Lecture 1 (第一周). 二次量子化.

参考: 教材

A.L. Fetter & J.D. Walecka. Quantum Theory of Many-Particle Systems.

Motivation: 为什么要引入二次量子化?

1. 方便描述多体体系，特别是粒子数不守恒的体系，例如量子场论 (相对论性).

(超导体; 化学势; ARPES).

2. 有些问题用一次量子化更方便 …

1. 玻色子:

1) Fock space:

一次量子化描述方式: $\Psi(\vec{r}_1, \cdots, \vec{r}_n)$.

$\Rightarrow$ $\vec{r}_1$ 处有1个 boson, $\vec{r}_2$ 处有1个 boson, ……

$$\Psi(\vec{r}_1, \cdots, \vec{r}_i, \cdots, \vec{r}_j, \cdots) = \Psi(\cdots, \vec{r}_j, \cdots, \vec{r}_i, \cdots).$$

一般地, 可以把位置 $\vec{r}$ 换成其它任意的量子数, 如动量 $\vec{k}$ 或抽象的模式 "a".

这里"模式" a 指的是一组正交归一基的标记. $\sum_a |a\rangle\langle a| = \mathbb{1}$

(单粒子 Hilbert space)

如 $\int d\vec{r}\, |\vec{r}\rangle\langle\vec{r}| = \mathbb{1}$, $\sum_{\vec{k}} |\vec{k}\rangle\langle\vec{k}| = \mathbb{1}$.

$a = 0, 1, 2, \cdots$

一个量子态: $a=0$ 有 n_0 个玻色子, $a=1$ 有 n_1 个玻色子, …

$(n_0, n_1, n_2, \cdots)$ 标记这样一个量子态, 记为 $|\{n_a\}\rangle$ 或 $|n_0, n_1, \cdots\rangle$.

$$\sum_{n_a=0}^{\infty} |\{n_a\}\rangle\langle\{n_a\}| = \mathbb{1}.$$

$$\langle\{n_a\}|\{m_a\}\rangle = \delta_{n_0,m_0}\delta_{n_1,m_1}\cdots = \prod_a \delta_{n_a,m_a}.$$

总粒子数 $N = \sum_a n_a$.

因此 $|\{n_a\}\rangle$ 可以用于描述一个粒子数不守恒的体系

2) 产生/湮灭算符

只考虑一个模式 α，可以略去模式的记号.

Fock space: $|0\rangle, |1\rangle, |2\rangle, \cdots$

算符: $\hat{n}$: $\hat{n}|n\rangle = n|n\rangle$.

产生/湮灭算符: $a^{+}|n\rangle \propto |n+1\rangle$; $a|n\rangle \propto |n\rangle$.

即: $|n\rangle \underset{a}{\overset{a^{+}}{\rightleftarrows}} |n+1\rangle$

— a^{+} 与 a 的作用必然不对易.

$$\begin{array}{ccc} |0\rangle & \xrightarrow{a^{+}} & |1\rangle \\ a\downarrow & & \downarrow a \\ \times & \xrightarrow{a^{+}} & |0\rangle \end{array}$$

$aa^{+}|0\rangle \propto |0\rangle$ 但是 $a^{+}a\,|0\rangle = 0$.

$\therefore\ aa^{+} \neq a^{+}a$.

(不对易源自 Fock space $|0\rangle, |1\rangle, \cdots$ 没有 $n<0$ 的态，因而 a 与 a^{+} 并不对称).

可以选择归一化常数, s.t. $[\hat{a}, \hat{a}^{+}] = 1$.

— $[\hat{a}, \hat{a}^{+}] = 1$ 的表示:

<u>定义</u> $\hat{n} = \hat{a}^{+}\hat{a}$

可证明 $[\hat{n}, \hat{a}] = -\hat{a}$; $[\hat{n}, \hat{a}^{+}] = \hat{a}^{+}$.

因此考虑 $\hat{n}$ 的本征态 $\hat{n}|n\rangle = n|n\rangle$.

$\Rightarrow\ \hat{n}\hat{a}|n\rangle = \hat{a}\hat{n}|n\rangle - \hat{a}|n\rangle = (n-1)\hat{a}|n\rangle$

因而 $\hat{a}|n\rangle$ 也是 $\hat{n}$ 的本征态，本征值为 $(n-1)$. 类似可证 $\hat{a}^{+}|n\rangle$ 本征值为 $(n+1)$.

