课堂练习

练习1：证明闭壳层体系中精确交换空穴密度的表达式$\rho_x(\boldsymbol{r}_1,\boldsymbol{r}_2)=-\frac{2|\rho_1(\boldsymbol{r}_1,\boldsymbol{r}_2)|^2}{\rho(\boldsymbol{r}_1)}$满足如下和规则（sum rule）

$$\int d\boldsymbol{r}_2\rho_x(\boldsymbol{r}_1,\boldsymbol{r}_2)=-1$$

证明：将题中条件代入待证明等式的左边，结合$\rho_1(\boldsymbol{r}_1,\boldsymbol{r}_2)$的定义$\rho_1(\boldsymbol{r}_1,\boldsymbol{r}_2)=\sum_i^{\frac{N}{2}}\psi_i(\boldsymbol{r}_1)\psi_i^*(\boldsymbol{r}_2)$，得

$$\int d\boldsymbol{r}_2\rho_x(\boldsymbol{r}_1,\boldsymbol{r}_2)=\int-\frac{2|\rho_1(\boldsymbol{r}_1,\boldsymbol{r}_2)|^2}{\rho(\boldsymbol{r}_1)}d\boldsymbol{r}_2=-2\int\frac{\rho_1(\boldsymbol{r}_1,\boldsymbol{r}_2)\rho_1^*(\boldsymbol{r}_1,\boldsymbol{r}_2)}{\rho(\boldsymbol{r}_1)}d\boldsymbol{r}_2$$
$$=-2\int\frac{\sum_{i,j}^{\frac{N}{2}}\psi_i(\boldsymbol{r}_1)\psi_i^*(\boldsymbol{r}_2)\psi_j^*(\boldsymbol{r}_1)\psi_j(\boldsymbol{r}_2)}{\rho(\boldsymbol{r}_1)}d\boldsymbol{r}_2=-\frac{2\sum_{i,j}^{\frac{N}{2}}\psi_i(\boldsymbol{r}_1)\psi_j^*(\boldsymbol{r}_1)\delta_{ij}}{\rho(\boldsymbol{r}_1)}$$
$$=-\frac{2\sum_{i}^{\frac{N}{2}}\psi_i(\boldsymbol{r}_1)\psi_i^*(\boldsymbol{r}_1)}{\rho(\boldsymbol{r}_1)}=-1$$

练习2：对于闭壳层体系，试证明$\rho_x(\boldsymbol{r}_1,\boldsymbol{r}_2)=-\frac{2|\rho(\boldsymbol{r}_1,\boldsymbol{r}_2)|^2}{\rho(\boldsymbol{r}_1)}$，其中$\rho(\boldsymbol{r}_1,\boldsymbol{r}_2)=\sum_i^{\frac{N}{2}}\psi_i(\boldsymbol{r}_1)\psi_i^*(\boldsymbol{r}_2)$

证明：精确交换空穴密度的定义为$\rho_x(\boldsymbol{r}_1,\boldsymbol{r}_2)=-\frac{\int ds_1\int ds_2|\rho(\boldsymbol{x}_1,\boldsymbol{x}_2)|^2}{\rho(\boldsymbol{r}_1)}$，其中

$\rho(\boldsymbol{x}_1,\boldsymbol{x}_2)=\sum_i^N\psi_i(\boldsymbol{x}_1)\psi_i^*(\boldsymbol{x}_2)$，因此代入得

