课堂练习

练习1：设由多电子波函数基组表示的矢量$|K\rangle = |\chi_i\chi_j\rangle, |L\rangle = |\chi_k\chi_l\rangle$，求$\langle K|L\rangle$

解：根据Slater行列式的表达式，我们知道$|K\rangle = \frac{1}{\sqrt{2!}}\begin{vmatrix} \chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1) \\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2) \end{vmatrix}$，

$|L\rangle = \frac{1}{\sqrt{2!}}\begin{vmatrix} \chi_k(\boldsymbol{x}_1) & \chi_l(\boldsymbol{x}_1) \\ \chi_k(\boldsymbol{x}_2) & \chi_l(\boldsymbol{x}_2) \end{vmatrix}$，因此

$$
\begin{aligned}
\langle K|L\rangle &= \iint \frac{1}{\sqrt{2!}}\begin{vmatrix} \chi_i^*(\boldsymbol{x}_1) & \chi_j^*(\boldsymbol{x}_1) \\ \chi_i^*(\boldsymbol{x}_2) & \chi_j^*(\boldsymbol{x}_2) \end{vmatrix} \cdot \frac{1}{\sqrt{2!}}\begin{vmatrix} \chi_k(\boldsymbol{x}_1) & \chi_l(\boldsymbol{x}_1) \\ \chi_k(\boldsymbol{x}_2) & \chi_l(\boldsymbol{x}_2) \end{vmatrix} d\boldsymbol{x}_1 d\boldsymbol{x}_2 \\
&= \iint \frac{1}{2}[\chi_i^*(\boldsymbol{x}_1)\chi_j^*(\boldsymbol{x}_2) - \chi_j^*(\boldsymbol{x}_1)\chi_i^*(\boldsymbol{x}_2)][\chi_k(\boldsymbol{x}_1)\chi_l(\boldsymbol{x}_2) - \chi_l(\boldsymbol{x}_1)\chi_k(\boldsymbol{x}_2)] d\boldsymbol{x}_1 d\boldsymbol{x}_2 \\
&= \frac{1}{2}[\int \chi_i^*(\boldsymbol{x}_1)\chi_k(\boldsymbol{x}_1)d\boldsymbol{x}_1 \int \chi_j^*(\boldsymbol{x}_2)\chi_l(\boldsymbol{x}_2)d\boldsymbol{x}_2 - \int \chi_j^*(\boldsymbol{x}_1)\chi_k(\boldsymbol{x}_1)d\boldsymbol{x}_1 \int \chi_i^*(\boldsymbol{x}_2)\chi_l(\boldsymbol{x}_2)d\boldsymbol{x}_2 \\
&\quad - \int \chi_i^*(\boldsymbol{x}_1)\chi_l(\boldsymbol{x}_1)d\boldsymbol{x}_1 \int \chi_j^*(\boldsymbol{x}_2)\chi_k(\boldsymbol{x}_2)d\boldsymbol{x}_2 + \int \chi_j^*(\boldsymbol{x}_1)\chi_l(\boldsymbol{x}_1)d\boldsymbol{x}_1 \int \chi_i^*(\boldsymbol{x}_2)\chi_k(\boldsymbol{x}_2)d\boldsymbol{x}_2] \\
&= \frac{1}{2}[\delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il} - \delta_{il}\delta_{jk} + \delta_{jl}\delta_{ik}] = \delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il}
\end{aligned}
$$

练习2：证明如果$|\Psi\rangle = |\chi_i\chi_j\dots\chi_l\rangle$和$|\Psi^{'}\rangle = |\chi_{i^{'}}\chi_{j^{'}}\dots\chi_{l^{'}}\rangle$是由正交归一轨道构成的两个Slater行列式波函数，如果它们由不同的单电子轨道组成，则有$\langle\Psi|\Psi^{'}\rangle = 0$；如果它们由相同的一组单电子轨道构成，则有$\langle\Psi|\Psi^{'}\rangle = (-1)^P$，这里$P$是将$i, j, \dots, l$变成$i^{'}, j^{'}, \dots, l^{'}$所需要进行互换的次数。

证明：据Slater行列式表达式，我们有$|\Psi\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1) & \dots & \chi_l(\boldsymbol{x}_1) \\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2) & \dots & \chi_l(\boldsymbol{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(\boldsymbol{x}_N) & \chi_j(\boldsymbol{x}_N) & \dots & \chi_l(\boldsymbol{x}_N) \end{vmatrix}$，

$|\Psi^{'}\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_{i^{'}}(\boldsymbol{x}_1) & \chi_{j^{'}}(\boldsymbol{x}_1) & \dots & \chi_{l^{'}}(\boldsymbol{x}_1) \\ \chi_{i^{'}}(\boldsymbol{x}_2) & \chi_{j^{'}}(\boldsymbol{x}_2) & \dots & \chi_{l^{'}}(\boldsymbol{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_{i^{'}}(\boldsymbol{x}_N) & \chi_{j^{'}}(\boldsymbol{x}_N) & \dots & \chi_{l^{'}}(\boldsymbol{x}_N) \end{vmatrix}$，因此它们的内积为

$$
\begin{aligned}
\langle\Psi|\Psi^{'}\rangle &= \int\cdots\int \frac{1}{N!}\begin{vmatrix} \chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1) & \dots & \chi_l(\boldsymbol{x}_1) \\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2) & \dots & \chi_l(\boldsymbol{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(\boldsymbol{x}_N) & \chi_j(\boldsymbol{x}_N) & \dots & \chi_l(\boldsymbol{x}_N) \end{vmatrix} \cdot \begin{vmatrix} \chi_{i^{'}}(\boldsymbol{x}_1) & \chi_{j^{'}}(\boldsymbol{x}_1) & \dots & \chi_{l^{'}}(\boldsymbol{x}_1) \\ \chi_{i^{'}}(\boldsymbol{x}_2) & \chi_{j^{'}}(\boldsymbol{x}_2) & \dots & \chi_{l^{'}}(\boldsymbol{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_{i^{'}}(\boldsymbol{x}_N) & \chi_{j^{'}}(\boldsymbol{x}_N) & \dots & \chi_{l^{'}}(\boldsymbol{x}_N) \end{vmatrix} d\boldsymbol{x}_1 d\boldsymbol{x}_2 \dots d\boldsymbol{x}_N \\
&= \int\cdots\int \frac{1}{N!}[\sum_P (-1)^P \chi_i(\boldsymbol{x}_{P_1})\chi_j(\boldsymbol{x}_{P_2})\dots\chi_l(\boldsymbol{x}_{P_N}) \sum_Q (-1)^Q \chi_{i^{'}}(\boldsymbol{x}_{Q_1})\chi_{j^{'}}(\boldsymbol{x}_{Q_2})\dots\chi_{l^{'}}(\boldsymbol{x}_{Q_N})] d\boldsymbol{x}_1 d\boldsymbol{x}_2 \dots d\boldsymbol{x}_N \\
&= \int\cdots\int \frac{1}{N!}[\sum_P (-1)^P \chi_{P_i}(\boldsymbol{x}_1)\chi_{P_j}(\boldsymbol{x}_2)\dots\chi_{P_l}(\boldsymbol{x}_N) \sum_Q (-1)^Q \chi_{Q_{i^{'}}}(\boldsymbol{x}_1)\chi_{Q_{j^{'}}}(\boldsymbol{x}_2)\dots\chi_{Q_{l^{'}}}(\boldsymbol{x}_N)] d\boldsymbol{x}_1 d\boldsymbol{x}_2 \dots d\boldsymbol{x}_N \\
&= \frac{1}{N!}\sum_P\sum_Q (-1)^{(P+Q)} \int \chi_{P_i}(\boldsymbol{x}_1)\chi_{Q_{i^{'}}}(\boldsymbol{x}_1)d\boldsymbol{x}_1 \int \chi_{P_j}(\boldsymbol{x}_2)\chi_{Q_{j^{'}}}(\boldsymbol{x}_2)d\boldsymbol{x}_2 \dots \int \chi_{P_l}(\boldsymbol{x}_N)\chi_{Q_{l^{'}}}(\boldsymbol{x}_N)d\boldsymbol{x}_N \\
&= \frac{1}{N!}\sum_P\sum_Q (-1)^{(P+Q)} \delta_{P_iQ_{i^{'}}}\delta_{P_jQ_{j^{'}}}\dots\delta_{P_lQ_{l^{'}}}
\end{aligned}
$$