若 $n \in \mathbb{N} = \{0, 1, 2, \cdots\}$, 我们得到一个有限维表示.

$\hat{a}|0\rangle = 0$. 故不存在 $|-1\rangle, \cdots$

— 归一化，要求 $\langle n|n\rangle = 1$.

$\hat{a}|n\rangle \propto |n-1\rangle$. 但也要求 $\langle n-1|n-1\rangle = 1$.

计算 $\|\hat{a}|n\rangle\|^2 = \langle n|\hat{a}^{+}\hat{a}|n\rangle = \langle n|\hat{n}|n\rangle = n$.

$\therefore\ \hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle$.

$\hat{a}^{+}|n\rangle \propto |n+1\rangle$. $\|\hat{a}^{+}|n\rangle\|^2 = \langle n|\hat{a}\hat{a}^{+}|n\rangle = \langle n|(\hat{a}^{+}\hat{a}+1)|n\rangle$
$= (n+1)$.

$\therefore \quad \hat{a}^+|n\rangle = \sqrt{n+1}\,|n+1\rangle.$

$$\begin{cases} \hat{a}\,|n\rangle = \sqrt{n}\,|n-1\rangle \\ \hat{a}^+|n\rangle = \sqrt{n+1}\,|n+1\rangle \\ a^+a\,|n\rangle = n\,|n\rangle \end{cases}$$

$$|n\rangle = \frac{1}{\sqrt{n}}\,a^+|n-1\rangle = \frac{1}{\sqrt{n(n-1)}}(a^+)^2|n-2\rangle = \cdots = \frac{1}{\sqrt{n!}}(a^+)^n|0\rangle.$$

Prop. 考虑 Fock 空间中状态 $|\phi\rangle$. $\hat{a}|\phi\rangle = 0 \Rightarrow |\phi\rangle \propto |0\rangle$.

这条性质很常用.

3) 多个模式；多体波函数

* 考虑一个系统有 M 个模式: $\alpha = 0, \dots, M$.

对于每个模式，有 Fock 空间和算符. $|n_\alpha\rangle$, $[\hat{a}_\alpha, \hat{a}_\alpha^+] = 1$.

整个系统: $|n_0, \dots, n_M\rangle = |n_0\rangle \otimes |n_1\rangle \otimes \cdots \otimes |n_M\rangle$.

$$\begin{cases} [\hat{a}_\alpha, \hat{a}_\beta^+] = \delta_{\alpha\beta} \\ [\hat{a}_\alpha, \hat{a}_\beta] = [\hat{a}_\alpha^+, \hat{a}_\beta^+] = 0 \\ \hat{n}_\alpha = \hat{a}_\alpha^+ \hat{a}_\alpha \\ \hat{N} = \sum_\alpha \hat{n}_\alpha \end{cases}$$

Ex. $\hat{a}_\alpha |n_0, \dots, n_\alpha, \dots, n_M\rangle = \sqrt{n_\alpha}\,|n_0, \dots, n_\alpha - 1, \dots, n_M\rangle.$

$\hat{a}_\alpha^+ |n_0, \dots, n_\alpha, \dots, n_M\rangle = \sqrt{n_\alpha + 1}\,|n_0, \dots, n_\alpha + 1, \dots, n_M\rangle.$

$\hat{n}_\alpha |n_0, \dots, n_\alpha, \dots, n_M\rangle = n_\alpha |n_0, \dots, n_\alpha, \dots, n_M\rangle.$

若 $\forall \alpha$, $\hat{a}_\alpha|\phi\rangle = 0$, 则 $|\phi\rangle \propto |0\rangle = |0, 0, \dots, 0\rangle$.

$$|n_0, \dots, n_M\rangle = \prod_\alpha \frac{1}{\sqrt{n_\alpha!}} (a_\alpha^+)^{n_\alpha} |0\rangle.$$

* 特别地，考虑空间坐标基底 $\alpha = \vec{r}$.

我们往往用特殊的符号 $\hat{\psi}(\vec{r})$, $\hat{\psi}^+(\vec{r})$ 来表示相应的产生/湮灭算符 $a_{\vec{r}}, a_{\vec{r}}^+$.

