氫原子的能量與波函數

氫原子中質子和電子相對運動的 Hamiltonian 是

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{Ze^2}{4\pi\varepsilon_0 r} \tag{1}$$

氫原子的薛丁格方程式在 xyz 座標下無法做變數分離，因此我們改用球座標。在球座標下，

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

與三度空間旋轉的薛丁格方程式比較，上式可寫成

$$\nabla^2 = \frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{1}{r^2\hbar^2}\hat{L}^2 \tag{3}$$

因此，氫原子的 Hamiltonian 可寫成

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{1}{2\mu r^2}\hat{L}^2-\frac{Ze^2}{4\pi\varepsilon_0 r} \tag{4}$$

我們現在假設氫原子的波函數可寫成

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \tag{5}$$

將(4),(5)帶入薛丁格方程式中得

$$-\frac{\hbar^2}{2\mu}\left(Y\frac{d^2}{dr^2}R+Y\frac{2}{r}\frac{d}{dr}R\right)+R\frac{1}{2\mu r^2}\hat{L}^2Y-\frac{Ze^2}{4\pi\varepsilon_0 r}RY = ERY \tag{6}$$

等號兩端同除 RY 得

$$-\frac{\hbar^2}{2\mu}\left(\frac{1}{R}\frac{d^2}{dr^2}R+\frac{1}{R}\frac{2}{r}\frac{d}{dr}R\right)+\frac{1}{2\mu r^2}\frac{1}{Y}\hat{L}^2Y-\frac{Ze^2}{4\pi\varepsilon_0 r}=E \qquad (7)$$

上式若成立則首先

$$\frac{1}{Y}\hat{L}^2Y=\text{constant} \qquad (8)$$

由三度空間的旋轉得知

$$Y=Y_{l,m_l}(\theta,\phi)=\text{spherical harmonics} \qquad (9)$$

$$\hat{L}^2Y_{l,m_l}=l(l+1)\hbar^2\,Y_{l,m_l} \qquad (10)$$

因此，(6)式可改寫成

$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2}R+\frac{2}{r}\frac{d}{dr}R\right)+\frac{l(l+1)\ \hbar^2}{2\mu\ \ r^2}R-\frac{Ze^2}{4\pi\varepsilon_0 r}R=ER \qquad (11)$$

(11)式稱為 radial equation，或可看成是在 r 方向運動的有效位能

$$V_{eff}(r)=\frac{l(l+1)\hbar^2}{2\mu r^2}-\frac{Ze^2}{4\pi\varepsilon_0 r} \qquad (12)$$

令 $e'=e/(4\pi\varepsilon_0)^{1/2};a=\hbar^2/\mu\ \ e'^2$ (13)

(11)式可改寫成

$$R''+\frac{2}{r}R'+\left[\frac{2E}{ae'^2}+\frac{2Z}{ar}-\frac{l(l+1)}{r^2}\right]R=0 \qquad (14)$$

當 r 很大時，(14) 式可近似成

$$R''+\frac{2E}{ae'^2}R=0 \qquad (15)$$

(15)式的解為 $(E<0)$

$$R=e^{-Cr}, C=\sqrt{-\frac{2E}{ae'^2}} \qquad (16)$$

現在我們假設(14)式真正的解可寫成：

$$R(r)=e^{-Cr}K(r) \qquad (17)$$

將(17)以及 R'，R'' 帶入(14)得到

$$r^2K''+(2r-2Cr^2)K'+\left[(2Z/a-2C)r-l(l+1)\right]K=0 \qquad (18)$$

我們令 K 為

$$K=r^s\sum_{j=0}^{\infty}b_jr^j=r^sM(r) \qquad (19)$$

帶回 (18) 式得到

$$r^2M''+[(2s+2)r-2Cr^2)]M'+[s^2+s+(2Z/a-2C-2Cs)r-l(l+1)]M=0 \qquad (20)$$

由(19)，當 $r=0$，$M(0)=b_0, M'(0)=b_1, M''(0)=2b_2$ (21)

帶入 (20) 得到：

$$\begin{aligned}&b_0(s^2+s-l^2-l)=0\\&s=l \text{ or } -l-1(\text{不合})\end{aligned} \qquad (22)$$

(20) 是可改寫成

$$r^2M''+[(2l+2)r-2Cr^2)]M'+(2Z/a-2C-2Cl)M=0 \qquad (23)$$

由 (19):

$$M(r)=\sum_{j=0}^{\infty} b_j r^j \tag{24}$$

將 M, M', M'' 帶入 (23)，整理後得到

$$\sum_{j=0}^{\infty}\left[j(j+1)b_{j+1}+2(l+1)(j+1)b_{j+1}+(2Z/a-2C-2Cl-2Cj)b_j\right]r^j=0 \tag{25}$$

