Variational Methods 变分法

$\hat{H}$. $|\varphi\rangle$. 有 $\frac{\langle\varphi|\hat{H}|\varphi\rangle}{\langle\varphi|\varphi\rangle} \geq E_0$

prove:

$\hat{H}|\varphi_n\rangle = E_n|\varphi_n\rangle$

$|\phi\rangle = \sum_n C_n|\varphi_n\rangle$

$\hat{H}|\phi\rangle = \sum_n C_n E_n|\varphi_n\rangle$

$\langle\phi|\hat{H}|\phi\rangle = \sum_n |C_n|^2 E_n$.

$$\frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\sum_n |C_n|^2 E_n}{\sum_n |C_n|^2} \geq E_0$$

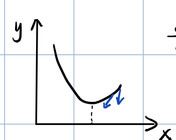
$E_n \geq E_0$.

$\sum_n |C_n|^2 E_n \geq \sum_n |C_n|^2 E_0$

$|\phi\rangle(x, y, z, \theta, \varphi)$ A set of parameters.

minimize $\frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}$

steapest descent



$\frac{\partial y}{\partial x}$. 在最小值时, $\frac{\partial y}{\partial x} = 0$.

$|\varphi\rangle = \sum_n C_n|\phi_n\rangle$ $\hat{H}$.

$y = \frac{\langle\varphi|\hat{H}|\varphi\rangle}{\langle\varphi|\varphi\rangle}$. $\frac{\partial y}{\partial C_i} = 0$ for i.

Langrange Multipler. 乘子.

$z = \langle\varphi|H|\varphi\rangle - \lambda(\langle\varphi|\varphi\rangle - 1)$

$\frac{\partial z}{\partial C_i} = 0$.

$\frac{\partial z}{\partial \lambda} = \langle\varphi|\varphi\rangle - 1 = 0$.

$\frac{\partial z}{\partial C_i} = \sum_n C_n^* H_{ni} - \lambda \sum_n C_n^* S_{ni}$ 变分. $\langle\varphi| = \sum_n \langle\phi_n|C_n^*$

$C^* \overleftarrow{H} = \lambda C^* \overleftarrow{S}$ $\langle\varphi|H|\varphi\rangle = \sum_{nm} C_n^* C_m H_{nm}$

$HC = \lambda SC$ $H_{nm} = \langle\phi_n|H|\phi_m\rangle$

$$\frac{\partial z}{\partial C_i^*} = \sum_m H_{im} C_m - \lambda \sum_m S_{im} C_m = 0 \qquad \langle \varphi | \varphi \rangle = \sum_{nm} C_n^* C_m S_{nm}$$

$$S^{\frac{1}{2}} S^{\frac{1}{2}} = S. \qquad S_{nm} = \langle \phi_n | \phi_m \rangle$$

$$S^{-\frac{1}{2}} H S^{-\frac{1}{2}} S^{\frac{1}{2}} C = \lambda S^{-\frac{1}{2}} S^{\frac{1}{2}} S^{\frac{1}{2}} C$$

$$\bar{H} \quad \bar{C} = \lambda \bar{C}.$$ λ is ground state erengy.

$$y = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}$$

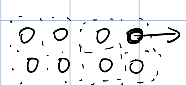
$$\frac{\partial y}{\partial C_i^*} = \frac{1}{\langle \phi | \phi \rangle} \left(\frac{\partial}{\partial C_i^*} \langle \phi | H | \phi \rangle - y \frac{\partial}{\partial C_i^*} \langle \phi | \phi \rangle \right)$$

$$\boxed{\frac{\partial y}{\partial C_i^*} = \frac{1}{\langle \phi | \phi \rangle} \cdot \frac{\partial}{\partial C_i^*} z}$$

prodideed $y = \lambda$.

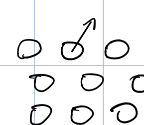
$$\frac{\partial y}{\partial C_i^*} = \frac{1}{\langle \phi | \phi \rangle} (HC - ySC) = 0.$$

$\lambda = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle}$ is the approsinated ground state energy.



$$H = \sum_i -\frac{\hbar^2}{2m} \nabla_i^2 + \sum_I -\frac{\hbar^2}{2M_I} \nabla_I^2 + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{I<J} \frac{Z_{Ie} Z_{Je}}{|\vec{R}_I - \vec{R}_J|} \text{ (大写: 原子核之间) } + \sum_{Ii} -\frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|}$$

$$= H_e + \sum_I -\frac{\hbar^2}{2M_I} \nabla_I^2.$$



波恩-奥本海默近似.