$\hat{n}(\vec{r}) = \hat{\psi}^+(\vec{r})\psi(\vec{r}).$

$[\psi(\vec{r}), \psi^+(\vec{r}')] = \delta(\vec{r} - \vec{r}')$; $[\psi(\vec{r}), \psi(\vec{r}')] = [\psi^+(\vec{r}), \psi^+(\vec{r}')] = 0.$

$[\hat{n}(\vec{r}), \psi(\vec{r}')] = -\delta(\vec{r} - \vec{r}')\psi(\vec{r}')$; $[\hat{n}(\vec{r}), \psi^+(\vec{r}')] = \delta(\vec{r} - \vec{r}')\psi^+(\vec{r}').$

* 多体波函数. $\cancel{\Psi(\vec{r}_1, \dots, \vec{r}_N) = \langle \Psi | n_{\vec{r}_1} = 1, \dots, n_{\vec{r}_N} = 1\rangle}$

$\cancel{= \langle 0 | \psi(\vec{r}_1) \cdots \psi(\vec{r}_N) | \Psi\rangle}$

$\cancel{= \langle \Psi | \psi^+(\vec{r}_1) \cdots \psi^+(\vec{r}_N) | 0\rangle}$.

4) 算符的一次量子化形式 ⇒ 二次量子化形式.

* Fock 空间的正则变换.

对于单体 Hilbert space, 我们可以在两组正交归一基之间进行正则变换

$\sum_\alpha |\alpha\rangle\langle\alpha| = \mathbb{1}$, $\langle\alpha|\beta\rangle = \delta_{\alpha\beta}$

$\sum_{\tilde\alpha} |\tilde\alpha\rangle\langle\tilde\alpha| = \mathbb{1}$, $\langle\tilde\alpha|\tilde\beta\rangle = \delta_{\tilde\alpha\tilde\beta}$.

$|\alpha\rangle = \sum_{\tilde\alpha} U_{\alpha\tilde\alpha} |\tilde\alpha\rangle = \sum_{\tilde\alpha} \langle\tilde\alpha|\alpha\rangle |\tilde\alpha\rangle$. $UU^+ = U^+U = \mathbb{1}$ (U 为 Unitary matrix).

作为单粒子态, $|\alpha\rangle$ 可以看成 Fock 空间中的 $|0, 0, \dots n_\alpha = 1, 0, \cdots\rangle$ 态

因此, $|\alpha\rangle = a_\alpha^+ |0\rangle$.

相应地, $|\tilde\alpha\rangle = a_{\tilde\alpha}^+ |0\rangle$.

$\therefore$ $a_\alpha^+|0\rangle = \sum_{\tilde\alpha} U_{\alpha\tilde\alpha}\, a_{\tilde\alpha}^+|0\rangle$.

$a_\alpha^+ = \sum_{\tilde\alpha} U_{\alpha\tilde\alpha}\, a_{\tilde\alpha}^+ = \sum_{\tilde\alpha} \langle\tilde\alpha|\alpha\rangle\, a_{\tilde\alpha}^+$

取 h.c., 得到 $a_\alpha = \sum_{\tilde\alpha} \langle\alpha|\tilde\alpha\rangle\, a_{\tilde\alpha}$.

特别地, 令 $\tilde\alpha = \vec r$: $a_\alpha = \int d\vec r\, \langle\alpha|\vec r\rangle\, \hat\psi(\vec r) = \int d\vec r\, \psi_\alpha^*(\vec r)\, \hat\psi(\vec r)$

反过来: $\psi(\vec r) = \sum_\alpha \psi_\alpha(\vec r)\, a_\alpha$.

这里 $\psi_\alpha(\vec r) = \langle\vec r|\alpha\rangle$ 为 $|\alpha\rangle$ 的波函数.

例: 取 $\alpha = \vec k$. $\psi_k(\vec r) = e^{i\vec k\cdot\vec r}$.

$\psi(\vec r) = \sum_k a_k e^{i\vec k\cdot\vec r}$.

* 单体算符:

考虑单体算符 $\hat O_1$. 多体的 $\hat O$ 为每个粒子的 $\hat O$ 的和.

