课堂练习

练习1：交换能的局域密度近似泛函写为$E_{\mathrm{X}}[\rho]=A_{\mathrm{X}}\int\rho(\mathbf{r})^{\frac{4}{3}}d\mathbf{r}$，现在：（1）写出$E_{\mathrm{X}}$对电子密度的泛函导数，即交换势$v_x(\mathbf{r})$；（2）$v_x(\mathbf{r})$仍可看作是密度的泛函，请推导出它对密度的泛函导数，也就是求E_{X}对电子密度的二阶泛函微分，由此得到的是交换核$f_x(\mathbf{r},\mathbf{r}')$(exchange kernel)，这是含时密度泛函理论中的一个重要量

解：（1）因为：

$$\delta E_{\mathrm{X}}[\rho]=E_{\mathrm{X}}[\rho+\delta\rho]-E_{\mathrm{X}}[\rho]=A_{\mathrm{X}}\int[(\rho+\delta\rho)^{\frac{4}{3}}-\rho^{\frac{4}{3}}]d\mathbf{r}=A_{\mathrm{X}}\int[\frac{4}{3}\rho^{\frac{1}{3}}\delta\rho+O(\delta\rho^2)]d\mathbf{r}\approx A_{\mathrm{X}}\int\frac{4}{3}\rho^{\frac{1}{3}}\delta\rho d\mathbf{r}$$

所以$\frac{\delta E_{\mathrm{X}}[\rho]}{\delta\rho}=\frac{4}{3}A_{\mathrm{X}}\rho(\mathbf{r})^{\frac{1}{3}}$，即交换势$v_x(\mathbf{r})=\frac{4}{3}A_{\mathrm{X}}\rho(\mathbf{r})^{\frac{1}{3}}$

（2）将交换势用狄拉克δ函数改写为积分形式，得$v_x(\mathbf{r})=\frac{4}{3}A_{\mathrm{X}}\int\rho(\mathbf{r}')^{\frac{1}{3}}\delta(\mathbf{r}-\mathbf{r}')d\mathbf{r}'$，从而：

$$\begin{aligned}\delta v_x(\mathbf{r})&=v_x[\rho+\delta\rho]-v_x[\rho]=\frac{4}{3}A_{\mathrm{X}}\int[(\rho+\delta\rho)^{\frac{1}{3}}-\rho^{\frac{1}{3}}]\delta(\mathbf{r}-\mathbf{r}')d\mathbf{r}'\\&=\frac{4}{3}A_{\mathrm{X}}\int[\frac{1}{3}\rho^{-\frac{2}{3}}+O(\delta\rho^2)]\delta(\mathbf{r}-\mathbf{r}')d\mathbf{r}'\approx\frac{4}{3}A_{\mathrm{X}}\int\frac{1}{3}\rho^{-\frac{2}{3}}\delta(\mathbf{r}-\mathbf{r}')d\mathbf{r}'\end{aligned}$$

所以$\frac{\delta v_x[\rho]}{\delta\rho}=\frac{4}{9}A_{\mathrm{X}}\rho^{-\frac{2}{3}}\delta(\mathbf{r}-\mathbf{r}')$，即交换核$f_x(\mathbf{r},\mathbf{r}')=\frac{4}{9}A_{\mathrm{X}}\rho^{-\frac{2}{3}}\delta(\mathbf{r}-\mathbf{r}')$

练习2：Thomas-Fermi-Weisacker(TFW)模型中，能量作为电子密度的泛函写为

$$E_{\mathrm{TFW}}[\rho]=C_{\mathrm{TF}}\int\rho(\mathbf{r})^{\frac{5}{3}}d\mathbf{r}+\lambda T_{\mathrm{W}}[\rho]+\int\rho(\mathbf{r})V_{\mathrm{ext}}(\mathbf{r})d\mathbf{r}+E_{\mathrm{H}}[\rho(\mathbf{r})]$$

其中$T_{\mathrm{W}}[\rho]$的表达式为$T_{\mathrm{W}}[\rho]=\frac{1}{8}\int\frac{\nabla\rho(\mathbf{r})\cdot\nabla\rho(\mathbf{r})}{\rho(\mathbf{r})}d\mathbf{r}$，$\lambda$是一个经验参数，一般取0.25。定义$\rho(\mathbf{r})=[\psi(\mathbf{r})]^2$，将上式表示为$\psi(\mathbf{r})$的泛函，推导出相应的Euler-Lagrange方程

