课堂练习

练习1：基于电子密度的定义$\begin{cases}\hat{\rho}(\boldsymbol{r})=\sum\limits_{i=1}^{N}\delta(\boldsymbol{r}_i-\boldsymbol{r})\\ \rho(\boldsymbol{r})=\langle\Psi|\hat{\rho}(\boldsymbol{r})|\Psi\rangle\end{cases}$，推导出行列式波函数所对应的电子密度表达式

解：如果$|\Psi\rangle$是行列式波函数，根据Slater-Condon规则，有：

$$\rho(\boldsymbol{r})=\langle\Psi|\hat{\rho}(\boldsymbol{r})|\Psi\rangle=\langle\Psi|\sum_{i=1}^{N}\delta(\boldsymbol{r}_i-\boldsymbol{r})|\Psi\rangle=\sum_{i=1}^{N}\int\psi_i(\boldsymbol{r}_i)\psi_i^*(\boldsymbol{r}_i)\delta(\boldsymbol{r}_i-\boldsymbol{r})d\boldsymbol{r}_i=\sum_{i=1}^{N}\psi_i(\boldsymbol{r})\psi_i^*(\boldsymbol{r})$$

练习2：用场算符如何表示电子密度？换言之，密度算符的二次量子化表示是什么？

解：对于一般的单体算符，其二次量子化表示为（记场算符为$\begin{cases}\hat{\psi}(\boldsymbol{x})=\sum\limits_i\chi(\boldsymbol{x})\hat{a}_i\\ \hat{\psi}^{\dagger}(\boldsymbol{x})=\sum\limits_i\chi^*(\boldsymbol{x})\hat{a}_i^{\dagger}\end{cases}$）

$$\hat{O}_1=\sum_{i,j}\langle i|\hat{O}_1|j\rangle\hat{a}_i^{\dagger}\hat{a}_j=\sum_{i,j}\int\chi_i^*(\boldsymbol{x})\hat{O}_1(\boldsymbol{x})\chi_j(\boldsymbol{x})d\boldsymbol{x}\hat{a}_i^{\dagger}\hat{a}_j=\int\hat{\psi}^{\dagger}(\boldsymbol{x})\hat{O}_1(\boldsymbol{x})\hat{\psi}(\boldsymbol{x})d\boldsymbol{x}$$

因此密度算符的二次量子化表示为

$$\hat{\rho}(\boldsymbol{x})=\int\hat{\psi}^{\dagger}(\boldsymbol{x}^{'})\delta(\boldsymbol{x}-\boldsymbol{x}^{'})\hat{\psi}(\boldsymbol{x}^{'})d\boldsymbol{x}^{'}=\hat{\psi}^{\dagger}(\boldsymbol{x})\hat{\psi}(\boldsymbol{x})$$

特别的，若不涉及自旋轨道，则密度算符的二次量子化表示为$\hat{\rho}(\boldsymbol{r})=\hat{\psi}^{\dagger}(\boldsymbol{r})\hat{\psi}(\boldsymbol{r})$

练习3：在Hohenberg-Kohn第一定理的推导中，设存在两个不同外场$v^{(1)}(\boldsymbol{r})$和$v^{(2)}(\boldsymbol{r})$（即满足$v^{(1)}(\boldsymbol{r})\neq v^{(2)}(\boldsymbol{r})+\mathrm{const}$），证明对应的基态波函数满足$\Psi^{(1)}\neq\Psi^{(2)}$

证明：将不同外场下的哈密尔顿算符表示出来，得$\hat{H}^{(1)}=\hat{T}+\hat{V}^{(1)}(\boldsymbol{r})+\hat{W}$，$\hat{H}^{(2)}=\hat{T}+\hat{V}^{(2)}(\boldsymbol{r})+\hat{W}$，其中$\hat{T}$为动能算符，$\hat{V}^{(1)}(\boldsymbol{r})$和$\hat{V}^{(2)}(\boldsymbol{r})$为不同的外场势能算符，$\hat{W}$为双电子算符。

假设在不同外场下，仍然有相同的基态波函数，我们有$\hat{H}^{(1)}|\Psi\rangle=E^{(1)}|\Psi\rangle$，$\hat{H}^{(2)}|\Psi\rangle=E^{(2)}|\Psi\rangle$，两式相减有：

$$(\hat{H}^{(1)}-\hat{H}^{(2)})|\Psi\rangle=[\hat{V}^{(1)}(\boldsymbol{r})-\hat{V}^{(2)}(\boldsymbol{r})]|\Psi\rangle=(E^{(1)}-E^{(2)})|\Psi\rangle$$

若采用二次量子化表象，则$\hat{V}^{(1)}(\boldsymbol{r})=\int\psi^{\dagger}(\boldsymbol{r})v^{(1)}(\boldsymbol{r})\psi(\boldsymbol{r})d\boldsymbol{r}$，$\hat{V}^{(2)}(\boldsymbol{r})=\int\psi^{\dagger}(\boldsymbol{r})v^{(2)}(\boldsymbol{r})\psi(\boldsymbol{r})d\boldsymbol{r}$，而在一次量子化表象下，$(\boldsymbol{r}_1,s_1,\boldsymbol{r}_2,s_2,\ldots,\boldsymbol{r}_N,s_N|\Phi\rangle=\Phi(\boldsymbol{r}_1,s_1,\boldsymbol{r}_2,s_2,\ldots,\boldsymbol{r}_N,s_N)$，$\psi^{\dagger}(\boldsymbol{r})\psi(\boldsymbol{r})=\sum\limits_{i=1}^{N}\delta(\boldsymbol{r}_i-\boldsymbol{r})$，因此左乘$(\boldsymbol{r}_1,s_1,\boldsymbol{r}_2,s_2,\ldots,\boldsymbol{r}_N,s_N|$，得（此处利用波函数不为零的性质）

