第六章　自旋与全同粒子

§6.1 电子自旋

（1）施特恩-格拉赫实验

（2）光谱的精细结构

（3）电子自旋假设

（4）回转磁比率

（1）施特恩-格拉赫实验

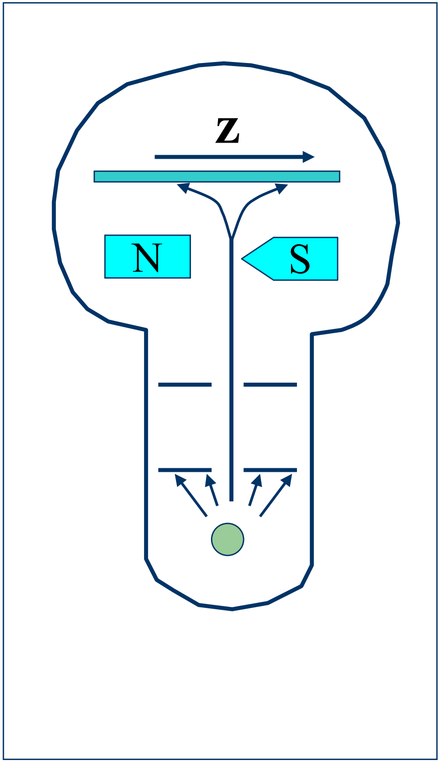
（a）实验现象

S态氢原子束通过狭缝和不均匀磁场，在感光板上出现两条分立的线

（b）结论

I. 氢原子有磁矩

II. 原子的磁矩只有两种取向，它们是空间量子化的



（c）讨论

$$U = -\vec{M} \bullet \vec{B} = -MB_z \cos\theta$$

$$F_z = -\frac{\partial U}{\partial z} = M\frac{\partial B_z}{\partial z}\cos\theta$$

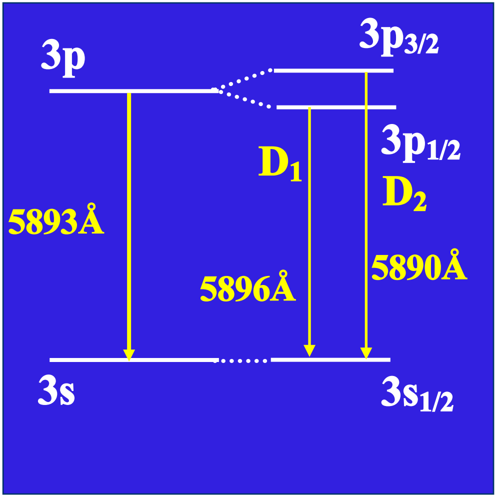
分析

如果原子磁矩可以取任何方向，cos θ 应当可以在区间(-1，+1)连续取值，结果应该是一个连续的带。但实验结果只有两条分立的线，对应 cos θ = -1 和+1。S态氢原子没有轨道磁矩，原子磁矩来自电子固有的磁矩，即自旋磁矩（原子核质量大，核磁矩贡献可忽略）

（2）精细光谱

钠原子光谱有一条明亮的黄线，对应的波长为**5893Å**

这条谱线由两条靠得很近的谱线组成，这种双谱线结构称为光谱线的精细结构



这种精细结构可以得出电子具有自旋的结论

(3) 电子自旋假设

1925年，乌伦贝克（Uhlenbeck）和哥德斯密脱（Goudsmit）提出了以下假设

i) 每个电子具有自旋角动量，它在空间任何方向上的投影只能取两个值：

$$\vec{S} \longrightarrow S_z = \pm\frac{\hbar}{2}$$

ii) 每个电子具有自旋磁矩，它与自旋角动量的关系是

$$\vec{M}_S = \frac{-e}{m_e}\vec{S} \quad (\mathrm{SI}) \qquad \vec{M}_S = \frac{-e}{m_s c}\vec{S} \quad (\mathrm{CGS})$$

自旋磁矩在空间任意方向的投影只能取两个值：

波尔磁子

$$M_{Sz} = \pm\frac{e\hbar}{2m_e c} = \pm M_B \qquad \textbf{(CGS)}$$

（4）回转磁比率

（a）电子

$$\frac{M_{Sz}}{S_z} = -\frac{e}{m_e c}$$

（b）轨道

$$\vec{M}_L = -\frac{e}{2m_e c}\vec{L}$$

$$\frac{M_L}{L} = -\frac{e}{2m_s c} = \frac{M_{SZ}}{2S_Z}$$

§6.2　电子的自旋算符和自旋函数

（1）自旋算符和泡利算符

（2）含自旋的体系波函数

（3）自旋的矩阵表示和泡利矩阵

（4）体系波函数的归一化和概率密度

（5）自旋波函数

（6）物理量的平均值

（1）自旋算符和泡利算符

电子具有自旋角动量这一特性纯粹是量子特性，它与坐标和动量无关，是电子内部状态的表征是描写电子状态的第四个变量.

自旋算符定义为 $\hat{\vec{S}}$

$\hat{\vec{L}}$	$\hat{\vec{S}}$
$\hat{\vec{L}} \times \hat{\vec{L}} = i\hbar \hat{\vec{L}}$	$\hat{\vec{S}} \times \hat{\vec{S}} = i\hbar \hat{\vec{S}}$
$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$	$[\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z$
$[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$	$[\hat{S}_y, \hat{S}_z] = i\hbar \hat{S}_x$
$[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$	$[\hat{S}_z, \hat{S}_x] = i\hbar \hat{S}_y$

$$\hat{S}^2\psi = (\hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2)\psi = \tfrac{3}{4}\hbar^2\psi \qquad \hat{S}_{x,y,z}\psi = \pm\frac{\hbar}{2}\psi$$

$$L^2 = l(l+1)\hbar^2 \Longrightarrow S^2 = s(s+1)\hbar^2 = \tfrac{3}{4}\hbar^2 \rightarrow s = \tfrac{1}{2}$$

自旋量子数只能取一个数值

泡利算符

$$\hat{\vec{S}} = \frac{\hbar}{2}\hat{\vec{\sigma}} \quad \Rightarrow \quad \begin{cases} S_x = \dfrac{\hbar}{2}\sigma_x \\ S_y = \dfrac{\hbar}{2}\sigma_y \\ S_z = \dfrac{\hbar}{2}\sigma_z \end{cases}$$

$$\hat{\vec{S}} \times \hat{\vec{S}} = i\hbar\hat{\vec{S}} \Rightarrow \hat{\vec{\sigma}} \times \hat{\vec{\sigma}} = 2i\hat{\vec{\sigma}} \quad \begin{cases} \hat{\sigma}_x\hat{\sigma}_y - \hat{\sigma}_y\hat{\sigma}_x = 2i\hat{\sigma}_z \\ \hat{\sigma}_y\hat{\sigma}_z - \hat{\sigma}_z\hat{\sigma}_y = 2i\hat{\sigma}_x \\ \hat{\sigma}_z\hat{\sigma}_x - \hat{\sigma}_x\hat{\sigma}_z = 2i\hat{\sigma}_y \end{cases}$$

$$\hat{\sigma}_x^2 = \hat{\sigma}_y^2 = \hat{\sigma}_z^2 = \mathrm{I}$$

反对易关系

$$\begin{cases} \hat{\sigma}_x\hat{\sigma}_y + \hat{\sigma}_y\hat{\sigma}_x = 0 \\ \hat{\sigma}_y\hat{\sigma}_z + \hat{\sigma}_z\hat{\sigma}_y = 0 \\ \hat{\sigma}_z\hat{\sigma}_x + \hat{\sigma}_x\hat{\sigma}_z = 0 \end{cases}$$

证明:

$$\hat{\sigma}_y\hat{\sigma}_z - \hat{\sigma}_z\hat{\sigma}_y = 2i\hat{\sigma}_x$$

$$\hat{\sigma}_y\hat{\sigma}_y\hat{\sigma}_z - \hat{\sigma}_y\hat{\sigma}_z\hat{\sigma}_y = 2i\hat{\sigma}_y\hat{\sigma}_x$$

σ ^{2}y=1

$$\hat{\sigma}_y^{\,2}\hat{\sigma}_z - \hat{\sigma}_y\hat{\sigma}_z\hat{\sigma}_y = 2i\hat{\sigma}_y\hat{\sigma}_x$$

$$\hat{\sigma}_z - \hat{\sigma}_y\hat{\sigma}_z\hat{\sigma}_y = 2i\hat{\sigma}_y\hat{\sigma}_x$$

$$\hat{\sigma}_y\hat{\sigma}_z\hat{\sigma}_y - \hat{\sigma}_z\hat{\sigma}_y^{\,2} = 2i\hat{\sigma}_x\hat{\sigma}_y$$

$$\hat{\sigma}_y\hat{\sigma}_z\hat{\sigma}_y - \hat{\sigma}_z = 2i\hat{\sigma}_x\hat{\sigma}_y$$

$$\hat{\sigma}_x\hat{\sigma}_y + \hat{\sigma}_y\hat{\sigma}_x = 0$$

$$\hat{\sigma}_x\hat{\sigma}_y = -\hat{\sigma}_y\hat{\sigma}_x$$

$$\begin{cases} \hat{\sigma}_x\hat{\sigma}_y - \hat{\sigma}_y\hat{\sigma}_x = 2i\hat{\sigma}_z \\ \hat{\sigma}_y\hat{\sigma}_z - \hat{\sigma}_z\hat{\sigma}_y = 2i\hat{\sigma}_x \\ \hat{\sigma}_z\hat{\sigma}_x - \hat{\sigma}_x\hat{\sigma}_z = 2i\hat{\sigma}_y \end{cases} \Rightarrow \begin{cases} \hat{\sigma}_x\hat{\sigma}_y = -\hat{\sigma}_y\hat{\sigma}_x = i\hat{\sigma}_z \\ \hat{\sigma}_y\hat{\sigma}_z = -\hat{\sigma}_z\hat{\sigma}_y = i\hat{\sigma}_x \\ \hat{\sigma}_z\hat{\sigma}_x = -\hat{\sigma}_x\hat{\sigma}_z = i\hat{\sigma}_y \end{cases}$$

（2）含自旋的体系波函数

$$\Psi = \Psi(x, y, z, S_z, t)$$

$$\begin{cases} \psi_1(\vec{r}, t) = \Psi(x, y, z, +\frac{\hbar}{2}, t) \\ \psi_2(\vec{r}, t) = \Psi(x, y, z, -\frac{\hbar}{2}, t) \end{cases}$$

旋量 $\Phi = \begin{pmatrix} \psi_1(\vec{r}, t) \\ \psi_2(\vec{r}, t) \end{pmatrix}$

$$\Phi_{\frac{1}{2}} = \begin{pmatrix} \psi_1(\vec{r}, t) \\ 0 \end{pmatrix} \qquad \Phi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ \psi_2(\vec{r}, t) \end{pmatrix}$$

（3）自旋的矩阵表示和泡利矩阵

（a）S_Z 矩阵

$$S_z = \frac{\hbar}{2}\begin{pmatrix} a & b \\ c & d \end{pmatrix} \longleftarrow \mathbf{S}_z\Phi_{\frac{1}{2}} = \frac{\hbar}{2}\Phi_{\frac{1}{2}} \quad \frac{\hbar}{2}\begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} \psi_1(\vec{r},t) \\ 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} \psi_1(\vec{r},t) \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} a\psi_1 \\ c\psi_1 \end{pmatrix} = \begin{pmatrix} \psi_1 \\ 0 \end{pmatrix} \longrightarrow \begin{cases} a = 1 \\ c = 0 \end{cases}$$

$$\frac{\hbar}{2}\begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} 0 \\ \psi_2(\vec{r},t) \end{pmatrix} = -\frac{\hbar}{2}\begin{pmatrix} 0 \\ \psi_2(\vec{r},t) \end{pmatrix} \Rightarrow \begin{pmatrix} b\psi_2 \\ d\psi_2 \end{pmatrix} = -\begin{pmatrix} 0 \\ \psi_2 \end{pmatrix} \Rightarrow \begin{cases} b = 0 \\ d = -1 \end{cases}$$

$$S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

（b）泡利算符的矩阵形式

$$\frac{\hbar}{2}\hat{\sigma}_z = S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \Rightarrow \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \hat{\sigma}_x = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

$$\hat{\sigma}_x = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \longrightarrow \hat{\sigma}_z\hat{\sigma}_x = -\hat{\sigma}_x\hat{\sigma}_z$$

