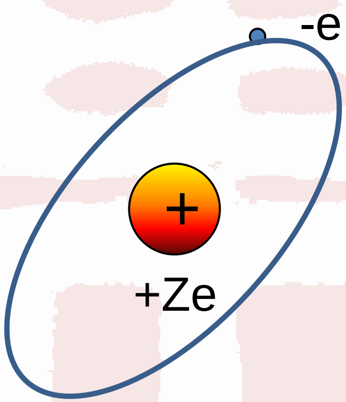
§ 2.6 单电子(H)原子—中心力场薛定谔方程

氢原子(类氢离子）的薛定谔方程

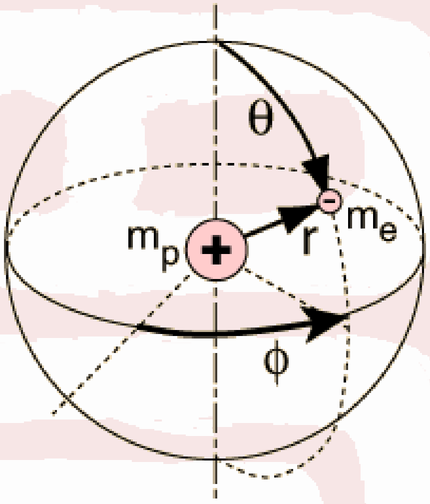


不含时的定态薛定谔方程

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(r)\right)u=Eu$$

其中库仑势

$$V(r)=-\frac{Ze^2}{4\pi\varepsilon_0 r}$$



From www.hyperphysics.phy-astr.gsu.edu

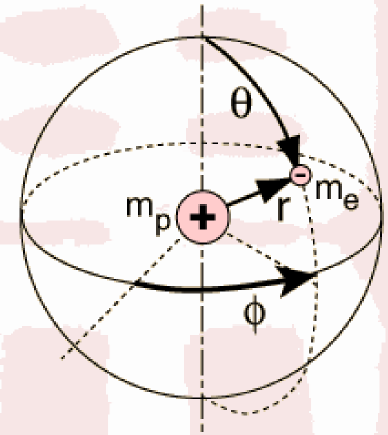
电子束缚在原子核的中心力场中，只与电子和原子核之间的径向距离有关。

§ 2.6 单电子(H)原子—中心力场薛定谔方程

分离变量

$$u(\mathbf{r}) = u(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$$

径向波函数　　角向波函数



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

$$=-\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)-\frac{1}{Y\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\equiv 常数\lambda$$

$$\begin{cases} \dfrac{1}{r^2}\dfrac{d}{dr}\left(r^2\dfrac{dR}{dr}\right)+\left[\dfrac{2m}{\hbar^2}(E-V(r))-\dfrac{\lambda}{r^2}\right]R=0 \\ -\dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\theta\dfrac{\partial Y}{\partial\theta}\right)-\dfrac{1}{\sin^2\theta}\dfrac{\partial^2 Y}{\partial\varphi^2}=\lambda Y \end{cases}$$

径向方程

角向方程

§ 2.6 单电子(H)原子—中心力场薛定谔方程

$$u(\mathbf{r}) = u_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi)$$

量子数

$$n = 1,2,3,\cdots$$
$$l = 0,1,2,\cdots,n-1$$
$$m = 0,\pm1,\pm2,\cdots\pm l$$

归一化条件

$$\int_0^\infty\int_0^\pi\int_0^{2\pi}|u_{nlm}(r,\theta,\varphi)|^2 r^2\sin\theta drd\theta d\varphi$$
$$=\int_0^\infty\int_0^\pi\int_0^{2\pi}|R_{nl}(r)Y_{lm}(\theta,\varphi)|^2 r^2\sin\theta drd\theta d\varphi$$
$$=\int_0^\infty R_{nl}^2(r)r^2dr\int_0^\pi\int_0^{2\pi}|Y_{lm}(\theta,\varphi)|^2\sin\theta d\theta d\varphi$$
$$=1$$

$$l = 0, 1, 2, 3, \cdots$$

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

$$Y_{0,0} = \frac{1}{(4\pi)^{1/2}}$$

$$Y_{1,0} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \quad Y_{1,\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$$

$$Y_{2,0} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \quad Y_{2,\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi} \quad Y_{2,\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$$

$$Y_{3,0} = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta) \quad Y_{3,\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$$

$$Y_{3,\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi} \quad Y_{3,\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$$

$$Y_{l,-m}(\theta,\phi) = (-1)^m Y_{lm}^*(\theta,\phi)$$

l = 0,1,2,3,4,5, … 分别称为 s, p, d, f, g, h, …态

§ 2.6 单电子(H)原子—径向方程

$$n = 1, 2, 3, \cdots$$

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

$$R_{10}(r) = 2(Z/a_0)^{3/2}\exp(-Zr/a_0)$$

$$R_{20}(r) = 2(Z/2a_0)^{3/2}(1 - Zr/2a_0)\exp(-Zr/2a_0)$$

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

$$R_{30}(r) = 2(Z/3a_0)^{3/2}(1 - 2Zr/3a_0 + 2Z^2r^2/27a_0^{\,2})\exp(-Zr/3a_0)$$

$$R_{31}(r) = \frac{4\sqrt{2}}{9}(Z/3a_0)^{3/2}(1 - Zr/6a_0)(Zr/a_0)\exp(-Zr/3a_0)$$

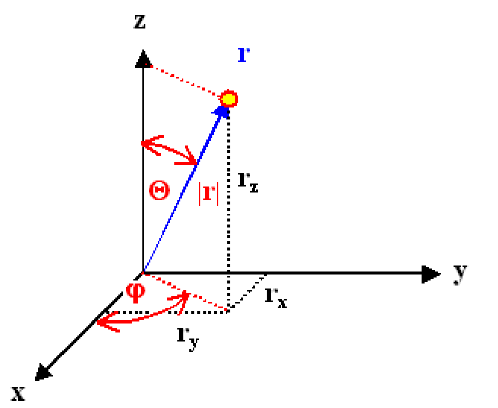
$$R_{32}(r) = \frac{4}{27\sqrt{10}}(Z/3a_0)^{3/2}(Zr/a_0)^2\exp(-Zr/3a_0)$$