若它们由不同的单电子轨道组成（或者说，至少存在两个波函数$\chi_k(\boldsymbol{x})$和$\chi_{k'}(\boldsymbol{x})$，使得$\chi_k(\boldsymbol{x}) \neq \chi_{k'}(\boldsymbol{x})$，但其余的波函数均满足$\chi_i(\boldsymbol{x}) \neq \chi_{i'}(\boldsymbol{x}), \chi_j(\boldsymbol{x}) = \chi_{j'}(\boldsymbol{x}), \ldots, \chi_l(\boldsymbol{x}) = \chi_{l'}(\boldsymbol{x})$），则经过配对后，$\delta_{P_i Q_{i'}}, \delta_{P_j Q_{j'}}, \ldots, \delta_{P_l Q_{l'}}$中至少有一个为0，从而$\langle\Psi|\Psi'\rangle = 0$

若它们由相同的一组单电子轨道构成，则经过配对后，必有$P_i = Q_{i'}, P_j = Q_{j'}, \ldots, P_l = Q_{l'}$，相应的，$P$等于从$\{i, j, \ldots, l\}$排列为$\{P_i, P_j, \ldots, P_l\}$所需的交换次数，$Q$等于从$\{i', j', \ldots, l'\}$排列为$\{Q_{i'}, Q_{j'}, \ldots, Q_{l'}\}$所需的交换次数（也等于从$\{Q_{i'}, Q_{j'}, \ldots, Q_{l'}\}$排列为$\{i', j', \ldots, l'\}$所需的交换次数），而$\{P_i, P_j, \ldots, P_l\}$与$\{Q_{i'}, Q_{j'}, \ldots, Q_{l'}\}$相同，因此$P+Q$相当于从$\{i, j, \ldots, l\}$排列为$\{i', j', \ldots, l'\}$所需的交换次数，而$\{i, j, \ldots, l\}$（或$\{i', j', \ldots, l'\}$）的排列总数有$N!$种，因此这时候$\langle\Psi|\Psi'\rangle = \frac{1}{N!} \cdot (-1)^{P'} N! = (-1)^{P'}$，此处$P'$表示将$\{i, j, \ldots, l\}$变成$\{i', j', \ldots, l'\}$所需要进行互换的次数，故原题得证

练习3：设考虑电子自旋的多电子Schroedinger方程为$\hat{H}\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = E\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$，证明在Hartree近似下，$E = \sum_i^N \varepsilon_i$

证明：在Hartree近似下，忽略多电子哈密顿算符中的两体项，有$\hat{H} = \sum_i^N \hat{h}(i)$，此时其本征解可以精确地写为$N$个单电子波函数（轨道）的乘积，并基于对泡利原理的考虑，要求这N个轨道都互不相同，从而有$\Psi^{\mathrm{HP}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = \chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)\ldots\chi_N(\boldsymbol{x}_N)$，其中$\chi_i$是单电子算符$\hat{h}$的本征函数，满足$\hat{h}(\boldsymbol{x})\chi_i(\boldsymbol{x}) = \varepsilon_i\chi_i(\boldsymbol{x})$。将以上条件代入多电子Schroedinger方程，得：

$$
\begin{aligned}
E\Psi^{\mathrm{HP}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = \hat{H}\Psi^{\mathrm{HP}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) &= \sum_i^N \hat{h}(i)[\chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)\ldots\chi_N(\boldsymbol{x}_N)] \\
&= \sum_i^N \chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)\ldots[\hat{h}(i)(\chi_i(\boldsymbol{x}_i))]\ldots\chi_N(\boldsymbol{x}_N) \\
&= \sum_i^N \chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)\ldots[\varepsilon_i(\chi_i(\boldsymbol{x}_i))]\ldots\chi_N(\boldsymbol{x}_N) \\
&= \sum_i^N \varepsilon_i\chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)\ldots\chi_N(\boldsymbol{x}_N) \\
&= (\sum_i^N \varepsilon_i) \cdot \Psi^{\mathrm{HP}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)
\end{aligned}
$$

对比等式两端可得$E = \sum_i^N \varepsilon_i$，证毕

练习4：H_2最小基组的哈密尔顿矩阵为$\mathbf{H} = \begin{pmatrix} \langle 1\bar{1}|\hat{H}|1\bar{1}\rangle & \langle 1\bar{1}|\hat{H}|2\bar{2}\rangle \\ \langle 2\bar{2}|\hat{H}|1\bar{1}\rangle & \langle 2\bar{2}|\hat{H}|2\bar{2}\rangle \end{pmatrix}$，请推导上式矩阵元根据分子轨道表示的表达式

解：由Slater行列式的定义，得

$$
\begin{aligned}
|1\bar{1}\rangle = \frac{1}{\sqrt{2!}}\begin{vmatrix} \chi_1(\boldsymbol{x}_1) & \chi_2(\boldsymbol{x}_1) \\ \chi_1(\boldsymbol{x}_2) & \chi_2(\boldsymbol{x}_2) \end{vmatrix} = \frac{1}{\sqrt{2!}}\begin{vmatrix} \psi_1(\boldsymbol{r}_1)\alpha(s_1) & \psi_1(\boldsymbol{r}_1)\beta(s_1) \\ \psi_1(\boldsymbol{r}_2)\alpha(s_2) & \psi_1(\boldsymbol{r}_2)\beta(s_2) \end{vmatrix} = \frac{1}{\sqrt{2!}}\psi_1(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)] \\
|2\bar{2}\rangle = \frac{1}{\sqrt{2!}}\begin{vmatrix} \chi_3(\boldsymbol{x}_1) & \chi_4(\boldsymbol{x}_1) \\ \chi_3(\boldsymbol{x}_2) & \chi_4(\boldsymbol{x}_2) \end{vmatrix} = \frac{1}{\sqrt{2!}}\begin{vmatrix} \psi_2(\boldsymbol{r}_1)\alpha(s_1) & \psi_2(\boldsymbol{r}_1)\beta(s_1) \\ \psi_2(\boldsymbol{r}_2)\alpha(s_2) & \psi_2(\boldsymbol{r}_2)\beta(s_2) \end{vmatrix} = \frac{1}{\sqrt{2!}}\psi_2(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2)[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)]
\end{aligned}
$$

因此记$\hat{H} = \hat{O}_1 + \hat{O}_2$，其中单电子算符$\hat{O}_1 = \sum_{i=1}^N \hat{h}_i$，双电子算符$\hat{O}_2 = \sum_{i<j} \hat{v}(\boldsymbol{r}_{ij}) = \sum_{i<j} \boldsymbol{r}_{ij}^{-1}$，则

