第六章 全同粒子

§ 6.1 Bose / Fermi 子

粒子1：$|k\rangle$，粒子2：$|k'\rangle$

两粒子态：$|k\rangle \otimes |k'\rangle$，$|k\rangle|k'\rangle$

对全同粒子：$|k\rangle|k'\rangle$ 与 $|k'\rangle|k\rangle$ 无法分辨

态写为 $|\psi\rangle = c_1 |k\rangle|k'\rangle + c_2 |k'\rangle|k\rangle$

定义交换算符：$\hat{P}|k\rangle|k'\rangle = |k'\rangle|k\rangle$

$\hat{P}|\psi\rangle = e^{i\theta}|\psi\rangle$ （全同粒子态交换不变）

$e^{i\theta}(c_1|k\rangle|k'\rangle + c_2|k'\rangle|k\rangle) = c_1|k'\rangle|k\rangle + c_2|k\rangle|k'\rangle$

解得 $\theta = 0, \pi$，$c_1 = c_2$ 或 $c_1 = -c_2$

构造全同粒子态：$|\psi_\pm\rangle = \frac{1}{\sqrt{2}}(|k\rangle|k'\rangle \pm |k'\rangle|k\rangle)$，分别对应（反）交换对称

全同粒子 $\begin{cases} \text{Bose 子} & \text{整数自旋} \quad \text{交换对称} \\ \text{Fermi 子} & \text{半整数自旋} \quad \text{交换反对称} \end{cases}$

对全同粒子系统，$[P, H] = 0$

Fermi 子：两个全同费米子不能占据同一个单粒子态。

$k = k' \rightarrow$ Pauli 不相容原理 $|\psi\rangle = \frac{1}{\sqrt{2}}(|k\rangle|k'\rangle - |k'\rangle|k\rangle) = 0$

N 个 Fermi 子：

设占据 $k_1 \cdots k_N$ 个单粒子态

$$|\psi\rangle = \frac{1}{\sqrt{N!}}\sum_P (-1)^{n_P}\hat{P}(|k_1\rangle|k_2\rangle \cdots |k_N\rangle)$$

$$= \frac{1}{\sqrt{N!}}\sum_P (-1)^{n_P}\hat{P}\,|k_1 k_2 \cdots k_N\rangle$$

选取坐标表象下的基矢：

$$|r_1, r_2 \cdots r_N\rangle = |r_1\rangle|r_2\rangle \cdots |r_N\rangle$$

$$|\psi\rangle = \frac{1}{\sqrt{N!}}\int d^3r_1 \cdots d^3r_N \sum_P (-1)^{n_P}\langle r_1, r_2 \cdots r_N|\hat{P}|k_1, k_2, \cdots k_N\rangle |r_1 \cdots r_N\rangle$$

$$= \int d^3r_1\, d^3r_2 \cdots d^3r_N\, \psi_{k_1,k_2\cdots k_N}(r_1, \cdots r_N)\,|r_1, r_2 \cdots r_N\rangle$$

其中 $\psi_{k_1,k_2\cdots k_N}(r_1, \cdots r_N) = \begin{vmatrix} \phi_{k_1}(r_1) & \phi_{k_1}(r_2) & \cdots & \phi_{k_1}(r_N) \\ \phi_{k_2}(r_1) & & & \vdots \\ \vdots & & & \\ \phi_{k_N}(r_1) & & \cdots & \phi_{k_N}(r_N) \end{vmatrix}$

Slater 行列式

N个Bose子：

可以有任意多个Bose子占据同一个单粒子态

N个Bose子占据m个单粒子态，设各态上粒子数为 $n_1 \cdots n_m$

$$N = n_1 + n_2 + \cdots + n_m$$

$$|\psi\rangle = \sqrt{\frac{\prod_i n_i!}{N!}} \sum_P \hat{P} \, (|1\rangle \cdots |m\rangle)$$