$$
\begin{aligned}
&(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N|[\hat{V}^{(1)}(\boldsymbol{r}) - \hat{V}^{(2)}(\boldsymbol{r})]|\Psi\rangle = (\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N|(E^{(1)} - E^{(2)})|\Psi\rangle \\
\Rightarrow &\int [v^{(1)}(\boldsymbol{r}) - v^{(2)}(\boldsymbol{r})] \sum_{i=1}^{N} \delta(\boldsymbol{r}_i - \boldsymbol{r}) \Psi(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N) d\boldsymbol{r} = (E^{(1)} - E^{(2)}) \Psi(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N) \\
\Rightarrow &\sum_{i=1}^{N} [v^{(1)}(\boldsymbol{r}_i) - v^{(2)}(\boldsymbol{r}_i)] \Psi(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N) = (E^{(1)} - E^{(2)}) \Psi(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N) \\
\Rightarrow &\sum_{i=1}^{N} [v^{(1)}(\boldsymbol{r}_i) - v^{(2)}(\boldsymbol{r}_i)] = E^{(1)} - E^{(2)} = \text{const}
\end{aligned}
$$

这与题设矛盾，因此不同外场下的基态波函数不同，证毕

练习4：Levy限制性搜索中的Ψ_ρ与HK第二定理证明过程中引入的Ψ_ρ有什么差别？

解：HK第二定理证明过程中引入的Ψ_ρ是由$\rho(\boldsymbol{r})$所确定的外势场$v(\boldsymbol{r})$所对应的哈密尔顿算符的基态波函数，它要求电子密度满足v-可表示性；而Levy限制性搜索中的Ψ_ρ是在限制Ψ的前提下给出指定的ρ，即$\Psi_\rho = \arg\min\limits_{\Psi\to\rho}\langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle$，因此电子密度只需要满足N-可表示性

练习5：写出用Kohn-Sham轨道能量表示的总能量表达式

解：根据Kohn-Sham方程，有$[-\frac{1}{2}\nabla^2 + v_s(\boldsymbol{r})]\psi_i(\boldsymbol{x}) = \varepsilon_i\psi_i(\boldsymbol{x})$，其中$v_s(\boldsymbol{r}) = v(\boldsymbol{r}) + v_{\mathrm{H}}(\boldsymbol{r}) + v_{\mathrm{xc}}(\boldsymbol{r})$，但是直接加和轨道能会发生重叠计算，因此将Kohn-Sham方程变形得

$$
-\frac{1}{2}\nabla^2\psi_i(\boldsymbol{x}) = [\varepsilon_i - v_s(\boldsymbol{r})]\psi_i(\boldsymbol{x}) = [\varepsilon_i - v(\boldsymbol{r}) - v_{\mathrm{H}}(\boldsymbol{r}) - v_{\mathrm{xc}}(\boldsymbol{r})]\psi_i(\boldsymbol{x})
$$

$$
\begin{aligned}
E[\rho] \equiv E_{\mathrm{HF}}[\rho] &= T_s[\rho] + \int \rho(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r} + E_H[\rho] + E_{xc}[\rho] \\
&= \sum_i^N \langle\psi_i| - \frac{1}{2}\nabla^2|\psi_i\rangle + \int \rho(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r} + E_H[\rho] + E_{xc}[\rho] \\
&= \sum_i^N \varepsilon_i - \sum_i^N \int |\psi_i(\boldsymbol{x})|^2[v(\boldsymbol{r}) + v_{\mathrm{H}}(\boldsymbol{r}) + v_{\mathrm{xc}}(\boldsymbol{r})]d\boldsymbol{x} + \int \rho(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r} + E_H[\rho] + E_{xc}[\rho] \\
&= \sum_i^N \varepsilon_i - \int \rho(\boldsymbol{r})[v(\boldsymbol{r}) + v_{\mathrm{H}}(\boldsymbol{r}) + v_{\mathrm{xc}}(\boldsymbol{r})]d\boldsymbol{r} + \int \rho(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r} + E_H[\rho] + E_{xc}[\rho] \\
&= \sum_i^N \varepsilon_i - \int \rho(\boldsymbol{r}) \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}d\boldsymbol{r}' - \int \rho(\boldsymbol{r})v_{\mathrm{xc}}(\boldsymbol{r})d\boldsymbol{r} + \frac{1}{2}\iint \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}d\boldsymbol{r}' + E_{\mathrm{xc}}[\rho] \\
&= \sum_i^N \varepsilon_i - \frac{1}{2}\iint \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}d\boldsymbol{r}' - \int \rho(\boldsymbol{r})v_{\mathrm{xc}}(\boldsymbol{r})d\boldsymbol{r} + E_{\mathrm{xc}}[\rho] \\
&= \sum_i^N \varepsilon_i - E_{\mathrm{H}}[\rho] - \int \rho(\boldsymbol{r})v_{\mathrm{xc}}(\boldsymbol{r})d\boldsymbol{r} + E_{\mathrm{xc}}[\rho]
\end{aligned}
$$