$$\langle 1\bar{1}|\hat{H}|1\bar{1}\rangle = \langle 1\bar{1}|\hat{O}_1+\hat{O}_2|1\bar{1}\rangle = \iint \frac{1}{2!}[\chi_1^*(\boldsymbol{x}_1)\chi_2^*(\boldsymbol{x}_2)-\chi_2^*(\boldsymbol{x}_1)\chi_1^*(\boldsymbol{x}_2)](\hat{O}_1+\hat{O}_2)[\chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)-\chi_2(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_2)]d\boldsymbol{x}_1 d\boldsymbol{x}_2$$
$$\langle 1\bar{1}|\hat{H}|2\bar{2}\rangle = \langle 1\bar{1}|\hat{O}_1+\hat{O}_2|2\bar{2}\rangle = \iint \frac{1}{2!}[\chi_1^*(\boldsymbol{x}_1)\chi_2^*(\boldsymbol{x}_2)-\chi_2^*(\boldsymbol{x}_1)\chi_1^*(\boldsymbol{x}_2)](\hat{O}_1+\hat{O}_2)[\chi_3(\boldsymbol{x}_1)\chi_4(\boldsymbol{x}_2)-\chi_3(\boldsymbol{x}_1)\chi_4(\boldsymbol{x}_2)]d\boldsymbol{x}_1 d\boldsymbol{x}_2$$
$$\langle 2\bar{2}|\hat{H}|1\bar{1}\rangle = \langle 2\bar{2}|\hat{O}_1+\hat{O}_2|1\bar{1}\rangle = \iint \frac{1}{2!}[\chi_3^*(\boldsymbol{x}_1)\chi_4^*(\boldsymbol{x}_2)-\chi_3^*(\boldsymbol{x}_1)\chi_4^*(\boldsymbol{x}_2)](\hat{O}_1+\hat{O}_2)[\chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)-\chi_2(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_2)]d\boldsymbol{x}_1 d\boldsymbol{x}_2$$
$$\langle 2\bar{2}|\hat{H}|2\bar{2}\rangle = \langle 2\bar{2}|\hat{O}_1+\hat{O}_2|2\bar{2}\rangle = \iint \frac{1}{2!}[\chi_3^*(\boldsymbol{x}_1)\chi_4^*(\boldsymbol{x}_2)-\chi_3^*(\boldsymbol{x}_1)\chi_4^*(\boldsymbol{x}_2)](\hat{O}_1+\hat{O}_2)[\chi_3(\boldsymbol{x}_1)\chi_4(\boldsymbol{x}_2)-\chi_4(\boldsymbol{x}_1)\chi_3(\boldsymbol{x}_2)]d\boldsymbol{x}_1 d\boldsymbol{x}_2$$

以$\langle 1\bar{1}|\hat{H}|1\bar{1}\rangle$为例，首先我们考虑单电子算符$\hat{O}_1$，为使单电子算符的作用项不为零，除单电子算符对应的波函数以外的波函数要一一对应，从而有：

$$\begin{aligned}
&\iint \frac{1}{2!}\chi_1^*(\boldsymbol{x}_1)\chi_2^*(\boldsymbol{x}_2)\hat{O}_1[\chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)]d\boldsymbol{x}_1 d\boldsymbol{x}_2 = \iint \frac{1}{2!}\chi_1^*(\boldsymbol{x}_1)\chi_2^*(\boldsymbol{x}_2)\{\hat{h}_1[\chi_1(\boldsymbol{x}_1)]\chi_2(\boldsymbol{x}_2)+\chi_1(\boldsymbol{x}_1)\hat{h}_2[\chi_2(\boldsymbol{x}_2)]\}d\boldsymbol{x}_1 d\boldsymbol{x}_2\\
&= \frac{1}{2}\int \chi_1^*(\boldsymbol{x}_1)\hat{h}_1[\chi_1(\boldsymbol{x}_1)]d\boldsymbol{x}_1\int \chi_2^*(\boldsymbol{x}_2)\chi_2(\boldsymbol{x}_2)d\boldsymbol{x}_2+\frac{1}{2}\int \chi_1^*(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_1)d\boldsymbol{x}_1\int \chi_2^*(\boldsymbol{x}_2)\hat{h}_2[\chi_2(\boldsymbol{x}_2)]d\boldsymbol{x}_2 = \frac{1}{2}(h_{11}+h_{\bar{1}\bar{1}}) = h_{11}\\
&\iint \frac{1}{2!}\chi_1^*(\boldsymbol{x}_1)\chi_2^*(\boldsymbol{x}_2)\hat{O}_1[\chi_2(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_2)]d\boldsymbol{x}_1 d\boldsymbol{x}_2 = \iint \frac{1}{2!}\chi_1^*(\boldsymbol{x}_1)\chi_2^*(\boldsymbol{x}_2)\{\hat{h}_2[\chi_2(\boldsymbol{x}_1)]\chi_1(\boldsymbol{x}_2)+\chi_2(\boldsymbol{x}_1)\hat{h}_1[\chi_1(\boldsymbol{x}_2)]\}d\boldsymbol{x}_1 d\boldsymbol{x}_2\\
&= \frac{1}{2}\int \chi_1^*(\boldsymbol{x}_1)\hat{h}_2[\chi_2(\boldsymbol{x}_1)]d\boldsymbol{x}_1\int \chi_2^*(\boldsymbol{x}_2)\chi_1(\boldsymbol{x}_2)d\boldsymbol{x}_2+\frac{1}{2}\int \chi_1^*(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_1)d\boldsymbol{x}_1\int \chi_2^*(\boldsymbol{x}_2)\hat{h}_1[\chi_1(\boldsymbol{x}_2)]d\boldsymbol{x}_2 = 0\\
&\iint \frac{1}{2!}\chi_2^*(\boldsymbol{x}_1)\chi_1^*(\boldsymbol{x}_2)\hat{O}_1[\chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)]d\boldsymbol{x}_1 d\boldsymbol{x}_2 = \iint \frac{1}{2!}\chi_2^*(\boldsymbol{x}_1)\chi_1^*(\boldsymbol{x}_2)\{\hat{h}_1[\chi_1(\boldsymbol{x}_1)]\chi_2(\boldsymbol{x}_2)+\chi_1(\boldsymbol{x}_1)\hat{h}_2[\chi_2(\boldsymbol{x}_2)]\}d\boldsymbol{x}_1 d\boldsymbol{x}_2\\
&= \frac{1}{2}\int \chi_2^*(\boldsymbol{x}_1)\hat{h}_1[\chi_1(\boldsymbol{x}_1)]d\boldsymbol{x}_1\int \chi_1^*(\boldsymbol{x}_2)\chi_2(\boldsymbol{x}_2)d\boldsymbol{x}_2+\frac{1}{2}\int \chi_2^*(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_1)d\boldsymbol{x}_1\int \chi_1^*(\boldsymbol{x}_2)\hat{h}_2[\chi_2(\boldsymbol{x}_2)]d\boldsymbol{x}_2 = 0\\
&\iint \frac{1}{2!}\chi_2^*(\boldsymbol{x}_1)\chi_1^*(\boldsymbol{x}_2)\hat{O}_1[\chi_2(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_2)]d\boldsymbol{x}_1 d\boldsymbol{x}_2 = \iint \frac{1}{2!}\chi_2^*(\boldsymbol{x}_1)\chi_1^*(\boldsymbol{x}_2)\{\hat{h}_2[\chi_2(\boldsymbol{x}_1)]\chi_1(\boldsymbol{x}_2)+\chi_2(\boldsymbol{x}_1)\hat{h}_1[\chi_1(\boldsymbol{x}_2)]\}d\boldsymbol{x}_1 d\boldsymbol{x}_2\\
&= \frac{1}{2}\int \chi_2^*(\boldsymbol{x}_1)\hat{h}_2[\chi_2(\boldsymbol{x}_1)]d\boldsymbol{x}_1\int \chi_1^*(\boldsymbol{x}_2)\chi_1(\boldsymbol{x}_2)d\boldsymbol{x}_2+\frac{1}{2}\int \chi_2^*(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_1)d\boldsymbol{x}_1\int \chi_1^*(\boldsymbol{x}_2)\hat{h}_1[\chi_1(\boldsymbol{x}_2)]d\boldsymbol{x}_2 = \frac{1}{2}(h_{\bar{1}\bar{1}}+h_{11}) = h_{11}
\end{aligned}$$

