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 $ho_x(m{r}_1,m{r}_2)=-rac{2|
ho_1(m{r}_1,m{r}_2)|^2}{
ho(m{r}_1)}$ 满足如下和规则(sum rule)

$$\int dm{r}_2
ho_x(m{r}_1,m{r}_2) = -1$$

证明:将题中条件代入待证明等式的左边,结合 $ho_1(m{r}_1,m{r}_2)$ 的定义 $ho_1(m{r}_1,m{r}_2)=\sum\limits_i^{rac{N}{2}}\psi_i(m{r}_1)\psi_i^*(m{r}_2)$,得

$$\int dm{r}_2
ho_x(m{r}_1,m{r}_2) = \int -rac{2|
ho_1(m{r}_1,m{r}_2)|^2}{
ho(m{r}_1)}dm{r}_2 = -2\int rac{
ho_1(m{r}_1,m{r}_2)
ho_1^*(m{r}_1,m{r}_2)}{
ho(m{r}_1)}dm{r}_2 \ = -2\int rac{\sum\limits_{i,j}^{rac{N}{2}}\psi_i(m{r}_1)\psi_i^*(m{r}_2)\psi_j^*(m{r}_1)\psi_j(m{r}_2)}{
ho(m{r}_1)}dm{r}_2 = -rac{2\sum\limits_{i,j}^{rac{N}{2}}\psi_i(m{r}_1)\psi_j^*(m{r}_1)\delta_{ij}}{
ho(m{r}_1)} \ = -rac{2\sum\limits_{i}^{rac{N}{2}}\psi_i(m{r}_1)\psi_i^*(m{r}_1)}{
ho(m{r}_1)} = -1$$

练习2: 对于闭壳层体系,试证明 $ho_x(m{r}_1,m{r}_2)=-rac{2|
ho(m{r}_1,m{r}_2)|^2}{
ho(m{r}_1)}$,其中

$$ho(oldsymbol{r}_1,oldsymbol{r}_2)=\sum_i^rac{N}{2}\psi_i(oldsymbol{r}_1)\psi_i^*(oldsymbol{r}_2)$$

证明:精确交换空穴密度的定义为 $\rho_x(m{r}_1,m{r}_2)=-rac{\int ds_1\int ds_2|
ho(m{x}_1,m{x}_2)|^2}{
ho(m{r}_1)}$,其中 $ho(m{x}_1,m{x}_2)=\sum\limits_{i=1}^N\psi_i(m{x}_1)\psi_i^*(m{x}_2)$,因此代入得

$$egin{align*}
ho_{m{x}}(m{r}_1,m{r}_2) &= -rac{\int ds_1 \int ds_2 |
ho(m{x}_1,m{x}_2)|^2}{
ho(m{r}_1)} = -rac{\int ds_1 \int ds_2
ho(m{x}_1,m{x}_2)
ho^*(m{x}_1,m{x}_2)}{
ho(m{r}_1)} \ &= -rac{\int ds_1 \int ds_2 \sum\limits_{i,j}^N \psi_i(m{x}_1)\psi_i^*(m{x}_2)\psi_j^*(m{x}_1)\psi_j(m{x}_2)}{
ho(m{r}_1)} \ &= -rac{\sum\limits_{i,j}^N \iint \psi_{[rac{i}{2}]}(m{r}_1)\sigma_i(s_1)\psi_{[rac{i}{2}]}^*(m{r}_2)\sigma_i^*(s_2)\psi_{[rac{j}{2}]}^*(m{r}_1)\sigma_j^*(s_1)\psi_{[rac{j}{2}]}(m{r}_2)\sigma_j(s_2)ds_1ds_2}{
ho(m{r}_1)} \ &= -rac{\sum\limits_{i,j}^N \psi_{[rac{i}{2}]}(m{r}_1)\psi_{[rac{i}{2}]}(m{r}_2)\psi_{[rac{j}{2}]}^*(m{r}_2)\phi_{[rac{j}{2}]}^*(m{r}_2)\delta_{j-2[rac{j}{2}],i-2[rac{i}{2}]}^*\delta_{i-2[rac{i}{2}],j-2[rac{j}{2}]}}{
ho(m{r}_1)} \ &= -rac{\sum\limits_{i,j}^N \psi_i(m{r}_1)\psi_i^*(m{r}_2)\psi_j^*(m{r}_1)\psi_j(m{r}_2)\delta_{1,1}^2 + \sum\limits_{i,j}^N \psi_i(m{r}_1)\psi_i^*(m{r}_2)\psi_j^*(m{r}_1)\psi_j(m{r}_2)\delta_{0,0}^2}{
ho(m{r}_1)} \ &= -rac{2|
ho(m{r}_1,m{r}_2)|^2}{
ho(m{r}_1)} \ &= -rac{2|
ho(m{r}_1,m{r}_2)|^2}{
ho(m{r}_1)} \ \end{split}$$