解：首先，对N个电子，其个数与电子密度的关系为$\int\rho(\mathbf{r})d\mathbf{r}=N$，用题目的定义，可改写为$\int\psi(\mathbf{r})^2d\mathbf{r}=N$；另一方面，能量作为电子密度的泛函可表示为$E_{\mathrm{TFW}}[\rho]=E_{\mathrm{TFW}}[\psi^2]$，从而设辅助泛函$L[\psi]=E_{\mathrm{TFW}}[\psi^2]-\mu[\int\psi(\mathbf{r})^2d\mathbf{r}-N]$，则对辅助泛函求微分得：

$$\frac{\delta L[\psi]}{\delta\psi}=\frac{\delta E_{\mathrm{TFW}}[\psi^2]}{\delta\psi}-2\mu\psi=\frac{\delta E_{\mathrm{TFW}}[\psi^2]}{\delta(\psi^2)}\frac{d(\psi^2)}{d\psi}-2\mu\psi=2\psi(\frac{\delta E_{\mathrm{TFW}}[\rho]}{\delta\rho}-\mu)$$

令$\frac{\delta L[\psi]}{\delta\psi}=0$，则有$\frac{\delta E_{\mathrm{TFW}}[\rho]}{\delta\rho}\psi=\mu\psi$。记$T_{\mathrm{TF}}[\rho]=C_{\mathrm{TF}}\int\rho(\mathbf{r})^{\frac{5}{3}}d\mathbf{r}$，$E_{\mathrm{ext}}[\rho]=\int\rho(\mathbf{r})V_{\mathrm{ext}}(\mathbf{r})d\mathbf{r}$，又知$E_{\mathrm{H}}[\rho]=\frac{1}{2}\iint\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$，因此这几项的微分分别为：

$$\begin{cases}\frac{\delta T_{\mathrm{TF}}[\rho]}{\delta\rho}=\frac{5}{3}C_{\mathrm{TF}}\rho(\mathbf{r})^{\frac{2}{3}}=\frac{5}{3}C_{\mathrm{TF}}\psi(\mathbf{r})^{\frac{4}{3}}\\\frac{\delta T_{\mathrm{W}}[\rho]}{\delta\rho}=\frac{1}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})^2}-\frac{1}{4}\frac{\nabla^2\rho(\mathbf{r})}{\rho(\mathbf{r})}\\\frac{\delta E_{\mathrm{ext}}[\rho]}{\delta\rho}=V_{\mathrm{ext}}(\mathbf{r})\\\frac{\delta E_{\mathrm{H}}[\rho]}{\delta\rho}=\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'=\int\frac{\psi(\mathbf{r}')^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\end{cases}$$

化解$\frac{\delta T_{\mathrm{W}}[\rho]}{\delta\rho}$需要将$\nabla\rho(\mathbf{r})$和$\nabla^2\rho(\mathbf{r})$变换为$\psi(\mathbf{r})$的泛函，而：

$$\begin{cases}\nabla\rho(\mathbf{r})=\nabla(\psi(\mathbf{r})^2)=2\psi(\mathbf{r})\nabla(\psi(\mathbf{r}))\\ \nabla^2\rho(\mathbf{r})=\nabla(\nabla\rho(\mathbf{r}))=\nabla(2\psi(\mathbf{r})\nabla(\psi(\mathbf{r})))=2|\nabla\psi(\mathbf{r})|^2+2\psi(\mathbf{r})\nabla^2(\psi(\mathbf{r}))\end{cases}$$

因此有：

$$\begin{aligned}\frac{\delta T_{\mathrm{W}}[\rho]}{\delta\rho}&=\frac{1}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})^2}-\frac{1}{4}\frac{\nabla^2\rho(\mathbf{r})}{\rho(\mathbf{r})}=\frac{\delta T_{\mathrm{W}}[\rho]}{\delta\rho}=\frac{1}{8}\frac{|2\psi(\mathbf{r})\nabla(\psi(\mathbf{r}))|^2}{\psi(\mathbf{r})^4}-\frac{1}{4}\frac{2|\nabla\psi(\mathbf{r})|^2+2\psi(\mathbf{r})\nabla^2(\psi(\mathbf{r}))}{\psi(\mathbf{r})^2}\\&=\frac{1}{2}\frac{|\nabla(\psi(\mathbf{r}))|^2}{\psi(\mathbf{r})^2}-\frac{1}{2}\frac{|\nabla(\psi(\mathbf{r}))|^2}{\psi(\mathbf{r})^2}-\frac{1}{2}\frac{\nabla^2(\psi(\mathbf{r}))}{\psi(\mathbf{r})}=-\frac{1}{2}\frac{\nabla^2(\psi(\mathbf{r}))}{\psi(\mathbf{r})}\end{aligned}$$