➤ 氢原子(类氢离子)处在束缚态 $u_{nlm}(r, \theta, \varphi)$，则在 (r, θ, φ) 点附近 $d\tau$ 体积元内电子出现的概率为：

$$\rho_{nlm}(r,\theta,\varphi)d\tau = |u_{nlm}(r,\theta,\varphi)|^2 r^2 \sin\theta dr d\theta d\varphi$$

$$= R_{nl}^2(r) r^2 dr |Y_{lm}(\theta,\varphi)|^2 d\Omega$$

径向分布　　　　角向分布



$$d\tau = dr \cdot r d\theta \cdot r\sin\theta d\varphi$$

$$= r^2 dr \frac{dS}{r^2} = r^2 dr d\Omega$$

角向分布函数 $W_{lm}(\theta, \varphi)$

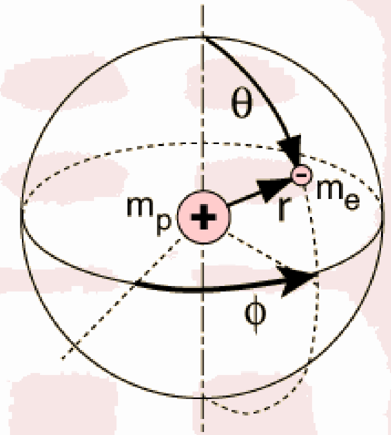
$$W_{lm}(\theta,\varphi)d\Omega = \left[\int_0^\infty |u_{nlm}(r,\theta,\varphi)|^2 r^2 dr\right] \sin\theta d\theta d\varphi$$

$$= \left[\int_0^\infty R_{nl}^2(r) r^2 dr\right] |Y_{lm}(\theta,\varphi)|^2 \sin\theta d\theta d\varphi$$

$$= |Y_{lm}(\theta,\varphi)|^2 d\Omega$$

§ 2.6 单电子(H)原子—H原子中电子的概率分布

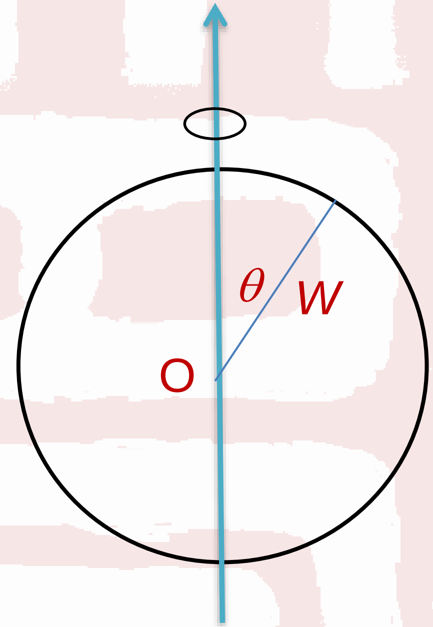
$$Y_{lm}(\theta,\varphi) = N_{lm} P_l^m(\cos\theta) e^{im\varphi}$$



角向分布函数

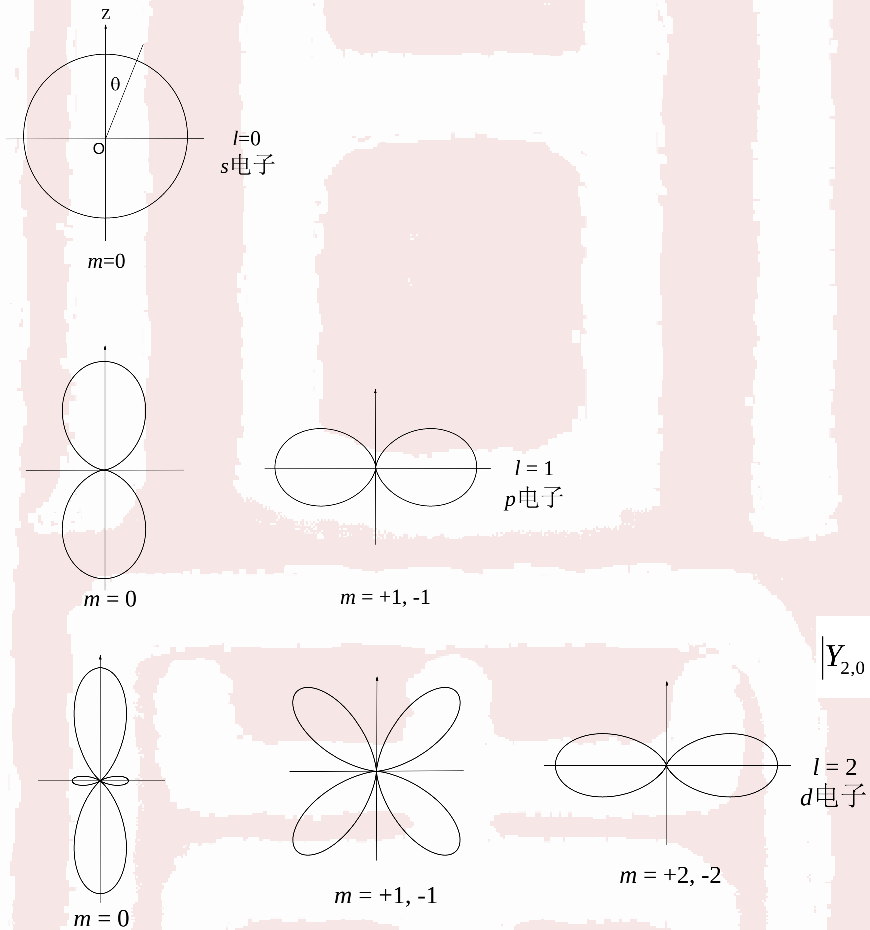
$$W_{lm}(\theta,\varphi) = |Y_{lm}(\theta,\varphi)|^2 = N_{lm}^2 |P_l^m(\cos\theta)|^2$$

角向分布函数表示：处在束缚态 $u_{nlm}(r, \theta, \varphi)$的氢原子(类氢离子)， 在$(\theta, \varphi)$方向单位立体角内电子出现的概率。



角向分布函数与方位角无关，具有旋转对称性。

§ 2.6 单电子(H)原子—H原子中电子的概率分布



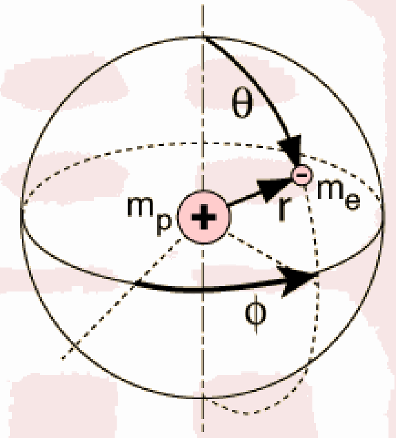
$$|Y_{0,0}|^2 = \frac{1}{4\pi}$$

$$|Y_{1,0}|^2 = \frac{3}{4\pi}\cos^2\theta \qquad |Y_{1,\pm1}|^2 = \frac{3}{8\pi}\sin^2\theta$$

$$|Y_{2,0}|^2 = \frac{5}{16\pi}(3\cos^2\theta - 1)^2 \qquad |Y_{2,\pm1}|^2 = \frac{15}{8\pi}\sin^2\theta\cos^2\theta$$

$$Y_{2,\pm2} = \frac{15}{32\pi}\sin^4\theta$$

$$W_{lm}(\theta,\varphi) = |Y_{lm}(\theta,\varphi)|^2$$



径向分布函数 $W_{nl}(r)$

$$W_{nl}(r)dr=\left[\int_0^{\pi}\int_0^{2\pi}|u_{nlm}(r,\theta,\varphi)|^2\sin\theta d\theta d\varphi\right]r^2dr$$

$$=\left[\int_0^{\pi}\int_0^{2\pi}|Y_{lm}(\theta,\varphi)|^2\sin\theta d\theta d\varphi\right]R_{nl}^2(r)r^2dr$$