我们取一个单体的正交归一基, 使得 $\hat O_1$ 在 $|\alpha\rangle$ 下对角化.

$\hat O_1|\alpha\rangle = \lambda_\alpha|\alpha\rangle$. $\langle\alpha|\hat O_1|\beta\rangle = \delta_{\alpha\beta}$.

$\therefore$ $\hat O = \sum_\alpha \hat n_\alpha \lambda_\alpha = \sum_\alpha \hat a_\alpha^+ \hat a_\alpha \lambda_\alpha = \sum_\alpha \hat a_\alpha^+ \langle\alpha|\hat O_1|\alpha\rangle \hat a_\alpha$

$= \sum_{\alpha\beta} \hat a_\alpha^+ \langle\alpha|\hat O_1|\beta\rangle \hat a_\beta$.

利用上面介绍的幺正变换, 可以证明 $\sum_{\alpha\beta} \hat a_\alpha^+ \langle\alpha|\hat O_1|\beta\rangle \hat a_\beta$ 在基底变换下不变.
另取一组基 $|\tilde\alpha\rangle$.

$\hat O = \sum_{\alpha\beta} \hat a_\alpha^+ \langle\alpha|\hat O_1|\beta\rangle \hat a_\beta = \sum_{\alpha\beta}\sum_{\tilde\alpha\tilde\beta} \hat a_{\tilde\alpha}^+ \langle\tilde\alpha|\alpha\rangle\langle\alpha|\hat O_1|\beta\rangle\langle\beta|\tilde\beta\rangle \hat a_{\tilde\beta}$

$= \sum_{\tilde\alpha\tilde\beta} \hat a_{\tilde\alpha}^+ \langle\tilde\alpha|\hat O_1|\tilde\beta\rangle \hat a_{\tilde\beta}$.

因此, $\hat O = \sum_{\alpha\beta} \hat a_\alpha^+ \langle\alpha|\hat O_1|\beta\rangle \hat a_\beta$ 在任意基矢下均成立.

特别地，取 $\alpha=\vec{r}$.

$$\hat{O}=\int d\vec{r}d\vec{r}'\ \psi^\dagger(\vec{r})\ \langle\vec{r}|O_1|\vec{r}'\rangle\ \psi(\vec{r}')$$

对于单体势能 $\langle r|\hat{O}_1|\vec{r}'\rangle=V(\vec{r})\delta(\vec{r}-\vec{r}')$.

$$\hat{V}=\int d\vec{r}\ \psi^\dagger(\vec{r})\ V(\vec{r})\psi(\vec{r}).$$

* 两体算符.

我们考虑简单的情形： $\hat{O}_2=\sum_{\alpha\beta}\lambda_{\alpha\beta}\ |\alpha\rangle\otimes|\beta\rangle\ \langle\alpha|\otimes\langle\beta|$

在某 basis 下对角的两体算符.

当 $\alpha=\vec{r}$ 时，这包含了 $\hat{U}_2=\int d\vec{r}d\vec{r}'\ |\vec{r},\vec{r}'\rangle\ U(\vec{r}-\vec{r}')\ \langle\vec{r},\vec{r}'|$

如 Coulomb 相互作用 $U(\vec{r}-\vec{r}')=\frac{e^2}{|\vec{r}-\vec{r}'|}$.

$$\hat{O}=\sum_{\alpha<\beta}n_\alpha n_\beta\lambda_{\alpha\beta}+\sum_{\alpha=\beta}\frac{n_\alpha(n_\alpha-1)}{2}\lambda_{\alpha\alpha}.$$
$$=\frac{1}{2}\sum_{\alpha\neq\beta}n_\alpha n_\beta\lambda_{\alpha\beta}+\frac{1}{2}\sum_{\alpha=\beta}n_\alpha(n_\alpha-1)\lambda_{\alpha\alpha}$$
$$=\frac{1}{2}\sum_{\alpha\neq\beta}a_\alpha^\dagger a_\alpha a_\beta^\dagger a_\beta\ \lambda_{\alpha\beta}+\frac{1}{2}\sum_{\alpha=\beta}\underbrace{a_\alpha^\dagger a_\alpha(a_\alpha^\dagger a_\alpha-1)}_{a_\alpha^\dagger a_\alpha^\dagger a_\alpha a_\alpha}\lambda_{\alpha\alpha}.$$
$$\cancel{=\frac{1}{2}\sum_{\alpha\beta}a_\beta^\dagger a_\alpha^\dagger a_\alpha a_\beta\lambda_{\alpha\beta}}$$
$$=\frac{1}{2}\sum_{\alpha\beta}a_\alpha^\dagger a_\beta^\dagger a_\beta a_\alpha\ \langle\alpha|\otimes\langle\beta|\ \hat{O}_2\ |\alpha\rangle\otimes|\beta\rangle.$$