因此$\langle 1\bar{1}|\hat{O}_1|1\bar{1}\rangle = 2h_{11}$
接下来考虑双电子算符$\hat{O}_2$，为使双电子算符的作用项不为零，除双电子算符对应的波函数以外的波函数要一一对应，从而有：

$$\begin{aligned}
&\iint \frac{1}{2!}\chi_1^*(\boldsymbol{x}_1)\chi_2^*(\boldsymbol{x}_2)\hat{O}_2[\chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)]d\boldsymbol{x}_1 d\boldsymbol{x}_2 = \frac{1}{2}\iint \frac{\chi_1^*(\boldsymbol{x}_1)\chi_2^*(\boldsymbol{x}_2)\chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)}{\boldsymbol{r}_{12}}d\boldsymbol{x}_1 d\boldsymbol{x}_2 = \frac{1}{2}V_{1\bar{1}1\bar{1}}\\
&\iint \frac{1}{2!}\chi_1^*(\boldsymbol{x}_1)\chi_2^*(\boldsymbol{x}_2)\hat{O}_2[\chi_2(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_2)]d\boldsymbol{x}_1 d\boldsymbol{x}_2 = \frac{1}{2}\iint \frac{\chi_1^*(\boldsymbol{x}_1)\chi_2^*(\boldsymbol{x}_2)\chi_2(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_2)}{\boldsymbol{r}_{12}}d\boldsymbol{x}_1 d\boldsymbol{x}_2 = \frac{1}{2}V_{1\bar{1}\bar{1}1} = 0\\
&\iint \frac{1}{2!}\chi_1^*(\boldsymbol{x}_1)\chi_2^*(\boldsymbol{x}_2)\hat{O}_2[\chi_2(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_2)]d\boldsymbol{x}_1 d\boldsymbol{x}_2 = \frac{1}{2}\iint \frac{\chi_1^*(\boldsymbol{x}_1)\chi_2^*(\boldsymbol{x}_2)\chi_2(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_2)}{\boldsymbol{r}_{12}}d\boldsymbol{x}_1 d\boldsymbol{x}_2 = \frac{1}{2}V_{1\bar{1}\bar{1}1} = 0\\
&\iint \frac{1}{2!}\chi_2^*(\boldsymbol{x}_1)\chi_1^*(\boldsymbol{x}_2)\hat{O}_2[\chi_2(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_2)]d\boldsymbol{x}_1 d\boldsymbol{x}_2 = \frac{1}{2}\iint \frac{\chi_2^*(\boldsymbol{x}_1)\chi_1^*(\boldsymbol{x}_2)\chi_2(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_2)}{\boldsymbol{r}_{12}}d\boldsymbol{x}_1 d\boldsymbol{x}_2 = \frac{1}{2}V_{\bar{1}1\bar{1}1} = \frac{1}{2}V_{1\bar{1}1\bar{1}}
\end{aligned}$$

因此$\langle 1\bar{1}|\hat{h}|1\bar{1}\rangle = \frac{1}{2}(V_{1\bar{1}1\bar{1}}+V_{\bar{1}1\bar{1}1}) = V_{1\bar{1}1\bar{1}}$，从而有$\langle 1\bar{1}|\hat{H}|1\bar{1}\rangle = 2h_{11}+V_{1\bar{1}1\bar{1}}$。同理可得
$\langle 1\bar{1}|\hat{H}|2\bar{2}\rangle = V_{1\bar{1}2\bar{2}}-V_{1\bar{1}\bar{2}2}$，$\langle 2\bar{2}|\hat{H}|1\bar{1}\rangle = V_{2\bar{2}1\bar{1}}-V_{2\bar{2}\bar{1}1}$，$\langle 2\bar{2}|\hat{H}|2\bar{2}\rangle = 2h_{22}+V_{2\bar{2}2\bar{2}}$

练习5：对于N电子闭壳层体系，从基于自旋轨道的HF基态能量表达式推导如下表达式

$$E_0 = 2\sum_a^{N/2} h_{aa}+\sum_{a,b}^{N/2}[2\langle ab|ab\rangle-\langle ab|ba\rangle] = 2\sum_a^{N/2} h_{aa}+\sum_{a,b}^{N/2}[2J_{ab}-K_{ab}]$$

其中J_{ab}为库仑积分，满足$J_{ab}=\langle ab|ab\rangle=\iint\frac{|\psi_i(\mathbf{r}_1)|^2|\psi_j(\mathbf{r}_2)|^2}{\mathbf{r}_{12}}d\mathbf{r}_1 d\mathbf{r}_2$；$K_{ab}$为交换积分，满足$K_{ab}=\langle ab|ba\rangle=\iint\frac{\psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_1)\psi_i(\mathbf{r}_2)}{\mathbf{r}_{12}}d\mathbf{r}_1 d\mathbf{r}_2$

解：N电子闭壳层体系对应的Slater行列式简记为$|\chi_1\chi_2\dots\chi_{N-1}\chi_N\rangle = |\psi_1\bar{\psi}_1\dots\psi_{N/2}\bar{\psi}_{N/2}\rangle$，根据Slater-Condon规则，单电子算符项为

$$\langle\psi_1\bar{\psi}_1\dots\psi_{N/2}\bar{\psi}_{N/2}|\hat{O}_1|\psi_1\bar{\psi}_1\dots\psi_{N/2}\bar{\psi}_{N/2}\rangle = \sum_{i=1}^{N/2}\langle\psi_1\bar{\psi}_1\dots\psi_{N/2}\bar{\psi}_{N/2}|\hat{h}_i+\hat{h}_{\bar{i}}|\psi_1\bar{\psi}_1\dots\psi_{N/2}\bar{\psi}_{N/2}\rangle$$
$$= \sum_{i=1}^{N/2}[\langle\psi_1\bar{\psi}_1\dots\psi_i\dots\psi_{N/2}\bar{\psi}_{N/2}|\psi_1\bar{\psi}_1\dots\hat{h}_i(\psi_i)\dots\psi_{N/2}\bar{\psi}_{N/2}\rangle + \langle\psi_1\bar{\psi}_1\dots\psi_{\bar{i}}\dots\psi_{N/2}\bar{\psi}_{N/2}|\psi_1\bar{\psi}_1\dots\hat{h}_{\bar{i}}(\psi_{\bar{i}})\dots\psi_{N/2}\bar{\psi}_{N/2}\rangle]$$
$$= \sum_{i=1}^{N/2}(\langle\psi_i|\hat{h}_i|\psi_i\rangle + \langle\psi_{\bar{i}}|\hat{h}_{\bar{i}}|\psi_{\bar{i}}\rangle) = \sum_{i=1}^{N/2}(h_{ii}+h_{\bar{i}\bar{i}}) = 2\sum_{i=1}^{N/2}h_{ii}$$