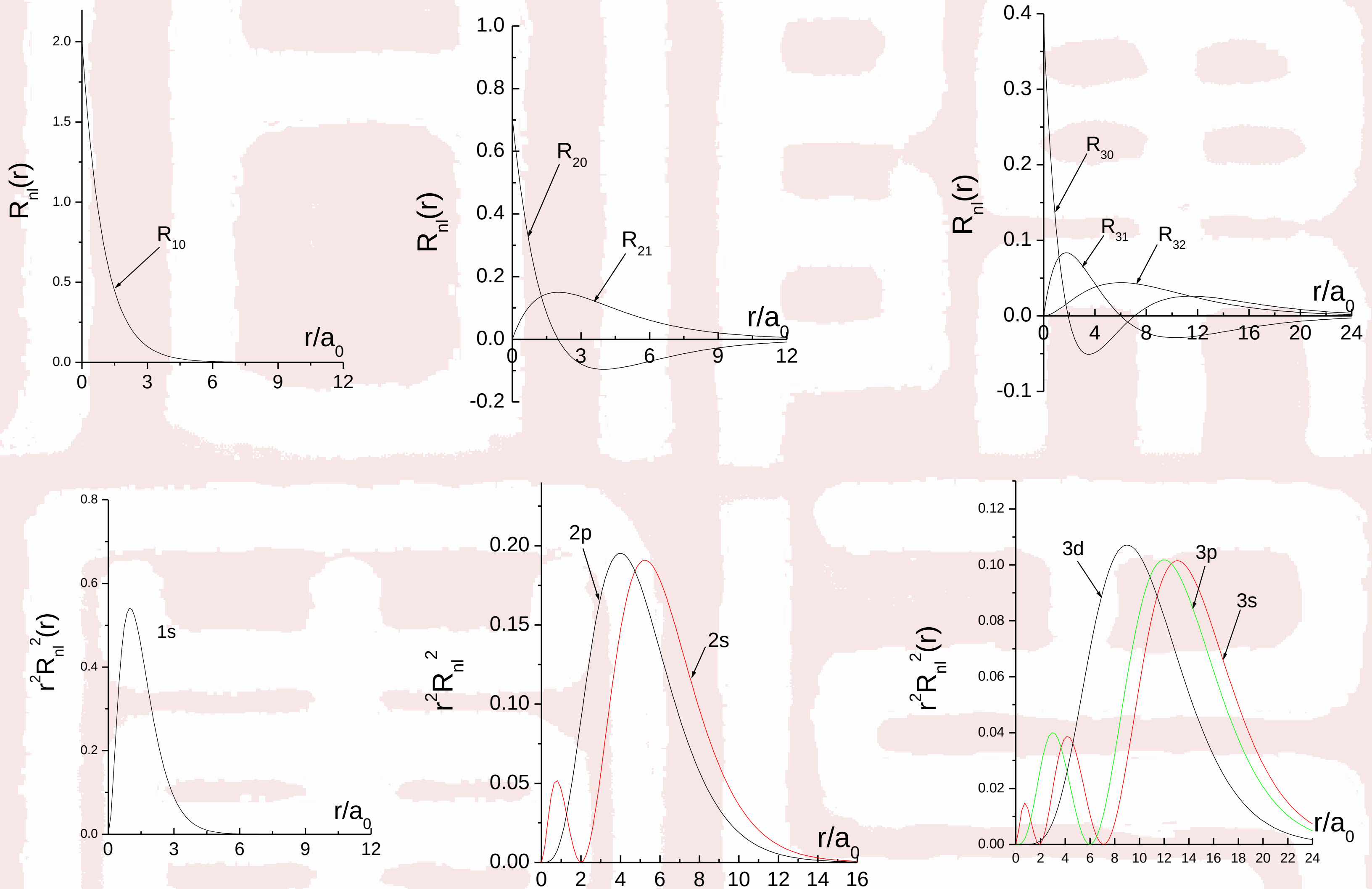
$$=R_{nl}^2(r)r^2dr$$

径向分布函数

$$W_{nl}(r)=R_{nl}^2(r)r^2$$

径向分布函数表示：处在束缚态 $u_{nlm}(r,\theta,\varphi)$的氢原子(类氢离子)，在半径 r 处单位厚度球壳内电子出现的概率。

§ 2.6 单电子(H)原子—H原子中电子的概率分布



§ 2.6 单电子(H)原子—H原子中电子的概率分布

(1) 只有$l = 0$的 s 态，径向波函数在$r = 0$处不为零。

(2) 最可几半径

$$\frac{dW_{n,n-1}(r)}{dr} = 0 \quad \Rightarrow \quad r_m = n^2 a_0$$

例如：氢原子处在1s 态时，电子最可几半径为 a_0

(3) 平均半径

$$\langle r \rangle_{nlm} = \int u_{nlm}^*(\mathbf{r}) r u_{nlm}(\mathbf{r}) d\tau$$

$$= \int_0^\infty |R_{nl}(r)|^2 r^3 dr$$

$$= \frac{n^2 a_0}{Z}\left\{1 + \frac{1}{2}\left[1 - \frac{l(l+1)}{n^2}\right]\right\}$$

例如：氢原子处在1s 态时，电子平均半径为 $3a_0/2$

(4) 其它常用的平均值

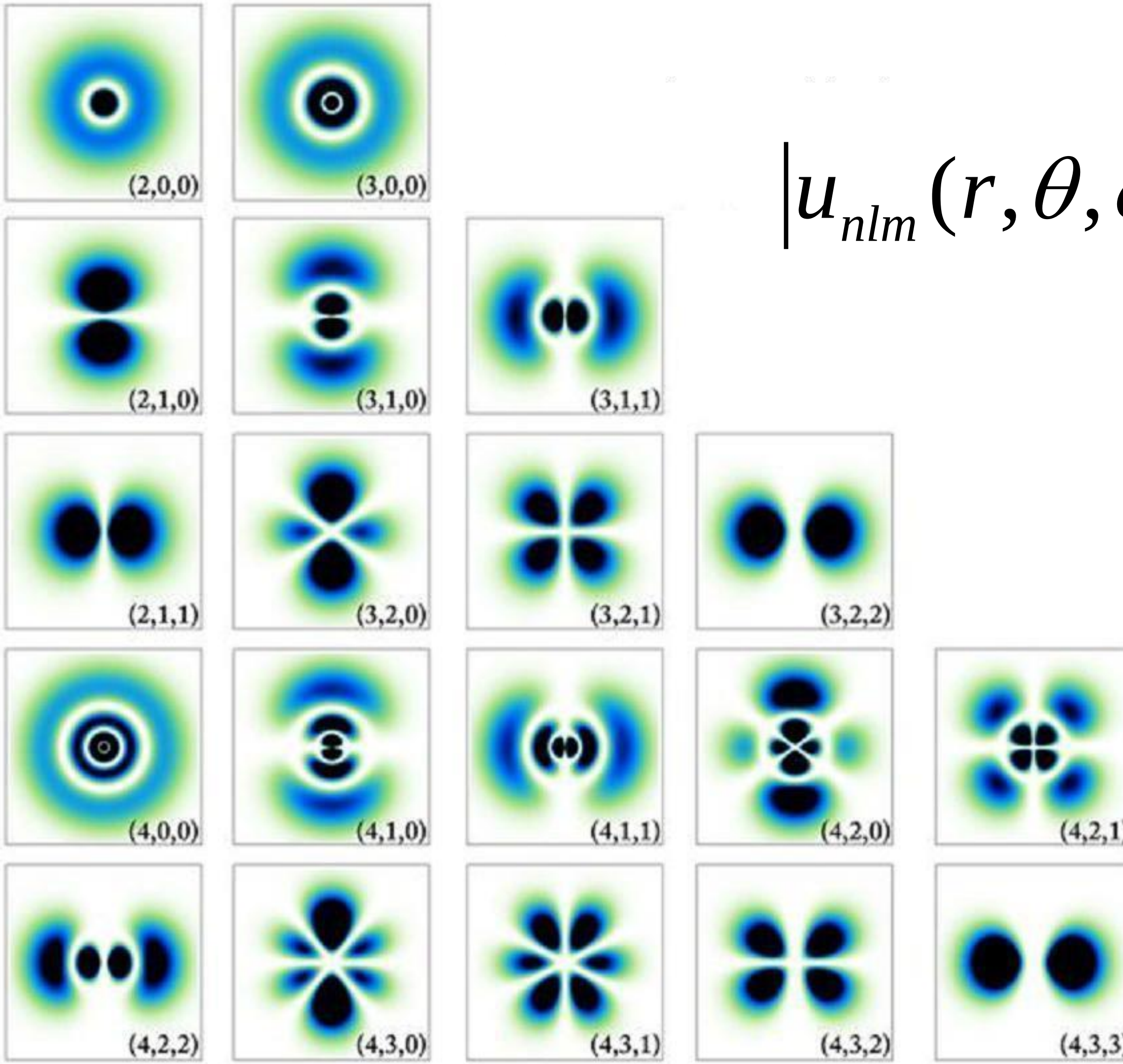
$$\langle r^2 \rangle_{nlm} = \frac{n^4 a_0^2}{Z^2}\left\{1+\frac{3}{2}\left[1-\frac{l(l+1)-1/3}{n^2}\right]\right\}$$

