Lecture 21-QM_II (13/09/00)

Saturday, December 4, 2021 3:00 PM

$$H = \sum_{i=1}^{N}\left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i}\right) + \sum_{\substack{ij \\ i>j}} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$H\Psi(1,\dots N) = E\Psi(1,\dots N)$$

✓ 1) $\Psi(1,\dots N) = \varphi_1(1)\,\varphi_2(2)\dots\varphi_N(N)$ تقریب Hartree ✓

$i = (\vec{x}_i, \vec{\sigma}_i)$

2) $= \frac{1}{\sqrt{N!}} \det\begin{pmatrix} \varphi_1(1) & \dots & \varphi_1(N) \\ \vdots & & \vdots \\ \varphi_N(1) & \dots & \varphi_N(N) \end{pmatrix}$ تقریب Hartree-Fock

تقریب هارتری :

قید $\int d^3x_i\, |\varphi_i(\vec{x}_i)|^2 = 1$ $\qquad \varphi_i(i) = \varphi_i(\vec{x}_i)\chi_i(m_{s_i})$

$$\langle \tilde{H} \rangle = \langle H \rangle - \sum_{i=1}^{N} \varepsilon_i \left(\int \underbrace{d^3x_i\, |\varphi_i(\vec{x}_i)|^2} - 1\right)$$

$$\Psi(1,\dots N) = \varphi_1(1)\dots\varphi_N(N)$$

$$\langle H \rangle = \langle \Psi(1,\dots N)|H|\Psi(1,\dots N)\rangle$$

$$\langle \tilde{H} \rangle = \sum_{i=1}^{N} \int d^3x_i\, \varphi_i^*(\vec{x}_i)\left(-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i}\right)\varphi_i(\vec{x}_i) + \frac{1}{2}\sum_{i\neq j}\int d^3x_i d^3x_j\, \varphi_i^*(\vec{x}_i)\varphi_j^*(\vec{x}_j)\frac{e^2}{|\vec{r}_i - \vec{r}_j|}\varphi_i(\vec{x}_i)\varphi_j(\vec{x}_j)$$

$$- \sum_{i=1}^{N} \varepsilon_i \int d^3x_i \left(|\varphi_i(x_i)|^2 - 1\right)$$

$$\frac{\delta G[\varphi_i(\vec{x}_i)]}{\delta \varphi_j(\vec{x}_j)} = \lim_{\lambda\to 0} \frac{G[\varphi_i(\vec{x}_i) + \lambda\delta_{ij}\delta(\vec{x}_i - \vec{x}_j)] - G[\varphi_i(\vec{x}_i)]}{\lambda}$$

$$\boxed{\frac{\delta \varphi_i^*(\vec{x}_i)}{\delta \varphi_j^*(\vec{x}_j)} = \delta_{ij}\,\delta(\vec{x}_i - \vec{x}_j)} \qquad \frac{d}{dx}f(x) = \lim_{\lambda\to 0}\frac{f(x+\lambda) - f(x)}{\lambda}$$

$$\frac{\delta\langle \tilde{H}\rangle}{\delta \varphi_k^*(\vec{x}_k)} = 0$$

جمله اول

$$\sum_{i=1}^{N}\int d^3x_i\, \delta_{ik}\,\delta(\vec{x}_i - \vec{x}_k)\left(-\frac{\hbar^2}{2m}\vec{\nabla}_i^2 - \frac{Ze^2}{r_i}\right)\varphi_i(\vec{x}_i)$$

$$= \left(-\frac{\hbar^2}{2m}\vec{\nabla}_k^2 - \frac{Ze^2}{r_k}\right)\varphi_k(\vec{x}_k)$$

جمله دوم

$$\frac{\delta}{\delta\varphi_k^*(x_k)} \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}}\int d^3x_i\, d^3x_j\, \varphi_i^*(x_i)\,\varphi_j^*(x_j)\frac{e^2}{|\vec{r}_i - \vec{r}_j|}\varphi_i(\vec{x}_i)\varphi_j(\vec{x}_j)$$

$$= \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}}\int \underbrace{d^3x_i}\, d^3x_j\, \delta_{ik}\,\delta(\vec{x}_i - \vec{x}_k)\,\varphi_j^*(\vec{x}_j)\frac{e^2}{|r_i - r_j|}\varphi_i(\vec{x}_i)\varphi_j(\vec{x}_j)$$

$$+ \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}}\int d^3x_i\, d^3x_j\, \varphi_i^*(\vec{x}_i)\,\delta_{jk}\,\delta(\vec{x}_j - \vec{x}_k)\frac{e^2}{|r_i - r_j|}\varphi_i(\vec{x}_i)\varphi_j(\vec{x}_j)$$

$$= \underbrace{\left(\sum_i \int d^3x_i\, \varphi_i^*(\vec{x}_i)\frac{e^2}{|\vec{r}_i - \vec{r}_k|}\varphi_i(\vec{x}_i)\right)}\varphi_k(\vec{x}_k)$$