双电子算符项为

$$\langle\psi_1\bar{\psi}_1\dots\psi_{N/2}\bar{\psi}_{N/2}|\hat{O}_2|\psi_1\bar{\psi}_1\dots\psi_{N/2}\bar{\psi}_{N/2}\rangle = \sum_{i<j}\langle\psi_1\bar{\psi}_1\dots\psi_{N/2}\bar{\psi}_{N/2}|\hat{v}(\boldsymbol{r}_{ij})|\psi_1\bar{\psi}_1\dots\psi_{N/2}\bar{\psi}_{N/2}\rangle$$
$$= \frac{1}{2}\sum_{i=1}^{N/2}\sum_{\sigma_i}\sum_{j=1}^{N/2}\sum_{\sigma_j}\langle i,\sigma_i,j,\sigma_j||i,\sigma_i,j,\sigma_j\rangle = \frac{1}{2}\sum_{i=1}^{N/2}\sum_{\sigma_i}\sum_{j=1}^{N/2}\sum_{\sigma_j}(\langle i,\sigma_i,j,\sigma_j|i,\sigma_i,j,\sigma_j\rangle - \langle i,\sigma_i,j,\sigma_j|j,\sigma_j,i,\sigma_i\rangle)$$
$$= \frac{1}{2}\sum_{i=1}^{N/2}\sum_{j=1}^{N/2}(\langle\psi_{i,\uparrow}\psi_{j,\uparrow}|\psi_{i,\uparrow}\psi_{j,\uparrow}\rangle + \langle\psi_{i,\uparrow}\psi_{j,\downarrow}|\psi_{i,\uparrow}\psi_{j,\downarrow}\rangle + \langle\psi_{i,\downarrow}\psi_{j,\uparrow}|\psi_{i,\downarrow}\psi_{j,\uparrow}\rangle + \langle\psi_{i,\downarrow}\psi_{j,\downarrow}|\psi_{i,\downarrow}\psi_{j,\downarrow}\rangle)$$
$$- \frac{1}{2}\sum_{i=1}^{N/2}\sum_{j=1}^{N/2}(\langle\psi_{i,\uparrow}\psi_{j,\uparrow}|\psi_{j,\uparrow}\psi_{i,\uparrow}\rangle + \langle\psi_{i,\uparrow}\psi_{j,\downarrow}|\psi_{j,\downarrow}\psi_{i,\uparrow}\rangle + \langle\psi_{i,\downarrow}\psi_{j,\uparrow}|\psi_{j,\uparrow}\psi_{i,\downarrow}\rangle + \langle\psi_{i,\downarrow}\psi_{j,\downarrow}|\psi_{j,\downarrow}\psi_{i,\downarrow}\rangle)$$
$$= \frac{1}{2}\sum_{i=1}^{N/2}\sum_{j=1}^{N/2}4\langle\psi_i\psi_j|\psi_i\psi_j\rangle - \frac{1}{2}\sum_{i=1}^{N/2}\sum_{j=1}^{N/2}2\langle\psi_i\psi_j|\psi_j\psi_i\rangle\text{（考虑电子自旋匹配，交换积分部分第2、3项为0）}$$
$$= 2\sum_{i=1}^{N/2}\sum_{j=1}^{N/2}J_{ij} - \sum_{i=1}^{N/2}\sum_{j=1}^{N/2}K_{ij} = \sum_{i=1}^{N/2}\sum_{j=1}^{N/2}(2J_{ij}-K_{ij})$$

两项加和为

$$\langle\psi_1\bar{\psi}_1\dots\psi_{N/2}\bar{\psi}_{N/2}|\hat{H}|\psi_1\bar{\psi}_1\dots\psi_{N/2}\bar{\psi}_{N/2}\rangle = \langle\psi_1\bar{\psi}_1\dots\psi_{N/2}\bar{\psi}_{N/2}|\hat{O}_1+\hat{O}_2|\psi_1\bar{\psi}_1\dots\psi_{N/2}\bar{\psi}_{N/2}\rangle$$
$$= 2\sum_{i=1}^{N/2}h_{ii} + \sum_{i=1}^{N/2}\sum_{j=1}^{N/2}(2J_{ij}-K_{ij})$$

练习6：证明即使空间轨道不是实函数，交换积分也一定是个实数

证明：（这部分的证明参考了知乎上的一个问答：[如何证明量子化学中的交换积分一定为正？]，以及计算化学公社的一个帖子：[请问如何证明交换积分一定为正？]）
首先我们知道泊松公式$-\nabla^2\psi(\mathbf{r}) = 4\pi\rho(\mathbf{r})$，其中$\psi(\mathbf{r})$为电势，$\rho(\mathbf{r})$为电子密度，两边作傅里叶变换，得

$$4\pi\rho(\boldsymbol{k}) = (2\pi)^{-\frac{3}{2}}\int(-\nabla^2\psi(\mathbf{r}))\cdot\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\mathbf{r}}d\mathbf{r} = (2\pi)^{-\frac{3}{2}}\boldsymbol{k}^2\psi(\boldsymbol{k})$$

取电荷分布为单位点电荷时（即$\rho(\mathbf{r}) = \delta(\mathbf{r})$时），泊松公式变为$-\nabla^2\frac{1}{\mathbf{r}} = 4\pi\delta(\mathbf{r})$，即$\psi(\mathbf{r}) = \frac{1}{\mathbf{r}}$；另一方面，对$4\pi\rho(\mathbf{r})$作傅里叶变换，则

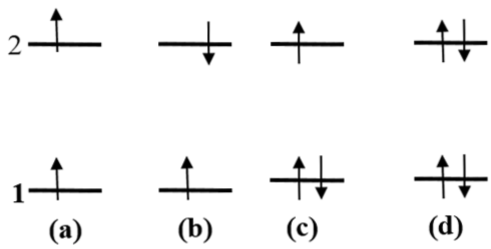
$$4\pi\rho(\boldsymbol{k}) = 4\pi\cdot(2\pi)^{-\frac{3}{2}}\int\rho(\mathbf{r})\cdot\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\mathbf{r}}d\mathbf{r} = 4\pi\cdot(2\pi)^{-\frac{3}{2}}\int\delta(\mathbf{r})\cdot\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\mathbf{r}}d\mathbf{r} = 4\pi\cdot(2\pi)^{-\frac{3}{2}}$$

因此$\psi(\boldsymbol{k}) = \frac{4\pi}{\boldsymbol{k}^2} \geq 0$。现在我们利用这个结论证明原命题。
交换积分的表达式为$K_{ab} = \langle ab|ba\rangle = \iint\frac{\psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_1)\psi_i(\mathbf{r}_2)}{\mathbf{r}_{12}}d\mathbf{r}_1d\mathbf{r}_2$，根据之前傅里叶变换的结果，有$\frac{1}{r_{12}} = \int\frac{4\pi}{\boldsymbol{k}^2}\cdot\mathrm{e}^{\mathrm{i}\boldsymbol{k}(\mathbf{r}_1-\mathbf{r}_2)}d\boldsymbol{k}$，代入可得

$$
\begin{aligned}
K_{ab} &= \iiint \psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_1)\psi_i(\mathbf{r}_2)\frac{4\pi}{\boldsymbol{k}^2}\cdot \mathrm{e}^{\mathrm{i}\boldsymbol{k}(\mathbf{r}_1-\mathbf{r}_2)}d\mathbf{r}_1 d\mathbf{r}_2 d\boldsymbol{k} = \int \frac{4\pi}{\boldsymbol{k}^2}d\boldsymbol{k}\int \psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1)\mathrm{e}^{\mathrm{i}\boldsymbol{k}\mathbf{r}_1}d\mathbf{r}_1\int \psi_j^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2)\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\mathbf{r}_2}d\mathbf{r}_2 \\
&= \int \frac{4\pi}{\boldsymbol{k}^2}|\int \psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1)\mathrm{e}^{\mathrm{i}\boldsymbol{k}\mathbf{r}_1}d\mathbf{r}_1|^2 d\boldsymbol{k} \geq 0
\end{aligned}
$$

从而交换积分为非负数，即交换积分为实数，证毕

练习7：写出图2所示各种构型所对应的总能量



解：根据Slater-Condon规则，对体系(a)，其总能量为$E_{(a)} = h_{11} + h_{22} + J_{12} - K_{12}$；对体系(b)，其总能量为$E_{(b)} = h_{11} + h_{22} + J_{12}$；对体系(c)，其总能量为$E_{(c)} = 2h_{11} + h_{22} + J_{11} + 2J_{12} - K_{12}$；对体系(d)，其总能量为$E_{(d)} = 2h_{11} + 2h_{22} + J_{11} + 4J_{12} + J_{22} - 2K_{12}$

练习8：推导Hartree近似下单电子轨道所满足的方程

$$
[-\frac{1}{2}\nabla^2 + V_{\text{eff},i}^{(\text{H})}(\mathbf{r})]\psi_i(\boldsymbol{x}) = \varepsilon_i\psi_i(\boldsymbol{x}) \quad (\text{其中} V_{\text{eff},i}^{(\text{H})}(\mathbf{r}) \equiv V_{\text{ext}}(r) + \sum_{j\neq i}\int \frac{\psi_j^*(\boldsymbol{x})\psi_j(\boldsymbol{x})}{|\mathbf{r}-\mathbf{r}'|}d\boldsymbol{x}')
$$