$$\left\langle \frac{1}{r} \right\rangle_{nlm} = \frac{Z}{a_0 n^2}$$

$$\left\langle \frac{1}{r^2} \right\rangle_{nlm} = \frac{Z^2}{a_0^2 n^3 (l+1/2)}$$

$$\left\langle \frac{1}{r^3} \right\rangle_{nlm} = \frac{Z^3}{a_0^3 n^3 l(l+1/2)(l+1)}$$

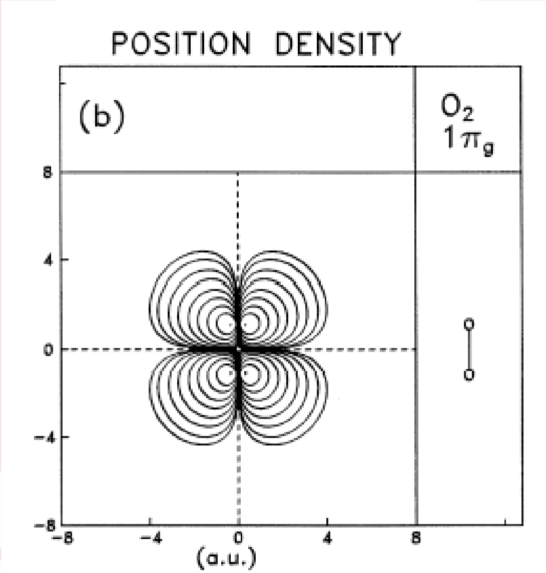
§ 2.6 单电子(H)原子—H原子中电子的概率分布



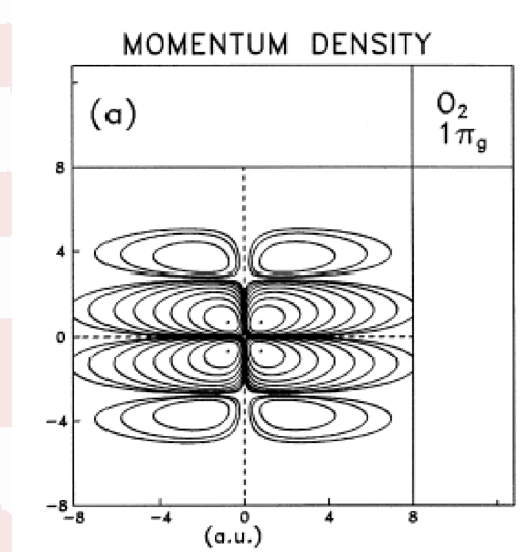
$$\left|u_{nlm}(r,\theta,\varphi)\right|^2$$

§ 2.6 单电子(H)原子—H原子中电子的概率分布

坐标空间和动量空间



FT

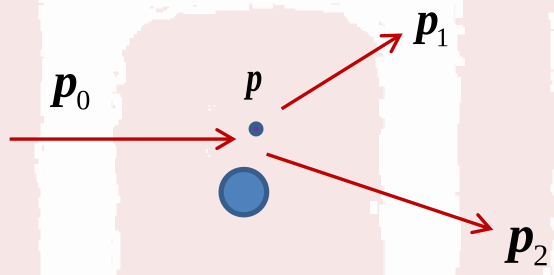


对于H原子：

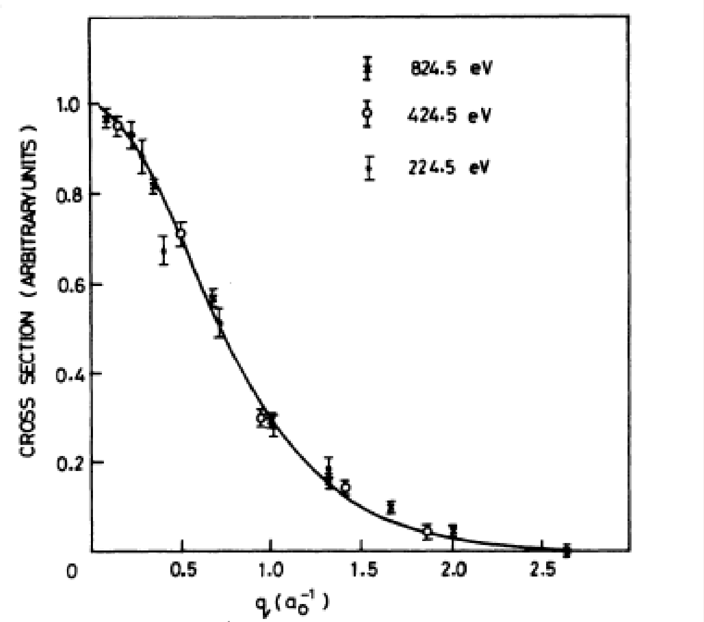
$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi}} e^{-r} \quad \xleftrightarrow{\text{FT}} \quad \phi_{1s}(p) = \frac{2^{3/2}}{\pi(1+p^2)^2}$$

$$\left|\phi_{1s}(p)\right|^2 = 8\pi^{-2}(1+p^2)^{-4}$$

$e^- + A$ (atoms, molecules, ...) $\rightarrow A^+ + e^-_1 + e^-_2$



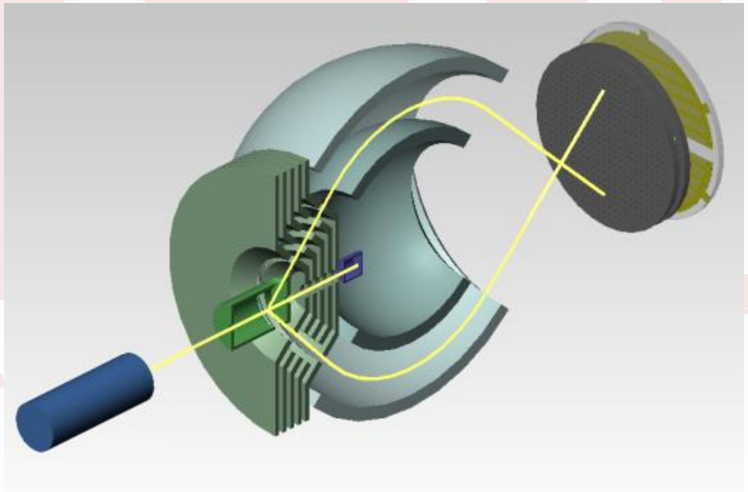
$$\boldsymbol{p}_0 + \boldsymbol{p} = \boldsymbol{p}_1 + \boldsymbol{p}_2$$