جلسه سوم

$$\frac{\delta}{\delta\varphi_k^*(\vec{x}_k)} \sum_i \varepsilon_i \left(\int d^3x_i \; \varphi_i^*(\vec{x}_i)\, \varphi_i(\vec{x}_i) - 1 \right)$$

$$= \sum_i \varepsilon_i \int d^3x_i \; \delta_{ik}\, \delta(\vec{x}_k - \vec{x}_i)\, \varphi_i(x_i) = \varepsilon_k \, \varphi_k(\vec{x}_k)$$

$$\frac{\delta \langle \tilde{H} \rangle}{\delta\varphi_k^*(\vec{x}_k)} = 0 \qquad r_k = |\vec{x}_k|$$

$$\left(\frac{-\hbar^2}{2m} \nabla_k^2 - \frac{Ze^2}{r_k} - \varepsilon_k + V_k(\vec{x}_k) \right) \varphi_k(\vec{x}_k) = 0$$

$$V_k(\vec{x}_k) = \sum_i \int d^3x_i \; \varphi_i^*(\vec{x}_i)\, \frac{e^2}{|\vec{r}_i - \vec{r}_k|}\, \varphi_i(\vec{x}_i) \quad ✓$$

$$\left(-\frac{\hbar^2}{2m} \nabla_k^2 - \frac{Ze^2}{r_k} + V_k(\vec{x}_k) \right) \varphi_k(\vec{x}_k) = \varepsilon_k \, \varphi_k(\vec{x}_k)$$

$$\psi(1 \dots N) = \varphi_1(\vec{x}_1) \dots \varphi_N(\vec{x}_N)$$ انتخاب اولیه •

تصویر (نمایش) شرودینگر :

$$i\hbar \frac{\partial}{\partial t} |\psi, t\rangle = H |\psi, t\rangle$$

عملگرها و از جمله H تابعیت زمان ندارد

$\langle \vec{x} | \psi, t \rangle = \psi(\vec{x}, t)$ تابعیت زمان دارد

$$\int_{t_0=0}^{t} \frac{\partial |\psi, t\rangle}{|\psi, t\rangle} = -\frac{i}{\hbar} \int_0^t H\, dt'$$

$$\ln \frac{|\psi, t\rangle}{|\psi, 0\rangle} = -\frac{i}{\hbar} H t \;\rightarrow\; |\psi, t\rangle = e^{-\frac{i}{\hbar} H t} |\psi, 0\rangle$$ عملگر تحول

$$|\psi, t\rangle = e^{-\frac{i}{\hbar} H (t - t_0)} |\psi, t_0\rangle$$

$$\mathcal{U}(t) \equiv e^{-\frac{i}{\hbar} \hat{H} t}$$ عملگر تحول زمان

$$\mathcal{U}\mathcal{U}^+ = 1$$

$$\mathcal{U}(t) = \sum_n \frac{1}{n!} \left(-i \hat{H} t \right)^n$$

$$\mathcal{U}^+ = \mathcal{U}^{-1}$$

$$\mathcal{U}^{-1} = e^{+\frac{i}{\hbar} H t}$$

$$\boxed{|\psi, t\rangle = \mathcal{U}(t)\, |\psi, 0\rangle}$$

غیر وابسته به زمان

$$\langle \hat{A}_s \rangle = {}_s\langle \psi, t | \hat{A}_s | \psi, t \rangle_s =$$

$$= {}_H\langle \psi, 0 | \underbrace{\mathcal{U}^+(t)\, \hat{A}_s\, \mathcal{U}(t)}_{\hat{A}_H(t)} | \psi, 0 \rangle_H \qquad |\psi\rangle_H = |\psi, 0\rangle_s$$

$$= {}_H\langle \psi | \hat{A}_H(t) | \psi \rangle_H$$ تحول زمانی شدن در تصویر هایزنبرگ

$$\boxed{\frac{d}{dt} A_H(t) = \frac{i}{\hbar} [\hat{H}_s, \hat{A}_H(t)] + \cancel{\left(\frac{\partial A_H(t)}{\partial t} \right)_H}}$$ اثبات