一般地， $\hat{O}=\frac{1}{2}\sum_{\alpha\beta\alpha'\beta'}a_{\alpha'}^\dagger a_{\beta'}^\dagger\ \langle\alpha'|\otimes\langle\beta'|\hat{O}_2|\alpha\rangle\otimes|\beta\rangle\ a_\beta a_\alpha.$

例： $U(\vec{r}-\vec{r}')=\frac{e^2}{|\vec{r}-\vec{r}'|}$

$$\hat{O}=\frac{1}{2}\int d\vec{r}d\vec{r}'\ \psi^\dagger(\vec{r})\psi^\dagger(\vec{r}')\frac{e^2}{|\vec{r}-\vec{r}'|}\psi(\vec{r}')\psi(\vec{r}).$$

5) 费米子.

* Fock space: $|0\rangle$ and $|1\rangle$. 泡利不相容原理.

$$c/c^\dagger.\quad \hat{n}=c^\dagger c.$$

$$\{c,c^\dagger\}=1.\qquad \{c,c\}=\{c^\dagger,c^\dagger\}=0\Rightarrow c^2=(c^\dagger)^2=0$$

$$0\leftarrow|0\rangle \underset{c^\dagger}{\overset{c}{\rightleftarrows}} |1\rangle\longrightarrow 0\qquad \begin{matrix}c|0\rangle=0 & c|1\rangle=0\\ c^\dagger|0\rangle=|1\rangle & c^\dagger|1\rangle=0.\end{matrix}$$

$$[\hat{n},c^\dagger]=c^\dagger\ ;\quad [\hat{n},c]=-c.$$

check: $\hat{n}|0\rangle=c^\dagger c|0\rangle=0.\qquad \hat{n}|1\rangle=c^\dagger c|1\rangle=|1\rangle.$

* 多个模式: Fock space $|\{n_\alpha\}\rangle$. $n_\alpha = 0$ or 1.

$$\{C_\alpha, C_\beta^\dagger\} = \delta_{\alpha\beta}$$

$$\{C_\alpha, C_\beta\} = \{C_\alpha^\dagger, C_\beta^\dagger\} = 0.$$

$$\hat{n}_\alpha = C_\alpha^\dagger C_\alpha.$$

$$|\{n_\alpha\}\rangle = (C_0^\dagger)^{n_0}(C_1^\dagger)^{n_1}\cdots(C_M^\dagger)^{n_M}|0\rangle = \prod_\alpha (C_\alpha^\dagger)^{n_\alpha}|0\rangle.$$

无需考虑 $\frac{1}{\sqrt{n_\alpha!}}$; 必须注意算符顺序.

* 幺正变换.

$$C_\alpha = \sum_{\tilde\alpha} \langle\alpha|\tilde\alpha\rangle C_{\tilde\alpha}.$$

$$\psi(\vec r) = \frac{1}{\sqrt V}\sum_k C_k e^{i\vec k\cdot\vec r}$$

* 算符: 单体 $\hat{O} = \sum_{\alpha\beta} C_\alpha^\dagger \langle\alpha|\hat{O}_1|\beta\rangle C_\beta$.