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} a & b \\ c & d \end{pmatrix} = -\begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \Rightarrow \begin{pmatrix} a & b \\ -c & -d \end{pmatrix} = \begin{pmatrix} -a & b \\ -c & d \end{pmatrix} \Rightarrow \begin{cases} a=0 \\ d=0 \end{cases}$$

$$\sigma_x = \begin{pmatrix} 0 & b \\ c & 0 \end{pmatrix} \quad \hat{\sigma}_x^+ = \hat{\sigma}_x \Rightarrow \begin{pmatrix} 0 & b \\ c & 0 \end{pmatrix}^+ = \begin{pmatrix} 0 & c^* \\ b^* & 0 \end{pmatrix} = \begin{pmatrix} 0 & b \\ c & 0 \end{pmatrix}$$

b = c*　　**c = b***

$$\sigma_x = \begin{pmatrix} 0 & c^* \\ c & 0 \end{pmatrix} \quad \sigma_x^{\ 2} = \begin{pmatrix} 0 & c^* \\ c & 0 \end{pmatrix}\begin{pmatrix} 0 & c^* \\ c & 0 \end{pmatrix} = \begin{pmatrix} |c|^2 & 0 \\ 0 & |c|^2 \end{pmatrix} = I \quad \Rightarrow |c|^2 = 1$$

$\sigma^2{}_x = \mathbf{I}$

若**c=exp[iα] (α为实数)**　$$\sigma_x = \begin{pmatrix} 0 & e^{-i\alpha} \\ e^{i\alpha} & 0 \end{pmatrix}$$

$$i\hat{\sigma}_y = \hat{\sigma}_z\hat{\sigma}_x \Rightarrow \hat{\sigma}_y = -i\hat{\sigma}_z\hat{\sigma}_x$$

$$\sigma_y = -i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & e^{-i\alpha} \\ e^{i\alpha} & 0 \end{pmatrix} = \begin{pmatrix} 0 & e^{i(-\alpha-\frac{\pi}{2})} \\ e^{i(\alpha+\frac{\pi}{2})} & 0 \end{pmatrix}$$

$\alpha = 0$，则有泡利矩阵

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

（4）体系波函数的归一化和概率密度

（a）归一化

$$\Phi = \begin{pmatrix} \psi_1(\vec{r},t) \\ \psi_2(\vec{r},t) \end{pmatrix} \qquad \int \Phi^+ \Phi d\tau = \int \begin{pmatrix} \psi_1^* & \psi_2^* \end{pmatrix} \begin{pmatrix} \psi_1(\vec{r},t) \\ \psi_2(\vec{r},t) \end{pmatrix} d\tau$$

$$= \int [|\psi_1|^2 + |\psi_2|^2] d\tau = 1$$

（b）概率密度

$$\omega(\vec{r},t) = \Phi^+\Phi = |\psi_1|^2 + |\psi_2|^2 = \omega_1(\vec{r},t) + \omega_2(\vec{r},t)$$

Sz = 1/2 $\quad \int \omega_1(\vec{r},t) d\tau$

Sz = – 1/2 $\quad \int \omega_2(\vec{r},t) d\tau$

（5）自旋波函数

$$\Phi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

通常情形下，电子的自旋状态对轨道运动有影响，从而 $\psi_1 \neq \psi_2$

当电子的自旋与轨道运动相互作用小到可以略去时，电子的自旋状态不影响轨道运动，ψ_1和 ψ_2对 **(x, y, z)**的依赖关系一样，体系波函数可写成如下形式:

$$\psi(\vec{r}, S_z, t) = \psi(\vec{r}, t)\chi(S_z)$$

$\chi(S_z)$ 是 $\hat{S}_z$的本征函数，即自旋波 函数

$$\hat{S}_z \chi(S_z) = \pm \frac{\hbar}{2} \chi(S_z)$$

$$\begin{cases} \hat{S}_z \chi_{\frac{1}{2}}(S_z) = \dfrac{\hbar}{2} \chi_{\frac{1}{2}}(S_z) \\ \hat{S}_z \chi_{-\frac{1}{2}}(S_z) = -\dfrac{\hbar}{2} \chi_{-\frac{1}{2}}(S_z) \end{cases}$$

$$\chi_{\frac{1}{2}} = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \qquad \chi_{-\frac{1}{2}} = \begin{pmatrix} a_3 \\ a_4 \end{pmatrix}$$

$$\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \Longrightarrow \begin{pmatrix} a_1 \\ -a_2 \end{pmatrix} = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \Rightarrow \begin{cases} a_1 = a_1 \\ a_2 = 0 \end{cases}$$

$$\begin{pmatrix} a_1^* & 0 \end{pmatrix}\begin{pmatrix} a_1 \\ 0 \end{pmatrix} = 1 \Rightarrow |a_1| = 1 \Rightarrow a_1 = 1$$

$$\chi_{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \chi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\chi_{-\frac{1}{2}}^{+}\chi_{\frac{1}{2}} = \begin{pmatrix} 0 & 1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0$$

（6）物理量的平均值

物理量 $G=\begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix}$

对自旋求平均

$$\Phi^+\hat{G}\Phi=\begin{pmatrix}\psi_1^* & \psi_2^*\end{pmatrix}\begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix}\begin{pmatrix}\psi_1 \\ \psi_2\end{pmatrix}=\begin{pmatrix}\psi_1^* & \psi_2^*\end{pmatrix}\begin{pmatrix} G_{11}\psi_1+G_{12}\psi_2 \\ G_{21}\psi_1+G_{22}\psi_2 \end{pmatrix}$$

$$=\psi_1^*G_{11}\psi_1+\psi_1^*G_{12}\psi_2+\psi_2^*G_{21}\psi_1+\psi_2^*G_{22}\psi_2$$

对坐标和自旋同时求平均

$$\overline{G}=\int\Phi^+\hat{G}\Phi d\tau=\int\begin{pmatrix}\psi_1^* & \psi_2^*\end{pmatrix}\begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix}\begin{pmatrix}\psi_1 \\ \psi_2\end{pmatrix}d\tau$$

$$=\int\ [\psi_1^*G_{11}\psi_1+\psi_1^*G_{12}\psi_2+\psi_2^*G_{21}\psi_1+\psi_2^*G_{22}\psi_2]d\tau$$

§6.3　简单塞曼效应

假设外磁场足够大，以致自旋和轨道运动相互作用能量和外磁场引起的附加能量比较起来可以略去

取磁场方向为z轴，则磁场引起的附加能量(CGS)是

$$U=-(\hat{\vec{M}}_L+\hat{\vec{M}}_S)\bullet\vec{B}=\frac{e}{2m_e c}(\hat{\vec{L}}+2\hat{\vec{S}})\bullet\vec{B}$$

$$=\frac{e}{2m_e c}(\hat{L}_z+2\hat{S}_z)B$$

体系的薛定谔方程为

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2+U(r)+\frac{eB}{2m_e c}(\hat{L}_z+2\hat{S}_z)\right)\Psi=E\Psi$$

$$\Psi = \psi_1 \chi_{\frac{1}{2}} = \begin{pmatrix} \psi_1 \\ 0 \end{pmatrix} \quad \text{或} \quad \Psi = \psi_2 \chi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ \psi_2 \end{pmatrix}$$

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + U(r) + \frac{eB}{2m_e c}(\hat{L}_z + 2\hat{S}_z) \right) \begin{pmatrix} \psi_1 \\ 0 \end{pmatrix} = E \begin{pmatrix} \psi_1 \\ 0 \end{pmatrix}$$

$$\because \quad \hat{S}_z \begin{pmatrix} \Psi_1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} \Psi_1 \\ 0 \end{pmatrix} \quad \therefore \quad \left(-\frac{\hbar^2}{2m_e}\nabla^2 + U(r) + \frac{eB}{2m_e c}(\hat{L}_z + \hbar) \right) \begin{pmatrix} \psi_1 \\ 0 \end{pmatrix} = E \begin{pmatrix} \psi_1 \\ 0 \end{pmatrix}$$

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + U(r) + \frac{eB}{2m_e c}(\hat{L}_z + \hbar) \right) \psi_1 = E\psi_1$$

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + U(r) + \frac{eB}{2m_e c}(\hat{L}_z - \hbar) \right) \psi_2 = E\psi_2$$

方程求解

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2+U(r)+\frac{eB}{2m_e c}(\hat{L}_z+\hbar)\right)\psi_1=E\psi_1$$

（a） **B=0**

$$\Psi_1=\Psi_2=\Psi_{nlm}=R_{nl}(r)Y_{lm}(\theta,\varphi)$$

a.I 氢原子

$$U(r)=-\frac{e^2}{r}\qquad E_n=-\frac{m_e e^4}{2\hbar^2 n^2}$$

a.II 类氢原子

Li, Na, ... 等碱金属原子，由于核外电子有屏蔽效应，能量不仅与**n**，而且与**l**有关

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2+U(r)\right)\psi_{nlm}=E_{nl}\psi_{nlm}$$

（b） B ≠0

对于 $\hat{L}_z\psi_{nlm} = \hat{L}_z R_{nl}(r)Y_{lm}(\theta,\varphi) = R_{nl}(r)\hat{L}_z Y_{lm}(\theta,\varphi)$

$= m\hbar R_{nl}(r)Y_{lm}(\theta,\varphi) = m\hbar\psi_{nlm}$

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + U(r) + \frac{eB}{2m_e c}(\hat{L}_z + \hbar)\right)\psi_{nlm} = E\psi_{nlm}$$

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + U(r)\right)\psi_{nlm} + \frac{eB}{2m_e c}(m\hbar + \hbar)\psi_{nlm} = E\psi_{nlm}$$

$$E_{nl}\psi_{nlm} + \frac{e\hbar B}{2m_e c}(m+1)\psi_{nlm} = E\psi_{nlm}$$

$$\Longrightarrow \quad E = E_{nl} + \frac{e\hbar B}{2m_e c}(m+1) \qquad S_z = \frac{\hbar}{2}$$

$$E = E_{nl} + \frac{e\hbar B}{2m_e c}(m-1) \qquad S_z = -\frac{\hbar}{2}$$

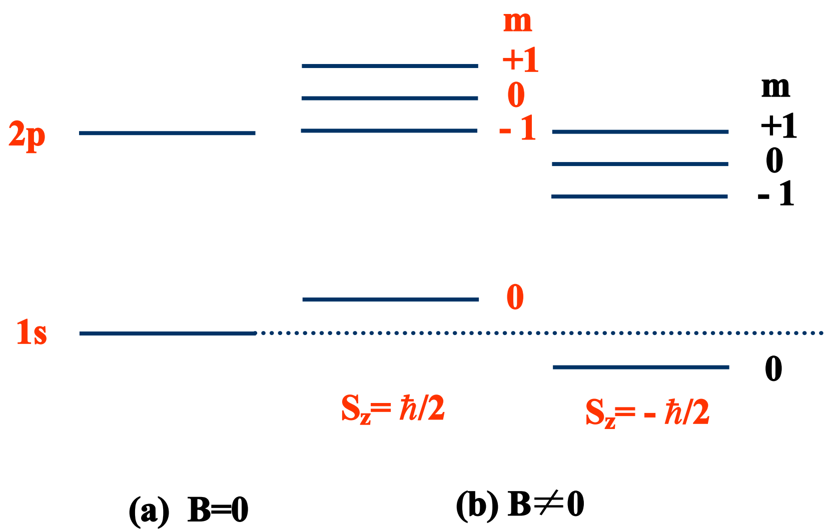
简单塞曼效应

$$E_{nlm}=\begin{cases}E_{nl}+\dfrac{e\hbar B}{2m_e c}(m+1) & S_z=\dfrac{\hbar}{2}\\ E_{nl}+\dfrac{e\hbar B}{2m_e c}(m-1) & S_z=-\dfrac{\hbar}{2}\end{cases}$$