每項係數均須為零，所以：

$$b_{j+1}=\frac{(2C+2Cl+2Cj-2Z/a)}{j(j+1)+2(l+1)(j+1)}b_j \tag{26}$$

由 (26) 所定義的無窮多項式在 r 很大時會發散，所以我們必須讓係數在 k 次方以後為零，由上式：

$$2C(1+l+k)=2Z/a,\ k=0,1,2,\cdots \tag{27}$$

令 $n\equiv k+l+1,\quad n=1,2,3,\cdots; l\le n-1$ (28)

$$Cn=Z/a$$

由 (16)

$$C^2=-\frac{2E}{ae'^2}=\frac{Z^2}{a^2n^2}$$
$$E_n=-\frac{Z^2}{n^2}\frac{e'^2}{2a}=-\frac{Z^2}{n^2}\frac{e^2}{8\pi\varepsilon_0 a} \tag{29}$$

由 (17), (19), (28)

$$R_{nl}(r)=r^l e^{-Zr/na}\sum_{j=0}^{n-l-1} b_j r^j \tag{30}$$

由 (26), (29)

$$b_{j+1} = \frac{2Z}{na}\frac{j+l+1-n}{j(j+1)+2(l+1)(j+1)}b_j \tag{31}$$

由(30), (31) 以及 normalization condition 我們可以得到以下 n = 1–3 完整的 $R_{nl}(r)$:

$$R_{10}(r) = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a} \tag{32}$$

$$R_{20}(r) = \frac{1}{\sqrt{8}}\left(\frac{Z}{a}\right)^{3/2}\left(2-\frac{Zr}{a}\right)e^{-Zr/2a} \tag{33}$$

$$R_{21}(r) = \frac{1}{\sqrt{24}}\left(\frac{Z}{a}\right)^{3/2}\frac{Zr}{a}e^{-Zr/2a} \tag{34}$$

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$$R_{30}(r) = \frac{2}{81\sqrt{3}}\left(\frac{Z}{a}\right)^{3/2}\left(27-18\frac{Zr}{a}+2\frac{Z^2r^2}{a^2}\right)e^{-Zr/3a} \tag{36}$$

$$R_{31}(r) = \frac{4}{81\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(6\frac{Zr}{a}+\frac{Z^2r^2}{a^2}\right)e^{-Zr/3a} \tag{37}$$

$$R_{32}(r) = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Z^2r^2}{a^2}\right)e^{-Zr/3a} \tag{38}$$

綜合上述的結果，氫原子的波函數為

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{nl}(r)Y_{l,m_l}(\theta,\phi) = R_{nl}(r)\Theta_{l,m_l}(\theta)\frac{1}{\sqrt{2\pi}}e^{im_l\phi} \tag{39}$$

除了波函數的型態外，量子數 n (principal quantum number) 決定總能量，量子數 l (angular momentum quantum number) 決定系統的角動量，量子數 m_l (magnetic quantum number) 決定角動量在 z 軸上的投影。

$$\hat{L}^2\psi_{n,l,m_l} = l(l+1)\hbar^2\,\psi_{n,l,m_l} \tag{40}$$

$$\hat{L}_z\psi_{n,l,m_l} = m_l\hbar\,\psi_{n,l,m_l} \tag{41}$$

由於能量只跟 n 有關，能階的 degeneracy 為

$$\text{degen} = \sum_{0}^{n-1} 2l+1 = n^2 \tag{42}$$

習慣上，我們將 $l = 0, 1, 2, 3$ 的波函數分別稱為 s, p, d, f wavefunctions or orbitals：

$$\psi_{100} = \psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a} \tag{43}$$

$$\psi_{200} = \psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(2-\frac{Zr}{a}\right)e^{-Zr/2a} \tag{44}$$

$$\psi_{210} = \psi_{2p_0} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\frac{Zr}{a}e^{-Zr/2a}\cos\theta \tag{45}$$

$$\psi_{21\pm1} = \psi_{2p_{\pm1}} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\frac{Zr}{a}e^{-Zr/2a}\sin\theta\, e^{\pm i\phi} \tag{46}$$

$$\psi_{300} = \psi_{3s} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^{2}\left(21-18\frac{Zr}{a}+2\frac{Z^2r^2}{a^2}\right)e^{-Zr/3a} \tag{47}$$

$$\psi_{310} = \psi_{3p_0} = \frac{1}{81}\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^{2}\left(6\frac{Zr}{a}-\frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}\cos\theta \tag{48}$$

$$\psi_{31\pm1} = \psi_{3p\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^{2}\left(6\frac{Zr}{a}-\frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}\sin\theta\, e^{\pm i\phi} \tag{49}$$

$$\psi_{320} = \psi_{3d_0} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^{2}e^{-Zr/3a}\left(3\cos^2\theta-1\right) \tag{50}$$

$$\psi_{32\pm1} = \psi_{3d_{\pm1}} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^{2}e^{-Zr/3a}\sin\theta\cos\theta\, e^{\pm i\phi} \tag{51}$$

$$\psi_{32\pm2} = \psi_{3d_{\pm1}} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^{2}e^{-Zr/3a}\sin^2\theta\, e^{\pm 2i\phi} \tag{52}$$