$H_e(\vec{R}_i)$ $\qquad \lambda = \frac{\langle \phi | H_e | \phi \rangle}{\langle \phi | \phi \rangle}$

$$\langle \chi | H_e = \langle \chi | E_0(R)$$

$\langle \chi | \frac{\partial H_e}{\partial R} | \chi \rangle = F = -\frac{\partial E_0}{\partial R_i}.$ Force.

Hellmon-Feynmann

$$E_0 = \langle \chi | H_e | \chi \rangle$$

$$\frac{\partial E_0}{\partial R_i} = \langle \frac{\partial}{\partial R_i} \chi | H | \chi \rangle + \langle \chi | \frac{\partial H_e}{\partial R_i} | \chi \rangle + \langle \chi | H_e | \frac{\partial}{\partial R_i} \chi \rangle$$

$$\langle \chi | H | \frac{\partial}{\partial R_i} \chi \rangle = E_0 \langle \chi | \frac{\partial}{\partial R_i} | \chi \rangle$$

$$\langle \frac{\partial}{\partial R_i} \chi | H | \chi \rangle = E_0 \langle \frac{\partial}{\partial R_i} \chi | \chi \rangle$$

$$\langle \chi | \frac{\partial}{\partial R_i} \chi \rangle + \langle \frac{\partial}{\partial R_i} \chi | \chi \rangle = \frac{\partial}{\partial R_i} (\langle \chi | \chi \rangle) = 0.$$

$$\frac{\langle\phi|\frac{\partial H_e}{\partial R_i}|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\partial\lambda}{\partial R_i}. \qquad \lambda = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}$$

$$\frac{\partial\lambda}{\partial R_i} = \frac{1}{\langle\phi|\phi\rangle}\left(\frac{\partial}{\partial R_i}\langle\phi|H|\phi\rangle - \lambda\frac{\partial}{\partial R_i}\langle\phi|\phi\rangle\right)$$

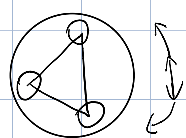
$$\langle\phi|\frac{\partial}{\partial R_i}H|\phi\rangle + \underline{\langle\frac{\partial}{\partial R_i}\phi|H|\phi\rangle + \langle\phi|H|\frac{\partial}{\partial R_i}\phi\rangle - \lambda\frac{\partial}{\partial R_i}\langle\phi|\phi\rangle}$$

$$\frac{\partial}{\partial R_i} = \frac{\partial}{\partial C_n}\frac{\partial C_n}{\partial R_i} \qquad \downarrow$$

$$\frac{\partial C_n}{\partial R_i}\frac{\partial}{\partial C_n}\left(\langle\phi|H|\phi\rangle - \lambda\langle\phi|\phi\rangle\right) = 0.$$

电子-电子. 核-核

$$H_e = \underbrace{\sum_i -\frac{\hbar^2}{2m}\nabla_i^2 + \sum_{ij}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}}_{F} + \underbrace{\sum_{I<J}\frac{Z_I Z_J e^2}{|\vec{R}_I-\vec{R}_J|}}_{V_{Ion}} + \underbrace{\sum_{Ii}\frac{Z_I e^2}{|\vec{r}_i-\vec{R}_I|}}_{V_{ext}=\sum_i V(r_i)}$$ 电子-核



$$[(1000)^3]^{10} = (10)^{90}.$$

Density Functional Theory   Walter Kohn
John Pople

$$H_e = F + V_{Ion} + V_{ext}$$

$$\hat{\rho} = |\varphi\rangle\langle\varphi|$$

$$\hat{\rho}(r,r') = \langle r|\varphi\rangle\langle\varphi|r'\rangle \qquad \langle\varphi|V_{ext}|\varphi\rangle = \int \underset{V(r)}{V_{ext}(r)}\,\varphi(r)\varphi^*(r)\,dr$$

$$\hat{\rho}(r) = \langle r|\varphi\rangle\langle\varphi|r\rangle = |\varphi(r)|^2 \qquad = \int V_{ext}(r)\,\rho(r)\,dr.$$

$$\langle\varphi|V_{ext}|\varphi\rangle = \int d\vec{r}_1^{\,3}\cdots d\vec{r}_n^{\,3}\;\varphi^*(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_n)\,\underbrace{V_{ext}(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_n)}_{\sum_i V(\vec{r}_i)}\,\varphi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_n)$$