§ 6.2 两电子系统

两电子系统态：

$$|\Psi\rangle = \sum_{s_{1z}, s_{2z}} \int d^3r_1\, d^3r_2\, \Psi(r_1, s_{1z}, r_2, s_{2z})\, |r_1, s_{1z}\rangle |r_2, s_{2z}\rangle$$

$$|\Psi\rangle = \sum_{s_{1z}, s_{2z}} \int d^3r_1\, d^3r_2\, \psi(r_1, r_2)\, \chi(s_{1z}, s_{2z})\, |r_1, r_2\rangle |s_{1z}, s_{2z}\rangle$$

$$= \sum_{s, s_z} \int d^3r_1\, d^3r_2\, \psi(r_1, r_2)\, |r_1, r_2\rangle |s, s_z\rangle$$ $\hat{S} = \hat{S}_1^2 + \hat{S}_2^2$, $\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z}$

假定两电子占据两单粒子态 $|k_1\rangle$, $|k_2\rangle$ 电子为费米子，波函数反对称.

(1) 自旋单重态 $|\Psi\rangle = \frac{1}{\sqrt{2}}(|k_1\rangle|k_2\rangle + |k_2\rangle|k_1\rangle)|00\rangle$

(2) 自旋三重态. $|\Psi\rangle = \frac{1}{\sqrt{2}}(|k_1\rangle|k_2\rangle - |k_2\rangle|k_1\rangle)$ $\begin{cases} |11\rangle \\ |10\rangle \\ |1-1\rangle \end{cases}$

例：考虑一维势井 $V(x) = \begin{cases} 0 & 0 \le x \le a \\ \infty & x<0, x>a \end{cases}$ 势井中有两个全同粒子

(1) 如果粒子自旋 $s=0$，写出体系最低两个能级，指出简并度、给出波函数、

$s=0$ 为 Bose子，且自旋部份只有交换对称一种情况

基态：两个粒子都处在最低能级.

$$\varepsilon_0 = 2E_1 = \frac{\pi^2\hbar^2}{ma^2}$$ $\psi_1(x)$ 为第一能级的空间波函数

$$\psi_0(x_1, x_2) = \psi_1(x_1)\,\psi_1(x_2)\,|00\rangle$$

第一激发态：一个在最低，一个在次低

$$\varepsilon_0 = E_1 + E_2 = \frac{5\pi^2\hbar^2}{2ma^2}$$

$$\psi_1(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\psi_1(x_1)\psi_2(x_2) + \psi_2(x_1)\psi_1(x_2)\right]|00\rangle$$

(2) 如果自旋 $s=\frac{1}{2}$ 呢？ $s=\frac{1}{2}$ 为 Fermi子

基态：$\varepsilon_0 = 2E_1 = \frac{\pi^2\hbar^2}{ma^2}$ 空间部份对称. 自旋部份反对称

$$\Psi_0(x_1, x_2) = \psi_1(x_1)\,\psi_1(x_2)\,|00\rangle$$

第一激发态：$\varepsilon_1 = E_1 + E_2 = \frac{5\pi^2\hbar^2}{2ma^2}$

$$\Psi_1(x_1, x_2) = \begin{cases} \frac{1}{\sqrt{2}}\left[\psi_1(x_1)\psi_2(x_2) + \psi_2(x_1)\psi_1(x_2)\right]|00\rangle \\ \frac{1}{\sqrt{2}}\left[\psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1)\right] \begin{cases} |11\rangle \\ |10\rangle \\ |1-1\rangle \end{cases} \end{cases}$$

§ 6.3 交换相互作用

考虑两个电子占据原子内两个正交轨道 $\phi_\alpha(r)$，$\phi_\beta(r)$，对应能量 $\varepsilon_\alpha, \varepsilon_\beta$

$$\hat{H} = \hat{H}_0(r_1) + \hat{H}_0(r_2) + \hat{H}_{int}(|r_1 - r_2|)$$

$$= \frac{\hat{p}_1^2}{2m} + V(r_1) + \frac{\hat{p}_2^2}{2m} + U(r_2) + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|r_1 - r_2|}$$

自旋单重态：$\psi_s(r_1, r_2) = \frac{1}{\sqrt{2}}\left[\phi_\alpha(r_1)\phi_\beta(r_2) + \phi_\beta(r_1)\phi_\alpha(r_2)\right]$ 空间部分对称