结果表明：在外磁场中，能级与m有关，原来m不同而能量相同的简并现象被外磁场消除。其次，由于外磁场的存在，能量与自旋有关。当原子处于s态时，l=m=0，原来的能级分裂为两个，如施特恩-格拉赫实验所观察到的。

$$E_{nlm}=E_{n00}=\begin{cases}E_{n0}+\dfrac{e\hbar B}{2m_e c} & (S_z=\dfrac{\hbar}{2})\\ E_{n0}-\dfrac{e\hbar B}{2m_e c} & (S_z=-\dfrac{\hbar}{2})\end{cases}$$

$$E_{nlm}=\begin{cases}E_{nl}+\dfrac{e\hbar B}{2m_e c}(m+1) & S_z=\dfrac{\hbar}{2}\\ E_{nl}+\dfrac{e\hbar B}{2m_e c}(m-1) & S_z=-\dfrac{\hbar}{2}\end{cases}$$



在强磁场中s项和p项的分裂

a. B = 0

$$\omega_0 = \frac{E_{nl} - E_{n'l'}}{\hbar}$$

b. B ≠ 0

$$\omega = \frac{E_{nlm} - E_{n'l'm'}}{\hbar} = \frac{1}{\hbar}\left(E_{nl} + \frac{e\hbar B}{2m_e c}(m \pm 1) - E_{n'l'} - \frac{e\hbar B}{2m_e c}(m' \pm 1) \right)$$

$$= \frac{E_{nl} - E_{n'l'}}{\hbar} + \frac{eB}{2m_e c}(m - m') = \omega_0 + \frac{eB}{2m_e c}\Delta m$$

$$\Delta m = 0, \pm 1 \;\; (\Delta l = \pm 1) \quad \omega = \begin{cases} \omega_0 \\ \omega_0 + \dfrac{eB}{2m_e c} \\ \omega_0 - \dfrac{eB}{2m_e c} \end{cases}$$

§6.4　两个角动量的耦合

（1）总角动量

（2）耦合和非耦合表象

（1）总角动量

$$\hat{\vec{J}}_1 \times \hat{\vec{J}}_1 = i\hbar \hat{\vec{J}}_1 \qquad \hat{\vec{J}}_2 \times \hat{\vec{J}}_2 = i\hbar \hat{\vec{J}}_2$$

$$\left[\hat{\vec{J}}_1, \quad \hat{\vec{J}}_2\right] = 0$$

（a） $\hat{\vec{J}} = \hat{\vec{J}}_1 + \hat{\vec{J}}_2$

$$\left[\hat{J}_x, \quad \hat{J}_y\right] = \left[\hat{J}_{1x} + \hat{J}_{2x}, \quad \hat{J}_{1y} + \hat{J}_{2y}\right] = \left[\hat{J}_{1x}, \quad \hat{J}_{1y}\right] + \left[\hat{J}_{1x}, \quad \hat{J}_{2y}\right] + \left[\hat{J}_{2x}, \quad \hat{J}_{1y}\right] + \left[\hat{J}_{2x}, \quad \hat{J}_{2y}\right]$$

$$= i\hbar \hat{J}_{1z} + 0 + 0 + i\hbar \hat{J}_{2z} = i\hbar(\hat{J}_{1z} + \hat{J}_{2z}) = i\hbar \hat{J}_z$$

$$\begin{cases} \left[\hat{J}_x, \quad \hat{J}_y\right] = i\hbar \hat{J}_z \\ \left[\hat{J}_y, \quad \hat{J}_z\right] = i\hbar \hat{J}_x \\ \left[\hat{J}_z, \quad \hat{J}_x\right] = i\hbar \hat{J}_y \end{cases} \longrightarrow \quad \hat{\vec{J}} \times \hat{\vec{J}} = i\hbar \hat{\vec{J}}$$

$(b) \quad \left[\hat{J}^2, \quad \hat{\vec{J}}\right] = 0$

$$\left[\hat{J}^2, \ \hat{J}_x\right] = \left[\hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2, \ \hat{J}_x\right] = \left[\hat{J}_x^2, \ \hat{J}_x\right] + \left[\hat{J}_y^2, \ \hat{J}_x\right] + \left[\hat{J}_z^2, \ \hat{J}_x\right]$$

$$= 0 + \hat{J}_y\left[\hat{J}_y, \ \hat{J}_x\right] + \left[\hat{J}_y, \ \hat{J}_x\right]\hat{J}_y + \hat{J}_z\left[\hat{J}_z, \ \hat{J}_x\right] + \left[\hat{J}_z, \ \hat{J}_x\right]\hat{J}_z$$

$$= -i\hbar\hat{J}_y\hat{J}_z - i\hbar\hat{J}_z\hat{J}_y + i\hbar\hat{J}_z\hat{J}_y + i\hbar\hat{J}_y\hat{J}_z$$

$$= 0$$

$$\hat{\vec{J}} \times \hat{\vec{J}} = i\hbar\hat{\vec{J}} \longrightarrow \left[\hat{J}^2, \quad \hat{J}_\alpha\right] = 0 \qquad \alpha = x, y, z$$

$(c)\ \left[\hat{J}^2,\quad \hat{J}_i^{\,2}\right]=0 \qquad i=1,2$

$$\left[\hat{J}^2,\quad \hat{J}_1^{\,2}\right]=\left[\hat{J}_1^{\,2}+\hat{J}_2^{\,2}+2\vec{J}_1\bullet\vec{J}_2,\quad \hat{J}_1^{\,2}\right]$$

$$=\left[\hat{J}_1^{\,2},\quad \hat{J}_1^{\,2}\right]+\left[\hat{J}_2^{\,2},\quad \hat{J}_1^{\,2}\right]+2\left[\hat{J}_{1x}\hat{J}_{2x}+\hat{J}_{1y}\hat{J}_{2y}+\hat{J}_{1z}\hat{J}_{2z},\quad \hat{J}_1^{\,2}\right]$$

$$=0+0+2\left[\hat{J}_{1x}\hat{J}_{2x},\quad \hat{J}_1^{\,2}\right]+2\left[\hat{J}_{1y}\hat{J}_{2y},\quad \hat{J}_1^{\,2}\right]+2\left[\hat{J}_{1z}\hat{J}_{2z},\quad \hat{J}_1^{\,2}\right]$$

$$=\mathbf{0}$$

$$\left[\hat{J}_{1x}\hat{J}_{2x},\quad \hat{J}_1^{\,2}\right]=\left[\hat{J}_{1y}\hat{J}_{2y},\quad \hat{J}_1^{\,2}\right]=\left[\hat{J}_{1z}\hat{J}_{2z},\quad \hat{J}_1^{\,2}\right]=0$$

$$\left[\hat{\boldsymbol{J}}^{\,2},\hat{\boldsymbol{J}}_i^{\,2}\right]=\mathbf{0}$$

$$\begin{cases}\left[\hat{\boldsymbol{J}}^{2},\quad \hat{\vec{\boldsymbol{J}}}_1\right]\neq 0\\ \left[\hat{\boldsymbol{J}}^{2},\quad \hat{\vec{\boldsymbol{J}}}_2\right]\neq 0\end{cases} \qquad \left[\hat{\boldsymbol{J}}_{1x}\hat{\boldsymbol{J}}_{2x}+\hat{\boldsymbol{J}}_{1y}\hat{\boldsymbol{J}}_{2y}+\hat{\boldsymbol{J}}_{1z}\hat{\boldsymbol{J}}_{2z},\quad \hat{\vec{\boldsymbol{J}}}_1\right]\neq 0$$

$$(d)\quad \left[\hat{J}_z \quad \hat{J}_i^{\,2}\right]=0 \qquad i=1,2.$$

$$\left[\hat{J}_z,\quad \hat{J}_1^{\,2}\right]=\left[\hat{J}_{1z}+\hat{J}_{2z},\quad \hat{J}_1^{\,2}\right]=\left[\hat{J}_{1z},\quad \hat{J}_1^{\,2}\right]+\left[\hat{J}_{2z},\quad \hat{J}_1^{\,2}\right]=0 \qquad \left[\hat{J}_z,\quad \hat{J}_2^{\,2}\right]=0$$

（2）耦合和非耦合表象

（a）本征函数

$$\hat{J}^{\,2},\hat{J}_z,\hat{J}_1^{\,2},\hat{J}_2^{\,2}$$

耦合表象基矢量

$$\hat{J}_1^{\,2},\hat{J}_{1z},\hat{J}_2^{\,2},\hat{J}_{2z}$$

非耦合表象基矢量

$$|\,j_1,j_2,j,m>$$

$$\hat{J}^2\,|\,j_1,j_2,j,m>=j(j+1)\hbar^2\,|\,j_1,j_2,j,m>$$

$$\hat{J}_z\,|\,j_1,j_2,j,m>=m\hbar\,|\,j_1,j_2,j,m>$$

$$|\,j_1,m_1,j_2,m_2>$$

$$=|\,j_1,m_1>|\,j_2,m_2>$$

这两套基矢量是正交归一和完备的，它们可以相互表示

$$|j_1,j_2,j,m> = \sum_{m_1 m_2} |j_1,m_1,j_2,m_2> \underline{<j_1,m_1,j_2,m_2|j_1,j_2,j,m>}$$

克来布希-高登系数

$$\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z} \rightarrow m = m_1 + m_2$$

$$\mathbf{m_1 = m - m_2}$$

$$|j_1,j_2,j,m> = \sum_{m_2} |j_1,m-m_2,j_2,m_2> \quad <j_1,m-m_2,j_2,m_2|j_1,j_2,j,m>$$

或

$$|j_1,j_2,j,m> = \sum_{m_1} |j_1,m_1,j_2,m-m_1> \quad <j_1,m_1,j_2,m-m_1|j_1,j_2,j,m>$$

（b）j的取值范围（j和j_1,j_2的关系）

i) 对于给定的 j_1 j_2 求 j_{max}

$\mathbf{m = j,\ j-1,\ \ldots,\ -j+1,\ -j \rightarrow m_{max} = j;}$

$\mathbf{m_1 = j_1,\ j_1-1,\ \ldots,\ -j_1+1,\ -j_1 \rightarrow (m_1)_{max} = j_1;}$

$\mathbf{m_2 = j_2,\ j_2-1,\ \ldots,\ -j_2+1,\ -j_2 \rightarrow (m_2)_{max} = j_2;}$

$$\mathbf{m = m_1 + m_2}$$

$$\mathbf{j_{max} = j_1 + j_2}$$

ii) 对于给定的 j_1 j_2求 j_{min}

$|j_1\ m_1\rangle, |j_2\ m_2\rangle$ 基矢的数目分别是 $2j_1+1$ 和 $2j_2+1$ ， 则

$$| j_1, m_1, j_2, m_2\rangle = |j_1, m_1\rangle\ |j_2, m_2\rangle$$

的数目是$(2j_1+1)(2j_2+1)$.

$$\sum_{j=j_{\min}}^{j_{\max}}(2j+1)=(j_{\max}+1)^2-j_{\min}{}^2=(j_1+j_2+1)^2-j_{\min}{}^2$$

$$(j_1+j_2+1)^2 - j_{min}{}^2 = (2j_1+1)(2j_2+1)$$

$$j_{min} = |j_1-j_2|$$

iii) j的取值

$$j = j_1+j_2,\ j_1+j_2-1,\ j_1+j_2-2,\ \ldots\ldots,\ |j_1 - j_2|$$

$$\Delta\ (j_1, j_2, j)$$

求得j和m后，解决了J^2和Jz的本征值问题

$$\hat{J}^2 \,|\, j_1, j_2, j, m> = j(j+1)\hbar^2 \,|\, j_1, j_2, j, m>$$

$$\hat{J}_z \,|\, j_1, j_2, j, m> = m\hbar \,|\, j_1, j_2, j, m>$$

它们的本征矢需知道耦合系数才能确定

$$|\, j_1, j_2, j, m> = \sum_{m_1} |\, j_1, m_1, j_2, m-m_1 >< \underline{j_1, m_1, j_2, m-m_1 \,|\, j_1, j_2, j, m>}$$

