2.2.1节 自旋轨道与空间轨道习题解析

练习2.1 $\langle \chi_{2i-1} | \chi_{2j-1} \rangle = \langle \psi_i^{\alpha} | \psi_j^{\alpha} \rangle = \delta_{ij} \cdot 1 = \delta_{ij}$； $\langle \chi_{2i} | \chi_{2j} \rangle = \langle \psi_i^{\beta} | \psi_j^{\beta} \rangle = \delta_{ij} \cdot 1 = \delta_{ij}$

$\langle \chi_{2i-1} | \chi_{2j} \rangle = \langle \psi_i^{\alpha} | \psi_j^{\beta} \rangle = S_{ij} \cdot 0 = 0$ ； $\langle \chi_{2i} | \chi_{2j-1} \rangle = \langle \psi_i^{\beta} | \psi_j^{\alpha} \rangle = S_{ij} \cdot 0 = 0$.

2.2.2节(Hartree积)习题解析

练习2.2. $\mathcal{H}\Psi^{HP} = \sum_{i=1}^{N} h(i)\Psi^{HP} = \sum_{i=1}^{N} \varepsilon_i \Psi^{HP} = \left(\sum_{i=1}^{N} \varepsilon_i\right)\Psi^{HP}$ $\quad \therefore E = \sum_{i=1}^{N} \varepsilon_i$.

2.2.3节（Slater行列式）习题解析

练习2.3 $\langle\Psi|\Psi\rangle=\int_{\Omega_1}dx_1\int_{\Omega_2}dx_2\frac{1}{\sqrt{2}}[\chi_i(1)\chi_j(2)-\chi_j(1)\chi_i(2)]^*\frac{1}{\sqrt{2}}[\chi_i(1)\chi_j(2)-\chi_j(1)\chi_i(2)]=\frac{1}{2}(1+0+0+1)=1.$

练习2.4 $\mathscr{H}\frac{1}{\sqrt{2}}(\chi_i(1)\chi_j(2)-\chi_j(1)\chi_i(2))=h(1)\frac{1}{\sqrt{2}}(\chi_i(1)\chi_j(2)-\chi_j(1)\chi_i(2))+h(2)\frac{1}{\sqrt{2}}(\chi_i(1)\chi_j(2)-\chi_j(1)\chi_i(2))$

$=\varepsilon_i\frac{1}{\sqrt{2}}\chi_i(1)\chi_j(2)-\varepsilon_j\frac{1}{\sqrt{2}}\chi_j(1)\chi_i(2)+\frac{1}{\sqrt{2}}\varepsilon_j\chi_i(1)\chi_j(2)-\frac{1}{\sqrt{2}}\varepsilon_i\chi_j(1)\chi_i(2)=(\varepsilon_i+\varepsilon_j)\frac{1}{\sqrt{2}}(\chi_i(1)\chi_j(2)-\chi_j(1)\chi_i(2)).$

从而$|\Psi^{HP}\rangle$能量为$\varepsilon_i+\varepsilon_j$.

练习2.5 $\langle K|L\rangle=\langle ij|kl\rangle\cancel{=\frac{1}{2}[\chi_i(1)\chi_j(2)-\chi_j(1)\chi_i(2)]^*}$

$=\frac{1}{2}\int_{\Omega_1}dx_1\int_{\Omega_2}dx_2[\chi_i(1)\chi_j(2)-\chi_j(1)\chi_i(2)]^*[\chi_k(1)\chi_l(2)-\chi_l(1)\chi_k(2)]=\frac{1}{2}[\langle ij|kl\rangle-\langle ij|lk\rangle-\langle ji|kl\rangle+\langle ji|lk\rangle]$

$=\frac{1}{2}[\delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk}-\delta_{jk}\delta_{il}+\delta_{jl}\delta_{ik}]=\delta_{ik}\delta_{jl}-\delta_{jk}\delta_{il}=\delta_{ij}^{kl}$

推广：我们知道，在平直空间张量分析中，$\delta_{ij}^{kl}\equiv\delta_{ik}\delta_{jl}-\delta_{jk}\delta_{il}$. 故而大胆猜测有

$$\langle\chi_{i_1}\chi_{i_2}\cdots\chi_{i_N}|\chi_{j_1}\chi_{j_2}\cdots\chi_{j_N}\rangle=\delta_{i_1i_2\cdots i_N}^{j_1j_2\cdots j_N}$$

证明：$\langle i_1i_2\cdots i_N|j_1j_2\cdots j_N\rangle=\frac{1}{N!}\sum_{i_1i_2\cdots i_N}\sum_{j_1j_2\cdots j_N}(-1)^{\tau(i_1i_2\cdots i_N)+\tau(j_1j_2\cdots j_N)}\cdot(-1)\delta_{i_1i_2\cdots i_N}^{j_1j_2\cdots j_N}=\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)+\tau(j_1j_2\cdots j_N)}\delta_{i_1}^{j_1}\delta_{i_2}^{j_2}\cdots\delta_{i_N}^{j_N}=\delta_{i_1i_2\cdots i_N}^{j_1j_2\cdots j_N}.$

2.5节(H$_2$模型的最小基)习题解析

练习2.6 $\langle\psi_1|\psi_1\rangle=\frac{1}{2(1+S_{12})}\int_{\Omega r_1}dr_1\int_{\Omega r_2}dr_2(\phi_1+\phi_2)^*(\phi_1+\phi_2)=\frac{1}{2(1+S_{12})}(1+S_{12}+S_{12}+1)=1$. 同理,$\langle\psi_2|\psi_2\rangle=1$.

$\langle\psi_1|\psi_2\rangle=\frac{1}{2\sqrt{1-S_{12}^2}}\int_{\Omega r_1}dr_1\int_{\Omega r_2}dr_2(\phi_1+\phi_2)^*(\phi_1-\phi_2)=\frac{1}{2\sqrt{1-S_{12}^2}}(1-S_{12}+S_{12}-1)=0$.

故ψ_1与ψ_2形成一个标准正交基.

2.2.7节（准确波函数的构建及组态相互作用）习题解析

练习2.7　苯分子有42个电子（1个碳原子提供6个，1个氢原子提供1个），却有36个原子轨道（1个碳原子提供1s，2s及2p三种5个轨道，1个氢原子提供1种1个s轨道。考虑到一个原子轨道可容纳一对电子（当然，自旋不能相同）。由电子的不可分辨性，有$C_{72}^{42}=1.64\times10^{20}$种方法，此即Full CI中行列式总数

单激发态需选1个电子填充另一组空轨道，从而有$C_{42}^{1}C_{30}^{1}=1260$种，

类似地，双激发态有$C_{32}^{2}C_{40}^{2}\doteq3.74\times10^{5}$种。

2.3.1节（H_2最小基矩阵元）习题解析

练习2.8 $\langle \Psi_{12}^{34} | \mathcal{O}_1 | \Psi_{12}^{34} \rangle = \langle \Psi_{12}^{34} | h(1) | \Psi_{12}^{34} \rangle + \langle \Psi_{12}^{34} | h(2) | \Psi_{12}^{34} \rangle$.

$\langle 2\bar{2} | h(1) | 2\bar{2} \rangle = \frac{1}{2} \int_{\Omega_1} dx_1 \int_{\Omega_2} dx_2 \, [\chi_3(1)\chi_4(2) - \chi_4(1)\chi_3(2)]^* h(1) [\chi_3(1)\chi_4(2) - \chi_4(1)\chi_3(2)]$

$= \frac{1}{2} \int_{\Omega_1} dx_1 [\chi_3^*(1) h(1) \chi_3(1) + \chi_4^*(1) h(1) \chi_4(1)] = \frac{1}{2} [\langle 3|h|3 \rangle + \langle 4|h|4 \rangle]$，同理，$\langle 2\bar{2} | h(2) | 2\bar{2} \rangle = \frac{1}{2} [\langle 3|h|3 \rangle + \langle 4|h|4 \rangle]$

$\therefore \langle 2\bar{2} | \mathcal{O}_1 | 2\bar{2} \rangle = \langle 2\bar{2} | h(1) | 2\bar{2} \rangle + \langle 2\bar{2} | h(2) | 2\bar{2} \rangle = \langle 3|h|3 \rangle + \langle 4|h|4 \rangle$.

而 $\langle 2\bar{2} | h(1) | \Psi_0 \rangle = \frac{1}{2} \int_{\Omega_1} dx_1 \int_{\Omega_2} dx_2 \, [\chi_3(1)\chi_4(2) - \chi_3(2)\chi_4(1)]^* h(1) [\chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(1)] = 0$. 同理，$\langle \Psi_{12}^{34} | h(2) | \Psi_0 \rangle = 0$.

