3. 交换相关能

3.1 E_{xc} 的一般表示式：

$$E[n] = \langle \Psi_{min}^{n} | T + V_{e-e} | \Psi_{min}^{n} \rangle + \int v_{ext}(\vec{r}) n(\vec{r}) d\vec{r}$$

$$= T_0[n] + \frac{e^2}{2}\int d\vec{r} d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r}-\vec{r}'|} + \int v_{ext}(\vec{r}) n(\vec{r}) d\vec{r} + E_x[n] + E_c[n]$$

设 $\varphi_i(\vec{r})$ 是 Kohn & Sham 方程的解：

$$\left\{ -\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2 + v_{coul}(\vec{r}) + v_{ext}(\vec{r}) + v_{xc}(\vec{r}) \right\} \varphi_i(\vec{r}) = \epsilon_i \varphi_i(\vec{r})$$

构造 Slater 行列式：

$$\Psi_0(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{i_1}(\vec{r}_1) & \varphi_{i_2}(\vec{r}_1) & \cdots\cdots & \varphi_{i_N}(\vec{r}_1) \\ \vdots & & & \vdots \\ \varphi_{i_1}(\vec{r}_N) & \varphi_{i_2}(\vec{r}_N) & \cdots\cdots & \varphi_{i_N}(\vec{r}_N) \end{vmatrix}$$

是无互作用多粒子系统的解。

$$n(\vec{r}) = N\int |\Psi(\vec{r}, \vec{r}_2, \cdots \vec{r}_N)|^2 d\vec{r}_2 \cdots d\vec{r}_N = \sum_{i=1}^{N} |\varphi_i(\vec{r})|^2$$

求期待值：

$$\langle \Psi_0 | T + V_{e-e} + V_{ext} | \Psi_0 \rangle = T_0[n] + \frac{e^2}{2}\sum_{i \neq j}\int \frac{|\varphi_i(\vec{r})|^2 |\varphi_j(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'$$

$$+ \frac{e^2}{2}\sum_{i \neq j}\int \frac{-\varphi_i^*(\vec{r})\varphi_j^*(\vec{r}')\varphi_i(\vec{r}')\varphi_j(\vec{r})}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}' + \sum_i \int v_{ext}(\vec{r}) |\varphi_i(\vec{r})|^2 d\vec{r}$$

$$\overset{\pm\, i=j\,项}{=\!=\!=} T_0[n] + \frac{e^2}{2}\int \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}' + \int v_{ext}(\vec{r}) n(\vec{r}) d\vec{r} + E_x[n]$$

$$E_x[n] = \frac{e^2}{2}\int \frac{-\left|\sum_{i=1}^{N} \varphi_i^*(\vec{r})\, \varphi_i(\vec{r}')\right|^2}{|\vec{r}-\vec{r}'|}\, d\vec{r}\, d\vec{r}'$$

或

$$\langle \Psi_0 | V_{e-e} | \Psi_0 \rangle = E_{coul}[n] + E_x[n]$$

$$E_c[n] = \langle \Psi^n_{min} | T + V_{e-e} | \Psi^n_{min} \rangle - T_0[n] - E_{coul}[n] - E_x[n]$$

$$E_{xc}[n] = \langle \Psi^n_{min} | T + V_{e-e} | \Psi^n_{min} \rangle - T_0[n] - E_{coul}[n]$$

构造：

$$F_\lambda[n] = \lim_{\Psi_\lambda \to n} \langle \Psi_\lambda | T + \lambda V_{e-e} | \Psi_\lambda \rangle = \langle \Psi^n_{\lambda,min} | T + \lambda V_{e-e} | \Psi^n_{\lambda,min} \rangle$$