该系数可以从专用表中查出. 以下列出了第二个角动量为电子自旋角动量$j_2 = 1/2$ 时的几个矢量耦合系数

$$< j_1, m-m_2, \tfrac{1}{2}, m_2 \mid j_1, \tfrac{1}{2}, j, m > \quad (j_1 > 0)$$

j	$m_2 = \frac{1}{2}$	$m_2 = -\frac{1}{2}$
$j_1 + \frac{1}{2}$	$\sqrt{\dfrac{j_1 + m + \frac{1}{2}}{2j_1 + 1}}$	$\sqrt{\dfrac{j_1 - m + \frac{1}{2}}{2j_1 + 1}}$
$j_1 - \frac{1}{2}$	$-\sqrt{\dfrac{j_1 - m + \frac{1}{2}}{2j_1 + 1}}$	$\sqrt{\dfrac{j_1 + m + \frac{1}{2}}{2j_1 + 1}}$

$$|j_1, \tfrac{1}{2}, j_1+\tfrac{1}{2}, m> \; = \sqrt{\frac{j_1+m+\frac{1}{2}}{2j_1+1}}\,|j_1, m-\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}> \; + \; \sqrt{\frac{j_1-m+\frac{1}{2}}{2j_1+1}}\,|j_1, m+\tfrac{1}{2}, \tfrac{1}{2}, -\tfrac{1}{2}>$$

$$|j_1, \tfrac{1}{2}, j_1-\tfrac{1}{2}, m> \; = -\sqrt{\frac{j_1-m+\frac{1}{2}}{2j_1+1}}\,|j_1, m-\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}> \; + \; \sqrt{\frac{j_1+m+\frac{1}{2}}{2j_1+1}}\,|j_1, m+\tfrac{1}{2}, \tfrac{1}{2}, -\tfrac{1}{2}>$$

§6.5 光谱的精细结构

这一节讨论在没有外场的情况下，电子自旋对类氢原子的能级和谱线的影响。

不考虑电子自旋与轨道相互作用的能量，类氢原子的哈密顿

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e}\nabla^2 + U(r) \qquad U(r) = -\frac{Ze_s^2}{r}$$

H_0, L^2, L_z, 和S_z相互对易，有共同本征函数（无耦合表象基矢）

$$\Phi_{nlm_lm_s}(r,\theta,\varphi,s_z) = R_{nl}(r)Y_{lm_l}(\theta,\varphi)\chi_{m_s} \Rightarrow |n,l,m_l,m_s>$$

$$E_n = -\frac{m_eZ^2e_s^4}{2\hbar^2n^2} \qquad n = 1,2,3,\cdots$$

能量简并度为n^2，考虑自旋后的简并度为$2n^2$

电子的总角动量算符为

$$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$$

由于L^2, J^2, Jz 和H_0相互对易 (S^2是常数，与任何算符都对易)，它们有共同本征函数（耦合表象基矢）

$$\Psi_{nljm}(r,\theta,\varphi,s_z) = R_{nl}(r)u_{ljm}(\theta,\varphi,s_z) \Rightarrow |n,l,j,m>$$

考虑自旋和轨道相互作用能，其表达式为

$$\hat{H}' = \frac{1}{2m_e^{\ 2}c^2}\frac{1}{r}\frac{dU}{dr}\hat{\vec{L}} \bullet \hat{\vec{S}} = \xi(r)\vec{L} \bullet \vec{S}$$

自旋轨道耦合项

体系哈密顿为

$$\hat{H} = \hat{H}_0 + \hat{H}' = -\frac{\hbar^2}{2m_e}\nabla^2 + U(r) + \xi(r)\vec{L} \bullet \vec{S}$$

由于H含有自旋-轨道耦合项，Lz、Sz和H不再对易，这时电子的态不能用量子数m_l和 m_s 来描写.

但 L^2, J^2, J_z 与H仍然对易，量子数 l, j, m可以描写电子的状态.

证明:

$$\hat{\vec{J}}^2=(\hat{\vec{L}}+\hat{\vec{S}})^2=\hat{L}^2+\hat{S}^2+2\hat{\vec{L}}\bullet\hat{\vec{S}}$$

$$\hat{\vec{L}}\bullet\hat{\vec{S}}=\tfrac{1}{2}[\hat{\vec{J}}^2-\hat{L}^2-\hat{S}^2]=\tfrac{1}{2}[\hat{\vec{J}}^2-\hat{L}^2-\tfrac{3}{4}\hbar^2]$$

$$[\hat{J}^2,\quad \hat{\vec{L}}\bullet\hat{\vec{S}}]=0$$

$$[\hat{J}_z,\quad \hat{\vec{L}}\bullet\hat{\vec{S}}]=0$$

$$[\hat{L}^2,\quad \hat{\vec{L}}\bullet\hat{\vec{S}}]=0$$

L^2, J^2, Jz 与 H’和H_0对易，因而与H对易.

微扰法求解

$$(\hat{H}_0+\hat{H}')\psi = E\psi$$

由于 H_0 的本征值是简并的，所以采用简并微扰方法求解

H_0 有两种波函数：耦合和非耦合表象波函数。其中耦合表象中 H' 矩阵是对角化的，可以省去解久期方程的步骤

若 $\psi=\sum_{ljm} C_{ljm}|n,l,j,m>$ 则

$$\sum_{ljm}[H'_{l'j'm',ljm}-E_n^{(1)}\delta_{l'l}\delta_{j'j}\delta_{m'm}]C_{ljm}=0$$

矩阵元

$$H'_{l'j'm',ljm}=<n,l',j',m'|\hat{H}'|n,l,j,m>$$

$$=\int_0^\infty R^*_{nl'}\xi(r)R_{nl}r^2dr<l',j',m'|\hat{\vec{L}}\bullet\hat{\vec{S}}|l,j,m>$$

$$\int_0^\infty R_{nl'}^* \xi(r) R_{nl} r^2 dr < l', j', m' | \hat{\vec{L}} \bullet \hat{\vec{S}} | l, j, m >$$

$$= < nl' | \xi(r) | nl > < l', j', m' | \tfrac{1}{2}[\hat{J}^2 - \hat{L}^2 - \tfrac{3}{4}\hbar^2] | l, j, m >$$

$$= < nl' | \xi(r) | nl > \tfrac{1}{2}[j(j+1) - l(l+1) - \tfrac{3}{4}]\hbar^2 < l', \tfrac{1}{2}, j', m' | l, \tfrac{1}{2}, j, m >$$

$$= < nl | \xi(r) | nl > \tfrac{1}{2}[j(j+1) - l(l+1) - \tfrac{3}{4}]\hbar^2 \delta_{l'l} \delta_{j'j} \delta_{m'm}$$

$$= H'_{nlj} \delta_{l'l} \delta_{j'j} \delta_{m'm}$$

$$= H'_{l'j'm',ljm}$$

$$H'_{nlj} = < nl | \xi(r) | nl > \tfrac{1}{2}[j(j+1) - l(l+1) - \tfrac{3}{4}]\hbar^2$$

$$< nl | \xi(r) | nl > = \int_0^\infty R_{nl}^* \xi(r) R_{nl} r^2 dr = \int_0^\infty R_{nl}^2 \xi(r) r^2 dr$$

$$\sum_{ljm} [H'_{l'j'm',ljm} - E_n^{(1)} \delta_{l'l} \delta_{j'j} \delta_{m'm}] C_{ljm} = \sum_{ljm} [H'_{nlj} - E_n^{(1)}] \delta_{l'l} \delta_{j'j} \delta_{m'm} C_{ljm} = 0$$

$$\sum_{ljm} [H'_{nlj} - E_n^{(1)}]\delta_{l'l}\delta_{j'j}\delta_{m'm}C_{ljm} = 0$$

$$[H'_{nl'j'} - E_n^{(1)}]C_{l'j'm'} = 0$$

$C_{ljm} \neq 0$

$$[H'_{nlj} - E_n^{(1)}]C_{ljm} = 0$$

$$[H'_{nlj} - E_n^{(1)}] = 0$$

$$E_n^{(1)} = E_{nlj}^{(1)} = H'_{nlj} = < nl \,|\, \xi(r) \,|\, nl > \tfrac{1}{2}[j(j+1) - l(l+1) - \tfrac{3}{4}]\hbar^2$$

自旋轨道耦合使原来简并的能级分裂开来，即简并被消除，但上式中不含量子数m，m可以取2j+1个值，还有2j+1度简并保留下来

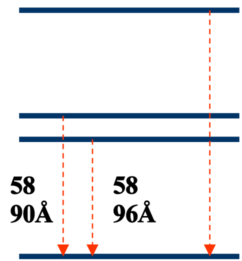
当n和l给定后，j可以取两个值：$j=l\pm1/2(l=0$除外)，即具有相同的量子数n,l的能级有两个，它们之间的差别很小，这就是产生光谱线精细结构的原因

$n=2,\ \ l=0,\ \ j=\frac{1}{2},\ \ 2^2S_{\frac{1}{2}}$

$n=2,\ \ l=1,\ \ j=\frac{3}{2},\ \ 2^2P_{\frac{3}{2}}$

$n=2,\ \ l=1,\ \ j=\frac{1}{2},\ \ 2^2P_{\frac{1}{2}}$

$n=1,\ \ l=0,\ \ j=\frac{1}{2},\ \ 1^2S_{\frac{1}{2}}$



钠原子2P项的精细结构

$$E_n^{(1)}=E_{nlj}^{(1)}=H'_{nlj}=<nl\,|\,\xi(r)\,|\,nl>\tfrac{1}{2}[j(j+1)-l(l+1)-\tfrac{3}{4}]\hbar^2$$

<ξ (r)>

$$U(r)=-\frac{Ze_s^{\ 2}}{r}\qquad \xi(r)=\frac{1}{2m_e^{\ 2}c^2}\frac{1}{r}\frac{dU}{dr}=\frac{Ze_s^{\ 2}}{2m_e^{\ 2}c^2}\frac{1}{r^3}$$

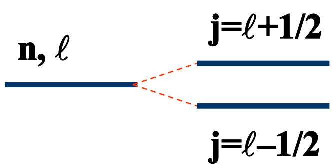
$$\langle \xi(r) \rangle = \int_0^\infty R_{nl}^2(r)\xi(r)r^2 dr = \frac{Ze_s^2}{2m_e^2c^2}\int_0^\infty \frac{R_{nl}^2(r)}{r}dr$$

$$= \frac{e_s^2}{2m_e^2c^2a_0^3}\frac{Z^4}{n^3 l(l+\frac{1}{2})(l+1)} \qquad a_0 = \frac{\hbar^2}{m_e e_s^2}$$

$$\begin{cases} E_{nl,j=l+\frac{1}{2}} = E_n^{(0)} + \frac{m_e c^2}{2}\left(\frac{\alpha Z}{n}\right)^4 \frac{n}{(2l+1)(l+1)} \\ E_{nl,j=l-\frac{1}{2}} = E_n^{(0)} - \frac{m_e c^2}{2}\left(\frac{\alpha Z}{n}\right)^4 \frac{n}{(2l+1)l} \end{cases}$$

$$\alpha = \frac{e_s^2}{\hbar c} = \frac{1}{137}$$

精细结构常数



波函数的零级近似可以是Ψ_{nljm}，也可以Ψ_{nljm}是对不同m的线性组合，它可用无耦合表象来表示，如下所示:

$$|n,l,l+\tfrac{1}{2},m> = \sqrt{\frac{l+m+\frac{1}{2}}{2l+1}}|n,l,m-\tfrac{1}{2},\tfrac{1}{2}> + \sqrt{\frac{l-m+\frac{1}{2}}{2l+1}}|n,l,m+\tfrac{1}{2},-\tfrac{1}{2}>$$

$$|n,l,l-\tfrac{1}{2},m> = -\sqrt{\frac{l-m+\frac{1}{2}}{2l+1}}|n,l,m-\tfrac{1}{2},\tfrac{1}{2}> + \sqrt{\frac{l+m+\frac{1}{2}}{2l+1}}|n,l,m+\tfrac{1}{2},-\tfrac{1}{2}>$$