解：根据改进的Hartree近似，假定多电子波函数可以表示为N个互相正交归一的单电子轨道的乘积，但这些轨道并不是单电子算符的本征函数，而是通过变分原理来确定，即
$E_0^{(\text{Hartree})} = \min\limits_{\langle\psi_i|\psi_j\rangle=\delta_{ij}}\langle\Psi^{\text{HP}}|\hat{H}|\Psi^{\text{HP}}\rangle$，其中$\Psi^{\text{HP}}(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N) = \chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)\ldots\chi_N(\boldsymbol{x}_N)$，而哈密尔顿算符可分为单体项和两体项，即$\hat{H} = \sum\limits_{i=1}^{N}\hat{h}_i + \sum\limits_{i<j}^{N}v_{ee}(\boldsymbol{r}_{ij})$，$\hat{h}_i = -\frac{1}{2}\nabla_i^2 + V_{\text{ext}}(\boldsymbol{r}_i)$，$v_{ee}(\boldsymbol{r}_{ij}) = \frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}$，根据拉格朗日乘数法，结合基矢正交归一的条件，有

$$
\begin{aligned}
L &= \langle\Psi^{\text{HP}}|\hat{H}|\Psi^{\text{HP}}\rangle - \sum_{i=1}^{N}\sum_{j=1}^{N}\lambda_{ij}\delta_{ij} \\
&= \sum_{i=1}^{N}\int \chi_i^*(\boldsymbol{x}_1)\hat{h}_i[\chi_i(\boldsymbol{x}_1)]d\boldsymbol{x}_1 + \sum_{i<j}\iint \frac{\chi_i^*(\boldsymbol{x}_1)\chi_j^*(\boldsymbol{x}_2)\chi_i(\boldsymbol{x}_1)\chi_j(\boldsymbol{x}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}d\boldsymbol{x}_1 d\boldsymbol{x}_2 - \sum_{i=1}^{N}\sum_{j=1}^{N}\lambda_{ij}\int \chi_i^*(\boldsymbol{x}_1)\chi_j(\boldsymbol{x}_1)d\boldsymbol{x}_1
\end{aligned}
$$

对L作关于波函数$\chi_i^*(\boldsymbol{x}_1)$的变分，并令变分为0，得

$$
\frac{\delta L}{\delta\chi_i^*(\boldsymbol{x}_1)} = \hat{h}_i[\chi_i(\boldsymbol{x}_1)] + \sum_{i\neq j}\int \frac{\chi_j^*(\boldsymbol{x}_2)\chi_j(\boldsymbol{x}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\chi_i(\boldsymbol{x}_1)d\boldsymbol{x}_2 - \lambda_{ii}\chi_i(\boldsymbol{x}_1) = 0
$$

移项得

$$
[\hat{h}_i + \sum_{i\neq j}\int \frac{\chi_j^*(\boldsymbol{x}_2)\chi_j(\boldsymbol{x}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}d\boldsymbol{x}_2]\chi_i(\boldsymbol{x}_1) = [-\frac{1}{2}\nabla_i^2 + V_{\text{ext}}(\boldsymbol{r}_i) + \sum_{i\neq j}\int \frac{\chi_j^*(\boldsymbol{x}_2)\chi_j(\boldsymbol{x}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}d\boldsymbol{x}_2]\chi_i(\boldsymbol{x}_1) = \lambda_{ii}\chi_i(\boldsymbol{x}_1)
$$

定义$V_{\text{eff},i}^{(\text{H})}(\boldsymbol{r}_i) \equiv V_{\text{ext}}(\boldsymbol{r}_i) + \sum\limits_{j\neq i}\int \frac{\chi_j^*(\boldsymbol{x}_2)\chi_j(\boldsymbol{x}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}d\boldsymbol{x}_1$，$\varepsilon_i = \lambda_{ii}$，则原题得证

练习9：以两电子体系波函数$|\Phi_0\rangle = |\chi_1\chi_2\rangle$直接推导$\langle\Phi_0|\hat{H}|\Phi_0\rangle \equiv \langle\Phi_0|\hat{O}_1 + \hat{O}_2|\Phi_0\rangle$，以验证Slater-Condon规则

解：仿照练习4，我们可以得到

$$\begin{aligned}\langle\Phi_0|\hat{O}_1|\Phi_0\rangle &= \langle\chi_1\chi_2|\hat{h}_1+\hat{h}_2|\chi_1\chi_2\rangle = \frac{1}{\sqrt{2!}}((\chi_1\chi_2|+(\chi_2\chi_1|)(\hat{h}_1+\hat{h}_2)\frac{1}{\sqrt{2!}}(|\chi_1\chi_2)+|\chi_2\chi_1)) \\ &= \frac{1}{2}[(\chi_1\chi_2|(\hat{h}_1+\hat{h}_2)|\chi_1\chi_2)+(\chi_1\chi_2|(\hat{h}_1+\hat{h}_2)|\chi_2\chi_1)+(\chi_2\chi_1|(\hat{h}_1+\hat{h}_2)|\chi_1\chi_2)+(\chi_2\chi_1|(\hat{h}_1+\hat{h}_2)|\chi_2\chi_1)] \\ &= \frac{1}{2}(h_{11}+h_{22})+0+0+\frac{1}{2}(h_{11}+h_{22}) = h_{11}+h_{22}\end{aligned}$$

$$\begin{aligned}\langle\Phi_0|\hat{O}_2|\Phi_0\rangle &= \langle\chi_1\chi_2|\hat{v}(\boldsymbol{r}_{12})|\chi_1\chi_2\rangle = \frac{1}{\sqrt{2!}}((\chi_1\chi_2|+(\chi_2\chi_1|)(\boldsymbol{r}_{12}^{-1})\frac{1}{\sqrt{2!}}(|\chi_1\chi_2)+|\chi_2\chi_1)) \\ &= \frac{1}{2}[(\chi_1\chi_2|\boldsymbol{r}_{12}^{-1}|\chi_1\chi_2)+(\chi_1\chi_2|\boldsymbol{r}_{12}^{-1}|\chi_2\chi_1)+(\chi_2\chi_1|\boldsymbol{r}_{12}^{-1}|\chi_1\chi_2)+(\chi_2\chi_1|\boldsymbol{r}_{12}^{-1}|\chi_2\chi_1)] \\ &= \frac{1}{2}[\langle 12||21\rangle+\langle 21||12\rangle] = \langle 12||21\rangle\end{aligned}$$

因此$\langle\Phi_0|\hat{H}|\Phi_0\rangle \equiv \langle\Phi_0|\hat{O}_1+\hat{O}_2|\Phi_0\rangle = h_{11}+h_{22}+\langle 12||21\rangle = \sum_{i=1}^{2}h_{ii}+\sum_{i<j}^{2}\langle ij||ji\rangle$，满足Slater-Condon规则

练习10：证明自旋阶梯（升降）算符$\hat{s}_\pm$与自旋z分量算符$\hat{s}_z$满足对易关系$[\hat{s}_z,\hat{s}_+]=\hat{s}_+,[\hat{s}_z,\hat{s}_-]=-\hat{s}_-$，简记为$[\hat{s}_z,\hat{s}_\pm]=\pm\hat{s}_\pm$（以上等式均采用原子单位制，即$\hbar=1$）

证明：我们知道$\hat{s}_\pm=\hat{s}_x\pm\mathrm{i}\hat{s}_y$，因此：

$$[\hat{s}_z,\hat{s}_\pm]=[\hat{s}_z,\hat{s}_x\pm\mathrm{i}\hat{s}_y]=[\hat{s}_z,\hat{s}_x]\pm\mathrm{i}[\hat{s}_z,\hat{s}_y]=\mathrm{i}(\hat{s}_y\mp\mathrm{i}\hat{s}_x)=\mp\hat{s}_x+\mathrm{i}\hat{s}_y=\pm\hat{s}_\pm$$

从而原题得证

练习11：以$|\alpha\rangle$和$|\beta\rangle$为基矢，写出$\hat{s}^2$，$\hat{s}_x$，$\hat{s}_y$，$\hat{s}_z$，$\hat{s}_+$和$\hat{s}_-$等算符的矩阵表示