两体: 假设 $\hat{O}_2 = \sum_{\alpha\beta} \lambda_{\alpha\beta} |\alpha\rangle\otimes|\beta\rangle\langle\alpha|\otimes\langle\beta|$.

$$\hat{O} = \frac{1}{2}\sum_{\alpha\neq\beta}\lambda_{\alpha\beta}\hat{n}_\alpha\hat{n}_\beta + \sum_{\alpha=\beta}\lambda_{\alpha\beta}\cancel{\frac{\hat{n}_\alpha(\hat{n}_\alpha-1)}{2}} \to 0$$

$$= \frac{1}{2}\sum_{\alpha\neq\beta} C_\alpha^\dagger C_\alpha C_\beta^\dagger C_\beta \lambda_{\alpha\beta} + \cancel{\frac{1}{2}\sum_{\alpha=\beta}\lambda_{\alpha\beta} C_\alpha^\dagger C_\alpha (C_\alpha^\dagger C_\alpha - 1)}$$

$$= \frac{1}{2}\sum_{\alpha\neq\beta} C_\alpha^\dagger C_\beta^\dagger \lambda_{\alpha\beta} C_\beta C_\alpha + \cancel{\frac{1}{2}\sum_{\alpha=\beta}\lambda_{\alpha\beta}}$$

$$= \frac{1}{2}\sum_{\alpha\beta\alpha'\beta'} C_\alpha^\dagger C_\beta^\dagger \langle\alpha|\otimes\langle\beta|\hat{O}_2|\alpha'\rangle\otimes|\beta'\rangle C_{\beta'}C_{\alpha'}.$$

例: $\hat{O} = \frac{1}{2}\int d\vec r d\vec r' \psi^\dagger(\vec r)\psi^\dagger(\vec r')\frac{e^2}{|\vec r-\vec r'|}\psi(\vec r')\psi(\vec r)$.

6) Slater 行列式.

例. 自由费米子 $H = \sum_k C_k^\dagger (\frac{k^2}{2m} - \mu) C_k$

FS: $|\vec k| < k_F$, $k_F^2/2m = \mu$.

基态: $|GS\rangle = \prod_{k<k_F} C_k^\dagger|0\rangle$.

我们经常考虑 Quadratic Hamiltonians $H = \sum_{ab} C_a^\dagger H_{ab} C_b$.

将 H 对角化: $\hat{H}_1 = \sum_\alpha \lambda_\alpha |\alpha\rangle\langle\alpha|$.

$$\hat{H} = \sum_\alpha \lambda_\alpha C_\alpha^\dagger C_\alpha.$$

$$|GS\rangle = \prod_{\lambda_\alpha<0} C_\alpha^\dagger|0\rangle$$

波函数. $\langle\vec r_1,\dots,\vec r_N|GS\rangle = \langle 0|\hat\psi(\vec r_1)\cdots\hat\psi(\vec r_N)\prod_{\lambda_\alpha<0}C_\alpha^\dagger|0\rangle$

$$= \sum_{\alpha_1\cdots\alpha_N}\langle 0|\underline{C_{\alpha_1}}\phi_{\alpha_1}(\vec r_1)\cdots C_{\alpha_N}\phi_{\alpha_N}(\vec r_N)\prod_{\lambda_\alpha<0}C_\alpha^\dagger|0\rangle$$

$C_{\alpha_1}\cdots C_{\alpha_N}$ 必须与 $\prod_{\lambda_\alpha<0}C_\alpha^\dagger$ 一一对应.

$$\{\alpha_1,\dots,\alpha_N\} = \{\alpha\,|\,\lambda_\alpha<0\}.$$

$\langle 0 | C_{\alpha_1} \cdots C_{\alpha_N} \prod_{\lambda_\alpha<0} C_\alpha^\dagger | 0 \rangle = \pm 1$. 取决于 $\{\alpha_1, \cdots, \alpha_N\} \to \{\alpha | \lambda_\alpha < 0\}$ 的置换的奇偶性.

$\therefore \langle \vec{r}_1, \cdots, \vec{r}_N | GS \rangle = \sum_{\{\alpha_1 \cdots \alpha_N\} = \{\alpha | \lambda_\alpha < 0\}} \mathrm{sgn}(\alpha_1, \cdots \alpha_N)\, \varphi_{\alpha_1}(\vec{r}_1) \cdots \varphi_{\alpha_N}(\vec{r}_N)$

$= \det [\varphi_{\alpha_i}(\vec{r}_j)]$.