以上讨论适用于$l>0$的情况，当$l=0$时，无自旋-轨道耦合，能级没有变化

作业

7.2
7.4
7.5

§6.6　全同粒子的特性

(1) 全同粒子和全同性原理

(2) 波函数的对称性

(3) 波函数对称性不随时间改变

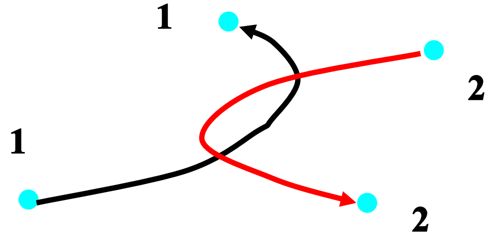
(4) 费米子和波色子

(1)　全同粒子和全同性原理

（a）全同粒子

质量、电荷、自旋和其它固有性质完全相同的微观粒子称为全同粒子

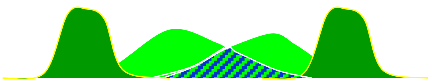
（b）与经典粒子的区别



$$\left\{\begin{array}{l}\text{位置}\\ \text{速度}\end{array}\right. \Rightarrow \text{轨道}$$

（c）微观粒子的不可区分性

微观粒子的运动 $\xrightarrow{\text{遵循}}$ 量子力学 $\longrightarrow$ 波函数



在波函数重叠区粒子不可区分

（d）全同粒子

对于全同粒子组成的体系，两全同粒子相互取代不引起物理状态的改变，这个论断称为全同性原理，它是量子力学的基本原理之一

(2)　波函数的对称性

（a）哈密顿的对称性

$$\hat{H}(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)=\sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m}\nabla_i^2+U(q_i,t)\right]+\sum_{i<j}^{N}W(q_i,q_j)$$

$$q_i\equiv\{\vec{r}_i,s_i\}$$

$$\hat{H}(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)=\hat{H}(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)$$

（b）波函数的对称性和反对称性

$$i\hbar\frac{\partial}{\partial t}\Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)$$

$$=\hat{H}(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)\Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)$$

$$i\hbar\frac{\partial}{\partial t}\Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)$$

$$=\hat{H}(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)\Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)$$

$$=\hat{H}(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)\Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)$$

$$\begin{cases}\Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)\\ \Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)\end{cases}$$

若**(i,j)**是方程的解，则**(j,i)**也是方程的解，根据全同性原理，二者描写的是同样一个状态，它们之间相差一个常数因子

$$\Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)=\lambda\Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)$$

$$\Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)=\lambda\Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)$$
$$=\lambda^2\Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)$$

$$\lambda^2=1 \quad \Rightarrow \quad \lambda=\pm 1$$

$\lambda=1$ $\quad \Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)=\Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)$

$\lambda=-1$ $\quad \Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)=-\Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)$

$$\hat{P}_{ij}\Phi(i,j)=\Phi(j,i)=\lambda\Phi(i,j)$$

$$\hat{P}_{ij}^2\Phi(i,j)=\hat{P}_{ij}\hat{P}_{ij}\Phi(i,j)=\lambda\hat{P}_{ij}\Phi(i,j)=\lambda^2\Phi(i,j)$$

$\lambda=\pm 1$,

对称波函数是算符 $\hat{P}_{ij}$ 的本征态

$\lambda=+1$;

交换对称波函数

$\lambda=-1$

交换反对称波函数

(3)　波函数对称性不随时间改变

证明

假定全同粒子体系波函数 **Φs** 在时刻**t**是对称的，则由于**H**的对称性，**HΦs**在这一时刻也是对称的

$$i\hbar\frac{\partial}{\partial t}\Phi_s = \hat{H}\Phi_s \qquad \textbf{t+dt} \qquad \Phi_s + \frac{\partial}{\partial t}\Phi_s dt$$

反对称情形也可如是证明。以此类推，在以后任何时刻波函数都是对称的或反对称的。描写全同粒子体系状态的波函数只能是对称的或反对称的，它们的对称性不随时间改变，如果体系在某一时刻处于对称（反对称）的态，则它将永远处于对称（反对称）的态上。

实验证明：电子、质子、中子这些自旋为（**h/4**π）的粒子以及其他自旋为（**h/4**π）奇数倍的粒子组成的全同粒子体系的波函数是反对称的，这类粒子服从费米-狄拉克统计，称为费米子;光子（自旋为**1**），基态氦原子（自旋为零）、α粒子（自旋为零）以及其他自旋为零或为（**h/2**π）整数倍的粒子，这类粒子服从玻色-爱因斯坦统计，称为玻色子。

§6.7 全同粒子体系波函数 泡利原理

（1）2个全同粒子体系波函数

（2）N个全同粒子体系波函数

（3）泡利原理

（1） 2个全同粒子体系波函数

(a) 对称和反对称波函数的组成

a.I 哈密顿（不考虑相互作用）

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{\hbar^2}{2\mu}\nabla_2^2 + V(q_1) + V(q_2)$$
$$= \hat{H}_0(q_1) + \hat{H}_0(q_2)$$

a.II 单粒子波函数

$\hat{H}_0$ 对全同粒子是相同的， 假定它不显含时间

$$\begin{cases} \hat{H}_0(q_1)\phi_i(q_1) = \varepsilon_i\phi_i(q_1) \\ \hat{H}_0(q_2)\phi_i(q_2) = \varepsilon_i\phi_i(q_2) \end{cases}$$

$\phi_i(q_n)$ $(n = 1,2,...)$

是单粒子波函数

a.III 交换简并

粒子1处于i态，2处于j态，则体系能量和波函数如下:

$$\begin{cases} E=\varepsilon_i+\varepsilon_j \\ \Phi\ (q_1,q_2)=\phi_i(q_1)\phi_j(q_2) \end{cases}$$

证明:

$$\hat{H}\Phi\ (q_1,q_2)=E\Phi\ (q_1,q_2)$$

$$[\hat{H}_0(q_1)+\hat{H}_0(q_2)]\Phi\ (q_1,q_2)=[\hat{H}_0(q_1)+\hat{H}_0(q_2)]\phi_i(q_1)\phi_j(q_2)$$

$$=[\hat{H}_0(q_1)\phi_i(q_1)]\phi_j(q_2)+\phi_i(q_1)[\hat{H}_0(q_2)\phi_j(q_2)]$$

$$=\varepsilon_i\phi_i(q_1)\phi_j(q_2)+\varepsilon_j\phi_i(q_1)\phi_j(q_2)$$

$$=(\varepsilon_i+\varepsilon_j)\phi_i(q_1)\phi_j(q_2)=E\Phi\ (q_1,q_2)$$

粒子1处于j态，2处于i态，则体系能量和波函数如下:

$$\begin{cases} E=\varepsilon_i+\varepsilon_j \\ \Phi\ (q_2,q_1)=\phi_i(q_2)\phi_j(q_1) \end{cases}$$

态 $\Phi\ (q_1,q_2)$和 $\Phi\ (q_2,q_1)$在能量上是简并的，它们可以通过交换 $q_1 \Leftrightarrow q_2$来实现，称为交换简并

a.IV 满足对称条件的波函数组成

i = j　(q1,q2) 和 (q2,q1)是对称波函数;
i ≠j　(q1,q2) 和 (q2,q1)的对称性不确定

根据全同粒子体系波函数的条件，构建对称性波函数

$$\Phi_S(q_1,q_2)=C[\Phi(q_1,q_2)+\Phi(q_2,q_1)]$$

$$\Phi_A(q_1,q_2)=C[\Phi(q_1,q_2)-\Phi(q_2,q_1)]$$

上述两个波函数都是**H**的本征函数，能量都为

$$E=\varepsilon_i+\varepsilon_j$$

两个费米子组成体系的波函数为反对称波函数，若它们状态相同，则波函数为零，无意义，因此，体系中两费米子不能处于同一状态，这是泡利原理在两粒子组成的体系中的表述

a.V 体系对称波函数和反对称波函数的归一化

首先: 若单粒子波函数是正交归一化的，则 $\Phi(q1, q2)$ 和 $\Phi(q2, q1)$也是正交归一化的

证明:

$$\iint \Phi^*(q_1,q_2)\Phi(q_1,q_2)dq_1dq_2 = \iint \phi_i^*(q_1)\phi_j^*(q_2)\phi_i(q_1)\phi_j(q_2)dq_1dq_2$$

$$= \int \phi_i^*(q_1)\phi_i(q_1)dq_1 \int \phi_j^*(q_2)\phi_j(q_2)dq_2 = 1$$

同理: $$\iint \Phi^*(q_2,q_1)\Phi(q_2,q_1)dq_1dq_2 = 1$$

但 $$\iint \Phi^*(q_2,q_1)\Phi(q_1,q_2)dq_1dq_2 = \iint \phi_i^*(q_2)\phi_j^*(q_1)\phi_i(q_1)\phi_j(q_2)dq_1dq_2$$

$$= \int \phi_j^*(q_1)\phi_i(q_1)dq_1 \int \phi_i^*(q_2)\phi_j(q_2)dq_2 = 0$$

同理:

$$\iint \Phi^*(q_1,q_2)\Phi(q_2,q_1)dq_1dq_2 = 0$$

其次:体系对称波函数和反对称波函数的的正交归一化

$$1=\iint \Phi_S{}^*\Phi_S dq_1dq_2$$

$$=C^2\iint [\Phi^*(q_1,q_2)+\Phi^*(q_2,q_1)][\Phi(q_1,q_2)+\Phi(q_2,q_1)]dq_1dq_2$$

$$=C^2\iint [\Phi^*(q_1,q_2)\Phi(q_1,q_2)+\Phi^*(q_2,q_1)\Phi(q_1,q_2)+$$

$$+\Phi^*(q_1,q_2)\Phi(q_2,q_1)+\Phi^*(q_2,q_1)\Phi(q_2,q_1)]dq_1dq_2$$

$$=C^2[1+0++0+1]=2C^2 \qquad \Rightarrow \qquad C=\frac{1}{\sqrt{2}}$$

$$\Phi_S(q_1,q_2)=\frac{1}{\sqrt{2}}[\Phi(q_1,q_2)+\Phi(q_2,q_1)]$$

同理 $\Phi_A(q_1,q_2)=\frac{1}{\sqrt{2}}[\Phi(q_1,q_2)-\Phi(q_2,q_1)]$

以上讨论适用于无相互作用情形，对有相互作用情形有

$$\begin{cases}\Phi(q_1,q_2)\neq\phi_i(q_1)\phi_j(q_2)\\ \Phi(q_2,q_1)\neq\phi_i(q_2)\phi_j(q_1)\end{cases} \quad \text{和} \quad \begin{cases}\hat{H}(q_1,q_2)\Phi(q_1,q_2)=E\Phi(q_1,q_2)\\ \hat{H}(q_1,q_2)\Phi(q_2,q_1)=E\Phi(q_2,q_1)\end{cases}$$

H有对称性

且 $\Phi_{S,A}(q_1,q_2)=\frac{1}{\sqrt{2}}[\Phi(q_1,q_2)\pm\Phi(q_2,q_1)]$

（2）N 个全同粒子体系波函数

（a）薛定谔方程求解

$$\hat{H}=\hat{H}_0(q_1)+\hat{H}_0(q_2)+\cdots+\hat{H}_0(q_N)=\sum_{n=1}^{N}\hat{H}_0(q_n)$$