由极值条件，对任意 $\langle \Psi^n |$：

$$\delta F_\lambda = \langle \Psi^n | T + \lambda V_{e-e} | \Psi^n \rangle - \langle \Psi^n_{\lambda,min} | T + \lambda V_{e-e} | \Psi^n_{\lambda,min} \rangle$$

$$\propto O[(\Psi^n - \Psi^n_{\lambda,min})^2]$$

$$E_{xc}(\lambda) = \langle \Psi^n_{\lambda,min} | T + \lambda V_{e-e} | \Psi^n_{\lambda,min} \rangle - T_0[n] - \lambda E_{coul}[n]$$

$$E_{xc} = E_{xc}(1) \; ; \qquad E_{xc}(0) = 0$$

$$\frac{d E_{xc}(\lambda)}{d\lambda} = \frac{E_{xc}(\lambda+d\lambda) - E_{xc}(\lambda)}{d\lambda} = \frac{1}{d\lambda}\Big\{ \langle \Psi^n_{\lambda+d\lambda,min} | T + (\lambda+d\lambda) V_{e-e} | \Psi^n_{\lambda+d\lambda,min} \rangle$$

$$- (\lambda + d\lambda) E_{coul} - \langle \Psi^{n}_{\lambda,min} | T + \lambda V_{e-e} | \Psi^{n}_{\lambda,min} \rangle + \lambda E_{coul} \Big\}$$

$$= \frac{1}{d\lambda} \Big\{ d\lambda \langle \Psi^{n}_{\lambda+d\lambda,min} | V_{e-e} | \Psi^{n}_{\lambda+d\lambda,min} \rangle - d\lambda E_{coul} +$$

$$+ \underbrace{\langle \Psi^{n}_{\lambda+d\lambda,min} | T + \lambda V_{e-e} | \Psi^{n}_{\lambda+d\lambda,min} \rangle - \langle \Psi^{n}_{\lambda,min} | T + \lambda V_{e-e} | \Psi^{n}_{\lambda,min} \rangle}_{\propto O[(\Psi^{n}_{\lambda+d\lambda,min} - \Psi^{n}_{\lambda,min})]^2 \propto Q(d\lambda)^2} \Big\}$$

$$= \langle \Psi^{n}_{\lambda,min} | V_{e-e} | \Psi^{n}_{\lambda,min} \rangle - E_{coul}$$

$$E_{xc}[n] = \int_0^1 d\lambda \Big\{ \langle \Psi^{n}_{\lambda,min} | V_{e-e} | \Psi^{n}_{\lambda,min} \rangle - E_{coul} \Big\} \qquad V_{e-e} = \frac{e^2}{2} \sum_{i \neq j}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

定义电子对密度：

$$P_\lambda(\vec{r}, \vec{r}') = N(N-1) \int |\Psi^{n}_{\lambda,min}(\vec{r}, \vec{r}', \vec{r}_3 \cdots \vec{r}_N)|^2 d\vec{r}_3 \cdots d\vec{r}_N$$

它代表在 $\vec{r}$ 处，$d\vec{r}$ 内有一个电子，同时在 $\vec{r}'$ 处，$d\vec{r}'$ 内另有一个电子的几率.

$$E_{xc}[n] = \int_0^1 d\lambda \Big\{ \int \frac{e^2}{2} \cdot \frac{P_\lambda(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' - \int \frac{e^2}{2} \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \Big\}$$

定义 $P_\lambda(\vec{r}, \vec{r}') = n(\vec{r}) \{ n(\vec{r}') + n_{xc,\lambda}(\vec{r}, \vec{r}') \}$

$$E_{xc}[n] = \int_0^1 d\lambda \int \frac{e^2}{2} \frac{n(\vec{r}) n_{xc,\lambda}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' = \int \frac{e^2}{2} \frac{n(\vec{r}) n_{xc}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$$

$$n_{xc}(\vec{r}, \vec{r}') = \int_0^1 d\lambda\, n_{xc,\lambda}(\vec{r}, \vec{r}')$$

$$= \int n(\vec{r})\, \epsilon_{xc}[\vec{r}, n]\, d\vec{r} \quad , \qquad \epsilon_{xc}[\vec{r}, n] = \frac{e^2}{2} \int \frac{n_{xc}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$$

每个电子的平均交换相关能.