从而 $\langle \Psi_{12}^{34} | \mathcal{O}_1 | \Psi_0 \rangle = 0$. 同理，$\langle \Psi_0 | \mathcal{O}_1 | \Psi_{12}^{34} \rangle = 0$.

练习2.9 同教材方法推导即可，注意重积分的值和积分变量无关，允许交换积分坐标。

$\langle \Psi_0 | \mathcal{O}_2 | \Psi_{12}^{34} \rangle = \frac{1}{2} \int_{\Omega_1} dx_1 \int_{\Omega_2} dx_2 \, [\chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2)]^* r_{12}^{-1} [\chi_3(1)\chi_4(2) - \chi_4(1)\chi_3(2)]$

$= \frac{1}{2} \int_{\Omega_1} dx_1 \int_{\Omega_2} dx_2 \, [\chi_1^*(1)\chi_2^*(2) r_{12}^{-1} \chi_3(1)\chi_4(2) - \chi_1^*(1)\chi_2^*(2) r_{12}^{-1} \chi_3(2)\chi_4(1) - \chi_2^*(1)\chi_1^*(2) r_{12}^{-1} \chi_3(1)\chi_4(2) + \chi_2^*(1)\chi_1^*(2) r_{12}^{-1} \chi_4(1)\chi_3(2)]$

$= \frac{1}{2} [\langle 12|34 \rangle + \langle 21|43 \rangle - \langle 12|43 \rangle - \langle 21|34 \rangle] = \frac{1}{2} [\langle 12|34 \rangle + \langle 12|34 \rangle - \langle 12|43 \rangle - \langle 12|43 \rangle] = \langle 12|34 \rangle - \langle 12|43 \rangle$.

$\therefore \langle \Psi_0 | \mathscr{H} | \Psi_{12}^{34} \rangle = \langle \Psi_0 | \mathcal{O}_1 | \Psi_{12}^{34} \rangle + \langle \Psi_0 | \mathcal{O}_2 | \Psi_{12}^{34} \rangle$. 由练习2.8得 $\langle \Psi_0 | \mathcal{O}_1 | \Psi_{12}^{34} \rangle = 0$. $\therefore \langle \Psi_0 | \mathscr{H} | \Psi_{12}^{34} \rangle = \langle 12|34 \rangle - \langle 12|43 \rangle$.

同理，$\langle \Psi_{12}^{34} | \mathscr{H} | \Psi_0 \rangle = \langle 34|12 \rangle - \langle 34|21 \rangle$. 由教材知，$\langle \Psi_0 | \mathscr{H} | \Psi_0 \rangle = \langle 1|h|1 \rangle + \langle 2|h|2 \rangle + \langle 12|12 \rangle - \langle 12|21 \rangle$.

同理 $\langle \Psi_{12}^{34} | \mathscr{H} | \Psi_0 \rangle = \langle \Psi_{12}^{34} | \mathcal{O}_1 | \Psi_{12}^{34} \rangle + \langle \Psi_{12}^{34} | \mathcal{O}_2 | \Psi_{12}^{34} \rangle = \langle 3|h|3 \rangle + \langle 4|h|4 \rangle + \langle 34|34 \rangle - \langle 34|43 \rangle$.

2.3.3节(矩阵元的一般规则)习题解析

练习2.10　先推导式(2.109a)与式(2.109b),再以之推导他式.

$\langle mm\|mm\rangle = \langle mm|mm\rangle - \langle mm|mm\rangle = 0$. 同理, $\langle nn\|nn\rangle = 0$. 式(2.109a)得证.

$\langle mn\|mn\rangle = \langle mn|mn\rangle - \langle mn|nm\rangle = \langle nm|nm\rangle - \langle nm|mn\rangle = \langle nm\|nm\rangle$. 式(2.109b)得证

从式(2.107)推导式(2.110)如下

$$\langle K|\mathscr{H}|K\rangle = \sum_m^N \langle m|h|m\rangle + \frac{1}{2}\sum_m^N\sum_n^N \langle mn\|mn\rangle = \sum_m^N \langle m|h|m\rangle + \sum_{n>m}^N\sum_m^N \langle mn\|mn\rangle$$

$$= \sum_m^N \langle m|h|m\rangle + \sum_{n>m}^N\sum_m^N [\langle mn|mn\rangle - \langle mn|nm\rangle] = \sum_m^N (m|h|m) + \sum_{n>m}^N\sum_m^N ([mm|nn] - [mn|nm])$$

练习2.11　利用练习2.10结论立得

$$\langle K|\mathscr{H}|K\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 3|h|3\rangle + \langle 12\|12\rangle + \langle 13\|13\rangle + \langle 23\|23\rangle.$$

练习2.12　利用矩阵元计算的一般规则计算即可. 教材式(2.111)–(2.114)已解释H_2最小基中$\langle\Psi_0|\mathscr{H}|\Psi_0\rangle$由来.而

$\langle\Psi_0|\mathcal{O}_1|\Psi_{12}^{34}\rangle = 0$,　$\langle\Psi_0|\mathcal{O}_2|\Psi_{12}^{34}\rangle = \langle 12\|34\rangle$　$\therefore \langle\Psi_0|\mathscr{H}|\Psi_{12}^{34}\rangle = \langle\Psi_0|\mathcal{O}_1|\Psi_{12}^{34}\rangle + \langle\Psi_0|\mathcal{O}_2|\Psi_{12}^{34}\rangle = \langle 12\|34\rangle$.

同理, $\langle\Psi_{12}^{34}|\mathscr{H}|\Psi_0\rangle = \langle 34\|12\rangle$., 而 $\langle\Psi_{12}^{34}|\mathcal{O}_1|\Psi_{12}^{34}\rangle = \langle 3|h|3\rangle + \langle 4|h|4\rangle$, $\langle\Psi_{12}^{34}|\mathcal{O}_2|\Psi_{12}^{34}\rangle = \langle 34\|34\rangle$

$\therefore \langle\Psi_{12}^{34}|\mathscr{H}|\Psi_{12}^{34}\rangle = \langle\Psi_{12}^{34}|\mathcal{O}_1|\Psi_{12}^{34}\rangle + \langle\Psi_{12}^{34}|\mathcal{O}_2|\Psi_{12}^{34}\rangle = \langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34\|34\rangle$.

练习2.13　利用规则计算即可。只是题目叙述不严谨, ab及rs应是紧临的两轨道, 否则不能应用表2.3.

当$a\neq b$, $r\neq s$时, $\langle\Psi_a^r|\mathcal{O}_1|\Psi_b^s\rangle$中有两电子不同, 从而$\langle\Psi_a^r|\mathcal{O}_1|\Psi_b^s\rangle = 0$;

当$a=b$, $r\neq s$时, $\langle\Psi_a^r|\mathcal{O}_1|\Psi_b^s\rangle = \langle\Psi_a^r|\mathcal{O}_1|\Psi_a^s\rangle$中有1电子不同, 从而$\langle\Psi_a^r|\mathcal{O}_1|\Psi_a^s\rangle = \langle r|h|s\rangle$;

当$a\neq b$, $r=s$时, $\langle\Psi_a^r|\mathcal{O}_1|\Psi_b^s\rangle = \langle\Psi_a^r|\mathcal{O}_1|\Psi_b^r\rangle = \langle\cdots\chi_r\cdots\chi_b\cdots|\mathcal{O}_1|\cdots\chi_a\cdots\chi_r\cdots\rangle = -\langle\cdots\chi_b\cdots\chi_r\cdots|\mathcal{O}_1|\cdots\chi_a\cdots\chi_r\cdots\rangle$

从而$\langle\Psi_a^r|\mathcal{O}_1|\Psi_b^s\rangle = -\langle b|h|a\rangle$;

当$a=b$, $r=s$时, $\langle\Psi_a^r|\mathcal{O}_1|\Psi_b^s\rangle = \langle\Psi_a^r|\mathcal{O}_1|\Psi_a^r\rangle = \sum_c^N \langle c|h|c\rangle - \langle a|h|a\rangle + \langle r|h|r\rangle$.

综上, 知原命题成立.