归一化因子: $\int_{\vec{r}_1 < \cdots < \vec{r}_N} d\vec{r}_1 \cdots d\vec{r}_N |\Psi(\vec{r}_1, \cdots, \vec{r}_N)|^2 = 1$

教书上取 $\int d\vec{r}_1 \cdots d\vec{r}_N |\Psi(\vec{r}_1, \cdots, \vec{r}_N)|^2 = 1 = N! \int_{\vec{r}_1 < \cdots < \vec{r}_N} d\vec{r}_1 \cdots d\vec{r}_N |\psi|^2$

按这个归一化方式, $|GS\rangle$ 波函数为

$\frac{1}{\sqrt{N!}} \langle \vec{r}_1, \cdots, \vec{r}_N | GS \rangle = \frac{1}{\sqrt{N!}} \det [\varphi_{\alpha_i}(\vec{r}_j)]$. Slater det

* 二次型 $\hat{H} = \sum_{\alpha\beta} C_\alpha^\dagger \langle \alpha | \hat{H}_1 | \beta \rangle C_\beta \iff$ 基态波函数 $|GS\rangle = \prod_{\lambda_\alpha < 0} C_\alpha^\dagger |0\rangle$

7) Hartree - Fock 近似.

$\hat{H}_1 = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})$.

$\hat{H}_2 = \frac{e^2}{|\vec{r} - \vec{r}'|}$.

$\hat{H} = \sum_\sigma \int d\vec{r}\, \psi_\sigma^\dagger(\vec{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi_\sigma(\vec{r})$

$+ \frac{1}{2} \sum_{\sigma\sigma'} \int d\vec{r}\, d\vec{r}'\, \psi_\sigma^\dagger(\vec{r}) \psi_{\sigma'}^\dagger(\vec{r}') \frac{e^2}{|\vec{r} - \vec{r}'|} \psi_{\sigma'}(\vec{r}') \psi_\sigma(\vec{r})$.

(平均场近似) Ansatz (变分波函数).

$|H_F\rangle = \prod_{\alpha \in A} C_\alpha^\dagger |0\rangle$ $\alpha \in A$ - 系列占据态, 不拘泥于完备基.

* Wick 定理.

Thm. 对于一个乘积态 $|\Phi\rangle = \prod_\alpha C_\alpha^\dagger |0\rangle$,

$\langle \Phi | C_1^\dagger C_2^\dagger C_3 C_4 | \Phi \rangle = \langle \Phi | C_1^\dagger C_4 | \Phi \rangle \langle \Phi | C_2^\dagger C_3 | \Phi \rangle$

$- \langle \Phi | C_1^\dagger C_3 | \Phi \rangle \langle \Phi | C_2^\dagger C_4 | \Phi \rangle$.

Proof. 首先考虑 $\langle C_\alpha^\dagger C_\beta^\dagger C_{\beta'} C_{\alpha'} \rangle$

(这里 $\langle \cdot \rangle = \langle \Phi | \cdot | \Phi \rangle$).

$\langle \Phi | C_\alpha^\dagger C_\beta^\dagger C_{\beta'} C_{\alpha'} | \Phi \rangle \neq 0$ 必须 $\{\alpha, \beta\} = \{\alpha', \beta'\} \subset A$.

若 $\alpha = \alpha', \beta = \beta'$: $\langle C_\alpha^\dagger C_\beta^\dagger C_{\beta'} C_{\alpha'} \rangle = \delta_{\alpha\alpha'} \delta_{\beta\beta'} = \langle C_\alpha^\dagger C_{\alpha'} \rangle \langle C_\beta^\dagger C_{\beta'} \rangle$

若 $\alpha = \beta', \alpha' = \beta$: $\langle C_\alpha^\dagger C_\beta^\dagger C_{\beta'} C_{\alpha'} \rangle = -\delta_{\alpha\beta'} \delta_{\beta\alpha'} = -\langle C_\alpha^\dagger C_{\beta'} \rangle \langle C_\beta^\dagger C_{\alpha'} \rangle$.

$\therefore \langle C_\alpha^\dagger C_\beta^\dagger C_{\beta'} C_{\alpha'} \rangle = \langle C_\alpha^\dagger C_{\alpha'} \rangle \langle C_\beta^\dagger C_{\beta'} \rangle - \langle C_\alpha^\dagger C_{\beta'} \rangle \langle C_\beta^\dagger C_{\alpha'} \rangle$.