从而：

$$\begin{aligned}\frac{\delta E_{\mathrm{TFW}}[\rho]}{\delta\rho}\psi&=(\frac{\delta T_{\mathrm{TF}}[\rho]}{\delta\rho}+\lambda\frac{\delta T_{\mathrm{W}}[\rho]}{\delta\rho}+\frac{\delta E_{\mathrm{ext}}[\rho]}{\delta\rho}+\frac{\delta E_{\mathrm{H}}[\rho]}{\delta\rho})\psi=(\frac{5}{3}C_{\mathrm{TF}}\psi^{\frac{4}{3}}-\frac{\lambda}{2}\frac{\nabla^2\psi}{\psi}+V_{\mathrm{ext}}+\int\frac{\psi^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}')\psi\\&=-\frac{\lambda}{2}\nabla^2\psi+(\frac{5}{3}C_{\mathrm{TF}}\psi^{\frac{4}{3}}+V_{\mathrm{ext}}+\int\frac{\psi^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}')\psi=\mu\psi\end{aligned}$$

记$\mu'=\frac{\mu}{\lambda}$，$H'=-\frac{1}{2}\nabla^2+\lambda^{-1}(\frac{5}{3}C_{\mathrm{TF}}\psi^{\frac{4}{3}}+V_{\mathrm{ext}}+\int\frac{\psi^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}')$，则最终得到Euler-Lagrange方程为$H'\psi=\mu'\psi$，以上方程未计及电子的自旋方向。

练习3：请推导出经典力学中角动量L_x和L_y的对易式和量子力学中角动量算符$\hat{L}_x$和$\hat{L}_y$的对易式

解：经典力学中，角动量$\boldsymbol{L}$被定义为$\boldsymbol{L}=\boldsymbol{x}\times\boldsymbol{p}=\begin{vmatrix}\boldsymbol{i}&\boldsymbol{j}&\boldsymbol{k}\\x&y&z\\p_x&p_y&p_z\end{vmatrix}$，因此$L_x=yp_z-zp_y$，$L_y=zp_x-xp_z$。根据经典对易关系，有$[r_i,p_j]=\delta_{ij}\ (i,j=x,y,z)$，其中$r_i$代表坐标轴为$i$时对应的坐标（例如$r_x$代表$x$），$\delta_{ij}=\begin{cases}0&(i\text{与}j\text{字母不同})\\1&(i\text{与}j\text{字母相同})\end{cases}$，因此有$[r_i,L_i]=[L_i,r_i]=0$，$[p_i,L_i]=[L_i,p_i]=0$，这是因为$L_i$的表达式中不包含$r_i$或$p_i$，并且有：

$$\begin{aligned}[L_x,L_y]&=[yp_z-zp_y,L_y]=[yp_z,L_y]-[zp_y,L_y]=y[p_z,L_y]+[y,L_y]p_z-z[p_y,L_y]-[z,L_y]p_y\\&=y[p_z,zp_x-xp_z]+0-0-[z,zp_x-xp_z]p_y=y([p_z,zp_x]-[p_z,xp_z])-([z,zp_x]-[z,xp_z])p_y\\&=y([p_z,z]p_x+z[p_z,p_x]-[p_z,x]p_z-x[p_z,p_z])-([z,z]p_x+z[z,p_x]-[z,x]p_z-x[z,p_z])p_y\\&=y(-1\cdot p_x+z\cdot 0-0\cdot p_z-x\cdot 0)-(0\cdot p_x+z\cdot 0-0\cdot p_z-x\cdot 1)p_y\\&=-yp_x+xp_y=L_z\end{aligned}$$

同样的，量子力学中，角动量算符$\hat{\boldsymbol{L}}$被定义为$\hat{\boldsymbol{L}}=\hat{\boldsymbol{x}}\times\hat{\boldsymbol{p}}=\begin{vmatrix}\boldsymbol{i}&\boldsymbol{j}&\boldsymbol{k}\\\hat{x}&\hat{y}&\hat{z}\\\hat{p}_x&\hat{p}_y&\hat{p}_z\end{vmatrix}$，因此$\hat{L}_x=\hat{y}\hat{p}_z-\hat{z}\hat{p}_y$，$\hat{L}_y=\hat{z}\hat{p}_x-\hat{x}\hat{p}_z$。根据量子对易关系，有$[\hat{r}_i,\hat{p}_j]=\mathrm{i}\hbar\delta_{ij}\ (i,j=x,y,z)$，其中$\hat{r}_i$代表坐标轴为$i$时对应的坐标算符（例如$\hat{r}_x$代表$\hat{x}$），$\delta_{ij}=\begin{cases}0&(i\text{与}j\text{字母不同})\\1&(i\text{与}j\text{字母相同})\end{cases}$，因此有$[\hat{r}_i,\hat{L}_i]=[\hat{L}_i,\hat{r}_i]=0$，$[\hat{p}_i,\hat{L}_i]=[\hat{L}_i,\hat{p}_i]=0$，这是因为$\hat{L}_i$的表达式中不包含$\hat{r}_i$或$\hat{p}_i$，并且有：