练习2.14　用定义验证即可, 带撇号的求和对除去a以外的所有项求和, 否则是对所有项求和.

$${}^N E_0 - {}^{N-1}E_0 = \left[\sum_b^N \langle b|h|b\rangle + \frac{1}{2}\sum_c^N\sum_d^N \langle cd\|cd\rangle\right] - \left[\sum_b^{N}{}' \langle b|h|b\rangle + \frac{1}{2}\sum_c^{N}{}'\sum_d^{N}{}' \langle cd\|cd\rangle\right]$$

$$= \langle a|h|a\rangle + \frac{1}{2}\sum_c^{N}{}' \langle ca\|ca\rangle + \frac{1}{2}\sum_d^{N}{}' \langle ad\|ad\rangle + \langle aa\|aa\rangle = \langle a|h|a\rangle + \sum_b^N \langle ab\|ab\rangle.$$

2.3.4节(矩阵元规则的推导)

练习2.15 $\mathscr{H}|\chi_i\chi_j\cdots\chi_k\rangle = \mathscr{H}\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N) = \sum_{i=1}^{N}h(i)\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N)$

$= \sum_{i=1}^{N}\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}h(i)\chi_{i_1}(1)\cdots\chi_{i_i}(i)\cdots\chi_{i_N}(N) = \frac{1}{\sqrt{N!}}\sum_{i=1}^{N}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\varepsilon_i\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N)$

$= \sum_{i=1}^{N}\varepsilon_i\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N) = \left(\sum_{i=1}^{N}\varepsilon_i\right)|\chi_i\chi_j\cdots\chi_k\rangle.$

练习2.16 由练习2.15. $\mathscr{H}|\chi_i\chi_j\cdots\chi_k\rangle = \left(\sum_{i=1}^{N}\varepsilon_i\right)|\chi_i\chi_j\cdots\chi_k\rangle$，由练习2.2. $\mathscr{H}|K^{HP}\rangle = \left(\sum_{i=1}^{N}\varepsilon_i\right)|K^{HP}\rangle$.

$\therefore \langle K|\mathscr{H}|L\rangle = \sum_{i=1}^{N}\varepsilon_i\langle K|L\rangle = \sum_{i=1}^{N}\varepsilon_i\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\langle i_1i_2\cdots i_N|L\rangle = \sum_{i=1}^{N}\varepsilon_i\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\delta^{L}_{i_1i_2\cdots i_N}.$

若$|K^{HP}\rangle$与$|L\rangle$不相同，即$\langle K^{HP}|L\rangle=0$. 则由相同种类轨道构成的$|K\rangle$必然有$\langle K|L\rangle=0$; 反之，若$\langle K^{HP}|L\rangle=1$或$\langle K^{HP}|L\rangle=-1$. 则$\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\delta^{L}_{i_1i_2\cdots i_N}$中有且仅有一项为1. 其余为0. 从而

$\langle K|\mathscr{H}|L\rangle = \frac{1}{\sqrt{N!}}\sum_{i=1}^{N}\varepsilon_i\langle K_i^{HP}|L\rangle = \frac{1}{\sqrt{N!}}\langle K^{HP}|L\rangle.$

证明单电子积分的运算规则的可参考外人读后感2.3.4节. 有详细同思路证明.

2.3.5节（从自旋轨道过渡到空间轨道）习题解析

习题2.17　依次化简练习2.9中的矩阵元，结果为

$$H(1,1)=\langle 1|h|1\rangle+\langle 2|h|2\rangle+\langle 12|12\rangle-\langle 12|21\rangle=[1|h|1]+[\bar{1}|h|\bar{1}]+[11|\bar{1}\bar{1}]-[1\bar{1}|\bar{1}1]$$
$$=(1|h|1)+(1|h|1)+(11|11)=2(1|h|1)+(11|11).$$

$$H(1,2)=\langle 12|34\rangle-\langle 12|43\rangle=[12|\bar{1}\bar{2}]-[1\bar{2}|\bar{1}2]=(12|12).$$

$$H(2,1)=\langle 34|12\rangle-\langle 34|21\rangle=[21|\bar{2}\bar{1}]-[2\bar{1}|\bar{2}1]=(21|21).$$

$$H(2,2)=\langle 3|h|3\rangle+\langle 4|h|4\rangle+\langle 34|34\rangle-\langle 34|43\rangle=[2|h|2]+[\bar{2}|h|\bar{2}]+[22|\bar{2}\bar{2}]-[2\bar{2}|\bar{2}2]$$
$$=(2|h|2)+(2|h|2)+(22|22)=2(2|h|2)+(22|22).$$

习题2.18　类比于教材中将电子脚标在闭壳层结构下折半为电子对脚标，我也如此处理。此外，由于对闭壳层系统，同一能级上电子能量（不论其自旋）相同，即成立$\varepsilon_i=\varepsilon_{\bar{i}}$，从而求和范围折半后，求和表达式的分母不变，从而在不改变结果的情况下，我将求和过程中出现的分母略去不写，以使过程简便，在最后结果中再加上它。那么，先分析求和范围变化，原求和裂为$2^4=16$组求和；而由求和表达式

$$\sum_{abrs}|\langle ab||rs\rangle|^2=\sum_{abrs}\langle ab||rs\rangle\langle sr||ab\rangle=\sum_{abrs}(\langle ab|rs\rangle-\langle ab|sr\rangle)(\langle rs|ab\rangle-\langle rs|ba\rangle)$$
$$=\sum_{abrs}([ar|bs]-[as|br])([ra|sb]-[rb|sa])=\sum_{abrs}\langle ab|rs\rangle(\langle rs|ab\rangle-\langle rs|ba\rangle)-\langle ab|sr\rangle(\langle rs|ab\rangle-\langle rs|ba\rangle).$$

的一般形式得到以下几点：

(1) 指标a,b,r,s中仅有1个和3个取自旋共轭的，每一项加数为0，从而相应的求和结果为0。
这由第二行第一个等号处表达式结果得到（对双电子积分，任一侧仅有一处有自旋共轭的值为0）。

(2) 指标a,b,r,s中的$abrs$与$\bar{a}\bar{b}\bar{r}\bar{s}$两项相加结果相等。
这由第二行第一个等号处表达式结果得到（对双电子积分$[ij|kl]=[\bar{i}\bar{j}|\bar{k}\bar{l}]=(ij|kl)$成立）。

(3) 指标a,b,r,s中仅有2个取自旋共轭的，$\bar{a}\bar{b}rs$及$ab\bar{r}\bar{s}$的求和中每一项加数为0，从而相应的求和结果为0；而$\bar{a}b\bar{r}s$与$a\bar{b}r\bar{s}$、$\bar{a}br\bar{s}$与$a\bar{b}\bar{r}s$两组求和的结果相等，可以直接合并。
这同样由第二行第一个等号处表达式结果得到（同结论(1)，得到结论前半部分，注意到对双电子积分$[\bar{i}j|k\bar{l}]=[i\bar{j}|\bar{k}l]=(ij|kl)=[ij|kl]$，从而得到此结论后半部分）。

用求和记号$\sum\cdot$表示用电子对（轨道）作脚标的求和，对a,b求和范围为$I_1^{N/2}$；对r,s求和范围为$I_{N/2+1}^{K}$。

$$\sum_{a\bar{b}r\bar{s}}^{\cdot}|\langle ab||rs\rangle|^2+\sum_{\bar{a}b\bar{r}s}^{\cdot}|\langle ab||rs\rangle|^2=2\sum_{\bar{a}b\bar{r}s}^{\cdot}\langle ab||rs\rangle=2\sum_{abrs}^{\cdot}([\bar{a}\bar{r}|bs]-[\bar{a}s|b\bar{r}])([\bar{r}\bar{a}|sb]-[\bar{r}b|s\bar{a}])$$

由双电子积分任一侧仅有一处为自旋共轭值为0，得$\left(\sum\limits_{\bar{a}b\bar{r}s}^{\cdot}+\sum\limits_{a\bar{b}r\bar{s}}^{\cdot}\right)|\langle ab||rs\rangle|^2=2\sum\limits_{abrs}^{\cdot}[ar|bs][ra|sb]$

从而，$\left(\sum\limits_{a\bar{b}r\bar{s}}^{\cdot}+\sum\limits_{\bar{a}b\bar{r}s}^{\cdot}\right)|\langle ab||rs\rangle|^2=2\sum\limits_{abrs}^{\cdot}\langle ab|rs\rangle\langle rs|ab\rangle$，同理，$\left(\sum\limits_{\bar{a}br\bar{s}}^{\cdot}+\sum\limits_{a\bar{b}\bar{r}s}^{\cdot}\right)|\langle ab||rs\rangle|^2=2\sum\limits_{abrs}^{\cdot}\langle ab|sr\rangle\langle rs|ba\rangle$。