对 $P_\lambda(\vec{r}, \vec{r}')$ 定义的两边对 $\vec{r}'$ 积分:

$$(N-1)\, n(\vec{r}) = n(\vec{r}) \left\{ N + \int n_{xc,\lambda}(\vec{r}, \vec{r}')\, d\vec{r}' \right\}$$

所以:

$$\int n_{xc,\lambda}(\vec{r}, \vec{r}')\, d\vec{r}' = -1 \Rightarrow \int n_{xc}(\vec{r}, \vec{r}')\, d\vec{r}' = -1$$

记: $n_{xc}(\vec{r}, \vec{r}') = n_x(\vec{r}, \vec{r}') + n_c(\vec{r}, \vec{r}')$

$$n_x(\vec{r}, \vec{r}') = n_{xc,\lambda=0}(\vec{r}, \vec{r}') = \left[P_{\lambda=0}(\vec{r}, \vec{r}') - n(\vec{r})\, n(\vec{r}') \right] / n(\vec{r})$$

$$P_{\lambda=0}(\vec{r}, \vec{r}') = N(N-1) \int |\psi_0(\vec{r}, \vec{r}', \vec{r}_3, \cdots \vec{r}_N)|^2 d\vec{r}_3 \cdots d\vec{r}_N$$

$$= n(\vec{r})\, n(\vec{r}') - \left| \sum_{i=1}^{N} \varphi_i^*(\vec{r})\, \varphi_i(\vec{r}') \right|^2$$

所以

$$n_x(\vec{r}, \vec{r}') = -\left| \sum_{i=1}^{N} \varphi_i^*(\vec{r})\, \varphi_i(\vec{r}') \right|^2 / n(\vec{r}) \leq 0$$

由 $n_x(\vec{r}, \vec{r}')$ 的定义:

$$\int n_x(\vec{r}, \vec{r}')\, d\vec{r}' = -1 \longrightarrow \int n_c(\vec{r}, \vec{r}')\, d\vec{r}' = 0.$$

$$\epsilon_{xc}[\vec{r}, n] = \frac{e^2}{2} \int \frac{n_x(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \frac{e^2}{2} \int \frac{n_c(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$$

较易求, 用 $\{\varphi_i(\vec{r})\}$ 较难求, 用 $\psi^{n}_{\lambda,min}(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N)$

3.2 局域密度近似 (Local Density Approximation, LDA).

用 $n=n(\vec{r})$ 的均匀(无外场)互作用电子气的 E_{xc} 表示系统的交换相关能. 均匀电子气 $v_{ext}(\vec{r})=0$, Kohn & Sham 方程的解为平面波:

$$\varphi_i(\vec{r})=\frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}} \qquad (|\vec{k}|\le k_F)$$

$$\epsilon_x^{LDA}(n)=\frac{e^2}{2}\int\frac{-\left|\sum_{\vec{k}}\frac{1}{V}e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}\right|^2/n}{|\vec{r}-\vec{r}'|}d\vec{r}'=-\frac{e^2}{2}\frac{1}{nV^2}\sum_{|\vec{k}|,|\vec{k}'|\le k_F}\int\frac{e^{i(\vec{k}-\vec{k}')(\vec{r}-\vec{r}')}}{|\vec{r}-\vec{r}'|}d\vec{r}'$$

$$=-\frac{3}{4}\pi e^2 k_F=-\frac{3}{4}\pi e^2\cdot 2\pi\left(\frac{3n}{4\pi^2}\right)^{1/3}=-\frac{3}{2}\pi^2 e^2\left(\frac{3n}{4\pi^2}\right)^{1/3} \quad (附录)$$

$\epsilon_c^{LDA}(n)$: 数值解, 量子 Monte Carlo, (Ceperley & Alder, 1980)
拟合: Vosko, Wilk & Nusair (VWN) (1980)

解析拟合:

$$\epsilon_c^{LDA}(n)=\frac{e^2}{2}A\left\{\ln\frac{y^2}{Y(y)}+\frac{2b}{Q}\operatorname{arctg}\frac{Q}{2y+b}-\frac{by_0}{Y(y_0)}\left[\ln\left(\frac{(y-y_0)^2}{Y(y)}\right)+\right.\right.$$

$$\left.\left.+\frac{2(b+2y_0)}{Q}\operatorname{arctg}\left(\frac{Q}{2y+b}\right)\right]\right\}$$

其中 $y=\sqrt{r_s}$ $\left[r_s=\left(\frac{3}{4\pi n}\right)^{1/3}\frac{1}{a_B}=\frac{me^2}{\hbar^2}\left(\frac{3}{4\pi n}\right)^{1/3}\right]$, $Y(y)=y^2+by+c$,

