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$|\Psi\rangle = |\chi_i \chi_j \ldots \chi_l\rangle$和$|\Psi'\rangle = |\chi_{i'} \chi_{j'} \ldots \chi_{l'}\rangle$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$i, j, \ldots, l$变成$i', j', \ldots, l'$所需要进行互换的次数。

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

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

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

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