對于任意 $C_1^\dagger C_2^\dagger C_3 C_4$, 将 C_i 展开至 C_α 下, 再用线性性质即可证明

用Wick定理，我们计算

$$E_{HF} = \langle HF | \hat{H} | HF \rangle = \int d\vec{r} \langle \psi^\dagger(\vec{r}) \left(-\frac{\hbar^2\nabla^2}{2m} + V\right) \psi(\vec{r}) \rangle$$

$$= \cancel{\sum_{\alpha\in A} \int d\vec{r}\, \phi_\alpha} \quad + \frac{1}{2} \int d\vec{r} d\vec{r}\,' \frac{e^2}{|\vec{r}-\vec{r}\,'|} \langle \psi^\dagger(\vec{r}) \psi^\dagger(\vec{r}\,') \psi(\vec{r}\,') \psi(\vec{r}) \rangle$$

$$\cancel{= \sum_{\alpha} \int d\vec{r} \langle \psi^\dagger_\alpha(\vec{r}) \left(-\frac{\nabla^2}{2m} + V\right) \psi_\alpha(\vec{r}) \rangle}$$

$$= \sum_{\alpha\in A} \int d\vec{r}\, \phi^*_\alpha(\vec{r}) \left(-\frac{\nabla^2}{2m} + V\right) \phi_\alpha(\vec{r})$$

$$+ \frac{1}{2} \int d\vec{r} d\vec{r}\,' \frac{e^2}{|\vec{r}-\vec{r}\,'|} \Big[\langle \psi^\dagger(\vec{r}) \psi(\vec{r}) \rangle \langle \psi^\dagger(\vec{r}\,') \psi(\vec{r}\,') \rangle - \langle \psi^\dagger(\vec{r}) \psi(\vec{r}\,') \rangle \langle \psi^\dagger(\vec{r}\,') \psi(\vec{r}) \rangle \Big]$$

$$= \sum_{\alpha\in A} \int d\vec{r}\, \phi^*_\alpha(\vec{r}) \left(-\frac{\hbar^2\nabla^2}{2m} + V\right) \phi_\alpha(\vec{r})$$

$$+ \frac{1}{2} \sum_{\alpha\beta\in A} \int d\vec{r} d\vec{r}\,' |\phi_\alpha(\vec{r})|^2 |\phi_\beta(\vec{r}\,')|^2 \frac{e^2}{|\vec{r}-\vec{r}\,'|}$$

$$\underbrace{- \frac{1}{2} \sum_{\alpha\beta\in A} \int d\vec{r} d\vec{r}\,' \phi^*_\alpha(\vec{r}) \phi^*_\beta(\vec{r}\,') \frac{e^2}{|\vec{r}-\vec{r}\,'|} \phi_\alpha(\vec{r}\,') \phi_\beta(\vec{r})}_{\text{交换相互作用}}$$

变分原理： $\min\ E_{HF} - \sum_{\alpha\in A} \epsilon_\alpha \int d\vec{r}\, |\phi_\alpha(\vec{r})|^2$

$$\frac{\delta E_{HF}}{\delta \phi^*_\alpha(\vec{r})} = \epsilon_\alpha \frac{\delta}{\delta \phi^*_\alpha(\vec{r})} \int d\vec{r}\, |\phi_\alpha(\vec{r})|^2 = \epsilon_\alpha \phi_\alpha(\vec{r})$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + \sum_\beta \int d\vec{r}\,' \phi^*_\beta(\vec{r}\,') \phi_\beta(\vec{r}\,') \frac{e^2}{|\vec{r}-\vec{r}\,'|} \right] \phi_\alpha(\vec{r})$$

$$- \sum_\beta \int d\vec{r}\,' \phi^*_\beta(\vec{r}\,') \phi_\alpha(\vec{r}\,') \phi_\beta(\vec{r}) \frac{e^2}{|\vec{r}-\vec{r}\,'|} = \epsilon_\alpha \phi_\alpha(\vec{r})$$

这里 $\langle \psi^\dagger(\vec{r}) \psi(\vec{r}\,') \rangle_{HF}$

$$= \sum_{\alpha\beta} \langle c^\dagger_\alpha c_\beta \rangle \phi^*_\alpha(\vec{r}) \phi_\beta(\vec{r}\,')$$

$$= \sum_{\alpha\in A} \phi^*_\alpha(\vec{r}) \phi_\alpha(\vec{r}\,').$$