课堂练习

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

解: (1) 因为:

$$\delta E_{
m X}[
ho] = E_{
m X}[
ho + \delta
ho] - E_{
m X}[
ho] = A_{
m X}\int [(
ho + \delta
ho)^{rac{4}{3}} -
ho^{rac{4}{3}}]d{f r} = A_{
m X}\int [rac{4}{3}
ho^{rac{1}{3}}\delta
ho + O(\delta
ho^2)]d{f r} pprox A_{
m X}\int rac{4}{3}
ho^{rac{1}{3}}\delta
ho d{f r}$$

所以
$$rac{\delta E_{
m X}[
ho]}{\delta
ho}=rac{4}{3}A_{
m X}
ho({f r})^{rac{1}{3}}$$
,即交换势 $v_x({f r})=rac{4}{3}A_{
m X}
ho({f r})^{rac{1}{3}}$

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

$$egin{aligned} \delta v_x(\mathbf{r}) &= v_x[
ho + \delta
ho] - v_x[
ho] = rac{4}{3}A_{ ext{X}}\int[(
ho + \delta
ho)^{rac{1}{3}} -
ho^{rac{1}{3}}]\delta(\mathbf{r} - \mathbf{r}^{'})d\mathbf{r}^{'} \ &= rac{4}{3}A_{ ext{X}}\int[rac{1}{3}
ho^{-rac{2}{3}} + O(\delta
ho^2)]\delta(\mathbf{r} - \mathbf{r}^{'})d\mathbf{r}^{'} pprox rac{4}{3}A_{ ext{X}}\intrac{1}{3}
ho^{-rac{2}{3}}\delta(\mathbf{r} - \mathbf{r}^{'})d\mathbf{r}^{'} \end{aligned}$$

所以
$$rac{\delta v_x[
ho]}{\delta
ho} = rac{4}{9} A_{
m X}
ho^{-rac{2}{3}} \delta({f r}-{f r}')$$
,即交换核 $f_x({f r},{f r}') = rac{4}{9} A_{
m X}
ho^{-rac{2}{3}} \delta({f r}-{f r}')$

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

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

其中 $T_{\mathrm{W}}[\rho]$ 的表达式为 $T_{\mathrm{W}}[\rho]=\frac{1}{8}\int \frac{\nabla \rho(\mathbf{r})\cdot\nabla \rho(\mathbf{r})}{\rho(\mathbf{r})}d\mathbf{r}$, λ 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 $\int
ho(\mathbf{r})d\mathbf{r}=N$,用题目的定义,可改写为 $\int \psi(\mathbf{r})^2 d\mathbf{r}=N$;另一方面,能量作为电子密度的泛函可表示为 $E_{\mathrm{TFW}}[
ho]=E_{\mathrm{TFW}}[\psi^2]$,从而设辅助泛函 $L[\psi]=E_{\mathrm{TFW}}[\psi^2]-\mu[\int \psi(\mathbf{r})^2 d\mathbf{r}-N]$,则对辅助泛函求微分得:

$$rac{\delta L[\psi]}{\delta \psi} = rac{\delta E_{ ext{TFW}}[\psi^2]}{\delta \psi} - 2 \mu \psi = rac{\delta E_{ ext{TFW}}[\psi^2]}{\delta (\psi^2)} rac{d(\psi^2)}{d \psi} - 2 \mu \psi = 2 \psi (rac{\delta E_{ ext{TFW}}[
ho]}{\delta
ho} - \mu)$$

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

$$\left\{egin{array}{l} rac{\delta T_{ ext{TF}}[
ho]}{\delta
ho} = rac{5}{3} C_{ ext{TF}}
ho(\mathbf{r})^{rac{2}{3}} = rac{5}{3} C_{ ext{TF}} \psi(\mathbf{r})^{rac{4}{3}} \ rac{\delta T_{ ext{W}}[
ho]}{\delta
ho} = rac{1}{8} rac{|
abla
ho(\mathbf{r})|^2}{
ho(\mathbf{r})^2} - rac{1}{4} rac{
abla^2
ho(\mathbf{r})}{
ho(\mathbf{r})} \ rac{\delta E_{ ext{ext}}[
ho]}{\delta
ho} = V_{ ext{ext}}(\mathbf{r}) \ rac{\delta E_{ ext{H}}[
ho]}{\delta
ho} = \int rac{
ho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' = \int rac{\psi(\mathbf{r}')^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \end{array}
ight.$$

化解 $\frac{\delta T_W[
ho]}{\delta
ho}$ 需要将 $\nabla
ho(\mathbf{r})$ 和 $\nabla^2
ho(\mathbf{r})$ 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:

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

从而:

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

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 $m{L}$ 被定义为 $m{L}=m{x} imesm{p}=\begin{vmatrix}m{i}&m{j}&m{k}\\x&y&z\\p_x&p_y&p_z\end{vmatrix}$,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

 $L_y=zp_x-xp_z$ 。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), $\delta_{ij}=egin{cases}0&(ieta j_{eta$ 母不同)} $1&(ieta j_{eta}$ 母相同),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:

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

同样的,量子力学中,角动量算符 $\hat{m{L}}$ 被定义为 $\hat{m{L}}=\hat{m{x}} imes\hat{m{p}}=\begin{vmatrix}m{i} & m{j} & m{k} \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix}$,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 $[\hat{r}_i,\hat{p}_j] = i\hbar\delta_{ij}\ (i,j=x,y,z)$,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}), $\delta_{ij} = \begin{cases} 0 & (i$ 与j字母不同),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:

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

练习4:证明在非简并微扰理论中,算符 $\hat{Q}_n=\hat{I}-\hat{P}_n=\sum\limits_{k\neq n}|k^{(0)}
angle\langle k^{(0)}|$ 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