从而由上面三条结论及上述对双自旋共轭部分求和之结果，得到（合并$abrs$与$\bar{a}\bar{b}\bar{r}\bar{s}$求和）

$$\sum_{abrs}|\langle ab||rs\rangle|^2=\left(\sum_{abrs}^{\cdot}+\sum_{\bar{a}\bar{b}\bar{r}\bar{s}}^{\cdot}+\sum_{\bar{a}b\bar{r}s}^{\cdot}+\sum_{\bar{a}br\bar{s}}^{\cdot}+\sum_{a\bar{b}r\bar{s}}^{\cdot}+\sum_{a\bar{b}\bar{r}s}^{\cdot}\right)|\langle ab||rs\rangle|^2$$
$$=2\sum_{abrs}^{\cdot}\langle ab|rs\rangle(\langle rs|ab\rangle-\langle rs|ba\rangle)-\langle ab|sr\rangle(\langle rs|ab\rangle-\langle rs|ba\rangle)+\langle ab|rs\rangle\langle rs|ab\rangle+\langle ab|sr\rangle\langle rs|ba\rangle$$
$$=2\sum_{abrs}^{\cdot}2\langle ab|rs\rangle\langle rs|ab\rangle-\langle ab|rs\rangle\langle rs|ba\rangle+2\langle ab|sr\rangle\langle rs|ba\rangle-\langle ab|sr\rangle\langle rs|ab\rangle.$$

$$=2\sum_{abrs} 2\langle ab|rs\rangle\langle rs|ab\rangle-\langle ab|rs\rangle\langle rs|ba\rangle+2\sum_{abrs} 2\langle ab|sr\rangle\langle rs|ba\rangle-\langle ab|sr\rangle\langle rs|ab\rangle.$$

(之所以此处分成两项，是希望通过交换角标r与s，将之合为一项。交换后一项的角标r与s，得)

$$=2\sum_{abrs} 2\langle ab|rs\rangle\langle rs|ab\rangle-\langle ab|rs\rangle\langle rs|ba\rangle+2\sum_{abrs} 2\langle ab|rs\rangle\langle sr|ba\rangle-\langle ab|rs\rangle\langle sr|ab\rangle$$

$$=2\sum_{abrs}\cancel{2}\langle ab|rs\rangle(2\langle rs|ab\rangle-\langle rs|ba\rangle)+2\sum_{abrs}\langle ab|rs\rangle(2\langle sr|ba\rangle-\langle sr|ab\rangle),$$ 之后利用$\langle ij|kl\rangle=\langle ji|lk\rangle$.

$$=2\sum_{abrs}\langle ab|rs\rangle(2\langle rs|ab\rangle-\langle rs|ba\rangle+2\sum_{abrs}\langle ab|rs\rangle(2\langle rs|ab\rangle-\langle rs|ba\rangle=4\sum_{abrs}\langle ab|rs\rangle(2\langle rs|ab\rangle-\langle rs|ab\rangle)$$

从而 $E_0^{(2)}=\frac{1}{4}\sum_{abrs}\frac{|\langle ab||rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}=\frac{1}{4}\sum_{abrs}\frac{4\langle ab|rs\rangle(2\langle rs|ab\rangle-\langle rs|ba\rangle)}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}=\sum_{a,b=1}^{N/2}\sum_{r,s=N/2+1}^{K}\frac{\langle ab|rs\rangle(2\langle rs|ab\rangle-\langle rs|ba\rangle)}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}.$

2.3.5

2.3.6节（库仑定律与交换积分）习题解析及2.3.7节（顶经典的行列式能量解读）习题解析

练习2.19 $J_{ii}=(ii|ii)=K_{ii}$

$J_{ij}^{*}=(ii|jj)^{*}=(ii|jj)=J_{ij}$ $\quad K_{ij}^{*}=(ij|ji)^{*}=(ji|ij)=(ij|ij)=K_{ij}$

$J_{ij}=(ii|jj)=(jj|ii)=J_{ji}$ $\quad K_{ij}=(ij|ji)=(ji|ij)=K_{ji}$.

练习2.20 $K_{ij}=(ij|ji)=(ij|ij)=(ji|ji)=\langle ii|jj\rangle=\langle jj|ii\rangle$.

练习2.21 注意利用练习2.20结论及练习2.17结论

$H(1,1)=2(1|h|1)+(11|11)=2h_{11}+J_{11}$

$H(1,2)=(12|12)=(12|21)=K_{12}$

$H(2,1)=(21|21)=(12|21)=K_{12}$

$H(2,2)=2(2|h|2)+(22|22)=2h_{22}+J_{22}$.

练习2.22 $E(|\Psi^{HP}_{\uparrow\downarrow}\rangle)=\langle\Psi^{HP}_{\uparrow\downarrow}|\mathscr{H}|\Psi^{HP}_{\uparrow\downarrow}\rangle=\int_{\Omega_1}dx_1\int_{\Omega_2}dx_2\,\psi_1^{*}(r_1)\alpha^{*}(\omega_1)\psi_2^{*}(r_2)\beta^{*}(\omega_2)\mathscr{H}[\psi_1(r_1)\alpha(\omega_1)\psi_2(r_2)\beta(\omega_2)]$

$=\int_{\Omega_{r_1}}dr_1\int_{\Omega_{r_2}}dr_2\,\psi_1^{*}(r_1)\psi_2^{*}(r_2)\mathscr{H}[\psi_1(r_1)\psi_2(r_2)]=\int_{\Omega_{r_1}}dr_1\int_{\Omega_{r_2}}dr_2\,\psi_1^{*}(r_1)\psi_2^{*}(r_2)(h(1)+h(2)+r_{12}^{-1})\psi_1(r_1)\psi_2(r_2)$

$=h_{11}+h_{22}+J_{11}$. 即$E(|\Psi^{HP}_{\uparrow\downarrow}\rangle)=h_{11}+h_{22}+J_{11}$，同理，$E(|\Psi^{HP}_{\downarrow\uparrow}\rangle)=h_{11}+h_{22}+J_{11}=E(\uparrow\downarrow)$

练习2.23 确定体系能量宜遵循个人设定的步骤，以免重复及遗漏

1. 先计算所有的单积分积分，顺序是从下向上依次写出；

2. 再计算所有的库仑积分，顺序是从下向上检查是否有能级有一对电子，若有即刻先写出这一对电子间的能量，排除外同能级的库仑积分后再以当前检查到的能级上的电子为一半，从下向上依次将之配对，此轮完成后不再理会这个电子，之后将此步骤应用于下一循环，至写出体系最后两电子构成的库仑积分。

3. 最后计算所有的交换积分，大体同第2步，只是两点不同：一是不再检查同一能级的一对电子（因为Pauli不相容原理不允许同自旋电子在同一轨道），二是检查二次（一次检查自旋为α，一次为β），且检查配对对象限于同自旋向电子，最后记得减去这一项的和！

(a) $E_a=(h_{11}+h_{22})+(J_{12})-(K_{12})=h_{11}+h_{22}+J_{12}-K_{12}$;

(b) $E_b=(h_{11}+h_{22})+(J_{12})+0=h_{11}+h_{22}+J_{12}$;

(c) $E_c=(2h_{11})+J_{11}+0=2h_{11}+J_{11}$;

(d) $E_d=(2h_{22})+J_{22}+0=2h_{22}+J_{22}$;

(e) $E_e=(2h_{11}+h_{22})+(J_{11}+2J_{12})-K_{12}=2h_{11}+h_{22}+J_{11}+2J_{12}-K_{12}$;

(f) $E_f=(h_{11}+2h_{22})+(J_{22}+2J_{12})-K_{12}=2h_{22}+h_{11}+J_{22}+2J_{12}-K_{12}$;

(g) $E_g=(2h_{11}+2h_{22})+(J_{11}+J_{22}+2J_{12}+2J_{21})-2K_{12}=2h_{11}+2h_{22}+J_{11}+J_{22}+4J_{12}-2K_{12}$.

2.4.1节(产生与湮灭算符及反对易关系)习题解析

练习2.24. 用式(2.194)即可,立即得到.

练习2.25. 用式(2.217)即可,立即得到.

练习2.26 $\langle\chi_i|\chi_j\rangle=\langle\ |a_i a_j^\dagger|\ \rangle=\langle\ |\delta_{ij}-a_j^\dagger a_i|\ \rangle=\delta_{ij}\langle\ |\ \rangle-\langle\ |a_j^\dagger a_i|\ \rangle=\delta_{ij}$.

练习2.27 首先,若$i\notin I_i^N \vee j\notin I_i^N$,则由于湮灭不存在对应能级的态结果为零,从而$\langle K|a_i^\dagger a_j|K\rangle=0$.

若$i\in I_i^N \wedge j\in I_i^N$. 再若$i\neq j$,则$\langle K|a_i^\dagger a_j|K\rangle$中有一电子同时位于二正交轨道,这并不被允许!此时仍有$\langle K|a_i^\dagger a_j|K\rangle=0$;否则$i=j$,使$\langle K|a_i^\dagger a_j|K\rangle=\langle K|a_i^\dagger a_i|K\rangle=\langle K|K\rangle=1$.

综上,原命题得证.