单粒子本征方程:

$$\begin{cases}\hat{H}_0(q_1)\phi_i(q_1)=\varepsilon_i\phi_i(q_1)\\ \hat{H}_0(q_2)\phi_j(q_2)=\varepsilon_j\phi_j(q_2)\\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\ \hat{H}_0(q_N)\phi_k(q_N)=\varepsilon_k\phi_k(q_N)\end{cases}$$

$$\hat{H}\Phi=E\Phi$$

$$\begin{cases}E=\varepsilon_i+\varepsilon_j+\cdots+\varepsilon_k\\ \Phi(q_1,q_2,\cdots q_N)=\phi_i(q_1)\phi_j(q_2)\cdots\phi_k(q_N)\end{cases}$$

（b）玻色子体系和波函数对称性

2个玻色子，体系对称波函数为

$$\Phi_S(q_1,q_2)=\frac{1}{\sqrt{2}}[\Phi(q_1,q_2)+\Phi(q_2,q_1)]=\frac{1}{\sqrt{2}}[\phi_i(q_1)\phi_j(q_2)+\phi_i(q_2)\phi_j(q_1)]$$

粒子1,2在态i， j的一种排列

N个玻色子，体系对称波函数为

$$\Phi_S(q_1,q_2\cdots q_N)=C\sum_p P[\phi_i(q_1)\phi_j(q_2)\cdots\phi_k(q_N)]$$

$$C=\sqrt{\frac{\prod_{k=1} n_k!}{N!}}$$

n_k 为处于单粒子**k**态的粒子数目

例如：N＝3的玻色子体系，有三个单粒子态 1, 2, 3, 现求该体系的对称波函数

I。n1=n2=n3=1

$$\Phi_S^{111}(q_1,q_2,q_3)=\frac{1}{\sqrt{3}}[\phi_1(q_1)\phi_2(q_2)\phi_3(q_3)+\phi_1(q_2)\phi_2(q_3)\phi_3(q_1)$$
$$+\phi_1(q_3)\phi_2(q_1)\phi_3(q_2)+\phi_1(q_3)\phi_2(q_2)\phi_3(q_1)$$
$$+\phi_1(q_2)\phi_2(q_1)\phi_3(q_3)+\phi_1(q_1)\phi_2(q_3)\phi_3(q_2)]$$

II。n1=3，n2=n3=0
n2=3，n1=n3=0
n3=3，n2=n1=0

$$\Phi_S^{300}(q_1,q_2,q_3)=\phi_1(q_1)\phi_1(q_2)\phi_1(q_3)$$
$$\Phi_S^{030}(q_1,q_2,q_3)=\phi_2(q_1)\phi_2(q_2)\phi_2(q_3)$$
$$\Phi_S^{003}(q_1,q_2,q_3)=\phi_3(q_1)\phi_3(q_2)\phi_3(q_3)$$

III。n1=2，n2=1，n3=0

$$\Phi_S^{210}(q_1,q_2,q_3)=\sqrt{\frac{2!1!0!}{3!}}[\phi_1(q_1)\phi_1(q_2)\phi_2(q_3)+\phi_1(q_1)\phi_1(q_3)\phi_2(q_2)+\phi_1(q_3)\phi_1(q_2)\phi_2(q_1)]$$

n1=1， n2=0， n3=2

$$\Phi_S^{102}(q_1,q_2,q_3)=\sqrt{\frac{1!0!2!}{3!}}[\phi_1(q_1)\phi_3(q_2)\phi_3(q_3)+\phi_1(q_2)\phi_3(q_1)\phi_3(q_3)+\phi_1(q_3)\phi_3(q_2)\phi_3(q_1)]$$

n1=0， n2=1， n3=2

$$\Phi_S^{012}(q_1,q_2,q_3)=\sqrt{\frac{0!1!2!}{3!}}[\phi_2(q_1)\phi_3(q_2)\phi_3(q_3)+\phi_2(q_2)\phi_3(q_1)\phi_3(q_3)+\phi_2(q_3)\phi_3(q_2)\phi_3(q_1)]$$

n1=0， n2=2， n3=1

$$\Phi_S^{021}(q_1,q_2,q_3)=\sqrt{\frac{0!2!1!}{3!}}[\phi_2(q_1)\phi_2(q_2)\phi_3(q_3)+\phi_2(q_1)\phi_2(q_3)\phi_3(q_2)+\phi_2(q_3)\phi_2(q_2)\phi_3(q_1)]$$

n1=1， n2=2， n3=0

$$\Phi_S^{120}(q_1,q_2,q_3)=\sqrt{\frac{1!2!0!}{3!}}[\phi_1(q_1)\phi_2(q_2)\phi_2(q_3)+\phi_1(q_2)\phi_2(q_1)\phi_2(q_3)+\phi_1(q_3)\phi_2(q_2)\phi_2(q_1)]$$

n1=2， n2=0， n3=1

$$\Phi_S^{201}(q_1,q_2,q_3)=\sqrt{\frac{2!0!1!}{3!}}[\phi_1(q_1)\phi_1(q_2)\phi_3(q_3)+\phi_1(q_1)\phi_1(q_3)\phi_3(q_2)+\phi_1(q_3)\phi_1(q_2)\phi_3(q_1)]$$

注意　以上实际是重复组合问题，计算公式为

$$C_m^{\tilde{n}} = C_{m+n-1}^n = \frac{(m+n-1)!}{n!(m-1)!}$$

$$C_3^{\tilde{3}} = C_{3+3-1}^3 = C_5^3$$

$$= \frac{5!}{3!(5-3)!} = 10$$

（c）费米子体系和反对称波函数

$$\Phi_A(q_1,q_2)=\frac{1}{\sqrt{2}}[\Phi\ (q_1,q_2)-\Phi\ (q_2,q_1)]=\frac{1}{\sqrt{2}}\begin{vmatrix}\phi_i(q_1) & \phi_i(q_2)\\ \phi_j(q_1) & \phi_j(q_2)\end{vmatrix}$$

$$\Phi_A(q_1,q_2\cdots q_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_i(q_1) & \phi_i(q_2) & \cdots & \phi_i(q_N)\\ \phi_j(q_1) & \phi_j(q_2) & \cdots & \phi_j(q_N)\\ \cdots & \cdots & \cdots & \cdots\\ \phi_k(q_1) & \phi_k(q_2) & \cdots & \phi_k(q_N)\end{vmatrix}$$

讨论

c.I Φ_A 是方程 $H\Phi_A=E\Phi_A$ 的解

c.II 斯莱特行列式为方程的解，交换任何两粒子，即调换两列，行列式改变符号，反对称函数

（3）泡利原理

（a）2费米子体系

$$\Phi_A(q_1,q_2)=\frac{1}{\sqrt{2}}[\phi_i(q_1)\phi_j(q_2)-\phi_i(q_2)\phi_j(q_1)]=\frac{1}{\sqrt{2}}\begin{vmatrix}\phi_i(q_1) & \phi_i(q_2)\\ \phi_j(q_1) & \phi_j(q_2)\end{vmatrix}$$

$$\Phi_A(q_1,q_2)=\frac{1}{\sqrt{2}}[\phi_i(q_1)\phi_i(q_2)-\phi_i(q_2)\phi_i(q_1)]=0$$

$$=\frac{1}{\sqrt{2}}\begin{vmatrix}\phi_i(q_1) & \phi_i(q_2)\\ \phi_i(q_1) & \phi_i(q_2)\end{vmatrix}$$

（b）N费米子体系

$$\Phi_A(q_1,q_2\cdots q_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_i(q_1) & \phi_i(q_2) & \cdots & \phi_i(q_N)\\ \phi_j(q_1) & \phi_j(q_2) & \cdots & \phi_j(q_N)\\ \cdots & \cdots & \cdots & \cdots\\ \phi_k(q_1) & \phi_k(q_2) & \cdots & \phi_k(q_N)\end{vmatrix}$$

$$\Phi_A(q_1,q_2\cdots q_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_i(q_1) & \phi_i(q_2) & \cdots & \phi_i(q_N)\\ \phi_i(q_1) & \phi_i(q_2) & \cdots & \phi_i(q_N)\\ \cdots & \cdots & \cdots & \cdots\\ \phi_k(q_1) & \phi_k(q_2) & \cdots & \phi_k(q_N)\end{vmatrix}=0$$

不能有两个或两个以上的费米子处于同一状态——泡利不相容原理----反对称波函数的要求

（c）无自旋-轨道相互作用情形

$$\Phi(\vec{r}_1,s_1;\vec{r}_2,s_2\cdots\vec{r}_N,s_N)=\phi(\vec{r}_1,\vec{r}_2,\cdots\vec{r}_N)\chi(s_1,s_2\cdots s_N)$$

如果粒子是费米子，上述体系波函数是反对称的

§6.8　两个电子的自旋函数

（1）两个电子波函数的组成

（2）总自旋S^2，Sz的本征函数

（3）两个电子波函数的再解释

（1）两个电子波函数的组成

哈密顿算符不含电子自旋相互作用项时

$$\chi(s_{1z},s_{2z})=\chi_{\alpha 1}(s_{1z})\chi_{\alpha 2}(s_{2z}) \qquad (\alpha_1,\alpha_2=\pm\tfrac{1}{2})$$

$$\chi_{\frac{1}{2}}(s_{1z})\chi_{\frac{1}{2}}(s_{2z}) \qquad \chi_{\frac{1}{2}}(s_{1z})\chi_{-\frac{1}{2}}(s_{2z})$$

$$\chi_{-\frac{1}{2}}(s_{1z})\chi_{\frac{1}{2}}(s_{2z}) \qquad \chi_{-\frac{1}{2}}(s_{1z})\chi_{-\frac{1}{2}}(s_{2z})$$

$$\begin{cases} \chi_s^{I}=\chi_{\frac{1}{2}}(s_{1z})\chi_{\frac{1}{2}}(s_{2z}) \\ \chi_s^{II}=\chi_{-\frac{1}{2}}(s_{1z})\chi_{-\frac{1}{2}}(s_{2z}) \\ \chi_s^{III}=\sqrt{\frac{1}{2}}[\chi_{\frac{1}{2}}(s_{1z})\chi_{-\frac{1}{2}}(s_{2z})+\chi_{\frac{1}{2}}(s_{2z})\chi_{-\frac{1}{2}}(s_{1z})] \end{cases}$$

$$\chi_A=\sqrt{\frac{1}{2}}[\chi_{\frac{1}{2}}(s_{1z})\chi_{-\frac{1}{2}}(s_{2z})-\chi_{\frac{1}{2}}(s_{2z})\chi_{-\frac{1}{2}}(s_{1z})]$$

（2）总自旋S^2，S_z的本征函数

（a）总自旋算符

$$\hat{\vec{S}} = \hat{\vec{s}}_1 + \hat{\vec{s}}_2 \qquad \hat{S}_z = s_{1z} + s_{2z} \qquad \hat{S}^2 = (\hat{\vec{s}}_1 + \hat{\vec{s}}_2)^2 = \hat{s}_1^2 + \hat{s}_2^2 + 2(\hat{\vec{s}}_1 \bullet \hat{\vec{s}}_2)$$

$$\hat{\vec{s}}_1 \bullet \hat{\vec{s}}_2 = \hat{s}_{1x}\hat{s}_{2x} + \hat{s}_{1y}\hat{s}_{2y} + \hat{s}_{1z}\hat{s}_{2z} \qquad \hat{S}^2 = \frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2 + 2(\hat{s}_{1x}\hat{s}_{2x} + \hat{s}_{1y}\hat{s}_{2y} + \hat{s}_{1z}\hat{s}_{2z})$$

$$= \frac{3}{2}\hbar^2 + 2(\hat{s}_{1x}\hat{s}_{2x} + \hat{s}_{1y}\hat{s}_{2y} + \hat{s}_{1z}\hat{s}_{2z})$$

$$\hat{S}_x\chi_{\frac{1}{2}} = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix}0\\ 1\end{pmatrix} = \frac{\hbar}{2}\chi_{-\frac{1}{2}} \qquad \hat{S}_x\chi_{-\frac{1}{2}} = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}0\\ 1\end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix}1\\ 0\end{pmatrix} = \frac{\hbar}{2}\chi_{\frac{1}{2}}$$

$$\hat{S}_y\chi_{\frac{1}{2}} = \frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix} = \frac{i\hbar}{2}\begin{pmatrix}0\\ 1\end{pmatrix} = \frac{i\hbar}{2}\chi_{-\frac{1}{2}} \qquad \hat{S}_y\chi_{-\frac{1}{2}} = \frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{pmatrix}0\\ 1\end{pmatrix} = -\frac{i\hbar}{2}\begin{pmatrix}1\\ 0\end{pmatrix} = -\frac{i\hbar}{2}\chi_{\frac{1}{2}}$$

$$\hat{S}_z\chi_{\frac{1}{2}} = \frac{\hbar}{2}\chi_{\frac{1}{2}} \qquad \hat{S}_z\chi_{-\frac{1}{2}} = -\frac{\hbar}{2}\chi_{-\frac{1}{2}}$$