$Q=(4c-b^2)^{1/2}$, $y_0=-0.10498$, $b=3.72744$, $c=12.93532$,

$A=0.0621814$.

$$\epsilon_{xc}^{LDA}[n(\vec{r})]=\epsilon_x^{LDA}[n(\vec{r})]+\epsilon_c^{LDA}[n(\vec{r})]$$

$$v_{xc}(\vec{r})=\frac{\delta E_{xc}}{\delta n(\vec{r})}=\epsilon_{xc}[n(\vec{r})]+n(\vec{r})\left.\frac{d\epsilon_{xc}(n)}{dn}\right|_{n=n(\vec{r})}$$

3.3 广义梯度近似 (Generalized Gradient Approximation, GGA):

$$E_{xc}^{GGA}=\int d\vec{r}\,n(\vec{r})\epsilon_{xc}^{GGA}(n,\nabla_{\vec{r}} n)=\int d\vec{r}\,d\vec{r}'\,\frac{e^2}{2}\,\frac{n(\vec{r})n_{xc}(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}$$

Gradient Expansion Approximation (GEA):

$$E_{xc}^{GEA}=\frac{e^2}{2}\int d\vec{r}\,d\vec{r}'\,\frac{n(\vec{r})n_{xc}(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}\,\underline{\underline{\vec{r}'=\vec{r}+\vec{u}}}\,\frac{e^2}{2}\int d\vec{r}\,d\vec{u}\,\frac{n(\vec{r})n_{xc}(\vec{r},\vec{r}+\vec{u})}{|\vec{u}|}$$

$$n_x^{GEA}(\vec{r},\vec{r}+\vec{u})=n_x^{LDA}(\vec{r},\vec{u})+\alpha_x(\vec{r},\vec{u})\,\vec{u}\cdot\nabla n(\vec{r})+\beta_x(\vec{r},\vec{u})\,(\vec{u}\cdot\nabla n(\vec{r}))^2+$$
$$+\gamma_x(\vec{r},\vec{u})\,\nabla n(\vec{r})\cdot\nabla n(\vec{r})$$

$$n_c^{GEA}(\vec{r},\vec{r}+\vec{u})=n_c^{LDA}(\vec{r},\vec{u})+\cdots\cdots$$

与实验比较，比LDA的结果反而更差。原因：LDA是对H的近似，但得出的 $n_x^{LDA}(\vec{r},\vec{u})$ 和 $n_c^{LDA}(\vec{r},\vec{u})$ 是H的严格解，所以满足条件：

$$n_x^{LDA}(\vec{r},\vec{u})\leq 0\ ;\quad \int n_x^{LDA}(\vec{r},\vec{u})\,d\vec{u}=-1\ ;\quad \int n_c^{LDA}(\vec{r},\vec{u})\,d\vec{u}=0$$

而GEA是对 $n_x(\vec{r},\vec{u})$ 和 $n_c(\vec{r},\vec{u})$ 的近似，严格解应包含 $\nabla n(\vec{r})$ 的无穷级项。所以近似后的 $n_x^{GEA}(\vec{r},\vec{u})$ 和 $n_c^{GEA}(\vec{r},\vec{u})$ 不再满足上述条件。相对于考虑 $\nabla n(\vec{r})$ 的贡献，这些条件的成立更为重要。

GGA：引入对 $n_x^{GEA}(\vec{r},\vec{u})$ 和 $n_c^{GEA}(\vec{r},\vec{u})$ 的附加修正，迫使其满足一般条件。但这些附加修正没有明显的物理意义，显得任意。

$$n_x^{GGA}(\vec{r},\vec{u}) = n_x^{GEA}(\vec{r},\vec{u})\,\theta[-n_x^{GEA}(\vec{r},\vec{u})]\,\theta(u_x^{cut}-u)$$

截断半径 u_x^{cut} 由以下方程的最小值给出：

$$\int_{|\vec{u}|\le u_x^{cut}} n_x^{GGA}(\vec{r},\vec{u})\,d\vec{u} = -1$$

$$n_c^{GGA}(\vec{r},\vec{u}) = n_c^{GEA}(\vec{r},\vec{u})\,\theta(u_c^{cut}-u)$$

截断半径 u_c^{cut} 由以下方程最小值给出：

$$\int_{|\vec{u}|\le u_c^{cut}} n_c^{GGA}(\vec{r},\vec{u})\,d\vec{u} = 0$$

$\epsilon_{xc}^{GGA}(n,\nabla n)$ 的表达式太复杂，从略.