练习2.28 设r.s为虚轨道指标,a.b为实轨道指标.

a. $a_r|\Psi_0\rangle$湮灭不存在r能级的态,结果为零.从而$\langle\Psi_0|a_r^\dagger=(a_r|\Psi_0\rangle)^\dagger=0^\dagger=0$.

b. $a_a^\dagger|\Psi_0\rangle$产生已存在a能级的态,结果为零.从而$\langle\Psi_0|a_a=(a_a^\dagger|\Psi_0\rangle)^\dagger=0^\dagger=0$.

c. $a_r^\dagger a_a|\Psi_0\rangle=|\Psi_a^r\rangle$.

d. $\langle\Psi_a^r|=(|\Psi_a^r\rangle)^\dagger=(a_r^\dagger a_a|\Psi_0\rangle)^\dagger=\langle\Psi_0|a_a^\dagger a_r$

e. $a_s^\dagger a_b a_r^\dagger a_a|\Psi_0\rangle=a_s^\dagger a_b|\Psi_a^r\rangle=|\Psi_{ab}^{rs}\rangle$.

$a_r^\dagger a_s^\dagger a_b a_a|\Psi_0\rangle=a_r^\dagger(\delta_{sb}-a_b a_s^\dagger)a_a|\Psi_0\rangle=-a_r^\dagger a_b a_s^\dagger a_a|\Psi_0\rangle=-|\Psi_{ba}^{rs}\rangle=|\Psi_{ab}^{rs}\rangle$.

f. $\langle\Psi_{ab}^{rs}|=(|\Psi_{ab}^{rs}\rangle)^\dagger=(a_s^\dagger a_b a_r^\dagger a_a|\Psi_0\rangle)^\dagger=\langle\Psi_0|a_a^\dagger a_r a_b^\dagger a_s$

$\langle\Psi_{ab}^{rs}|=(|\Psi_{ab}^{rs}\rangle)^\dagger=(a_r^\dagger a_s^\dagger a_b a_a|\Psi_0\rangle)^\dagger=\langle\Psi_0|a_a^\dagger a_b^\dagger a_s a_r$

2.4.2节(二次量子化算符与其矩阵元)习题解析

练习2.29. $\langle\Psi_0|\mathscr{O}_1|\Psi_0\rangle = \langle\Psi_0|\sum_{ij}\langle i|h|j\rangle a_i^\dagger a_j|\Psi_0\rangle = \sum_{ij}\langle i|h|j\rangle\langle\Psi_0|a_i^\dagger a_j|\Psi_0\rangle$ 利用练习2.27结论,

$\therefore$ $\therefore \langle\Psi_0|\mathscr{O}_1|\Psi_0\rangle = \sum_a \langle a|h|a\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle$.

练习2.30 $\langle\Psi_a^r|\mathscr{O}_1|\Psi_0\rangle = \langle\Psi_a^r|\sum_i\sum_j\langle i|h|j\rangle a_i^\dagger a_j|\Psi_0\rangle = \sum_{ij}\langle i|h|j\rangle\langle\Psi_0|a_a^\dagger a_r a_i^\dagger a_j|\Psi_0\rangle$

显然$|\Psi_0\rangle$中必须得有j能级的电子.否则$a_j|\Psi_0\rangle=0$. 从而j只能在占据态求和,不妨记j为b.

$\therefore \langle\Psi_a^r|\mathscr{O}_1|\Psi_0\rangle = \sum_i\sum_b\langle i|h|b\rangle\langle\Psi_0|a_a^\dagger a_r a_i^\dagger a_b|\Psi_0\rangle = \sum_i\sum_b\langle i|h|b\rangle\langle\Psi_0|a_a^\dagger(\delta_{ir} - a_i^\dagger a_r)a_b|\Psi_0\rangle$

$= \sum_{ib}\langle i|h|b\rangle[\delta_{ir}\langle\Psi_0|a_a^\dagger a_b|\Psi_0\rangle - \langle\Psi_0|a_a^\dagger a_i^\dagger a_r a_b|\Psi_0\rangle]$ (由于Ψ_0没有r能级电子,及利用练习2.27结论)

$= \sum_{ib}\langle i|h|b\rangle\delta_{ir}\delta_{ab} = \langle r|h|a\rangle$.

练习2.31 $\langle\Psi_a^r|\mathscr{O}_2|\Psi_0\rangle = \langle\Psi_0|a_a^\dagger a_r\frac{1}{2}\sum_{ijkl}\langle ij|kl\rangle a_i^\dagger a_j^\dagger a_l a_k|\Psi_0\rangle = \frac{1}{2}\sum_{ijkl}\langle ij|kl\rangle\langle\Psi_0|a_a^\dagger a_r a_i^\dagger a_j^\dagger a_l a_k|\Psi_0\rangle$.

同练习2.30. 则k.l只能在占据态中求和.不妨记为c.d.

$\therefore \langle\Psi_a^r|\mathscr{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{ijcd}\langle ij|cd\rangle\langle\Psi_0|a_a^\dagger a_r a_i^\dagger a_j^\dagger a_d a_c|\Psi_0\rangle = \frac{1}{2}\sum_{ijcd}\langle ij|cd\rangle\langle\Psi_0|a_a^\dagger(\delta_{ir} - a_i^\dagger a_r)a_j^\dagger a_d a_c|\Psi_0\rangle$.

$= \frac{1}{2}\sum_{ijcd}\langle ij|cd\rangle[\delta_{ir}\langle\Psi_0|a_a^\dagger a_j^\dagger a_d a_c|\Psi_0\rangle - \langle\Psi_0|a_a^\dagger a_i^\dagger a_r a_j^\dagger a_d a_c|\Psi_0\rangle]$

$= \frac{1}{2}\sum_{ijcd}\langle ij|cd\rangle[\delta_{ir}\langle\Psi_0|a_a^\dagger a_j^\dagger a_d a_c|\Psi_0\rangle - \langle\Psi_0|a_a^\dagger a_i^\dagger(\delta_{rj} - a_j^\dagger a_r)a_d a_c|\Psi_0\rangle]$ (由于$|\Psi_0\rangle$无r能级电子,则末项为0)

$= \frac{1}{2}\sum_{ijcd}\langle ij|cd\rangle[\delta_{ir}\delta_{jd}\delta_{ac} - \delta_{rj}\delta_{id}\delta_{ac} - 0] = \frac{1}{2}\sum_d[\langle rd|ad\rangle - \langle dr|ad\rangle] = \frac{1}{2}\sum_b[\langle rb|ab\rangle - \langle rb|ba\rangle] = \frac{1}{2}\sum_b\langle rb||ab\rangle$.

2.5.1节(自旋算符)习题解析

练习2.32 a) $S_+|\alpha\rangle = S_x|\alpha\rangle + iS_y|\alpha\rangle = \frac{1}{2}|\beta\rangle - \frac{1}{2}|\beta\rangle = 0$; $S_+|\beta\rangle = S_x|\beta\rangle + iS_y|\beta\rangle = \frac{1}{2}|\alpha\rangle + \frac{1}{2}|\alpha\rangle = |\alpha\rangle$

$S_-|\alpha\rangle = S_x|\alpha\rangle - iS_y|\alpha\rangle = \frac{1}{2}|\beta\rangle + \frac{1}{2}|\beta\rangle = |\beta\rangle$; $S_-|\beta\rangle = S_x|\beta\rangle - iS_y|\beta\rangle = \frac{1}{2}|\alpha\rangle - \frac{1}{2}|\alpha\rangle = 0$.

b) $S_+S_- - S_z + S_z^2 = (S_x+iS_y)(S_x-iS_y) - S_z + S_z^2 = S_x^2+S_y^2+i(S_yS_x-S_xS_y) - S_z + S_z^2 = S_x^2+S_y^2+S_z^2 = S^2$

$S_-S_+ + S_z + S_z^2 = (S_x-iS_y)(S_x+iS_y) + S_z + S_z^2 = S_x^2+S_y^2+i(S_xS_y-S_yS_x) + S_z + S_z^2 = S_x^2+S_y^2+S_z^2 = S^2$

练习2.33. 首先，$|\alpha\rangle$及$|\beta\rangle$构成自旋空间的一个基(此空间为一个线性空间)，而S^2, S_z, S_+, S_-为其上的线性变换。

由式(2.245a)，得 $S^2(|\alpha\rangle, |\beta\rangle) = (|\alpha\rangle, |\beta\rangle)\begin{pmatrix} \frac{3}{4} & 0 \\ 0 & \frac{3}{4} \end{pmatrix}$，从而$S^2$在基$|\alpha\rangle, |\beta\rangle$上的矩阵表示为$\frac{3}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$。

当然，此表示是在基为$|\alpha\rangle, |\beta\rangle$顺序及原子单位制下的表示，更换基及单位制可能使矩阵表示形式变化。

同理，$S_z(|\alpha\rangle, |\beta\rangle) = (|\alpha\rangle, |\beta\rangle)\begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$，从而$S_z$在基$|\alpha\rangle, |\beta\rangle$上的矩阵表示为$\frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$。

类似地，S_+、S_-在基$|\alpha\rangle, |\beta\rangle$下的矩阵表示分别为$\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$，$\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$。

练习2.34. 先来证明两个引理。

引理1：$[AB, C] = A[B, C] + [A, C]B$，其中$A, B, C$间有结合律(可任意结合)及分配律(双分配)。

证明：$[AB, C] = ABC - CAB = ABC - ACB + ACB - CAB = A(BC-CB) + (AC-CA)B = A[B, C] + [A, C]B$.

