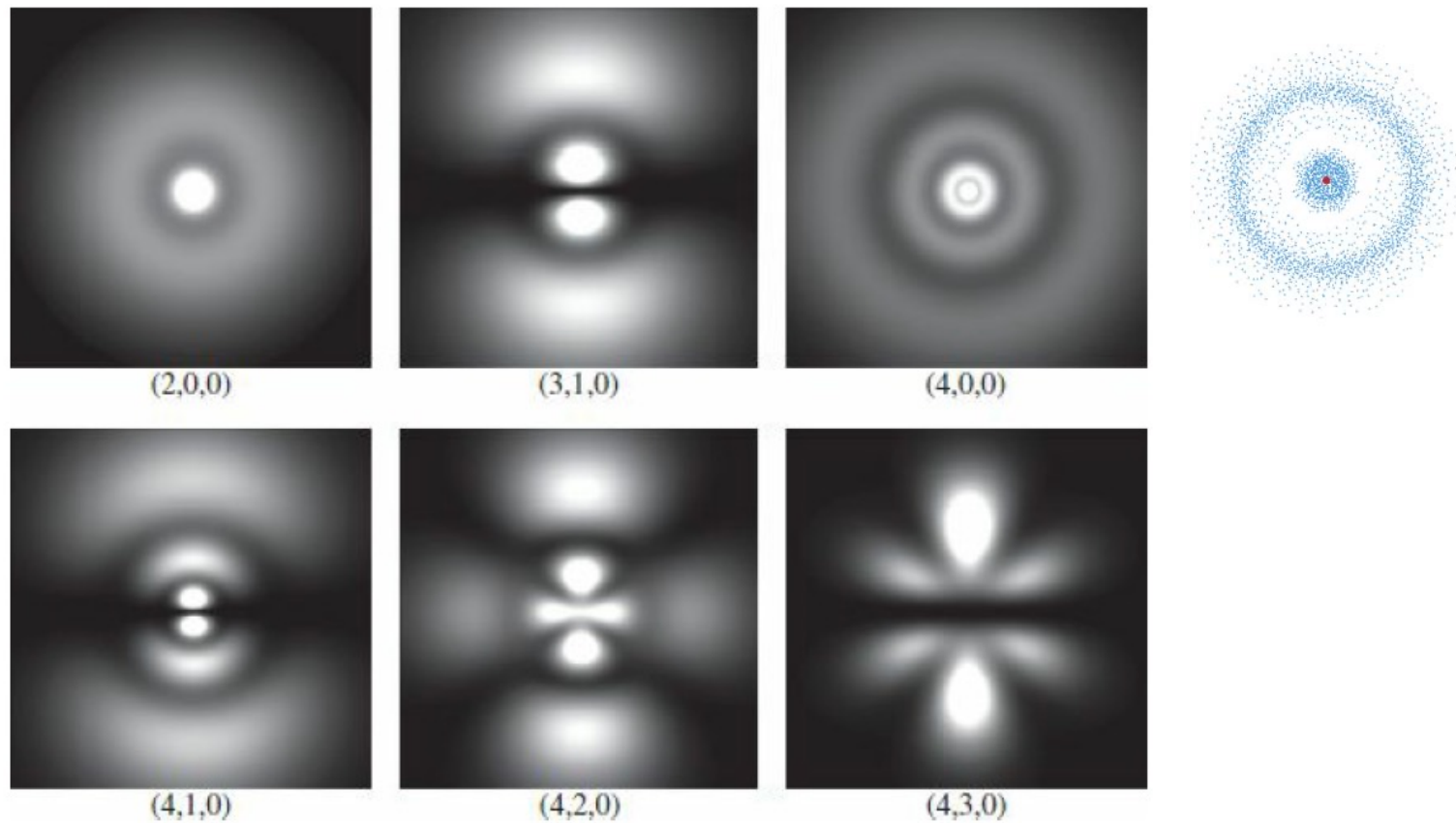
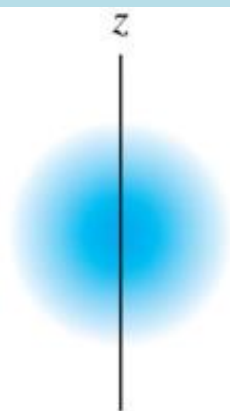
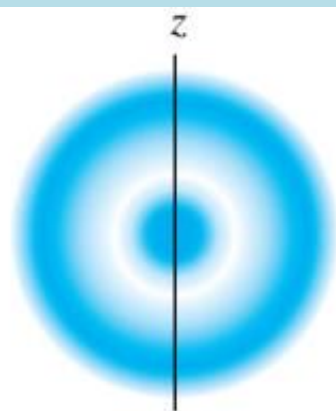


Figure 4.8: Density plots for the first few hydrogen wave functions, labeled by  $(n, \ell, m)$ . Printed by permission using “Atom in a Box” by Dauger Research. You can make your own plots by going to: <http://dauger.com>.