利用上述式子可求出S^2和S_Z在四个态中的本征值，例如

$$\hat{S}^2\chi_S^I$$

$$=[\tfrac{3}{2}\hbar^2+2(\hat{s}_{1x}\hat{s}_{2x}+\hat{s}_{1y}\hat{s}_{2y}+\hat{s}_{1z}\hat{s}_{2z})]\chi_S^I$$

$$=\tfrac{3}{2}\hbar^2\chi_S^I+2(\hat{s}_{1x}\hat{s}_{2x}+\hat{s}_{1y}\hat{s}_{2y}+\hat{s}_{1z}\hat{s}_{2z})[\chi_{\frac{1}{2}}(s_{1z})\chi_{\frac{1}{2}}(s_{2z})]$$

$$=\tfrac{3}{2}\hbar^2\chi_S^I+2[\hat{s}_{1x}\chi_{\frac{1}{2}}(s_{1z})\hat{s}_{2x}\chi_{\frac{1}{2}}(s_{2z})+\hat{s}_{1y}\chi_{\frac{1}{2}}(s_{1z})\hat{s}_{2y}\chi_{\frac{1}{2}}(s_{2z})+\hat{s}_{1z}\chi_{\frac{1}{2}}(s_{1z})\hat{s}_{2z}\chi_{\frac{1}{2}}(s_{2z})]$$

$$=\tfrac{3}{2}\hbar^2\chi_S^I+2[\frac{\hbar^2}{4}\chi_{-\frac{1}{2}}(s_{1z})\chi_{-\frac{1}{2}}(s_{2z})-\frac{\hbar^2}{4}\chi_{-\frac{1}{2}}(s_{1z})\chi_{-\frac{1}{2}}(s_{2z})+\frac{\hbar^2}{4}\chi_{\frac{1}{2}}(s_{1z})\chi_{\frac{1}{2}}(s_{2z})]$$

$$=\tfrac{3}{2}\hbar^2\chi_S^I+2[\frac{\hbar^2}{4}\chi_{\frac{1}{2}}(s_{1z})\chi_{\frac{1}{2}}(s_{2z})]=\tfrac{3}{2}\hbar^2\chi_S^I+\frac{\hbar^2}{2}\chi_S^I=2\hbar^2\chi_S^I$$

$$\hat{S}_z\chi_S^I=(\hat{s}_{1z}+\hat{s}_{2z})\chi_{\frac{1}{2}}(s_{1z})\chi_{\frac{1}{2}}(s_{2z})=\tfrac{1}{2}\hbar\chi_{\frac{1}{2}}(s_{1z})\chi_{\frac{1}{2}}(s_{2z})+\tfrac{1}{2}\hbar\chi_{\frac{1}{2}}(s_{1z})\chi_{\frac{1}{2}}(s_{2z})=\hbar\chi_S^I$$

χ_S^I是算符$\hat{S}^2$和$\hat{S}_z$的本征函数，量子数分 别为$S=1$和$m_s=1$

同理可求得其余三个态的本征值

$$\begin{cases}\hat{S}^2\chi_S^{II} = 2\hbar^2\chi_S^{II} \\ \hat{S}_z\chi_S^{II} = -\hbar\chi_S^{II}\end{cases} \qquad \begin{cases}\hat{S}^2\chi_S^{III} = 2\hbar^2\chi_S^{III} \\ \hat{S}_z\chi_S^{III} = 0\,\chi_S^{III}\end{cases} \quad \text{和} \quad \begin{cases}\hat{S}^2\chi_A = 0 \\ \hat{S}_z\chi_A = 0\end{cases}$$

结果汇总如下表所示

	$\hat{S}^2$	S	$\hat{S}_z$	m_S	$^{2S+1}\chi_{m_S}$
χ_S^I	$2\hbar^2$	1	$\hbar$	1	$^3\chi_1$
χ_S^{II}	$2\hbar^2$	1	$-\hbar$	-1	$^3\chi_{-1}$
χ_S^{III}	$2\hbar^2$	1	0	0	$^3\chi_0$
χ_A	0	0	0	0	$^1\chi_0$

（3）两个电子波函数的再解释

对耦合情形的理解

$$\chi_{m_{1s}}(s_{1z}) = |\, s_1 m_{1s} > \qquad \chi_{m_{2s}}(s_{2z}) = |\, s_2 m_{2s} >$$

（a）无耦合 $\quad |\, s_1 m_{1s} s_2 m_{2s} >=|\, s_1 m_{1s} >|\, s_2 m_{2s} >$

（b）耦合 $\quad \hat{\vec{S}} = \hat{\vec{s}}_1 + \hat{\vec{s}}_2 \qquad \hat{S}_z = \hat{s}_{1z} + \hat{s}_{2z}$

耦合基矢 $\quad |\, s_1 \quad s_2 \quad S \quad m_s >$

（c）关系

C—G

$$|\, s_1 \quad s_2 \quad S \quad m_s >= \sum_{m_{1s} m_{2s}} |\, s_1 m_{1s} s_2 m_{2s} >< s_1 m_{1s} s_2 m_{2s} \,|\, s_1 \quad s_2 \quad S \quad m_s >$$

$$= \sum_{m_{2s}=-\frac{1}{2}}^{\frac{1}{2}} |\, s_1 \quad m_s - m_{2s} \quad s_2 \quad m_{2s} >< s_1 \quad m_s - m_{2s} \quad s_2 \quad m_{2s} \,|\, s_1 \quad s_2 \quad S \quad m_s >$$

$$= |\, s_1 \quad m_s + \tfrac{1}{2} \quad \tfrac{1}{2} \quad -\tfrac{1}{2} >< s_1 \quad m_s + \tfrac{1}{2} \quad \tfrac{1}{2} \quad -\tfrac{1}{2} \,|\, s_1 \quad \tfrac{1}{2} \quad S \quad m_s >$$

$$+ |\, s_1 \quad m_s - \tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2} >< s_1 \quad m_s - \tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2} \,|\, s_1 \quad \tfrac{1}{2} \quad S \quad m_s >$$

$m_s = m_{1s} + m_{2s}$

$$|s_1 \quad s_2 \quad S \quad m_s> \quad =|s_1 \quad m_s+\tfrac{1}{2} \quad \tfrac{1}{2} \quad -\tfrac{1}{2}><s_1 \quad m_s+\tfrac{1}{2} \quad \tfrac{1}{2} \quad -\tfrac{1}{2}|s_1 \quad \tfrac{1}{2} \quad S \quad m_s>$$

$$+|s_1 \quad m_s-\tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2}><s_1 \quad m_s-\tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2}|s_1 \quad \tfrac{1}{2} \quad S \quad m_s>$$

$I. \quad S=s_1+\tfrac{1}{2}$

$$|s_1 \quad \tfrac{1}{2} \quad s_1+\tfrac{1}{2} \quad m_s> \quad =\sqrt{\frac{s_1+m_s+\frac{1}{2}}{2s_1+1}}|s_1 \quad m_s-\tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2}>+\sqrt{\frac{s_1-m_s+\frac{1}{2}}{2s_1+1}}|s_1 \quad m_s+\tfrac{1}{2} \quad \tfrac{1}{2} \quad -\tfrac{1}{2}>$$

$s_1=\tfrac{1}{2}$

$$|\tfrac{1}{2} \quad \tfrac{1}{2} \quad 1 \quad m_s> \quad = \quad \sqrt{\frac{1+m_s}{2}}|\tfrac{1}{2} \quad m_s-\tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2}>+\sqrt{\frac{1-m_s}{2}}|\tfrac{1}{2} \quad m_s+\tfrac{1}{2} \quad \tfrac{1}{2} \quad -\tfrac{1}{2}>$$

$S=1, \quad m_s=1, 0, \quad -1$

ms =1

$$|\tfrac{1}{2} \quad \tfrac{1}{2} \quad 1 \quad 1> \;=\; |\tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2}> \;=\; |\tfrac{1}{2} \quad \tfrac{1}{2}>_1|\tfrac{1}{2} \quad \tfrac{1}{2}>_2=\chi_{\frac{1}{2}}(s_{1z})\chi_{\frac{1}{2}}(s_{2z})$$

ms = 0

$$|\tfrac{1}{2} \quad \tfrac{1}{2} \quad 1 \quad 0> \;=\; \sqrt{\tfrac{1}{2}}|\tfrac{1}{2} \quad -\tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2}>+\sqrt{\tfrac{1}{2}}|\tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2} \quad -\tfrac{1}{2}>$$

$$=\sqrt{\tfrac{1}{2}} \quad |\tfrac{1}{2} \quad -\tfrac{1}{2}>_1|\tfrac{1}{2} \quad \tfrac{1}{2}>_2+\sqrt{\tfrac{1}{2}}|\tfrac{1}{2} \quad \tfrac{1}{2}>_1|\tfrac{1}{2} \quad -\tfrac{1}{2}>_2$$

$$= \sqrt{\tfrac{1}{2}}[\chi_{-\frac{1}{2}}(s_{1z})\chi_{\frac{1}{2}}(s_{2z})+\chi_{\frac{1}{2}}(s_{1z})\chi_{-\frac{1}{2}}(s_{2z})]$$

ms =-1

$$|\tfrac{1}{2} \quad \tfrac{1}{2} \quad 1 \quad -1> \;=\; |\tfrac{1}{2} \quad -\tfrac{1}{2} \quad \tfrac{1}{2} \quad -\tfrac{1}{2}> \;=\; |\tfrac{1}{2} \quad -\tfrac{1}{2}>_1|\tfrac{1}{2} \quad -\tfrac{1}{2}>_2=\chi_{-\frac{1}{2}}(s_{1z})\chi_{-\frac{1}{2}}(s_{2z})$$

$$\hat{S}^2\ {}^3\chi_{m_s} = \hat{S}^2 \,|\tfrac{1}{2} \quad \tfrac{1}{2} \quad 1 \quad m_s> \ = 1(1+1)\hbar^2 \,|\tfrac{1}{2} \quad \tfrac{1}{2} \quad 1 \quad m_s> = 2\hbar^2\ {}^3\chi_{m_s}$$

$$\hat{S}_z\ {}^3\chi_{m_s} = \hat{S}_z \,|\tfrac{1}{2} \quad \tfrac{1}{2} \quad 1 \quad m_s> \ = m_s\hbar \,|\tfrac{1}{2} \quad \tfrac{1}{2} \quad 1 \quad m_s> = m_s\hbar\ {}^3\chi_{m_s}$$

II. $S = s_1 - \frac{1}{2}$

$$|s_1 \quad \tfrac{1}{2} \quad s_1 - \tfrac{1}{2} \quad m_s> = -\sqrt{\frac{s_1 - m_s + \frac{1}{2}}{2s_1+1}}\,|s_1 \quad m_s - \tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2}> + \sqrt{\frac{s_1 + m_s + \frac{1}{2}}{2s_1+1}}\,|s_1 \quad m_s + \tfrac{1}{2} \quad \tfrac{1}{2} \quad -\tfrac{1}{2}>$$