引理2：$[A^2, A] = 0$.

证明：$[A^2, A] = A[A, A] + [A, A]A = 0$.

由以上两个引理之得

$[S^2, S_z] = [S_x^2, S_z] + [S_y^2, S_z] + [S_z^2, S_z] = S_x[S_x, S_z] + [S_x, S_z]S_x + S_y[S_y, S_z] + [S_y, S_z]S_y = -iS_xS_y - iS_yS_x + iS_yS_x + iS_xS_y$
$= 0$. 即得$[S^2, S_z] = 0 \Leftrightarrow S^2, S_z$有交换律.

练习2.35 先证明：若线性变换$\mathcal{A}$与$\mathcal{H}$可交换，则$\mathcal{A}|\Phi\rangle$同$|\Phi\rangle$一样是属于$\mathcal{H}$本征值E的本征函数.

$\mathcal{H}(\mathcal{A}|\Phi\rangle) = \mathcal{A}\mathcal{H}|\Phi\rangle = \mathcal{A}E|\Phi\rangle = E(\mathcal{A}|\Phi\rangle)$. 从而命题得证.

若$|\Phi\rangle$是非兼并的，则$\mathcal{H}$中属于本征值E的特征子空间(维数为1)。取$|\Phi\rangle$即为该子空间的一个基，从而$\mathcal{A}|\Phi\rangle$作为该子空间中的一个向量，必定可以被$|\Phi\rangle$线性表出；

若$|\Phi\rangle$是兼并的，由$\mathcal{H}$是Hermite变换，从而若兼并度为n，则属于本征值E的本征子空间(维数为n)(由Zorn引理，可证明任一线性空间必有一个基)，故可取找到Hermite变换$\mathcal{H}$的属于本征值E的n个本征函数做为本征值为E的特征子空间的一个基，使得通过合适的线性组合后得到$\mathcal{A}|\Phi\rangle$.

练习2.36 由于$\mathcal{A}$为Hermite变换，故本征值必为实数，从而$a_1 \in \mathbb{R}$，$a_2 \in \mathbb{R}$。再由于$\mathcal{A}\mathcal{H} = \mathcal{H}\mathcal{A}$，由练习2.35中非兼并的情形，由于$\mathcal{A}\mathcal{H}|\Psi_1\rangle = \mathcal{H}\mathcal{A}|\Psi_1\rangle = a_1\mathcal{H}|\Psi_1\rangle$，~~得到~~ $\mathcal{H}|\Psi_1\rangle$是$\mathcal{A}$的属于本征值$a_1$的本征值函数，从而$\exists\, b \in \mathbb{C}$ s.t. $\mathcal{H}|\Psi_1\rangle = b_1|\Psi_1\rangle$. 由此$\langle\Psi_1|\mathcal{H}|\Psi_2\rangle = b_1\langle\Psi_1|\Psi_2\rangle$. 而恒正空间中(西空间中)，Hermite变换属于不同本征值的特征向量必正交，从而$\langle\Psi_1|\mathcal{H}|\Psi_2\rangle = b_1\langle\Psi_1|\Psi_2\rangle = b_1 \cdot 0 = 0$.

练习2.37 下文中$N_i^{\alpha/\beta}$表示取$S_z(i)/M_{s_i}(i)$中的电子取向的自旋量子数，可能为$+\frac{1}{2}(\alpha)$，也可能为$-\frac{1}{2}(\beta)$。

$$\varphi_z|\chi_i\chi_j\cdots\chi_k\rangle = \sum_{i=1}^{N} S(i)\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N) = \sum_{i=1}^{N}\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)} S_z(i)[\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N)]$$

$$= \sum_{i=1}^{N}\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\frac{N^\alpha - N^\beta}{2}[\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N)] = \frac{N^\alpha - N^\beta}{2}\cdot\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}[\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N)] = \frac{N^\alpha - N^\beta}{2}|\chi_i\chi_j\cdots\chi_k\rangle.$$

现在证明一下教材中出现的一些式子

式(2.251)：$\varphi_+\varphi_- - \varphi_z + \varphi_z^2 = \left(\sum_{i=1}^{N} S_+(i)\right)\left(\sum_{j=1}^{N} S_-(j)\right) - \left(\sum_{i=1}^{N} S_z(i)\right) + \left(\sum_{i=1}^{N} S_z(i)\right)\left(\sum_{j=1}^{N} S_z(j)\right) = \sum_{i=1}^{N}\sum_{j=1}^{N} S_+(i)S_-(j) - \sum_{i=1}^{N} S_z(i) + \sum_{i=1}^{N}\sum_{j=1}^{N} S_z(i)S_z(j)$

$$= \sum_{i=1}^{N}\sum_{j=1}^{N}[S_x(i)+iS_y(i)][S_x(j)-iS_y(j)] - \sum_{i=1}^{N} S_z(i) + \sum_{i=1}^{N}\sum_{j=1}^{N} S_z(i)S_z(j)$$

$$= \sum_{i=1}^{N}\sum_{j=1}^{N}\{S_x(i)S_x(j) + S_y(i)S_y(j) + S_z(i)S_z(j) + i[S_y(i)S_x(j) - S_x(i)S_y(j)]\} - \sum_{i=1}^{N} S_z(i).$$

注意到 $S_y(i)S_x(j) - S_x(i)S_y(j)$ 交换角标 i,j 后 $S_y(j)S_x(i) - S_x(j)S_y(i)$ 是前者的反算符（对 i,j 分别成自旋，显然可交换），

从而 $\sum_{i=1}^{N}\sum_{j=1}^{N} i[S_y(i)S_x(j) - S_x(i)S_y(j)] = i\sum_{i=1}^{N}[S_y(i)S_x(i) - S_x(i)S_y(i)] = -i\sum_{i=1}^{N}[S_x(i), S_y(i)] = \sum_{i=1}^{N} S_z(i)$ 与最后一项抵消.

$\therefore \varphi_+\varphi_- - \varphi_z + \varphi_z^2 = \sum_{i=1}^{N}\sum_{j=1}^{N}[S_x(i)S_x(j) + S_y(i)S_y(j) + S_z(i)S_z(j)] = \left[\sum_{i=1}^{N}[S_x(i)\hat{i} + S_y(i)\hat{j} + S_z(i)\hat{k}]\right]\cdot\sum_{j=1}^{N}[S_x(j)\hat{i} + S_y(j)\hat{j} + S_z(j)\hat{k}] = \varphi^2.$

式(2.251)得证

~~式(2.253a)：$\varphi^2 = \left(\sum_{i=1}^{N}\vec{S}(i)\right)\cdot\left(\sum_{j=1}^{N}\vec{S}(j)\right) = \sum_{i=1}^{N}\sum_{j=1}^{N}[S_x(i)S_x(j) + S_y(i)S_y(j) + S_z(i)S_z(j)]$. 这个变换形式未免过于复杂，故先取出一部分研究.~~

~~$S_x(i)S_x(j)|\Phi\rangle = S_x(i)S_x(j)\sum_{i_1i_2\cdots i_N}\frac{1}{\sqrt{N!}}(-1)^{\tau(i_1i_2\cdots i_N)}\psi_{i_1}(1)\psi_{i_2}(2)\cdots\psi_{i_N}(N)\omega_{i_1}(1)\omega_{i_2}(2)\cdots\omega_{i_N}(N)$. 先考虑 $i\neq j$ 情形，则~~

~~$S_x(i)S_x(j)|\Phi\rangle = \left[\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\psi_{i_1}(1)\psi_{i_2}(2)\cdots\psi_{i_N}(N)\cdots\omega_{i_i}^*(i)\cdots\omega_{i_j}^*(j)\cdots\omega_{i_N}(N)\right]\frac{1}{4}$，而交换 i,j 位置，得~~

~~$S_x(j)S_x(i)|\Phi\rangle = \left[\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\psi_{i_1}(1)\psi_{i_2}(2)\cdots\psi_{i_N}(N)\omega_{i_1}(1)\cdots\omega_{i_j}^*(j)\cdots\omega_{i_i}^*(i)\cdots\omega_{i_N}(N)\right]\frac{1}{4}$（此处需在逆序数中易位 i 与 j）~~