$$\rho_x(\boldsymbol{r}_1,\boldsymbol{r}_2)=-\frac{\int ds_1\int ds_2|\rho(\boldsymbol{x}_1,\boldsymbol{x}_2)|^2}{\rho(\boldsymbol{r}_1)}=-\frac{\int ds_1\int ds_2\rho(\boldsymbol{x}_1,\boldsymbol{x}_2)\rho^*(\boldsymbol{x}_1,\boldsymbol{x}_2)}{\rho(\boldsymbol{r}_1)}$$
$$=-\frac{\int ds_1\int ds_2\sum_{i,j}^N\psi_i(\boldsymbol{x}_1)\psi_i^*(\boldsymbol{x}_2)\psi_j^*(\boldsymbol{x}_1)\psi_j(\boldsymbol{x}_2)}{\rho(\boldsymbol{r}_1)}$$
$$=-\frac{\sum_{i,j}^N\iint\psi_{[\frac{i}{2}]}(\boldsymbol{r}_1)\sigma_i(s_1)\psi_{[\frac{i}{2}]}^*(\boldsymbol{r}_2)\sigma_i^*(s_2)\psi_{[\frac{j}{2}]}^*(\boldsymbol{r}_1)\sigma_j^*(s_1)\psi_{[\frac{j}{2}]}(\boldsymbol{r}_2)\sigma_j(s_2)ds_1ds_2}{\rho(\boldsymbol{r}_1)}$$
$$=-\frac{\sum_{i,j}^N\psi_{[\frac{i}{2}]}(\boldsymbol{r}_1)\psi_{[\frac{i}{2}]}^*(\boldsymbol{r}_2)\psi_{[\frac{j}{2}]}^*(\boldsymbol{r}_1)\psi_{[\frac{j}{2}]}(\boldsymbol{r}_2)\delta_{j-2[\frac{j}{2}],i-2[\frac{i}{2}]}\delta_{i-2[\frac{i}{2}],j-2[\frac{j}{2}]}}{\rho(\boldsymbol{r}_1)}$$
$$=-\frac{\sum_{i,j}^{\frac{N}{2}}\psi_i(\boldsymbol{r}_1)\psi_i^*(\boldsymbol{r}_2)\psi_j^*(\boldsymbol{r}_1)\psi_j(\boldsymbol{r}_2)\delta_{1,1}^2+\sum_{i,j}^{\frac{N}{2}}\psi_i(\boldsymbol{r}_1)\psi_i^*(\boldsymbol{r}_2)\psi_j^*(\boldsymbol{r}_1)\psi_j(\boldsymbol{r}_2)\delta_{0,0}^2}{\rho(\boldsymbol{r}_1)}$$
$$=-\frac{2\sum_{i,j}^{\frac{N}{2}}\psi_i(\boldsymbol{r}_1)\psi_i^*(\boldsymbol{r}_2)\psi_j^*(\boldsymbol{r}_1)\psi_j(\boldsymbol{r}_2)}{\rho(\boldsymbol{r}_1)}=-\frac{2|\rho(\boldsymbol{r}_1,\boldsymbol{r}_2)|^2}{\rho(\boldsymbol{r}_1)}$$

练习3：DFT相关能(correlation energy)定义为

$$E_c[\rho]=\langle\Psi_\rho|\hat{T}+\hat{V}_{ee}|\Psi_\rho\rangle-\langle\Phi_\rho|\hat{T}+\hat{V}_{ee}|\Phi_\rho\rangle$$

试证明$E_c[\rho]\le 0$

证明：我们先回到普适泛函的定义

$$F_\lambda[\rho(\boldsymbol{r})]\equiv\min_{\Psi\to\rho}\langle\Psi|\hat{T}+\lambda\hat{V}_{ee}|\Psi\rangle\equiv\langle\Psi_\rho^\lambda|\hat{T}+\lambda\hat{V}_{ee}|\Psi_\rho^\lambda\rangle$$

显然，当λ分别为0和1时，有

$$\begin{aligned}F_{\lambda=0}[\rho]&\equiv\langle\Psi_\rho^{\lambda=0}|\hat{T}|\Psi_\rho^{\lambda=0}\rangle=\langle\Phi_\rho|\hat{T}|\Phi_\rho\rangle\equiv T_s[\rho]\\F_{\lambda=1}[\rho]&\equiv\langle\Psi_\rho^{\lambda=1}|\hat{T}+\hat{V}_{ee}|\Psi_\rho^{\lambda=1}\rangle\equiv T[\rho]+V_{ee}[\rho]\end{aligned}$$

其中$|\Psi\rangle$与$|\Phi\rangle$对应于相同电子密度，而根据Levy限制性搜索，$|\Psi\rangle=\arg\min_\rho\langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle$（对应于$\lambda=1$的情形），因此$F_{\lambda=1}[\rho]=\langle\Psi_\rho|\hat{T}+\hat{V}_{ee}|\Psi_\rho\rangle\le\langle\Phi_\rho|\hat{T}+\hat{V}_{ee}|\Phi_\rho\rangle$，即$E_c[\rho]\le 0$，当且仅当体系只有单电子时取等号。