练习3: DFT相关能(correlation energy)定义为

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

试证明 $E_c[\rho] < 0$

证明: 我们先回到普适泛函的定义

$$F_{\lambda}[
ho(m{r})] \equiv \min_{\Psi
ightarrow
ho} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi
angle \equiv \langle \Psi_{
ho}^{\lambda} | \hat{T} + \lambda \hat{V}_{ee} | \Psi_{
ho}^{\lambda}
angle$$

显然, 当 λ 分别为0和1时, 有

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

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 $F_{\lambda=1}[\rho]=\langle\Psi_{\rho}|\hat{T}+\hat{V}_{ee}|\Psi_{\rho}\rangle\leq\langle\Phi_{\rho}|\hat{T}+\hat{V}_{ee}|\Phi_{\rho}\rangle$,即 $E_{c}[\rho]\leq0$,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

$$E_{\mathrm{x}}^{(DFT)} = \langle \Phi_{
ho_0} | \hat{V}_{ee} | \Phi_{
ho_0}
angle - E_{\mathrm{H}}[
ho] \ E_{\mathrm{x}}^{(HF)} = \langle \Phi_{\mathrm{o}}^{(\mathrm{HF})} | \hat{V}_{ee} | \Phi_{\mathrm{o}}^{(\mathrm{HF})}
angle - E_{\mathrm{H}}[
ho_{\mathrm{HF}}] \$$

证明如果 $ho_0(m{r})\simeq
ho_{
m HF}(m{r})$,则有 $E_{
m x}^{(DFT)}>E_{
m x}^{(HF)}$

证明: (未完待续)

练习5: 在自旋密度泛函理论的推导中,证明 $m(m{r})=eta_e[
ho^eta(m{r})ho^lpha(m{r})]$

证明: 电子磁化密度算符的定义式为 $\hat{m{m}}(m{r}) = -2eta_e\sum_i^N\hat{m{s}}_i\delta(m{r}-m{r}_i)$,其期望值为

 $m{m}(m{r})=\langle\Psi_0|\hat{m{m}}(m{r})|\Psi_0
angle$,假定磁场只在z方向上的分量不为零,即 $m{B}(m{r})=B(m{r})m{e}_z$,此时电子磁化密度也只有z方向上分量,即 $m{m}(m{r})=m(m{r})m{e}_z$,从而 $\hat{m{m}}(m{r})$ 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

$$egin{aligned} m(oldsymbol{r}) &= \langle \Psi_0 | \hat{m}_z(oldsymbol{r}) | \Psi_0
angle = -2eta_e \langle \Psi_0 | \sum_i^N \hat{s}_{zi} \delta(oldsymbol{r} - oldsymbol{r}_i) | \Psi_0
angle = -2eta_e \sum_i^N \langle \Psi_0 | \hat{s}_{zi} \delta(oldsymbol{r} - oldsymbol{r}_i) | \Psi_0
angle \ &= -2eta_e \sum_i^N \int rac{1}{N} \sum_j^N \psi_i(oldsymbol{x}_j) \hat{s}_{zi} \delta(oldsymbol{r} - oldsymbol{r}_i) \psi_i(oldsymbol{x}_j) doldsymbol{x}_i = -2eta_e \sum_i^N \int rac{Nm_{s,i}}{N} \sum_j^N \psi_i(oldsymbol{x}_j) \delta(oldsymbol{r} - oldsymbol{r}_i) \psi_i^*(oldsymbol{x}_j) doldsymbol{x}_i \ &= -2eta_e \left[\sum_i^N \int m_{s,i} \sum_j^N \psi_i^{\sigma_i}(oldsymbol{r}_j) \sigma_i(s_j) \delta(oldsymbol{r} - oldsymbol{r}_i) \psi_{[\frac{i}{2}]}^*(oldsymbol{r}_j) \sigma_i^*(s_j) doldsymbol{r}_i ds_i \ &= -2eta_e \left[\sum_i^{N_{lpha}} rac{1}{2} \psi_i^{lpha}(oldsymbol{r}) \psi_i^{lpha*}(oldsymbol{r}) - \sum_i^{N_{eta}} rac{1}{2} \psi_i^{eta}(oldsymbol{r}) \psi_i^{eta*}(oldsymbol{r})
ight] = eta_e [
ho^{eta}(oldsymbol{r}) -
ho^{lpha}(oldsymbol{r})
ight] \end{aligned}$$