$$\frac{d}{dt} \hat{A}_H(t) = \frac{d}{dt} \mathcal{U}^+(t)\, A_s\, \mathcal{U}(t) = \frac{d}{dt} \left(e^{\frac{i}{\hbar} H_s t} A_s\, e^{-\frac{i}{\hbar} H_s t} \right)$$

$$= \frac{i}{\hbar} H_s \underbrace{\mathcal{U}^+(t) A_s\, \mathcal{U}(t)}_{A_H(t)} + \left(\frac{-i}{\hbar} \right) \underbrace{\mathcal{U}^+(t)\, A_s}_{A_H} \underbrace{\mathcal{U}(t)\mathcal{U}^+(t)}_{=1} \underbrace{H_s\, \mathcal{U}(t)}_{H_s}$$

$$H_H(t) = \mathcal{U}^+(t)\, H_s\, \mathcal{U}(t) = e^{\frac{i H_s t}{\hbar}} H_s\, e^{-\frac{i H_s t}{\hbar}} = H_s$$

$A_H \qquad\qquad H_s$

$$H_H(t) = U^{+}(t)\, H_s\, U(t) = e^{\frac{iH_s t}{\hbar}}\, H_s\, e^{-\frac{iH_s t}{\hbar}} = H_s$$

$$= \frac{i}{\hbar}\left(H_s\, A_H(t) - A_H(t)\, H_s\right) = \frac{i}{\hbar}\,[\underset{H_H(t)}{H_s}, A_H(t)]$$

$$\frac{d}{dt} A_H(t) = \frac{i}{\hbar}\,[H_H(t), A_H(t)]$$

- $|\psi,0\rangle_s = |\psi\rangle_H \qquad\qquad |\psi,t\rangle = \mathcal{U}(t)\,|\psi,0\rangle$

  $|\psi\rangle_H = \mathcal{U}^{+}(t)\,|\psi,t\rangle$

  $\frac{d}{dt}|\psi\rangle_H = 0$

✓ $\underset{\text{interaction}}{|\psi,t\rangle_I} = e^{iH_0 t/\hbar}\,|\psi,t\rangle_s$ ارزی تصویر برهمکنش

〃 دیراک

$$O_I(t) = e^{iH_0 t/\hbar}\, O_s\, e^{-iH_0 t/\hbar} \qquad\qquad H = H_0 + V(t)$$

✓ $i\hbar \frac{\partial}{\partial t}|\psi,t\rangle_I = V(t)\,|\psi,t\rangle_I \quad \leftarrow$

$$\frac{d}{dt} O_I(t) = \frac{i}{\hbar}\,[H_0, O_I(t)]$$

- $i\hbar \frac{\partial}{\partial t}|\psi,t\rangle_s = \hat{H}\,|\psi,t\rangle_s$

$$\int_0^t \frac{\partial|\psi,t\rangle_s}{|\psi,t\rangle_s} = \frac{-i}{\hbar}\int_0^t \hat{H}(t')\,dt'$$

$$\ln\frac{|\psi,t\rangle_s}{|\psi,0\rangle_s} = \frac{-i}{\hbar} H_0 t - \frac{i}{\hbar}\int^t V(t')\,dt'$$

$$|\psi,t\rangle_s = e^{-\frac{i}{\hbar}H_0 t - \frac{i}{\hbar}\int_0^t V(t')dt'}\,|\psi,0\rangle_s \qquad 0 = [H_0, V(t)]$$

$$\rightarrow |\psi,t\rangle_s = e^{-\frac{i}{\hbar}H_0 t}\, e^{-\frac{i}{\hbar}\int V(t')dt'}\,|\psi,0\rangle_s$$

✓ $\boxed{|\psi,t\rangle_I \equiv e^{+\frac{i}{\hbar}H_0 t}\,|\psi,t\rangle_s} = e^{-\frac{i}{\hbar}\int_0^t V(t')dt'}\,|\psi,0\rangle_s$

$$i\hbar\frac{d}{dt}|\psi,t\rangle_I = i\hbar\,\frac{i}{\hbar}H_0\, e^{\frac{i}{\hbar}H_0 t}\,|\psi,t\rangle_s + e^{\frac{i}{\hbar}H_0 t}\, i\hbar\frac{d}{dt}|\psi,t\rangle_s$$

$$= -H_0\,|\psi,t\rangle_I + e^{iH_0 t/\hbar}\,\underset{H_0 + V(t)}{H}\,|\psi,t\rangle_s$$

$$= \left\{-H_0 + (H_0 + V(t))\right\}|\psi,t\rangle_I$$

$$\boxed{i\hbar\frac{d}{dt}|\psi,t\rangle_I = V(t)\,|\psi,t\rangle_I}$$