练习4：HF中的交换能与DFT的交换能是否有确定的大小关系？现给出两者的表达式

$$\begin{aligned}E_{\mathrm{x}}^{(DFT)}&=\langle\Phi_{\rho_0}|\hat{V}_{ee}|\Phi_{\rho_0}\rangle-E_{\mathrm{H}}[\rho]\\E_{\mathrm{x}}^{(HF)}&=\langle\Phi_0^{(\mathrm{HF})}|\hat{V}_{ee}|\Phi_0^{(\mathrm{HF})}\rangle-E_{\mathrm{H}}[\rho_{\mathrm{HF}}]\end{aligned}$$

证明如果$\rho_0(\boldsymbol{r})\simeq\rho_{\mathrm{HF}}(\boldsymbol{r})$，则有$E_{\mathrm{x}}^{(DFT)}>E_{\mathrm{x}}^{(HF)}$

证明：（未完待续）

练习5：在自旋密度泛函理论的推导中，证明$m(\boldsymbol{r})=\beta_e[\rho^\beta(\boldsymbol{r})-\rho^\alpha(\boldsymbol{r})]$

证明：电子磁化密度算符的定义式为$\hat{\boldsymbol{m}}(\boldsymbol{r})=-2\beta_e\sum_i^N\hat{\boldsymbol{s}}_i\delta(\boldsymbol{r}-\boldsymbol{r}_i)$，其期望值为$\boldsymbol{m}(\boldsymbol{r})=\langle\Psi_0|\hat{\boldsymbol{m}}(\boldsymbol{r})|\Psi_0\rangle$，假定磁场只在z方向上的分量不为零，即$\boldsymbol{B}(\boldsymbol{r})=B(\boldsymbol{r})\boldsymbol{e}_z$，此时电子磁化密度也只有z方向上分量，即$\boldsymbol{m}(\boldsymbol{r})=m(\boldsymbol{r})\boldsymbol{e}_z$，从而$\hat{\boldsymbol{m}}(\boldsymbol{r})$中只剩下$\hat{m}_z$的部分（对应的电子自旋算符为$\hat{s}_z$），假设$|\Psi_0\rangle$为Slater行列式波函数，则

$$\begin{aligned}m(\boldsymbol{r})=\langle\Psi_0|\hat{m}_z(\boldsymbol{r})|\Psi_0\rangle&=-2\beta_e\langle\Psi_0|\sum_i^N\hat{s}_{zi}\delta(\boldsymbol{r}-\boldsymbol{r}_i)|\Psi_0\rangle=-2\beta_e\sum_i^N\langle\Psi_0|\hat{s}_{zi}\delta(\boldsymbol{r}-\boldsymbol{r}_i)|\Psi_0\rangle\\&=-2\beta_e\sum_i^N\int\frac{1}{N}\sum_j^N\psi_i^*(\boldsymbol{x}_j)\hat{s}_{zi}\delta(\boldsymbol{r}-\boldsymbol{r}_i)\psi_i(\boldsymbol{x}_j)d\boldsymbol{x}_i=-2\beta_e\sum_i^N\int\frac{Nm_{s,i}}{N}\sum_j^N\psi_i(\boldsymbol{x}_j)\delta(\boldsymbol{r}-\boldsymbol{r}_i)\psi_i^*(\boldsymbol{x}_j)d\boldsymbol{x}_i\\&=-2\beta_e\sum_i^N\iint m_{s,i}\sum_j^N\psi_{[\frac{i}{2}]}^{\sigma_i}(\boldsymbol{r}_j)\sigma_i(s_j)\delta(\boldsymbol{r}-\boldsymbol{r}_i)\psi_{[\frac{i}{2}]}^*(\boldsymbol{r}_j)\sigma_i^*(s_j)d\boldsymbol{r}_ids_i\\&=-2\beta_e\Big[\sum_i^{N_\alpha}\frac{1}{2}\psi_i^\alpha(\boldsymbol{r})\psi_i^{\alpha*}(\boldsymbol{r})-\sum_i^{N_\beta}\frac{1}{2}\psi_i^\beta(\boldsymbol{r})\psi_i^{\beta*}(\boldsymbol{r})\Big]=\beta_e[\rho^\beta(\boldsymbol{r})-\rho^\alpha(\boldsymbol{r})]\end{aligned}$$