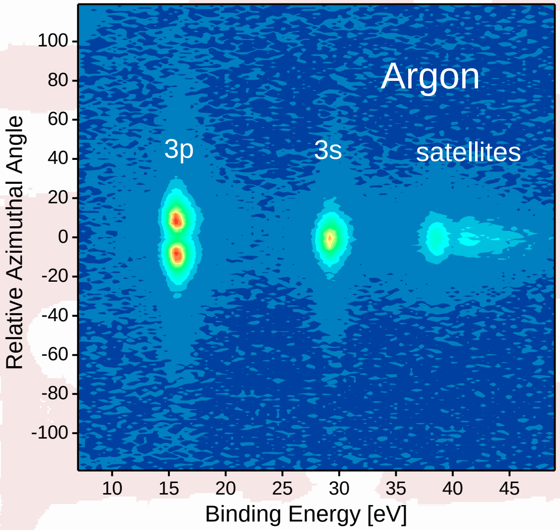


Eric Weigold (1937-)

Ian McCarthy (1930-2005)

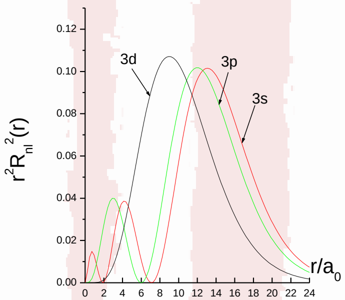
§ 2.6 单电子(H)原子—H原子中电子的概率分布

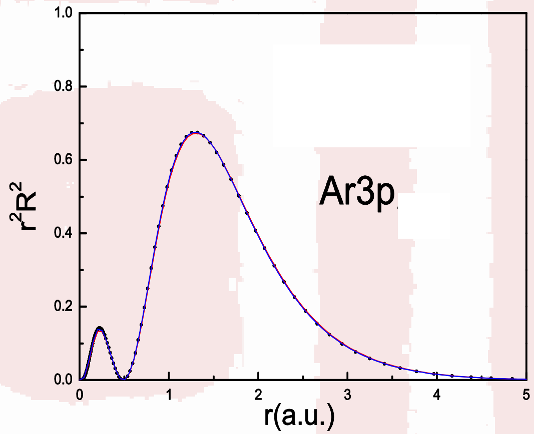


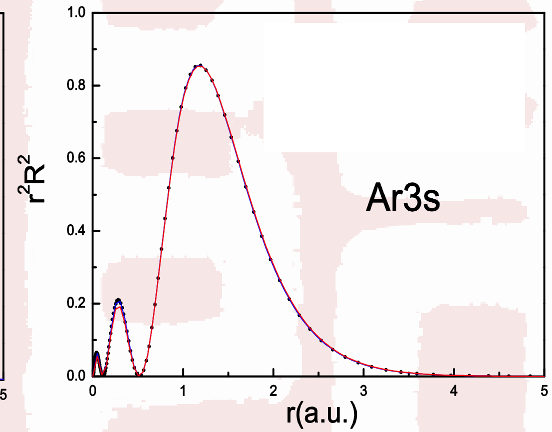


Argon

position space



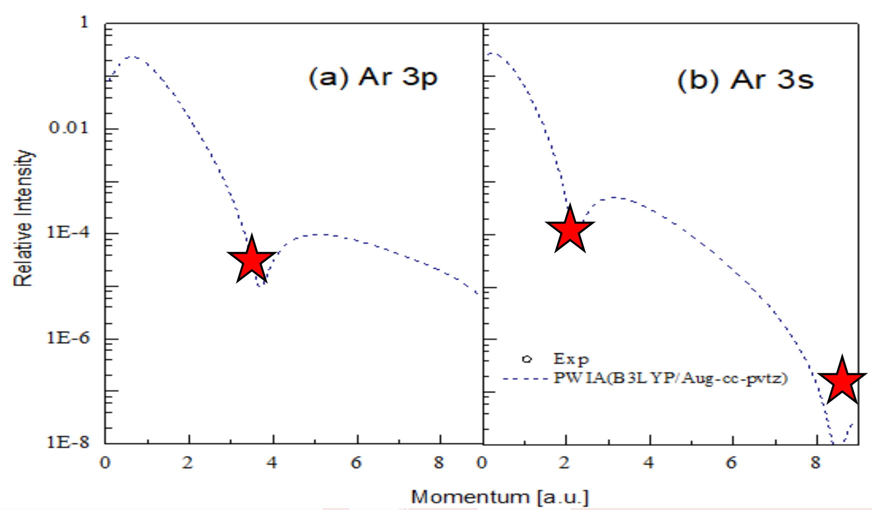




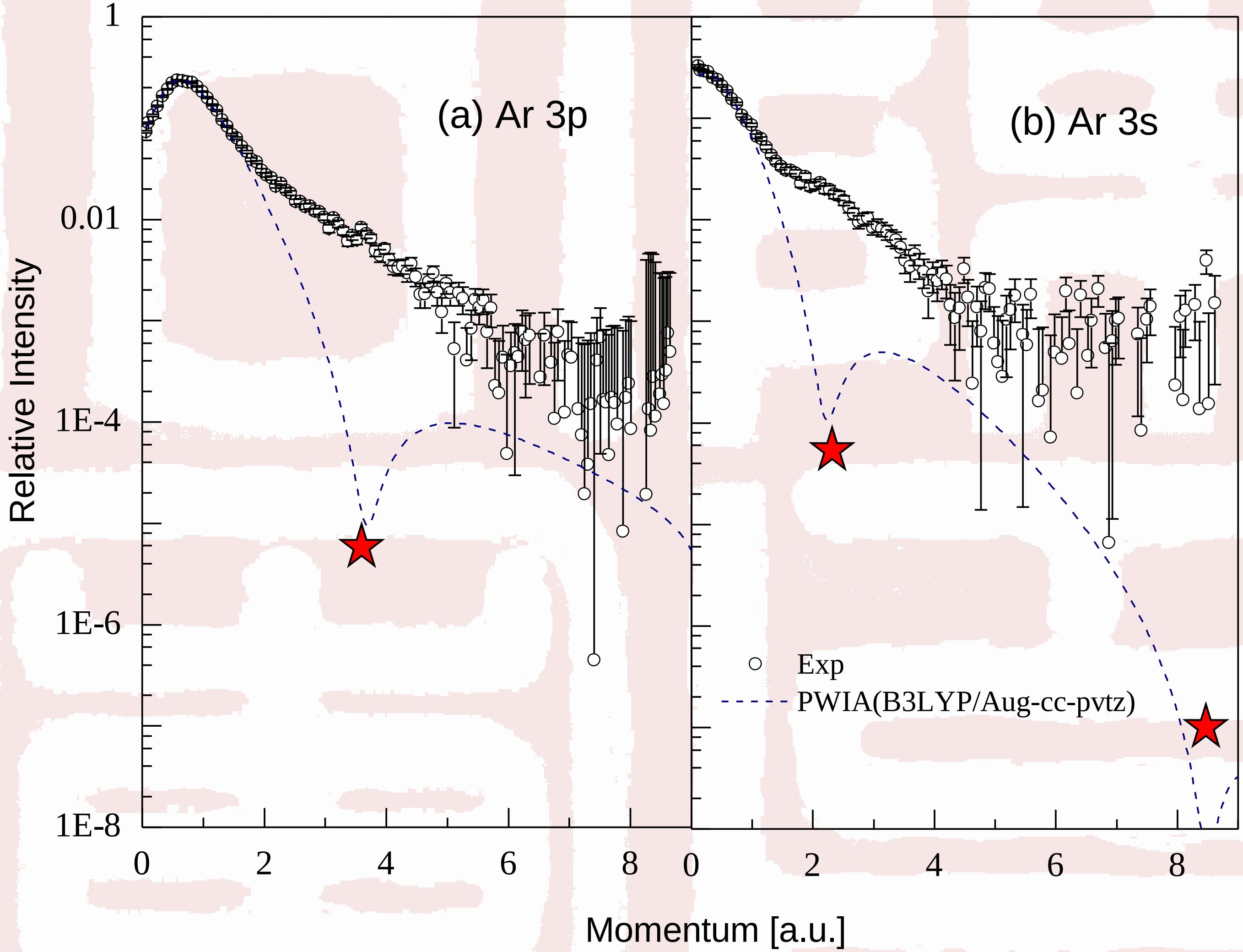
FT

$$\psi_{nlm}(\mathbf{r}) = N_{nlm}R_{nl}(r)Y_{lm}(\Omega_r) \Longleftrightarrow \phi_{nlm}(\mathbf{p}) = N_{nlm}P_{nl}(p)Y_{lm}(\Omega_p)$$

momentum space

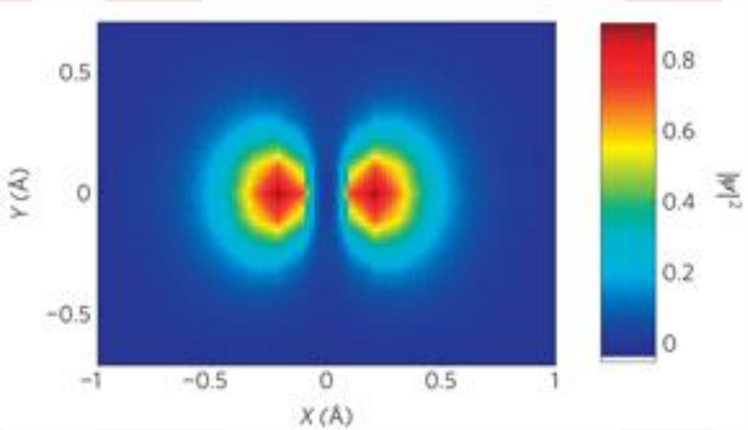


§ 2.6 单电子(H)原子—H原子中电子的概率分布



§ 2.6 单电子(H)原子—H原子中电子的概率分布

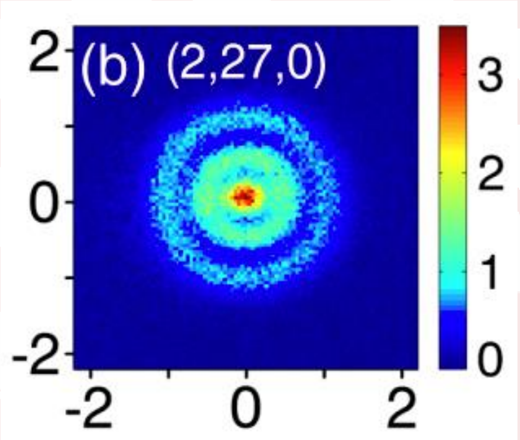