~~$= \frac{1}{4}\frac{-1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}\tau^{(i_1\cdots i_i\cdots i_j\cdots i_N)}\psi_{i_1}(1)\cdots\psi_{i_N}(N)\omega_{i_1}(1)\cdots\omega_{i_i}^*(i)\cdots\omega_{i_j}^*(j)\cdots\omega_{i_N}(N) = -S_x(i)S_x(j)|\Phi\rangle.$~~

~~从而 $\forall i,j\in I^N$，$i\neq j$，$S_x(i)S_x(j) + S_x(j)S_x(i)|\Phi\rangle = 0$. 同样的方法可以去证明 $S_y(i)S_y(j) + S_y(j)S_y(i)|\Phi\rangle = S_z(i)S_z(j) + S_z(j)S_z(i)|\Phi\rangle = 0$.~~

~~从而只需讨论 $S_x^2(i) + S_y^2(i) + S_z^2(i)|\Phi\rangle$，而 $S_x^2(i)|\Phi\rangle = \frac{1}{4}|\Phi\rangle$，$S_y^2(i)|\Phi\rangle = \frac{1}{4}|\Phi\rangle$，$S_z^2(i)|\Phi\rangle = \frac{1}{4}|\Phi\rangle$.~~

~~$\therefore S_x^2(i) + S_y^2(i) + S_z^2(i)|\Phi\rangle = \frac{3}{4}|\Phi\rangle$~~

2.5.2节(受限行列式及自旋适应构象)习题解析

习题2.38　先证明对闭壳层行列式，$\mathscr{S}_+|\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\cdots\rangle=0$.

$$\mathscr{S}_+|ij\cdots k\rangle=\sum_{i=1}^{N}S_+(i)\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N)=\sum_{i=1}^{N}\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}S_+(i)[\chi_{i_1}(1)\chi_{i_2}(2)\cdots\chi_{i_N}(N)]$$

$$=\sum_{i=1}^{N}\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\psi_{i_1}(1)\psi_{i_2}(2)\cdots\psi_{i_N}(N)\prod_{j=1}^{N}{}'\omega_{i_j}(j)\,S_+(i)\,\omega_{i_i}(i)$$

$$=\sum_{i=1}^{N}\frac{1}{\sqrt{N!}}\sum_{i_1i_2\cdots i_N}(-1)^{\tau(i_1i_2\cdots i_N)}\psi_{i_1}(1)\psi_{i_2}(2)\cdots\psi_{i_N}(N)\prod_{j=1}^{N}{}'\omega_{i_j}(j)\,\delta_{\omega_i}^{\beta}\,\omega_{i_i}(\alpha)$$

从而对一对电子来讲，若ω_i为α，则$\delta_{\omega_i}^{\beta}=\delta_{\alpha}^{\beta}=0$；若$\omega_i=\beta$，则前面乘积中有$\omega_{i_i'}(\alpha)$与之相同，使得这一项违反Pauli不相容原理，从而为0. 由于体系为闭壳层，所有电子配对，从而$\sum_{i=1}^{N}$后加数全为0. 从而$\mathscr{S}_+|ij\cdots k\rangle=0$. 于是$\mathscr{S}_-\mathscr{S}_+|\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\cdots\rangle=0$. 而由式(2.254)，闭壳层必有$N^{\alpha}=N^{\beta}$. 于是$\mathscr{S}_z|\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\cdots\rangle=0$，从而对$\mathscr{S}_z^2$有$\mathscr{S}_z^2|\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\cdots\rangle=\mathscr{S}_z(\mathscr{S}_z|\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\cdots\rangle)=\mathscr{S}_z0=0$. 从而

$$\mathscr{S}^2|\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\cdots\rangle=\mathscr{S}_-\mathscr{S}_+|\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\cdots\rangle+\mathscr{S}_z|\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\cdots\rangle+\mathscr{S}_z^2|\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\cdots\rangle=0+0+0=0.$$

练习2.39　先证明$|\Psi_{\bar 1}^{\bar 2}\rangle=-\frac{1}{\sqrt2}[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)]\beta(1)\beta(2)$与$|\Psi_1^2\rangle=\frac{1}{\sqrt2}[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)]\alpha(1)\alpha(2)$是三重态.

$\cancel{\mathscr{S}_-\mathscr{S}_+=-\frac{1}{\sqrt2}[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)]\mathscr{S}_-[S_+(1)+S_+(2)][\alpha(1)\beta(2)+\beta(1)\alpha(2)]=}$

$$\mathscr{S}_-\mathscr{S}_+|\Psi_{\bar 1}^{\bar 2}\rangle=-\frac{1}{\sqrt2}[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)]\mathscr{S}_-[S_+(1)+S_+(2)]\beta(1)\beta(2)$$

$$=-\frac{1}{\sqrt2}[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)][S_-(1)+S_-(2)][\alpha(1)\beta(2)+\beta(1)\alpha(2)]$$

$$=-\frac{1}{\sqrt2}[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)][\beta(1)\beta(2)+\beta(1)\beta(2)]=2|\Psi_{\bar 1}^{\bar 2}\rangle.$$

$$\mathscr{S}_z|\Psi_{\bar 1}^{\bar 2}\rangle=-\frac{1}{\sqrt2}[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)][S_z(1)+S_z(2)]\beta(1)\beta(2)=-\frac{1}{\sqrt2}[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)](-\tfrac12\beta(1)\beta(2)-\tfrac12\beta(1)\beta(2))=-|\Psi_{\bar 1}^{\bar 2}\rangle$$

$$\mathscr{S}_z^2|\Psi_{\bar 1}^{\bar 2}\rangle=\mathscr{S}_z(\mathscr{S}_z|\Psi_{\bar 1}^{\bar 2}\rangle)=-\mathscr{S}_z|\Psi_{\bar 1}^{\bar 2}\rangle=|\Psi_{\bar 1}^{\bar 2}\rangle.$$

$$\therefore\ \mathscr{S}^2|\Psi_{\bar 1}^{\bar 2}\rangle=\mathscr{S}_-\mathscr{S}_+|\Psi_{\bar 1}^{\bar 2}\rangle+\mathscr{S}_z|\Psi_{\bar 1}^{\bar 2}\rangle+\mathscr{S}_z^2|\Psi_{\bar 1}^{\bar 2}\rangle=2|\Psi_{\bar 1}^{\bar 2}\rangle=1(1+1)|\Psi_{\bar 1}^{\bar 2}\rangle.$$

同理论证有 $\mathscr{S}_-\mathscr{S}_+|\Psi_1^2\rangle=0$，$\mathscr{S}_z|\Psi_1^2\rangle=|\Psi_1^2\rangle$，$\mathscr{S}_z^2|\Psi_1^2\rangle=|\Psi_1^2\rangle$，从而$\mathscr{S}^2|\Psi_1^2\rangle=2|\Psi_1^2\rangle=1(1+1)|\Psi_1^2\rangle$.

~~再来~~论证$|{}^3\Psi_1^2\rangle=\frac{1}{\sqrt2}(|\Psi_{\bar 1}^{\bar 2}\rangle-|\Psi_1^2\rangle)$是三重态. 由于$|{}^3\Psi_1^2\rangle=\frac12[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)][\alpha(1)\beta(2)+\beta(1)\alpha(2)]$

$$\mathscr{S}_-\mathscr{S}_+|{}^3\Psi_1^2\rangle=\frac12[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)]\mathscr{S}_-[S_+(1)+S_+(2)][\alpha(1)\beta(2)+\beta(1)\alpha(2)]$$

$$=\frac12[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)][S_-(1)+S_-(2)][\alpha(1)\alpha(2)+\alpha(1)\alpha(2)]$$

$$=2\cdot\frac12[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)][\beta(1)\alpha(2)+\alpha(1)\beta(2)]=2|{}^3\Psi_1^2\rangle.$$

$$\mathscr{S}_z|{}^3\Psi_1^2\rangle=\frac12[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)][S_z(1)+S_z(2)][\alpha(1)\beta(2)+\beta(1)\alpha(2)]$$

$$=\frac12[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)][\tfrac12\alpha(1)\beta(2)-\tfrac12\beta(1)\alpha(2)+\alpha(1)\cdot-\tfrac12\beta(2)+\beta(1)\cdot\tfrac12\alpha(2)]=0,$$ 故 $\mathscr{S}_z^2|{}^3\Psi_1^2\rangle=\mathscr{S}_z\cdot0=0$.