讨论：GGA 在量子化学对分子的计算比较成功，LDA 对分子结合能的估计过高。在原子计标中 GGA 比 LDA 给出较好的原子总能量，但对电离能和亲和能的计算与 LDA 类似。在固体中，GGA 对晶格常数的计标有时比 LDA 好些，有时差些。

3.4 附录

$$\epsilon_x^{LDA}(n) = -\frac{e^2}{2}\frac{1}{nV^2}\sum_{|\vec{k}|,|\vec{k}'|\le k_F}\int\frac{e^{i(\vec{k}-\vec{k}')\cdot(\vec{r}-\vec{r}')}}{|\vec{r}-\vec{r}'|}d\vec{r}' = -\frac{e^2}{2}\frac{V}{N}\int_{|\vec{k}|,|\vec{k}'|\le k_F}\frac{d\vec{k}\,d\vec{k}'}{(2\pi)^6}\cdot\frac{4\pi}{|\vec{k}-\vec{k}'|^2}$$

$$= -\frac{1}{2}\frac{V}{N}\int_{|\vec{k}|\le k_F}\frac{d\vec{k}}{(2\pi)^3}\cdot\frac{e^2}{2\pi}k_F\left[\frac{k_F^2-k^2}{k_F k}\ln\left|\frac{k_F+k}{k_F-k}\right|+2\right] \quad (\text{蔡} P.155)$$

$$= -\frac{e^2}{4\pi}\cdot\frac{V}{N}\cdot\frac{k_F}{(2\pi)^3}\cdot 4\pi^2\left\{\frac{2}{3}k_F^3+\int_0^{k_F}\frac{k}{k_F}(k_F+k)(k_F-k)\ln\frac{k_F+k}{k_F-k}\cdot dk\right\}$$

$$= -\frac{e^2\pi k_F}{n}\frac{1}{(2\pi)^3}\left\{\frac{2}{3}k_F^3+\int_0^{k_F}\frac{dk'}{k_F}(2k_F-k')(k_F-k')k'\ln\frac{2k_F-k'}{k'}\right\}$$

$$= -\frac{\pi e^2 k_F}{n}\cdot\frac{1}{(2\pi)^3}\left\{\frac{2}{3}k_F^3+\frac{1}{k_F}\int_0^{k_F}dk\left(2k_F^2k-3k_Fk^2+k^3\right)\ln\frac{2k_F-k}{k}\right\}$$

$$= -\frac{\pi e^2 k_F}{n}\frac{1}{(2\pi)^3}\left\{\frac{2}{3}k_F^3+\frac{1}{k_F}\left[-\int_0^{k_F}(k_F^2k^2-k_Fk^3+\frac{1}{4}k^3)\left(-\frac{1}{2k_F-k}-\frac{1}{k}\right)dk\right]\right\}$$

$$= -\frac{\pi e^2 k_F}{n}\frac{1}{(2\pi)^3}\left\{\frac{2}{3}k_F^3+\frac{1}{2}\int_0^{k_F}k(2k_F-k)dk\right\}$$

$$= -\frac{\pi e^2 k_F}{n}\cdot\frac{1}{(2\pi)^3}\left(\frac{2}{3}k_F^3+\frac{1}{3}k_F^3\right) = -\frac{\pi e^2 k_F}{n}\cdot\frac{k_F^3}{(2\pi)^3}$$

而

$$N=\frac{V}{(2\pi)^3}\int_0^{k_F}4\pi^2k^2dk=\frac{V}{(2\pi)^3}\cdot\frac{4\pi^2k_F^3}{3} \Rightarrow n=\frac{4\pi^2}{3}\cdot\frac{k_F^3}{(2\pi)^3}$$

所以

$$\epsilon_x(n) = -\frac{3\pi e^2}{4}k_F = -\frac{3}{2}\pi^2e^2\left(\frac{3n}{4\pi^2}\right)^{1/3}$$