$$\begin{aligned}[\hat{L}_x,\hat{L}_y]&=[\hat{y}\hat{p}_z-\hat{z}\hat{p}_y,\hat{L}_y]=[\hat{y}\hat{p}_z,\hat{L}_y]-[\hat{z}\hat{p}_y,\hat{L}_y]=\hat{y}[\hat{p}_z,\hat{L}_y]+[\hat{y},\hat{L}_y]\hat{p}_z-\hat{z}[\hat{p}_y,\hat{L}_y]-[\hat{z},\hat{L}_y]\hat{p}_y\\&=\hat{y}[\hat{p}_z,\hat{z}\hat{p}_x-\hat{x}\hat{p}_z]+0-0-[\hat{z},\hat{z}\hat{p}_x-\hat{x}\hat{p}_z]\hat{p}_y=\hat{y}([\hat{p}_z,\hat{z}\hat{p}_x]-[\hat{p}_z,\hat{x}\hat{p}_z])-([\hat{z},\hat{z}\hat{p}_x]-[\hat{z},\hat{x}\hat{p}_z])\hat{p}_y\\&=\hat{y}([\hat{p}_z,\hat{z}]\hat{p}_x+\hat{z}[\hat{p}_z,\hat{p}_x]-[\hat{p}_z,\hat{x}]\hat{p}_z-\hat{x}[\hat{p}_z,\hat{p}_z])-([\hat{z},\hat{z}]\hat{p}_x+\hat{z}[\hat{z},\hat{p}_x]-[\hat{z},\hat{x}]\hat{p}_z-\hat{x}[\hat{z},\hat{p}_z])\hat{p}_y\\&=\hat{y}(-\mathrm{i}\hbar\hat{p}_x+\hat{z}\cdot 0-0\cdot\hat{p}_z-\hat{x}\cdot 0)-(0\cdot\hat{p}_x+\hat{z}\cdot 0-0\cdot\hat{p}_z-\mathrm{i}\hbar\hat{x})\hat{p}_y\\&=\mathrm{i}\hbar(-\hat{y}\hat{p}_x+\hat{x}\hat{p}_y)=\mathrm{i}\hbar\hat{L}_z\end{aligned}$$

练习4：证明在非简并微扰理论中，算符$\hat{Q}_n=\hat{I}-\hat{P}_n=\sum\limits_{k\neq n}|k^{(0)}\rangle\langle k^{(0)}|$为幂等算符，即$(\hat{Q}_n)^m=\hat{Q}_n$，其中$m\in\mathbb{Z},m\geq 2$

证明：首先，对于$m=2$的情形，有：

$$(\hat{Q}_n)^2=(\sum_{k\neq n}|k^{(0)}\rangle\langle k^{(0)}|)(\sum_{l\neq n}|l^{(0)}\rangle\langle l^{(0)}|)=\sum_{k\neq n}\sum_{l\neq n}|k^{(0)}\rangle\langle k^{(0)}|l^{(0)}\rangle\langle l^{(0)}|=\sum_{k\neq n}\sum_{l\neq n}\delta_{k^{(0)},l^{(0)}}|k^{(0)}\rangle\langle l^{(0)}|=\sum_{k\neq n}|k^{(0)}\rangle\langle k^{(0)}|=\hat{Q}_n$$

其次，若$m=m_0$的情形成立，则当$m=m_0+1$时，有：

$$(\hat{Q}_n)^{m_0+1}=\hat{Q}_n(\hat{Q}_n)^{m_0}=\hat{Q}_n\hat{Q}_n=(\sum_{k\neq n}|k^{(0)}\rangle\langle k^{(0)}|)(\sum_{l\neq n}|l^{(0)}\rangle\langle l^{(0)}|)=\sum_{k\neq n}|k^{(0)}\rangle\langle k^{(0)}|=\hat{Q}_n$$

综上，根据数学归纳法，得算符$\hat{Q}_n$为幂等算符