强激光场中的高次谐波谱



Ne 2*p* orbital

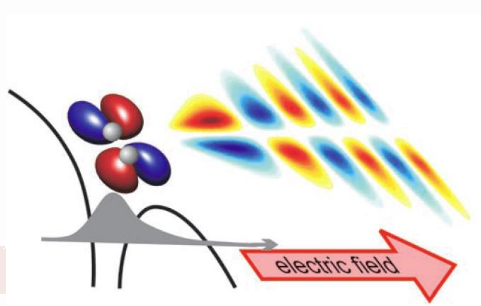
Nat. Phys. 5, 412 (2009).

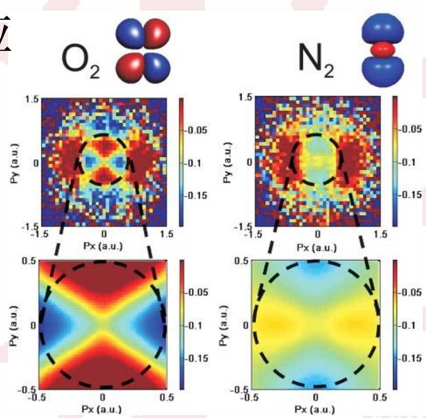
氢原子轨道的光电离显微成像



PRL 110, 213001 (2013)

强激光场中的电子隧道效应





Science 320 (2008) 1478

§ 2.6 单电子(H)原子—量子数的物理意义

$$u(\mathbf{r}) = u_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi)$$

量子数

$$n = 1, 2, 3, \cdots$$

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

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

(1) 主量子数 n 和氢原子能级

$$n=\frac{Ze^2}{4\pi\varepsilon_0\hbar}\left(-\frac{m_e}{2E}\right)^{1/2} \Rightarrow E_n=-\frac{1}{2n^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\frac{m_e}{\hbar^2}$$