最后论证$|{}^1\Psi_1^2\rangle=\frac{1}{\sqrt2}(|\Psi_{\bar 1}^{\bar 2}\rangle+|\Psi_1^2\rangle)=\frac12[\psi_1(1)\psi_2(2)+\psi_1(2)\psi_2(1)][\alpha(1)\beta(2)-\beta(1)\alpha(2)]$

$$\mathscr{S}_-\mathscr{S}_+|{}^1\Psi_1^2\rangle=\frac{1}{\sqrt2}[\psi_1(1)\psi_2(2)+\psi_1(2)\psi_2(1)]\mathscr{S}_-[S_+(1)+S_+(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)]$$

$$=\frac12[\psi_1(1)\psi_2(2)+\psi_2(1)\psi_1(2)][S_-(1)+S_-(2)][-\alpha(1)\alpha(2)+\alpha(1)\alpha(2)]=0.$$

$$\mathscr{S}_z|{}^1\Psi_1^2\rangle=\frac{1}{\sqrt2}[\psi_1(1)\psi_2(2)+\psi_1(2)\psi_2(1)][S_z(1)+S_z(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)]$$

$$=\frac{1}{\sqrt2}[\psi_1(1)\psi_2(2)+\psi_1(2)\psi_2(1)][\tfrac12\alpha(1)\beta(2)+\tfrac12\alpha(1)\beta(2)+\alpha(1)\cdot-\tfrac12\beta(2)-\beta(1)\cdot\tfrac12\alpha(2)]=|{}^1\Psi_1^2\rangle.$$ 故 $\mathscr{S}_z^2|{}^1\Psi_1^2\rangle=|{}^1\Psi_1^2\rangle$.

$$\therefore\ \mathscr{S}^2|{}^1\Psi_1^2\rangle=\mathscr{S}_-\mathscr{S}_+|{}^1\Psi_1^2\rangle+\mathscr{S}_z|{}^1\Psi_1^2\rangle+\mathscr{S}_z^2|{}^1\Psi_1^2\rangle=2|{}^1\Psi_1^2\rangle=1(1+1)|{}^1\Psi_1^2\rangle.$$

练习2.40 $\langle {}^1\Psi_1^2|\mathscr{H}|{}^1\Psi_1^2\rangle = \frac{1}{2}(\langle\Psi_{\bar 1}^{\bar 2}| + \langle\Psi_1^2|)\mathscr{H}(|\Psi_1^2\rangle + |\Psi_{\bar 1}^{\bar 2}\rangle) = \frac{1}{2}[E(|\Psi_{\bar 1}^{\bar 2}\rangle) + E(|\Psi_1^2\rangle) + \langle\Psi_{\bar 1}^{\bar 2}|\mathscr{H}|\Psi_1^2\rangle + \langle\Psi_1^2|\mathscr{H}|\Psi_{\bar 1}^{\bar 2}\rangle]$

$E(|\Psi_{\bar 1}^{\bar 2}\rangle) = h_{11} + h_{22} + J_{12}$, $E(|\Psi_1^2\rangle) = h_{11} + h_{22} + J_{12}$, $\langle\Psi_{\bar 1}^{\bar 2}|\mathscr{H}|\Psi_1^2\rangle = \langle 1\bar 2|\mathscr{O}_1|2\bar 1\rangle + \langle 1\bar 2|\mathscr{O}_2|2\bar 1\rangle$

而$\langle 1\bar 2|\mathscr{O}_1|2\bar 1\rangle = 0$, $\langle 1\bar 2|\mathscr{O}_2|2\bar 1\rangle = \langle 1\bar 2|2\bar 1\rangle = [12|\bar 2\bar 1] = (12|21) = K_{12}$. 同理, $\langle\Psi_1^2|\mathscr{H}|\Psi_{\bar 1}^{\bar 2}\rangle = K_{21} = K_{12}$

$\therefore \langle {}^1\Psi_1^2|\mathscr{H}|{}^1\Psi_1^2\rangle = \frac{1}{2}(h_{11} + h_{22} + J_{12} + h_{11} + h_{22} + J_{12} + K_{12} + K_{12}) = h_{11} + h_{22} + J_{12} + K_{12}$.

同理, $\langle {}^3\Psi_1^2|\mathscr{H}|{}^3\Psi_1^2\rangle = \frac{1}{2}(\langle\Psi_{\bar 1}^{\bar 2}| - \langle\Psi_1^2|)\mathscr{H}(|\Psi_{\bar 1}^{\bar 2}\rangle - |\Psi_1^2\rangle) = \frac{1}{2}[E(|\Psi_{\bar 1}^{\bar 2}\rangle) + E(|\Psi_1^2\rangle) - \langle\Psi_1^2|\mathscr{H}|\Psi_{\bar 1}^{\bar 2}\rangle - \langle\Psi_{\bar 1}^{\bar 2}|\mathscr{H}|\Psi_1^2\rangle]$

$= \frac{1}{2}[h_{11} + h_{22} + J_{12} + h_{11} + h_{22} + J_{12} - K_{12} - K_{12}] = h_{11} + h_{22} + J_{12} - K_{12}$.

从空间函数上, $|{}^3\Psi_1^2\rangle$为相减.相应积分结果小于相加的$|{}^1\Psi_1^2\rangle$.

2.5.2

2.5.3节(不受限行列式)习题解析.

练习2.41. a.注意到$\mathscr{S}^2=\mathscr{S}_-\mathscr{S}_++\mathscr{S}_z+\mathscr{S}_z^2$，而$\mathscr{S}_z|K\rangle=0$. $\mathscr{S}_z^2|K\rangle=\mathscr{S}_z\cdot 0=0$. 故$|K\rangle$为$\mathscr{S}^2$本征函数$\Leftrightarrow|K\rangle$为$\mathscr{S}_-\mathscr{S}_+$的本征函数.

$\mathscr{S}_-\mathscr{S}_+|K\rangle=\mathscr{S}_-[S_+(1)+S_+(2)]\frac{1}{\sqrt{2}}[\psi_1^\alpha(1)\alpha(1)\psi_1^\beta(2)\beta(2)-\psi_1^\beta(1)\beta(1)\psi_1^\alpha(2)\alpha(2)]$

$=[S_-(1)+S_-(2)]\frac{1}{\sqrt{2}}[\psi_1^\alpha(1)\alpha(1)\psi_1^\beta(2)\alpha(2)-\psi_1^\beta(1)\alpha(1)\psi_1^\alpha(2)\alpha(2)]=\frac{1}{\sqrt{2}}[\psi_1^\alpha(1)\psi_1^\beta(2)-\psi_2^\beta(1)\psi_1^\alpha(2)][S_-(1)+S_-(2)]\alpha(1)\alpha(2)$.

$=\frac{1}{\sqrt{2}}[\psi_1^\alpha(1)\psi_1^\beta(2)-\psi_1^\beta(1)\psi_1^\alpha(2)][\beta(1)\alpha(2)+\alpha(1)\beta(2)]=|\psi_1^\alpha\bar{\psi}_1^\beta\rangle-|\psi_1^\beta\bar{\psi}_1^\alpha\rangle$

$\therefore|K\rangle$是$\mathscr{S}^2$的本征函数$\Leftrightarrow|K\rangle$是$\mathscr{S}_-\mathscr{S}_+$的本征函数$\Leftrightarrow\psi_1^\alpha=\psi_1^\beta$.

b. $\langle K|\mathscr{S}^2|K\rangle=\frac{1}{2}\int_{\Omega_1}dx_1\int_{\Omega_2}dx_2[\psi_1^\alpha(1)\alpha(1)\psi_1^\beta(2)\beta(2)-\psi_1^\beta(1)\beta(1)\psi_1^\alpha(2)\alpha(2)]^*\mathscr{S}^2[\psi_1^\alpha(1)\alpha(1)\psi_1^\beta(2)\beta(2)-\psi_1^\beta(1)\beta(1)\psi_1^\alpha(2)\alpha(2)]$

$=\frac{1}{2}\int_{\Omega_1}dx\int_{\Omega_2}dx_2[\psi_1^\alpha(1)\alpha(1)\psi_1^\beta(2)\beta(2)-\psi_1^\beta(1)\beta(1)\psi_1^\alpha(2)\alpha(2)]^*[\psi_1^\alpha(1)\beta(1)\psi_1^\beta(2)\alpha(2)+\psi_1^\alpha(1)\alpha(1)\psi_1^\beta(2)\beta(2)-\psi_1^\beta(1)\beta(1)\psi_1^\alpha(2)\alpha(2)-\psi_1^\beta(1)\alpha(1)\psi_2^\alpha(2)\beta(2)]$

$=\frac{1}{2}[0+1+0-|S_{11}^{\alpha\beta}|^2-|S_{11}^{\beta\alpha}|^2-0+1+0]=1-|S_{11}^{\alpha\beta}|^2$