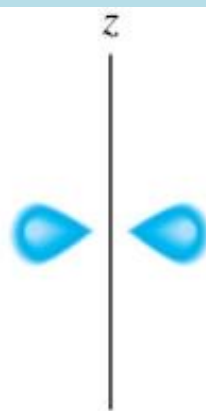




$1s, m_l = 0$



$2s, m_l = 0$



$2p, m_l = \pm 1$



$2p, m_l = 0$



$3p, m_l = 0$



$3p, m_l = \pm 1$



$3d, m_l = 0$



$3d, m_l = \pm 1$



$3d, m_l = \pm 2$

有時候會以陰影區域來標定一定大小以上的機率密度：

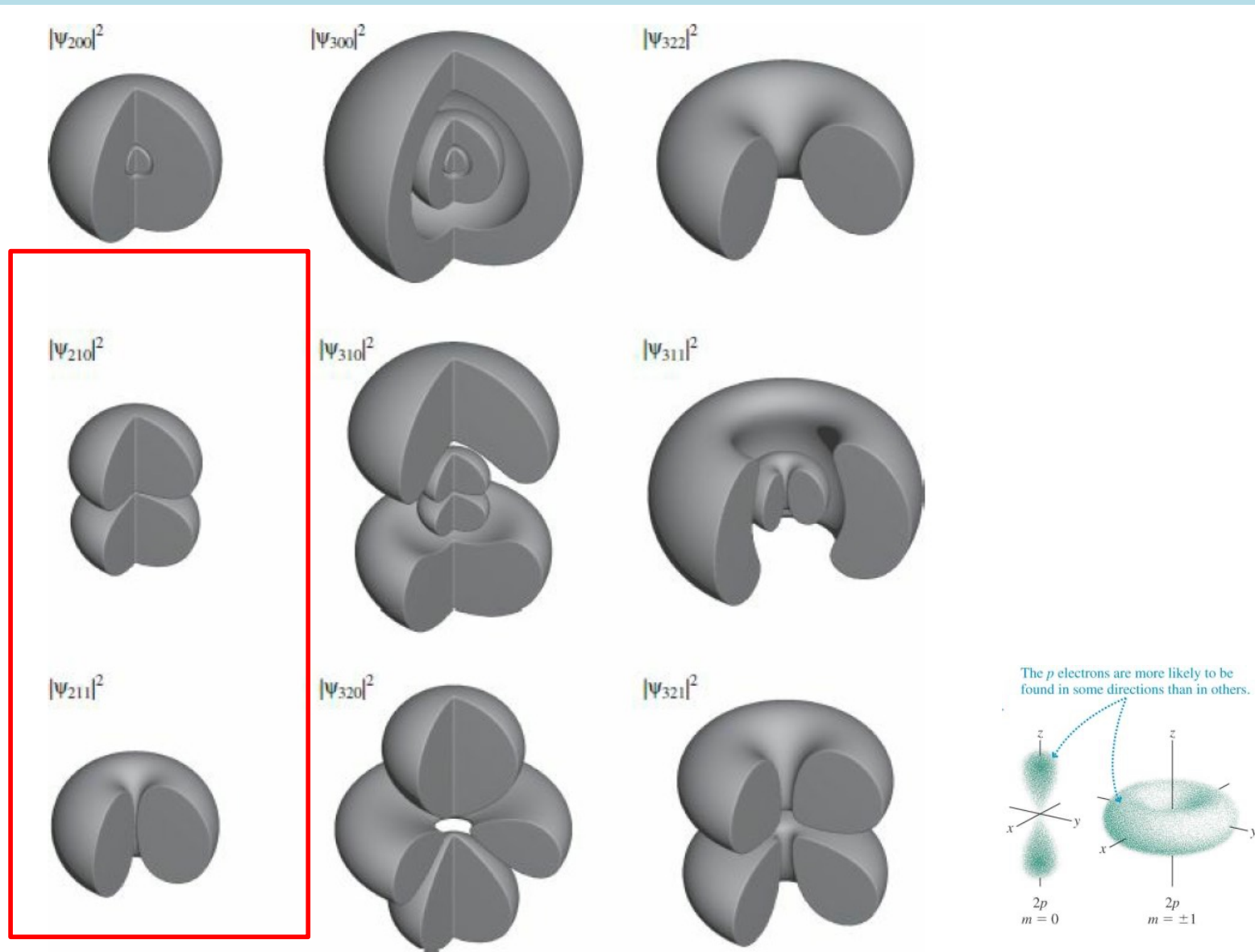
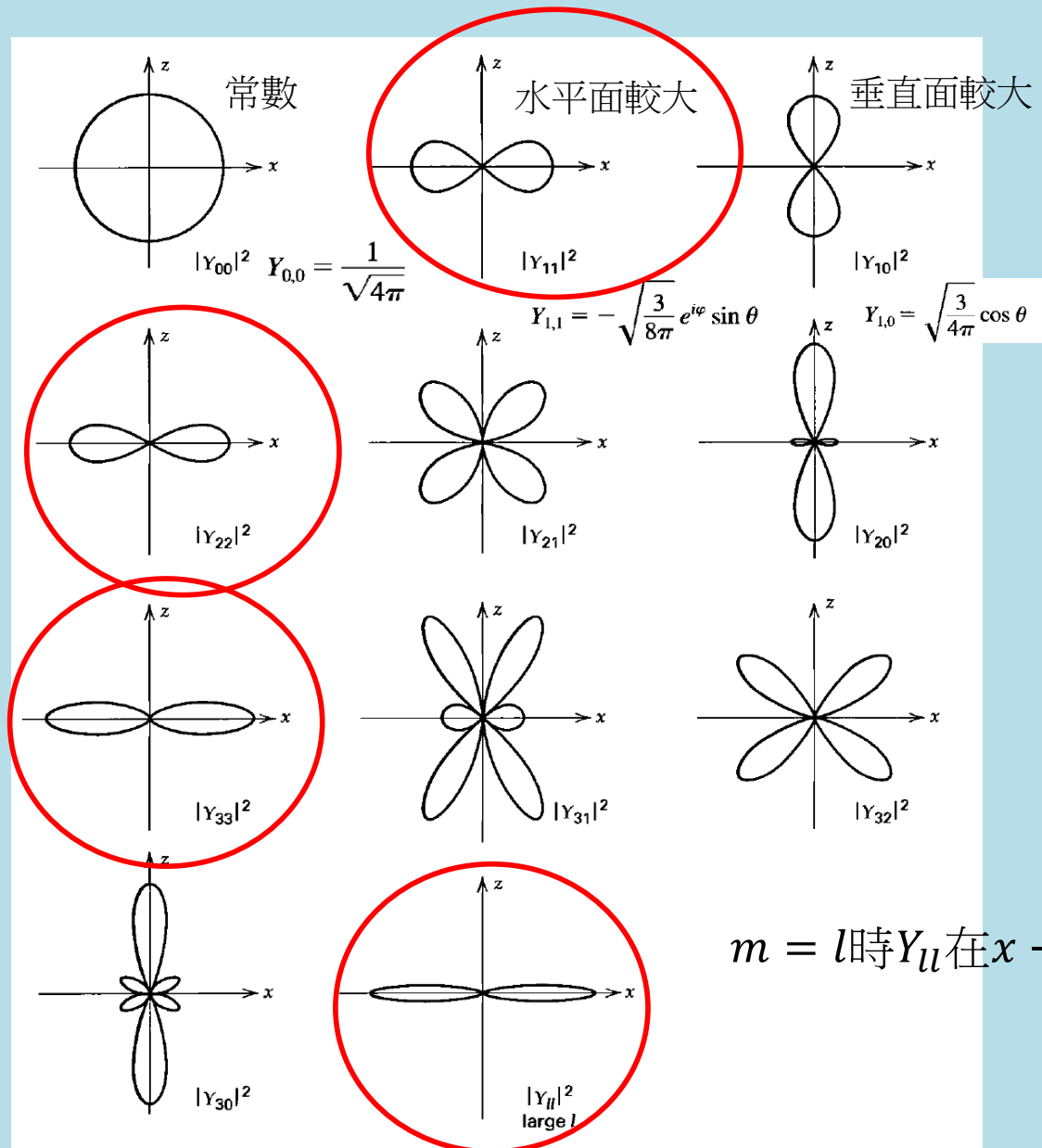


Figure 4.9: Shaded regions indicate significant electron density ( $|\psi|^2 > 0.25/\text{nm}^3$ ) for the first few hydrogen wave functions. The region  $0 < \phi < \pi/2$  has been cut away;  $|\psi|^2$  has azimuthal symmetry in all cases.



$m = l$ 時 $Y_{ll}$ 在 $x - y$ 水平面最大，而且越來越扁。

**Figure 8-4** Distributions of  $|Y_{lm}(\theta, \phi)|^2$ . The sketches represent sections of the distributions made in the  $z$ - $x$  plane. It should be understood that the three-dimensional distributions are obtained by rotating the figures about the  $z$ -axis.