$s_1 = \frac{1}{2}$ **$S = 0, \quad m_s = 0$**

$$|\tfrac{1}{2} \quad \tfrac{1}{2} \quad 0 \quad 0> \ = \ -\sqrt{\tfrac{1}{2}}\,|\tfrac{1}{2} \quad -\tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2}> + \sqrt{\tfrac{1}{2}}\,|\tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2} \quad -\tfrac{1}{2}>$$

$$= -\sqrt{\tfrac{1}{2}}\,|\tfrac{1}{2} \quad -\tfrac{1}{2}>_1 |\tfrac{1}{2} \quad \tfrac{1}{2}>_2 + \sqrt{\tfrac{1}{2}}\,|\tfrac{1}{2} \quad \tfrac{1}{2}>_1 |\tfrac{1}{2} \quad -\tfrac{1}{2}>_2$$

$$= \sqrt{\tfrac{1}{2}}[\chi_{\frac{1}{2}}(s_{1z})\chi_{-\frac{1}{2}}(s_{2z}) - \chi_{-\frac{1}{2}}(s_{1z})\chi_{\frac{1}{2}}(s_{2z})]$$

$$\hat{S}^2\ {}^1\chi_0 = \hat{S}^2 \,|\tfrac{1}{2} \quad \tfrac{1}{2} \quad 0 \quad 0> \ = 0(0+1)\hbar^2 \,|\tfrac{1}{2} \quad \tfrac{1}{2} \quad 0 \quad 0> = 0$$

$$\hat{S}_z\ {}^1\chi_0 = \hat{S}_z \,|\tfrac{1}{2} \quad \tfrac{1}{2} \quad 0 \quad 0> \ = 0\hbar \,|\tfrac{1}{2} \quad \tfrac{1}{2} \quad 0 \quad 0> = 0$$

§6.9　氦原子(微扰法)

电子自旋和泡利不相容原理考虑进去，可以得出与实验符合很好的结果

（1）氦原子哈密顿算符

（2）微扰法求解氦原子能级和波函数

（3）讨论

（1）氦原子哈密顿算符

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e_s^2}{r_1} - \frac{2e_s^2}{r_2} + \frac{e_s^2}{r_{12}}$$

$$\Phi(\vec{r}_1, \vec{r}_2, s_{1z}, s_{2z}) = \psi(\vec{r}_1, \vec{r}_2)\chi(s_{1z}, s_{2z})$$

$$\hat{H}\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

（2）微扰法求解氦原子能级和波函数

（a）零级和微扰哈密顿算符

$$\hat{H} = \hat{H}^{(0)} + \hat{H}'$$

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e_s^{\ 2}}{r_1} - \frac{2e_s^{\ 2}}{r_2} = \hat{H}_1^{(0)} + \hat{H}_2^{(0)}$$

$$\hat{H}' = \frac{e_s^{\ 2}}{r_{12}}$$

$$\left[-\frac{\hbar^2}{2m}\nabla_\alpha^2 - \frac{2e_s^{\ 2}}{r_\alpha}\right]\psi_n(\vec{r}_\alpha) = \varepsilon_n \psi_n(\vec{r}_\alpha) \qquad (\alpha = 1,2.)$$

$$\varepsilon_n = -\frac{mZ^2 e_s^{\ 4}}{2\hbar^2 n^2} \qquad (n = 1,2\cdots)$$

$$\psi_n(\vec{r}_\alpha) = \psi_{nlm}(\vec{r}_\alpha) \qquad (\alpha = 1,2.)$$

（b）对称和反对称零级本征函数

对称本征函数

$$\psi_S^{(0)}(\vec{r}_1,\vec{r}_2)=\psi_n(\vec{r}_1)\psi_n(\vec{r}_2)$$

$$\psi_S^{(0)}(\vec{r}_1,\vec{r}_2)=\sqrt{\tfrac{1}{2}}[\psi_n(\vec{r}_1)\psi_m(\vec{r}_2)+\psi_n(\vec{r}_2)\psi_m(\vec{r}_1)] \qquad m\neq n$$

反对称本征函数

$$\psi_A^{(0)}(\vec{r}_1,\vec{r}_2)=\sqrt{\tfrac{1}{2}}[\psi_n(\vec{r}_1)\psi_m(\vec{r}_2)-\psi_n(\vec{r}_2)\psi_m(\vec{r}_1)] \qquad m\neq n$$

（c）状态能量的修正

$$E_{nm}^{(0)}=\varepsilon_n+\varepsilon_m$$

$$E_{11}^{(0)}=\varepsilon_1+\varepsilon_1=-\frac{4me_s^{\ 4}}{\hbar^2}$$

$$\psi_S^{(0)}(\vec{r}_1,\vec{r}_2)=\psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)=\frac{8}{\pi a_0^3}e^{-2(r_1+r_2)/a_0}$$

$$E_{11}^{(1)}=\iint \psi_S^{(0)^*}(\vec{r}_1,\vec{r}_2)\frac{e_s^{\ 2}}{r_{12}}\psi_S^{(0)}(\vec{r}_1,\vec{r}_2)d\tau_1 d\tau_2$$

$$=\left.\frac{5Ze_s^{\ 2}}{8a_0}\right|_{Z=2}=\frac{5e_s^{\ 2}}{4a_0}=\frac{5me_s^{\ 4}}{4\hbar^2} \qquad a_0=\frac{\hbar^2}{me_s^{\ 2}}$$

$$E_0\approx E_{11}^{(0)}+E_{11}^{(1)}=\varepsilon_1+\varepsilon_1+E_{11}^{(1)}=-\frac{4me_s^{\ 4}}{\hbar^2}+\frac{5me_s^{\ 4}}{4\hbar^2}=-\frac{11me_s^{\ 4}}{4\hbar^2}$$

$$=-2.75\frac{e_s^{\ 2}}{a_0}=-74.83\,eV$$

$$E_0(\exp)=-2.904\frac{e_s^{\ 2}}{a_0}=-78.98\,eV$$ 误差是 **5.3 %**

（d）激发态能量的一级修正

m ≠ n

$$E_{nm}^{(1)} = \iint \psi_{\substack{S\\A}}^{(0)^*}(\vec{r}_1,\vec{r}_2)\frac{e^2}{r_{12}}\psi_{\substack{S\\A}}^{(0)}(\vec{r}_1,\vec{r}_2)d\tau_1 d\tau_2$$

$$= \frac{1}{2}\iint [\psi_n^*(\vec{r}_1)\psi_m^*(\vec{r}_2)\pm\psi_n^*(\vec{r}_2)\psi_m^*(\vec{r}_1)]\frac{e^2}{r_{12}}[\psi_n(\vec{r}_1)\psi_m(\vec{r}_2)\pm\psi_n(\vec{r}_2)\psi_m(\vec{r}_1)]d\tau_1 d\tau_2$$

$$= \underbrace{\frac{1}{2}\iint \frac{e^2}{r_{12}}|\psi_n(\vec{r}_1)|^2 \psi_m(\vec{r}_2)|^2 d\tau_1 d\tau_2}_{K} + \underbrace{\frac{1}{2}\iint \frac{e^2}{r_{12}}|\psi_n(\vec{r}_2)|^2 \psi_m(\vec{r}_1)|^2 d\tau_1 d\tau_2}_{K}$$

$$\pm \underbrace{\frac{1}{2}\iint \frac{e^2}{r_{12}}\psi_n^*(\vec{r}_1)\psi_m^*(\vec{r}_2)\psi_n(\vec{r}_2)\psi_m(\vec{r}_1)d\tau_1 d\tau_2}_{J} \pm \underbrace{\frac{1}{2}\iint \frac{e^2}{r_{12}}\psi_n^*(\vec{r}_2)\psi_m^*(\vec{r}_1)\psi_n(\vec{r}_1)\psi_m(\vec{r}_2)d\tau_1 d\tau_2}_{J}$$

$$= K \pm J$$

$$\begin{cases} E_S = \varepsilon_n + \varepsilon_m + K + J \\ E_A = \varepsilon_n + \varepsilon_m + K - J \end{cases} \qquad (m \neq n)$$

（e）氦原子的波函数

$$\Phi_I = \psi_S^{(0)}(\vec{r}_1, \vec{r}_2)\chi_A(s_{1z}, s_{2z}) = \psi_S^{(0)\,1}\chi_0$$

$$\Phi_{II} = \psi_A^{(0)}(\vec{r}_1, \vec{r}_2)\chi_S(s_{1z}, s_{2z}) = \psi_A^{(0)\,3}\chi_{m_s} \qquad (m_s = 0, \pm 1.)$$

I——单态 II——三重态

（f） K和J的物理意义

库仑能

$$\begin{cases}\rho_{nn}(\vec{r}_1) = -e\psi_n^*(\vec{r}_1)\psi_n(\vec{r}_1) \\ \rho_{mm}(\vec{r}_2) = -e\psi_m^*(\vec{r}_2)\psi_m(\vec{r}_2)\end{cases}$$

$$K = \iint \frac{1}{r_{12}}\rho_{nn}(\vec{r}_1)\rho_{mm}(\vec{r}_2)d\tau_1 d\tau_2$$

交换密度

交换能

$$\begin{cases}\rho_{mn}(\vec{r}_1) = -e\psi_m^*(\vec{r}_1)\psi_n(\vec{r}_1) \\ \rho_{mn}^*(\vec{r}_2) = -e\psi_m(\vec{r}_2)\psi_n^*(\vec{r}_2)\end{cases}$$

$$J = \iint \frac{1}{r_{12}}\rho_{mn}(\vec{r}_1)\rho_{mn}^*(\vec{r}_2)d\tau_1 d\tau_2$$

（3）讨论

（a）交换能是量子力学中特有的结果

K和J来自库仑力. J来自全同粒子体系波函数的对称性，是量子力学的特殊结果

（b）J

$$J=\iint \frac{1}{r_{12}}\rho_{mn}(\vec{r}_1)\rho_{mn}{}^{*}(\vec{r}_2)d\tau_1 d\tau_2 \quad \begin{cases}\rho_{mn}(\vec{r}_1)=-e\psi_m^{*}(\vec{r}_1)\psi_n(\vec{r}_1)\\ \rho_{mn}{}^{*}(\vec{r}_2)=-e\psi_m(\vec{r}_2)\psi_n^{*}(\vec{r}_2)\end{cases}$$

J反映了m和n态波函数的重合程度

（c）m≠n, 氦原子激发态的四重简并可用简并微扰处理

$$\Phi_I = \psi_S^{(0)}(\vec{r}_1,\vec{r}_2)\chi_A(s_{1z},s_{2z}) = \psi_S^{(0)\,1}\chi_0$$

$$\Phi_{II} = \psi_A^{(0)}(\vec{r}_1,\vec{r}_2)\chi_S(s_{1z},s_{2z}) = \psi_A^{(0)\,3}\chi_{m_s} \qquad (m_s = 0,\pm1.)$$

$$\begin{cases} \psi_S^{(0)}(\vec{r}_1,\vec{r}_2) = \sqrt{\frac{1}{2}}[\psi_n(\vec{r}_1)\psi_m(\vec{r}_2) + \psi_n(\vec{r}_2)\psi_m(\vec{r}_1)] \\ \psi_A^{(0)}(\vec{r}_1,\vec{r}_2) = \sqrt{\frac{1}{2}}[\psi_n(\vec{r}_1)\psi_m(\vec{r}_2) - \psi_n(\vec{r}_2)\psi_m(\vec{r}_1)] \end{cases} \qquad m \neq n$$

$H_{ij}' = 0$， $H_{22}' = H_{33}' = H_{44}'$

$$\begin{cases} E_1^{(1)} = H'_{11} = K + J \\ E_2^{(1)} = H'_{22} = H'_{33} = H'_{44} = K - J \end{cases}$$

作业

7.6
7.8