自旋三重态：$\psi_a(r_1, r_2) = \frac{1}{\sqrt{2}}\left[\phi_\alpha(r_1)\phi_\beta(r_2) - \phi_\beta(r_1)\phi_\alpha(r_1)\right]$ 空间部分反对称

$$\langle \psi_s | \hat{H} | \psi_s \rangle = \varepsilon_\alpha + \varepsilon_\beta + U_{\alpha\beta} + J_{\alpha\beta}$$

$$\langle \psi_a | \hat{H} | \psi_a \rangle = \varepsilon_\alpha + \varepsilon_\beta + U_{\alpha\beta} - J_{\alpha\beta}$$

其中 $$U_{\alpha\beta} = \frac{e^2}{4\pi\varepsilon_0}\int d^3r_1\, d^3r_2 \frac{|\phi_\alpha(r_1)|^2 |\phi_\beta(r_2)|^2}{|r_1 - r_2|}$$

$$J_{\alpha\beta} = \frac{e^2}{4\pi\varepsilon_0}\int d^3r_1\, d^3r_2 \frac{\phi_\alpha^*(r_1)\phi_\beta(r_1)\phi_\alpha(r_2)\phi_\beta^*(r_2)}{|r_1 - r_2|}$$

推导：$\langle \psi_s | \hat{H} | \psi_s \rangle$

$$= \int d^3r_1\, d^3r_2\, \psi_s^*(r_1, r_2)\, \hat{H}\, \psi_s(r_1, r_2)$$

$$= \int d^3r_1\, d^3r_2 \frac{1}{\sqrt{2}}\left[\psi_\alpha^*(r_1)\psi_\beta^*(r_2) + \psi_\beta^*(r_1)\psi_\alpha^*(r_2)\right]\left[\frac{\hat{p}_1^2}{2m} + V(r_1) + \frac{\hat{p}_2^2}{2m} + U(r_2) + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|r_1 - r_2|}\right]$$

$$\frac{1}{\sqrt{2}}\left[\psi_\alpha(r_1)\psi_\beta(r_2) + \psi_\beta(r_1)\psi_\alpha(r_2)\right]$$

$$= \frac{1}{2}\int d^3r_1\, d^3r_2 \Big\{ \psi_\alpha^*(r_1)\left[\frac{\hat{p}_1^2}{2m} + V(r_1)\right]\psi_\alpha(r_1)\,\psi_\beta^*(r_2)\psi_\beta(r_2) \quad = \varepsilon_\alpha$$

$$+ \psi_\beta^*(r_1)\psi_\beta(r_1)\psi_\alpha^*(r_2)\left[\frac{\hat{p}_2^2}{2m} + V(r_1)\right]\psi_\alpha(r_2) \quad = \varepsilon_\alpha$$

$$+ \psi_\alpha^*(r_1)\psi_\alpha(r_1)\psi_\beta^*(r_2)\left[\frac{\hat{p}_2^2}{2m} + V(r_2)\right]\psi_\beta(r_2)$$

$$+ \psi_\beta^*(r_1)\left[\frac{\hat{p}_1^2}{2m} + V(r_1)\right]\psi_\beta(r_1)\psi_\alpha^*(r_2)\psi_\alpha(r_2) \Big\}$$

$$+ \psi_\alpha^*(r_1)\left[\frac{\hat{p}_1^2}{2m} + V(r_1)\right]\psi_\beta(r_1)\psi_\beta^*(r_2)\left[\frac{\hat{p}_2^2}{2m} + V(r_2)\right]\psi_\alpha(r_2) \quad \text{交叉项} = 0$$

$$+ \psi_\beta^*(r_1)\left[\frac{\hat{p}_1^2}{2m} + V(r_1)\right]\psi_\alpha(r_1)\psi_\alpha^*(r_2)\left[\frac{\hat{p}_2^2}{2m} + V(r_2)\right]\psi_\beta(r_2) \quad = 0$$

$$+ \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|r_1 - r_2|}\Big[\underbrace{\psi_\alpha^*(r_1)\psi_\alpha(r_1)\psi_\beta^*(r_2)\psi_\beta(r_2)}_{U_{\alpha\beta}} + \underbrace{\psi_\alpha^*(r_1)\psi_\beta(r_1)\psi_\beta^*(r_2)\psi_\alpha(r_2)}_{J_{\alpha\beta}}$$

$$\underbrace{+ \psi_\beta^*(r_1)\psi_\alpha(r_1)\psi_\alpha^*(r_2)\psi_\beta(r_2)}_{J_{\alpha\beta}} + \underbrace{\psi_\beta^*(r_1)\psi_\beta(r_1)\psi_\alpha^*(r_2)\psi_\alpha(r_2)}_{U_{\alpha\beta}}\Big]$$

将交换能看作自旋空间有效交换作用的本征值.