如果  $l$  同時也是最大值  $n - 1$ ，機率密度會集中於一個圓。

$n = 45, l = 44, m = 44$

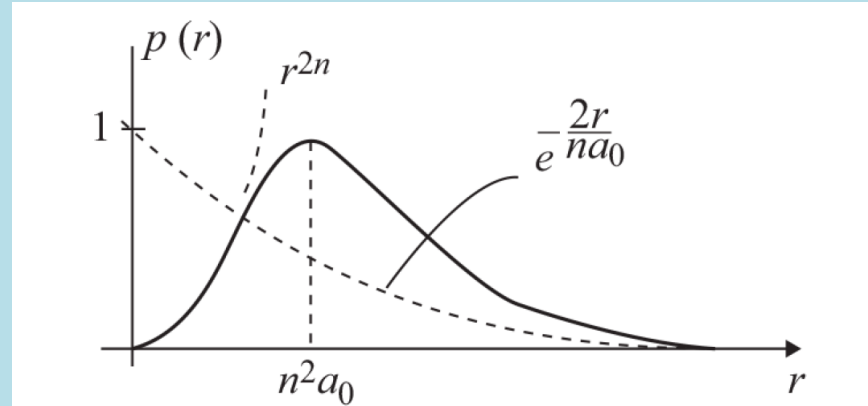
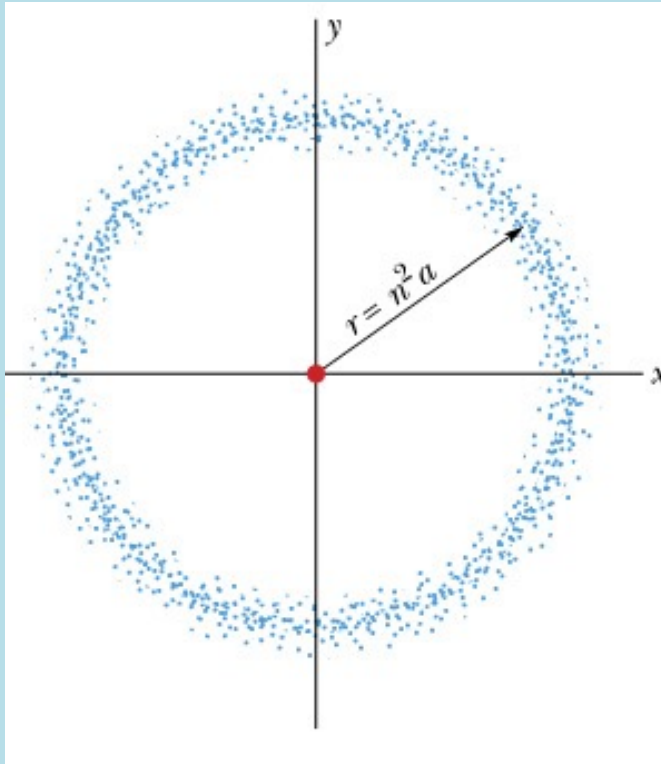


Figure 11.4

The radial probability distribution  $p(r)$  for an energy eigenstate with principal quantum number  $n$  and  $\ell = n - 1$  vanishes for  $r = 0$  and approaches zero as  $r \rightarrow \infty$ . For the intermediate value  $r = n^2 a_0$ , it reaches its peak value.

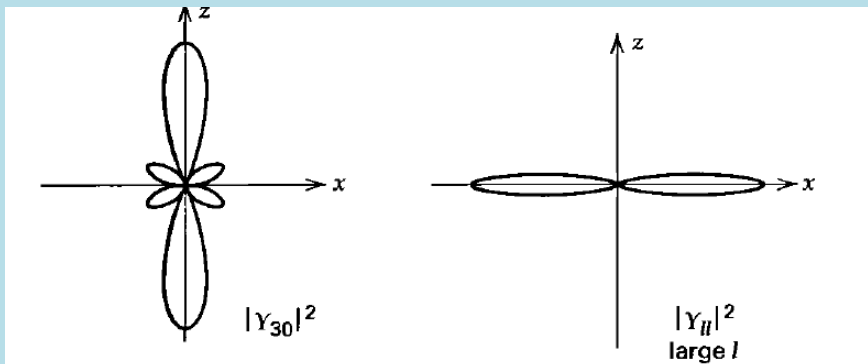


Figure 8-4 Distributions of  $|Y_{lm}(\theta, \phi)|^2$ . The sketches represent sections in the  $z$ - $x$  plane. It should be understood that the three-dimensional distribution is obtained by rotating the figures about the  $z$ -axis.

當量子數很大時，機率密度會集中於  $x - y$  平面上。