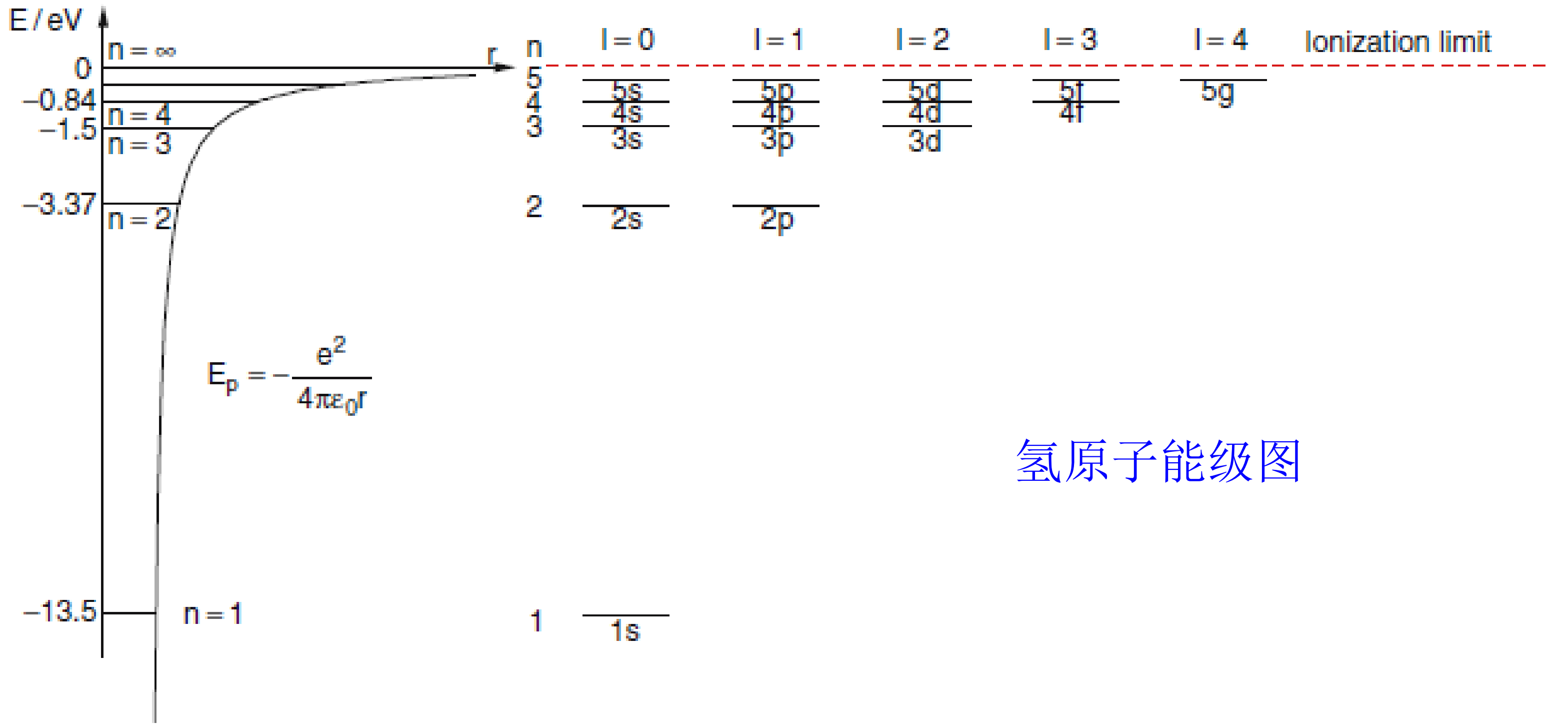
$$=-\frac{e^2}{(4\pi\varepsilon_0)a_0}\frac{Z^2}{2n^2}$$

$$=-\frac{1}{2}m_e\alpha^2c^2\frac{Z^2}{n^2} \qquad n=1,2,3,\cdots$$

氢原子能量是量子化的， 与Bohr理论结果一致；

氢原子能量取决于量子数 n，称为主量子数；

§ 2.6 单电子(H)原子—量子数的物理意义



氢原子能级图

对于给定的量子数 n， $l = 0, 1, 2, \cdots, n-1$

对于量子数 l， $m = 0, \pm 1, \pm 2, \cdots \pm l$

共有： $\sum_{l=0}^{n-1}(2l+1) = n^2$ 个不同的状态。

它们都有相同的能量，称它们是 n^2 重简并的。

(2) 轨道量子数(角量子数) l和轨道角动量的大小

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

两边同乘 $R_{nl}(r)$

$$R_{nl}(r)\hat{L}^2 Y_{lm}(\theta,\varphi) = l(l+1)\hbar^2 R_{nl}(r) Y_{lm}(\theta,\varphi)$$

$$\hat{L}^2 R_{nl}(r) Y_{lm}(\theta,\varphi) = l(l+1)\hbar^2 R_{nl}(r) Y_{lm}(\theta,\varphi)$$

$$\hat{L}^2 u_{nlm}(r,\theta,\varphi) = l(l+1)\hbar^2 u_{nlm}(r,\theta,\varphi)$$

所以 $u_{nlm}(r,\theta,\varphi)$ 是 $\hat{L}^2$ 的本征态，相应的本征值为 $l(l+1)\hbar^2$

量子数 l 描述电子做轨道运动角动量的大小，称为轨道角动量量子数，
简称轨道量子数或角量子数。

$$L = \sqrt{l(l+1)}\hbar \qquad l = 0,1,2,\cdots,n-1$$

角动量可以等于0

比较Bohr的量子假设：$L = n\hbar$

§ 2.6 单电子(H)原子—量子数的物理意义

(3) 磁量子数 m 与轨道角动量的z分量

角向函数是球谐函数

$$Y_{lm}(\theta,\varphi) = N_{lm}P_l^m(\cos\theta)e^{im\varphi}$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$$

$$\Rightarrow \quad \hat{L}_z Y_{lm}(\theta,\varphi) = m\hbar\, Y_{lm}(\theta,\varphi)$$

两边同乘 $R_{nl}(r)$，得 $\hat{L}_z u_{nlm}(r,\theta,\phi) = m\hbar\, u_{nlm}(r,\theta,\phi)$

所以 $u_{nlm}(r,\theta,\varphi)$ 也是 $\hat{L}_z$ 的本征态，相应的本征值为$m\hbar$

量子数 m 描述电子轨道角动量 z 分量，称为磁量子数。

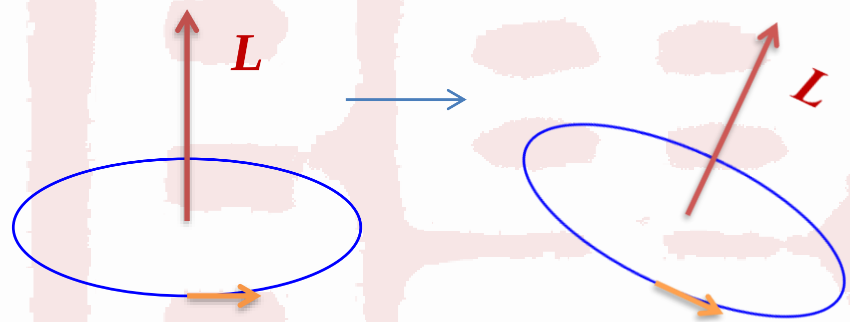
$$L_z = m\hbar \qquad m = 0, \pm 1, \pm 2, \cdots \pm l$$

§2.6 单电子(H)原子—量子数的物理意义

(4) 角动量矢量 $\boldsymbol{L}$

经典的角动量矢量：

大小和方向可以取任意值。



经典角动量

量子的角动量矢量：

大小量子化：

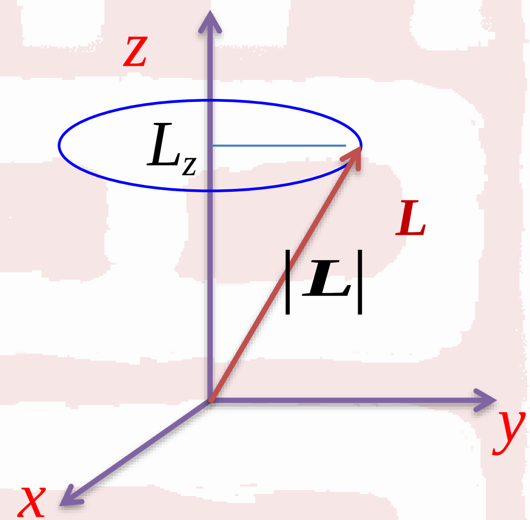
$$L=\sqrt{l(l+1)}\hbar \qquad l=0,1,2,\cdots,n-1$$