$$\int d\vec{r}_1^{\,3}\underbrace{d\vec{r}_2^{\,3}\cdots d\vec{r}_n^{\,3}}\;V(\vec{r}_1)\,|\varphi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_n)|^2$$

$$\rho(r_1) = \int d\vec{r}_2^{\,3}\cdots d\vec{r}_n^{\,3}\,|\varphi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_n)|^2$$

$$= \int d\vec{r}_1^{\,3}\,V(\vec{r}_1)\,\rho(\vec{r}_1)$$

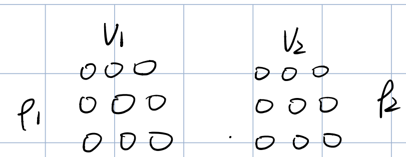
$$= \sum_i d\vec{r}_i^{\,3}\,V(r_i)\,\rho(r_i)$$

$$= \int \rho(r)V(r)\,dr. \qquad \rho(r) = \sum_i \rho(r_i)$$

If φ_1 is a ground state for V_1.

φ_2 is a ground state for V_2.

then $\rho_1 \neq \rho_2$.



$\rho_1 = \rho_2$. $V_1 = V_2 + C$

$E_1 = \int \varphi_1^* (F + V_1) \varphi_1$

$E_2 = \int \varphi_2^* (F + V_2) \varphi_2$

$\int \varphi_1^* (F+V_2) \varphi_1^* > \int \varphi_2^* (F+V_2) \varphi_2^* = E_2$.

$\int \varphi_2^* (F + V_1) \varphi_2 > E_1$

$$\begin{cases} \int \varphi_1^* F \varphi_1 + \int V_2 \rho_1 > \int \varphi_2^* F \varphi_2 + \int V_2 \rho_2 \\ \int \varphi_2^* F \varphi_2 + \int \rho_2 V_1 > \int \varphi_1^* F \varphi_1 + \int V_1 \rho_2 \end{cases}$$

相加

Now if we assume $\rho_1 = \rho_2$.

$\int (V_1 + V_2) \rho > \int (V_1 + V_2) \rho$

controdiction

if $\rho_1 \neq \rho_2$. $V_1 \neq V_2 + C$. $E_1 \neq E_2$

$H = F + V$.

normalization

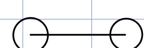
$- \lambda (\int \rho(r) dr - N)$

$E[\rho] = F[\rho] + \int V(r) \rho(r) dr$ (F: two part)

$= T[\rho] + \frac{e^2}{2} \int \frac{\rho(r) \rho(r')}{|r - r'|} dr\, dr' + E_{xc}[\rho] + \int V(r) \rho(r) dr$

$\langle \psi | V_c | \psi \rangle = \int \sum_{i<j} \frac{|\psi(\vec{r}_1, \dots, \vec{r}_n)|^2}{|\vec{r}_i - \vec{r}_j|^2} d\vec{r}_1 \dots \vec{r}_n$

$\int \rho\, dr = N$



$\frac{\delta E[\rho]}{\delta \rho} = 0$.

$\frac{\partial T}{\partial \rho} + e^2 \int dr' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{xc}}{\delta \rho} + V(\vec{r}) = 0$.

ρ: function

E: function of ρ

assume $\rho = \sum_i^N |u_i|^2$

$T[\rho] = -\frac{\hbar^2}{2m} \sum_{i=1}^N \int u_i^* \nabla^2 u_i dr$.

$\frac{\partial E}{\partial u_i^*(r)} = -\frac{\hbar^2}{2m} \nabla^2 u_i^{(r)} + \int e^2 \sum_{j=1}^N \frac{|u_j|^2}{|\vec{r} - \vec{r}'|} d\vec{r}'\, u_i(r) + V_{ex}(r) u_i(r) + V u_i(r) = 0$.

denfinition $\frac{\partial E_{xc}}{\partial u_i^*} = V_{xc} u_i(\vec{r})$

$\left(-\frac{\hbar^2}{2m} \nabla^2 + \int e^2 \sum_{j=1}^N \frac{|u_j|^2}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{ex} + V\right) u_i = \lambda u_i$

Kohn-Sham Equation

(guess)

$U_i \rightarrow \rho = \sum_{i=1}^{N} |U_i|^2$

$\rightarrow H_{DFT} \rightarrow \lambda U_i$