解：首先我们知道，$|\frac{1}{2},\frac{1}{2}\rangle=|\alpha\rangle$，$|\frac{1}{2},-\frac{1}{2}\rangle=|\beta\rangle$，因此有：

$$\langle\alpha|\hat{s}_z|\alpha\rangle=\frac{1}{2}\hbar\langle\alpha|\alpha\rangle=\frac{1}{2}\hbar \quad \langle\alpha|\hat{s}_z|\beta\rangle=-\frac{1}{2}\hbar\langle\alpha|\beta\rangle=0 \quad \langle\beta|\hat{s}_z|\alpha\rangle=\frac{1}{2}\hbar\langle\beta|\alpha\rangle=0 \quad \langle\beta|\hat{s}_z|\beta\rangle=-\frac{1}{2}\hbar\langle\beta|\beta\rangle=-\frac{1}{2}\hbar$$

且有：

$$\langle\alpha|\hat{s}^2|\alpha\rangle=\frac{1}{2}\cdot\frac{3}{2}\hbar^2\langle\alpha|\alpha\rangle=\frac{3}{4}\hbar^2 \quad \langle\alpha|\hat{s}_z|\beta\rangle=\frac{1}{2}\cdot\frac{3}{2}\hbar^2\langle\alpha|\beta\rangle=0 \quad \langle\beta|\hat{s}_z|\alpha\rangle=\frac{1}{2}\cdot\frac{3}{2}\hbar^2\langle\beta|\alpha\rangle=0 \quad \langle\beta|\hat{s}_z|\beta\rangle=\frac{1}{2}\cdot\frac{3}{2}\hbar^2\langle\beta|\beta\rangle=\frac{3}{4}\hbar^2$$

因此$\hat{s}_z$和$\hat{s}^2$的矩阵表示为$\boldsymbol{s}_z=\frac{1}{2}\hbar\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$，$\boldsymbol{s}_z=\frac{3}{4}\hbar^2\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$

接下来考虑$\hat{s}_+$和$\hat{s}_-$，根据下一个练习的结论（证明已给出），我们有：

$$\langle\alpha|\hat{s}_+|\alpha\rangle=\langle\alpha|\cdot\mathbf{0}=0 \quad \langle\alpha|\hat{s}_+|\beta\rangle=\hbar\langle\alpha|\alpha\rangle=\hbar \quad \langle\beta|\hat{s}_+|\alpha\rangle=\langle\beta|\cdot\mathbf{0}=0 \quad \langle\beta|\hat{s}_+|\beta\rangle=\hbar\langle\beta|\alpha\rangle=0$$

$$\langle\alpha|\hat{s}_-|\alpha\rangle=\hbar\langle\alpha|\beta\rangle=0 \quad \langle\alpha|\hat{s}_-|\beta\rangle=\langle\alpha|\cdot\mathbf{0}=0 \quad \langle\beta|\hat{s}_-|\alpha\rangle=\hbar\langle\beta|\beta\rangle=\hbar \quad \langle\beta|\hat{s}_-|\beta\rangle=\langle\beta|\cdot\mathbf{0}=0$$

因此$\hat{s}_+$和$\hat{s}_-$的矩阵表示为$\boldsymbol{s}_+=\hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}$，$\boldsymbol{s}_-=\hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}$

由$\hat{s}_\pm=\hat{s}_x\pm\mathrm{i}\hat{s}_y$，得$\hat{s}_x=\frac{1}{2}(\hat{s}_++\hat{s}_-)$，$\hat{s}_y=-\frac{\mathrm{i}}{2}(\hat{s}_+-\hat{s}_-)$，从而$\hat{s}_x$和$\hat{s}_y$的矩阵表示为

$$\boldsymbol{s}_x=\frac{1}{2}(\boldsymbol{s}_++\boldsymbol{s}_-)=\frac{1}{2}[\hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}+\hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}]=\frac{1}{2}\hbar\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$$

$$\boldsymbol{s}_y=-\frac{\mathrm{i}}{2}(\boldsymbol{s}_+-\boldsymbol{s}_-)=-\frac{\mathrm{i}}{2}[\hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}-\hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}]=\frac{1}{2}\hbar\begin{pmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{pmatrix}$$

练习12：证明如下等式：（1）$\hat{s}^2=\hat{s}_+\hat{s}_- - \hbar\hat{s}_z+\hat{s}_z^2$；（2）$\hat{s}_+|\alpha\rangle=\mathbf{0}$，$\hat{s}_+|\beta\rangle=|\alpha\rangle$，$\hat{s}_-|\alpha\rangle=|\beta\rangle$，$\hat{s}_-|\beta\rangle=\mathbf{0}$（以上等式均采用原子单位制，即$\hbar=1$）

证明：

（1）我们知道

$$\hat{s}^2=\hat{s}_x^2+\hat{s}_y^2+\hat{s}_z^2=(\hat{s}_x+\mathrm{i}\hat{s}_y)(\hat{s}_x-\mathrm{i}\hat{s}_y)+\mathrm{i}[\hat{s}_x,\hat{s}_y]+\hat{s}_z^2=\hat{s}_+\hat{s}_-+\mathrm{i}\cdot\mathrm{i}\hbar\hat{s}_z+\hat{s}_z^2=\hat{s}_+\hat{s}_- - \hbar\hat{s}_z+\hat{s}_z^2$$

因此原题得证，类似的，有

$$\hat{s}^2=\hat{s}_x^2+\hat{s}_y^2+\hat{s}_z^2=(\hat{s}_x-\mathrm{i}\hat{s}_y)(\hat{s}_x+\mathrm{i}\hat{s}_y)-\mathrm{i}[\hat{s}_x,\hat{s}_y]+\hat{s}_z^2=\hat{s}_-\hat{s}_+-\mathrm{i}\cdot\mathrm{i}\hbar\hat{s}_z+\hat{s}_z^2=\hat{s}_-\hat{s}_++\hbar\hat{s}_z+\hat{s}_z^2$$

（2）因为

$$\begin{cases}\hbar\hat{s}_+|\frac{1}{2},m_s\rangle=[\hat{s}_z,\hat{s}_+]|\frac{1}{2},m_s\rangle=(\hat{s}_z\hat{s}_+-\hat{s}_+\hat{s}_z)|\frac{1}{2},m_s\rangle=\hat{s}_z\hat{s}_+|\frac{1}{2},m_s\rangle-\hat{s}_+\hat{s}_z|\frac{1}{2},m_s\rangle=\hat{s}_z\hat{s}_+|\frac{1}{2},m_s\rangle-m_s\hbar\hat{s}_+|\frac{1}{2},m_s\rangle\\ \hbar\hat{s}_-|\frac{1}{2},m_s\rangle=-[\hat{s}_z,\hat{s}_-]|\frac{1}{2},m_s\rangle=-(\hat{s}_z\hat{s}_--\hat{s}_-\hat{s}_z)|\frac{1}{2},m_s\rangle=-\hat{s}_z\hat{s}_-|\frac{1}{2},m_s\rangle+\hat{s}_-\hat{s}_z|\frac{1}{2},m_s\rangle=-\hat{s}_z\hat{s}_-|\frac{1}{2},m_s\rangle+m_s\hbar\hat{s}_-|\frac{1}{2},m_s\rangle\end{cases}$$