练习6:证明在SDFT中,精确交换空穴密度可以表达为

$$ho_x(m{r}_1,m{r}_2)=-rac{\sum_{\sigma}|
ho_1^{\sigma}(m{r}_1,m{r}_2)|^2}{
ho(m{r}_1)}$$
,其中 $ho_1^{\sigma}(m{r}_1,m{r}_2)=\sum_i^{N^{\sigma}}\psi_i^{\sigma}(m{r}_1)\psi_i^{\sigma*}(m{r}_2)$

证明: 仿照练习2, 我们有

$$egin{align*}
ho_x(m{r}_1,m{r}_2) &= -rac{\int ds_1 \int ds_2 \left|
ho(m{x}_1,m{x}_2)
ight|^2}{
ho(m{r}_1)} = -rac{\int ds_1 \int ds_2
ho(m{x}_1,m{x}_2)
ho^*(m{x}_1,m{x}_2)}{
ho(m{r}_1)} \ &= -rac{\int ds_1 \int ds_2 \sum\limits_{i,j}^N \psi_i(m{x}_1) \psi_i^*(m{x}_2) \psi_j^*(m{x}_1) \psi_j(m{x}_2)}{
ho(m{r}_1)} \ &= -rac{\int ds_1 \int ds_2 \sum\limits_{i,j}^N \psi_i(m{x}_1) \psi_i^*(m{x}_2) \psi_j^*(m{x}_1) \psi_j(m{x}_2)}{
ho(m{r}_1)} \ &= -rac{\sum\limits_{i,j}^N \iint \psi_{\left[rac{i}{2}
ight]}^{\sigma_i}(m{r}_1) \sigma_i(s_1) \psi_{\left[rac{i}{2}
ight]}^{\sigma_i*}(m{r}_2) \sigma_i^*(s_2) \psi_{\left[rac{j}{2}
ight]}^{\sigma_j*}(m{r}_1) \sigma_j^*(s_1) \psi_{\left[rac{j}{2}
ight]}^{\sigma_j}(m{r}_2) \sigma_j(s_2) ds_1 ds_2}{
ho(m{r}_1)} \ &= -rac{\sum\limits_{i,j}^N \psi_{\left[rac{i}{2}
ight]}^{\sigma_i}(m{r}_1) \psi_{\left[rac{j}{2}
ight]}^{\sigma_j*}(m{r}_1) \psi_{\left[rac{j}{2}
ight]}^{\sigma_j}(m{r}_2) \delta_{j-\left[rac{j}{2}
ight],i-\left[rac{i}{2}
ight]} \delta_{i-\left[rac{i}{2}
ight],j-\left[rac{j}{2}
ight]}}{
ho(m{r}_1)} \ &= -rac{\sum\limits_{i,j} \psi_{\left[rac{i}{2}
ight]}^{\sigma_i}(m{r}_1,m{r}_2) \left|^2}{
ho(m{r}_1)} \ &= -rac{\sum\limits_{\sigma} \left|
ho_1^\sigma(m{r}_1,m{r}_2)
ight|^2}{
ho(m{r}_1,m{r}_2,m{r}_2, \m{r}_2, \m{r}_2,$$