方向

$$L_z=m\hbar \qquad m=0,\pm1,\pm2,\cdots\pm l$$

L_x, L_y 没有确定取值，但有确定的期望值：

$$\langle L_x\rangle=\langle L_y\rangle=0$$

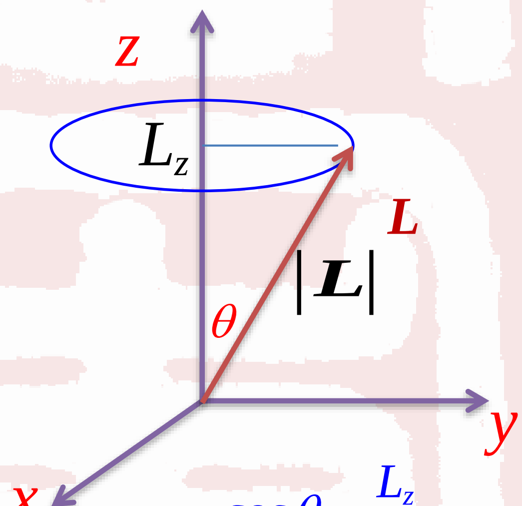


量子角动量的矢量模型

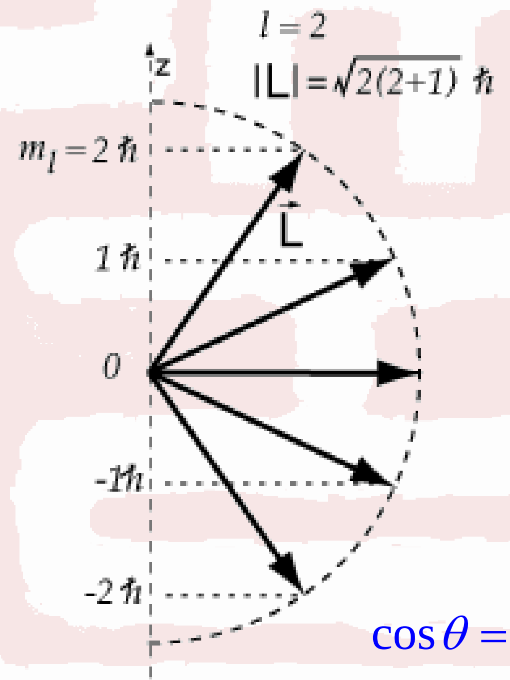
(5) 空间取向量子化

$$L = \sqrt{l(l+1)}\hbar \qquad L_z = m\hbar$$

对于给定量子数 l， $m = 0, \pm 1, \pm 2, \cdots \pm l$



$$\cos\theta = \frac{L_z}{|\boldsymbol{L}|}$$



$$\cos\theta = \frac{0, \pm\hbar, \pm 2\hbar}{|\boldsymbol{L}|}$$

Vector Model for Orbital Angular Momentum

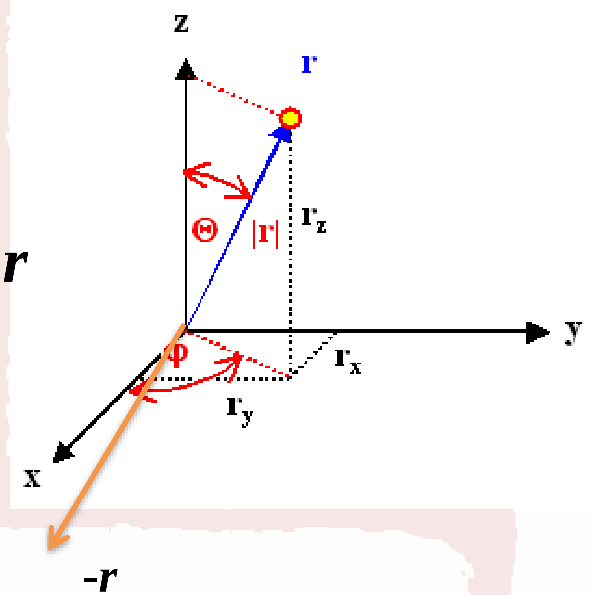
§ 2.6 单电子(H)原子—H原子波函数的宇称

宇称：空间反演的对称性。

设 $\hat{P}$ 为宇称算符，定义为：

$$\hat{P}\varphi(\mathbf{r}) = \varphi(-\mathbf{r})$$

空间反演操作：$\boldsymbol{r} \rightarrow -\boldsymbol{r}$



再做一次空间反演操作，有

$$\hat{P}^2\varphi(\mathbf{r}) = \hat{P}\varphi(-\mathbf{r}) = \varphi(\mathbf{r})$$

宇称算符的本征方程

$$\hat{P}\varphi(\mathbf{r}) = \eta\varphi(\mathbf{r})$$

$$\hat{P}^2\varphi(\mathbf{r}) = \hat{P}\left(\eta\varphi(\mathbf{r})\right) = \eta\hat{P}\varphi(\mathbf{r}) = \eta^2\varphi(\mathbf{r})$$

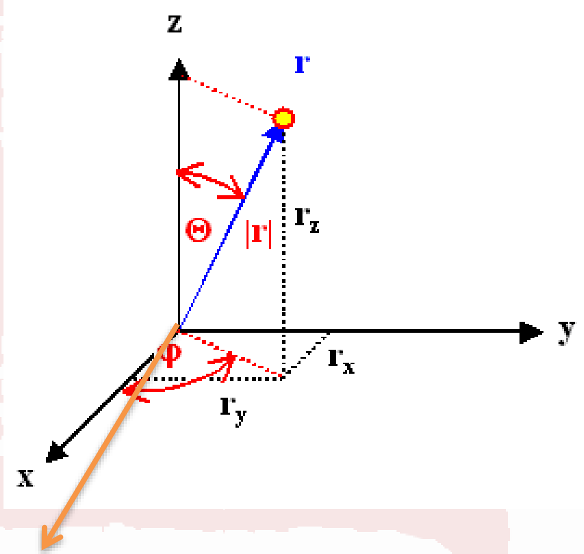
⇒ $\eta^2 = 1$ ⇒ $\eta = \pm 1$

所以 $\hat{P}\varphi(\mathbf{r}) = \pm\varphi(\mathbf{r})$

§ 2.6 单电子(H)原子—H原子波函数的宇称

$\eta = +1$　空间反演对称，体系具有偶宇称；

$\eta = -1$　空间反演反对称，体系具有奇宇称；



在球坐标下，空间反演操作相当于变换：

$$(r,\ \theta,\ \varphi)\ \rightarrow (r,\ \pi\text{-}\theta,\ \pi+\varphi)$$

对于氢原子(类氢离子)波函数

$$\hat{P}\left[R_{nl}(r)Y_{lm}(\theta,\phi)\right] = R_{nl}(r)Y_{lm}(\pi-\theta,\phi+\pi)$$

$$= R_{nl}(r)(-1)^l Y_{lm}(\theta,\phi)$$

宇称取决于 $(-1)^l$