所以有$\begin{cases}\hat{s}_z\hat{s}_+|\frac{1}{2},m_s\rangle=(m_s+1)\hbar\hat{s}_+|\frac{1}{2},m_s\rangle\\ \hat{s}_z\hat{s}_-|\frac{1}{2},m_s\rangle=(m_s-1)\hbar\hat{s}_-|\frac{1}{2},m_s\rangle\end{cases}$，从而有$\begin{cases}\hat{s}_+|\frac{1}{2},m_s\rangle=s_{+,m_s}|\frac{1}{2},m_s+1\rangle\\ \hat{s}_-|\frac{1}{2},m_s\rangle=s_{-,m_s}|\frac{1}{2},m_s-1\rangle\end{cases}$，又知$\begin{cases}\hat{s}_+^\dagger=\hat{s}_x^\dagger+(\mathrm{i}\hat{s}_y)^\dagger=\hat{s}_x-\mathrm{i}\hat{s}_y=\hat{s}_-\\ \hat{s}_-^\dagger=\hat{s}_x^\dagger-(\mathrm{i}\hat{s}_y)^\dagger=\hat{s}_x+\mathrm{i}\hat{s}_y=\hat{s}_+\end{cases}$，且

$$\begin{cases}\langle\frac{1}{2},m_s|\hat{s}_+\hat{s}_-|\frac{1}{2},m_s\rangle=\langle\frac{1}{2},m_s|(\hat{s}^2+\hbar\hat{s}_z-\hat{s}_z^2)|\frac{1}{2},m_s\rangle=\langle\frac{1}{2},m_s|\hat{s}^2|\frac{1}{2},m_s\rangle+\langle\frac{1}{2},m_s|\hbar\hat{s}_z|\frac{1}{2},m_s\rangle-\langle\frac{1}{2},m_s|\hat{s}_z^2|\frac{1}{2},m_s\rangle\\ \langle\frac{1}{2},m_s|\hat{s}_-\hat{s}_+|\frac{1}{2},m_s\rangle=\langle\frac{1}{2},m_s|(\hat{s}^2-\hbar\hat{s}_z-\hat{s}_z^2)|\frac{1}{2},m_s\rangle=\langle\frac{1}{2},m_s|\hat{s}^2|\frac{1}{2},m_s\rangle-\langle\frac{1}{2},m_s|\hbar\hat{s}_z|\frac{1}{2},m_s\rangle-\langle\frac{1}{2},m_s|\hat{s}_z^2|\frac{1}{2},m_s\rangle\end{cases}$$

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$$\begin{cases}\langle\frac{1}{2},m_s|\hat{s}_+\hat{s}_-|\frac{1}{2},m_s\rangle=(\langle\frac{1}{2},m_s|\hat{s}_-^\dagger)(\hat{s}_-|\frac{1}{2},m_s\rangle)=\langle\frac{1}{2},m_s-1||s_{-,m_s}|^2|\frac{1}{2},m_s-1\rangle=|s_{-,m_s}|^2=(\frac{3}{4}+m_s-m_s^2)\hbar^2\\ \langle\frac{1}{2},m_s|\hat{s}_-\hat{s}_+|\frac{1}{2},m_s\rangle=(\langle\frac{1}{2},m_s|\hat{s}_+^\dagger)(\hat{s}_+|\frac{1}{2},m_s\rangle)=\langle\frac{1}{2},m_s+1||s_{+,m_s}|^2|\frac{1}{2},m_s+1\rangle=|s_{+,m_s}|^2=(\frac{3}{4}-m_s-m_s^2)\hbar^2\end{cases}$$

从而得$\begin{cases}|s_{+,m_s}|=\sqrt{\frac{3}{4}-m_s(m_s+1)}\hbar\\ |s_{-,m_s}|=\sqrt{\frac{3}{4}-m_s(m_s-1)}\hbar\end{cases}$，假设$s_{+,m_s}$和$s_{-,m_s}$均为正实数，则$\begin{cases}\hat{s}_+|\frac{1}{2},m_s\rangle=\sqrt{\frac{3}{4}-m_s(m_s+1)}\hbar|\frac{1}{2},m_s+\frac{1}{2}\rangle\\ \hat{s}_-|\frac{1}{2},m_s\rangle=\sqrt{\frac{3}{4}-m_s(m_s-1)}\hbar|\frac{1}{2},m_s-\frac{1}{2}\rangle\end{cases}$，因此

$$\begin{cases}\hat{s}_+|\alpha\rangle=\sqrt{\frac{3}{4}-\frac{1}{2}\cdot(\frac{1}{2}+1)}\hbar|\frac{1}{2},\frac{3}{2}\rangle=\mathbf{0}\\ \hat{s}_+|\beta\rangle=\sqrt{\frac{3}{4}-(-\frac{1}{2})\cdot(-\frac{1}{2}+1)}\hbar|\alpha\rangle=\hbar|\alpha\rangle\\ \hat{s}_-|\alpha\rangle=\sqrt{\frac{3}{4}-\frac{1}{2}\cdot(\frac{1}{2}-1)}\hbar|\beta\rangle=\hbar|\beta\rangle\\ \hat{s}_-|\beta\rangle=\sqrt{\frac{3}{4}-(-\frac{1}{2})\cdot(-\frac{1}{2}-1)}\hbar|\frac{1}{2},-\frac{3}{2}\rangle=\mathbf{0}\end{cases}$$

特别地，当采用原子单位制时，即有第（2）题的等式

练习13：证明单Slater行列式波函数是$\hat{S}_z$本征态，满足

$$\hat{S}_z|\chi_i\chi_j\ldots\chi_k\rangle=\frac{1}{2}(N^\alpha-N^\beta)|\chi_i\chi_j\ldots\chi_k\rangle\equiv M_s|\chi_i\chi_j\ldots\chi_k\rangle$$

其中N^σ（$\sigma=\alpha$或β）为行列式中具有自旋为σ的单电子轨道的数目

证明：易知

$$\hat{S}_z|\chi_i\chi_j\dots\chi_k\rangle=\hat{S}_z\frac{1}{\sqrt{N!}}\begin{vmatrix}\chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1) & \dots & \chi_k(\boldsymbol{x}_1)\\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2) & \dots & \chi_k(\boldsymbol{x}_2)\\ \vdots & \vdots & \ddots & \vdots\\ \chi_i(\boldsymbol{x}_N) & \chi_j(\boldsymbol{x}_N) & \dots & \chi_k(\boldsymbol{x}_N)\end{vmatrix}=\frac{1}{\sqrt{N!}}\hat{S}_z\sum_P(-1)^P\chi_i(\boldsymbol{x}_{P_1})\chi_j(\boldsymbol{x}_{P_2})\dots\chi_k(\boldsymbol{x}_{P_N})$$

而$\hat{S}_z$的表达式为$\hat{S}_z=\sum\limits_{l=1}^{N}\hat{\boldsymbol{s}}_{z,l}$，因此有：

$$\begin{aligned}\hat{S}_z|\chi_i\chi_j\dots\chi_k\rangle&=\frac{1}{\sqrt{N!}}\sum_{l=1}^{N}\hat{s}_{z,l}\sum_P(-1)^P\chi_i(\boldsymbol{x}_{P_1})\chi_j(\boldsymbol{x}_{P_2})\dots\chi_k(\boldsymbol{x}_{P_N})=\frac{1}{\sqrt{N!}}\sum_P(-1)^P\sum_{l=1}^{N}\chi_i(\boldsymbol{x}_{P_1})\chi_j(\boldsymbol{x}_{P_2})\dots[\hat{s}_{z,l}\chi_l(\boldsymbol{x}_{P_l})]\dots\chi_k(\boldsymbol{x}_{P_N})\\&=\frac{1}{\sqrt{N!}}\sum_P(-1)^P\sum_{l=1}^{N}m_{s,l}[\chi_i(\boldsymbol{x}_{P_1})\chi_j(\boldsymbol{x}_{P_2})\dots\chi_l(\boldsymbol{x}_{P_l})\dots\chi_k(\boldsymbol{x}_{P_N})]=\frac{\frac{\hbar}{2}(N^\alpha-N^\beta)}{\sqrt{N!}}\sum_P(-1)^P\chi_i(\boldsymbol{x}_{P_1})\chi_j(\boldsymbol{x}_{P_2})\dots\chi_k(\boldsymbol{x}_{P_N})\\&=\frac{1}{2}(N^\alpha-N^\beta)|\chi_i\chi_j\dots\chi_k\rangle\end{aligned}$$

故原题得证