$(\hat{S}_1+\hat{S}_2)^2 = \hat{S}_1^2+\hat{S}_2^2+2\hat{S}_1\cdot\hat{S}_2 = \frac{3}{2}\hbar^2+2\hat{S}_1\cdot\hat{S}_2$

有效交换作用: $\hat{S}_1\cdot\hat{S}_2$

$\langle\psi_s|\hat{H}|\psi_s\rangle = \varepsilon_\alpha+\varepsilon_\beta+U_{\alpha\beta}-\frac{1}{2}J_{\alpha\beta}-2J_{\alpha\beta}\langle\psi_s|\frac{1}{\hbar^2}\hat{S}_1\cdot\hat{S}_2|\psi_s\rangle$

$\langle\psi_a|\hat{H}|\psi_a\rangle = \varepsilon_\alpha+\varepsilon_\beta+U_{\alpha\beta}-\frac{1}{2}J_{\alpha\beta}-2J_{\alpha\beta}\langle\psi_a|\frac{1}{\hbar^2}\hat{S}_1\cdot\hat{S}_2|\psi_a\rangle$

推导: $\langle\psi_s|\hat{S}_1\cdot\hat{S}_2|\psi_s\rangle$

$= \frac{1}{2}\langle\psi_s|\hat{S}^2-\hat{S}_1^2-\hat{S}_2^2|\psi_s\rangle$

$= \frac{1}{2}(0-\frac{3}{4}\hbar^2-\frac{3}{4}\hbar^2) = -\frac{3}{4}\hbar^2$

$\langle\psi_a|\hat{S}_1\cdot\hat{S}_2|\psi_a\rangle = \frac{1}{2}(2-\frac{3}{4}-\frac{3}{4})\hbar^2 = \frac{1}{4}\hbar^2$

$\hookrightarrow \hat{H}_{ex} = -2J(\frac{1}{\hbar^2}\hat{S}_1\cdot\hat{S}_2+\frac{1}{4})$

$J>0$ 铁磁交换作用

$J<0$ 反铁磁交换作用

对原子轨道上的两电子

$$J_{\alpha\beta} = \frac{e^2}{4\pi\varepsilon_0}\int d^3r_1\, d^3r_2\, \frac{\Phi^*(r_1)\,\Phi(r_2)}{|r_1-r_2|}$$

$\Phi(r) = \varphi_\alpha(r_1)\,\varphi_\beta^*(r_2)$

$$= \frac{e^2}{4\pi\varepsilon_0}\int\frac{d^3k}{(2\pi)^{3/2}}\,d^3r_1\,\Phi^*(r_1)\,\Phi(k)\int d^3r_2\,\frac{e^{i\vec{k}\cdot\vec{r}_2}}{|\vec{r}_1-\vec{r}_2|}$$

$\Phi(r_2) = \frac{1}{(2\pi)^{3/2}}\int d^3k\,\Phi(k)\,e^{i\vec{k}\cdot\vec{r}_2}$

$$= \frac{e^2}{4\pi\varepsilon_0}\int\frac{d^3k}{(2\pi)^{3/2}}\,\frac{4\pi}{k^2}\,\Phi(k)\int d^3r_1\,\Phi^*(r_1)\,e^{i\vec{k}\cdot\vec{r}_1}$$

$\int\frac{e^{i\vec{k}\cdot\vec{r}}}{|\vec{r}|} = \frac{4\pi}{k^2}$

$$= \frac{e^2}{4\pi\varepsilon_0}\int\frac{d^3k}{(2\pi)^{3/2}}\,\frac{4\pi^2}{k^2}|\Phi(k)|^2 > 0$$

$\Phi^*(k) = \frac{1}{(2\pi)^{3/2}}\int d^3r\,\Phi^*(r)\,e^{i\vec{k}\cdot\vec{r}}$

$\Rightarrow$ 原子内不同轨道电子自旋之间铁磁交换作用.