练习6：证明在SDFT中，精确交换空穴密度可以表达为$\rho_x(\boldsymbol{r}_1,\boldsymbol{r}_2)=-\frac{\sum_\sigma|\rho_1^\sigma(\boldsymbol{r}_1,\boldsymbol{r}_2)|^2}{\rho(\boldsymbol{r}_1)}$，其中$\rho_1^\sigma(\boldsymbol{r}_1,\boldsymbol{r}_2)=\sum_i^{N^\sigma}\psi_i^\sigma(\boldsymbol{r}_1)\psi_i^{\sigma*}(\boldsymbol{r}_2)$

证明：仿照练习2，我们有

$$\rho_x(\boldsymbol{r}_1,\boldsymbol{r}_2) = -\frac{\int ds_1 \int ds_2 |\rho(\boldsymbol{x}_1,\boldsymbol{x}_2)|^2}{\rho(\boldsymbol{r}_1)} = -\frac{\int ds_1 \int ds_2 \rho(\boldsymbol{x}_1,\boldsymbol{x}_2)\rho^*(\boldsymbol{x}_1,\boldsymbol{x}_2)}{\rho(\boldsymbol{r}_1)}$$

$$= -\frac{\int ds_1 \int ds_2 \sum_{i,j}^{N} \psi_i(\boldsymbol{x}_1)\psi_i^*(\boldsymbol{x}_2)\psi_j^*(\boldsymbol{x}_1)\psi_j(\boldsymbol{x}_2)}{\rho(\boldsymbol{r}_1)}$$

$$= -\frac{\sum_{i,j}^{N} \iint \psi^{\sigma_i}_{[\frac{i}{2}]}(\boldsymbol{r}_1)\sigma_i(s_1)\psi^{\sigma_i *}_{[\frac{i}{2}]}(\boldsymbol{r}_2)\sigma_i^*(s_2)\psi^{\sigma_j *}_{[\frac{j}{2}]}(\boldsymbol{r}_1)\sigma_j^*(s_1)\psi^{\sigma_j}_{[\frac{j}{2}]}(\boldsymbol{r}_2)\sigma_j(s_2)ds_1 ds_2}{\rho(\boldsymbol{r}_1)}$$

$$= -\frac{\sum_{i,j}^{N} \psi^{\sigma_i}_{[\frac{i}{2}]}(\boldsymbol{r}_1)\psi^{\sigma_i *}_{[\frac{i}{2}]}(\boldsymbol{r}_2)\psi^{\sigma_j *}_{[\frac{j}{2}]}(\boldsymbol{r}_1)\psi^{\sigma_j}_{[\frac{j}{2}]}(\boldsymbol{r}_2)\delta_{j-[\frac{j}{2}],i-[\frac{i}{2}]}\delta_{i-[\frac{i}{2}],j-[\frac{j}{2}]}}{\rho(\boldsymbol{r}_1)}$$

$$= -\frac{\sum_{i,j}^{N_\alpha} \psi^{\alpha}_{[\frac{i}{2}]}(\boldsymbol{r}_1)\psi^{\alpha}_{[\frac{i}{2}]}(\boldsymbol{r}_2)\psi^{\alpha *}_{[\frac{j}{2}]}(\boldsymbol{r}_1)\psi^{\alpha}_{[\frac{j}{2}]}(\boldsymbol{r}_2) + \sum_{i,j}^{N_\beta} \psi^{\beta}_{[\frac{i}{2}]}(\boldsymbol{r}_1)\psi^{\beta}_{[\frac{i}{2}]}(\boldsymbol{r}_2)\psi^{\beta}_{[\frac{j}{2}]}(\boldsymbol{r}_1)\psi^{\beta}_{[\frac{j}{2}]}(\boldsymbol{r}_2)}{\rho(\boldsymbol{r}_1)}$$

$$= -\frac{\sum_\sigma |\rho_1^\sigma(\boldsymbol{r}_1,\boldsymbol{r}_2)|^2}{\rho(\boldsymbol{r}_1)}$$