$\oplus \quad x_2 \quad \ominus \qquad\qquad \oplus \quad x_1 \quad \ominus$

$\longleftarrow \quad R \quad \longrightarrow$

$$\int_{x_2}^{x_1} -(-Cx_1)\,dx_1 = \frac{1}{2}Cx_1^2$$

$$\boxed{H_0 = \frac{P_1^2}{2m} + \frac{1}{2}Cx_1^2 + \frac{P_2^2}{2m} + \frac{1}{2}Cx_2^2} \quad \frac{2e^2}{R}x_1x_2 \rightarrow \frac{2e^2}{R}\left(\frac{1}{2}\right)\left[x_s^2 - x_a^2\right]$$

$H = H_0 + H_1$

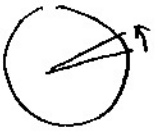
$$\begin{cases} x_s = \frac{1}{\sqrt{2}}(x_1 + x_2) \Rightarrow & x_1 = \frac{1}{\sqrt{2}}(x_s + x_a) \qquad P_1 = \frac{1}{\sqrt{2}}(P_s + P_a) \\ x_a = \frac{1}{\sqrt{2}}(x_1 - x_2) \Rightarrow & x_2 = \frac{1}{\sqrt{2}}(x_s - x_a) \qquad P_2 = \frac{1}{\sqrt{2}}(P_s - P_a) \end{cases}$$

$$= \boxed{\frac{P_s^2}{2m} + \frac{1}{2}\left[C + \frac{2e^2}{R}\right]x_s^2 + \frac{P_a^2}{2m} + \frac{1}{2}\left[C - \frac{2e^2}{R}\right]x_a^2}$$

$$E = \hbar w_s\left[n_s + \frac{1}{2}\right] \qquad \frac{1}{e^{h\nu_s/KT} - 1}$$ 에 따라 E 변화 안다 (통계열역학).

$h\nu_s$ integer

frequency $\quad mr(2\pi\nu)^2 = C \quad \nu = \frac{1}{2\pi}\sqrt{\frac{C}{m}}$



$$\therefore \quad \nu_s = \frac{1}{2\pi}\sqrt{\frac{C + \frac{2e^2}{R}}{m}}$$

$$E^c - E^{no.c} = \hbar\sqrt{\frac{C + \frac{2e^2}{R}}{m}}\left[n_s + \frac{1}{2}\right] + \hbar\sqrt{\frac{C - \frac{2e^2}{R}}{m}}\left[n_a + \frac{1}{2}\right] - 2\hbar\sqrt{\frac{C}{m}}\left[\frac{1}{2}\right] = \frac{A}{R^6}$$

$$\sqrt{\frac{2mE}{\hbar}}\, L = 2\pi n.$$

$$E = \frac{\hbar^2}{2m}\left(\frac{2\pi n}{Lx}\right)^2, \quad k_n = \frac{2\pi n}{L}$$

$$\boxed{\phi(r) = \frac{1}{\sqrt{V}} e^{i2\pi\left(\frac{n_x}{Lx}x + \frac{n_y}{Ly}y + \frac{n_z}{Lz}z\right)}} \quad e^{ik \cdot r_1} \quad (x, y, z)$$

$$\left(\frac{2\pi n_x}{Lx}, \frac{2\pi n_y}{Ly}, \frac{2\pi n_z}{Lz}\right)$$

$$\int \phi^*(r)\,\phi(r)\, d^3r = 1 \Rightarrow VC^2 = 1 \quad C = \frac{1}{\sqrt{V}}$$

$$\rho_1(r_1 r_2) = \sum_{i=1}^{N} \phi_i^*(r_2)\phi(r_1) = \frac{2}{V}\sum_{i=1}^{N/2} e^{ik\cdot(r_1 - r_2)}$$

(N counting)

$$\approx \frac{2}{V}\int$$

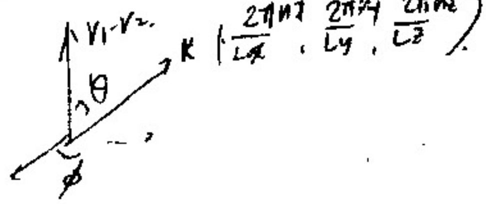
$$* = \frac{2}{V}\left(\frac{L}{2\pi}\right)^3 \int e^{ik\cdot(r_1 - r_2)}\, dk_x\, dk_y\, dk_z$$

$$* = \frac{1}{4\pi^3}\int_0^{k_F} k^2 dk \int_0^{\pi} e^{ik(r_1 - r_2)} \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

spherical

when $r_1 = r_2$,

$$\frac{1}{4\pi^3}\cdot\frac{4}{3}\underbrace{k_F^3\,\pi}_{\text{근거성}} = \rho(r)_{r_1 = r_2 = r = \frac{r_1 + r_2}{2}}.$$



(K.E, exchange) → first density of theory. improve.

DFT.

many body

$$E = \langle \psi(x_1, x_2 \cdots x_N) | H | \psi(x_1, x_2 \cdots x_N) \rangle = \sum_{i=1}^{N} \langle \phi_i | \left(-\frac{\hbar^2}{2m}\nabla^2 + \sum_{a} \frac{q_a(-e)}{4\pi\epsilon_0 |R_a - r|} \right) | \phi_i \rangle$$

$$+ \frac{1}{2} \left[\sum_{j}^{N} \sum_{i=1}^{N} \left(\langle \phi_i \phi_j | \frac{1}{4\pi\epsilon_0 |r_1 - r_2|} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \frac{1}{4\pi\epsilon_0 |r_1 - r_2|} | \phi_j \phi_i \rangle \right) \right] + \sum_{\alpha} \sum_{\beta} \frac{q_a q_\beta}{4\pi\epsilon_0 |R_a - R_\beta|}$$

구성되는 전자 orbital

$$\frac{\det}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \cdots & \phi_N(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \cdots & \phi_N(x_2) \\ \vdots & & & \vdots \\ \phi_1(x_N) & \phi_2(x_N) & \cdots & \phi_N(x_N) \end{vmatrix}$$

(1) $\sum_i \int \phi_i^*(r) \left[-\frac{\hbar^2}{2m}\nabla^2 \right] \phi(r)\, d^3r$

(2) $\sum \sum \int \underbrace{\phi_i^*(x_1)}_{\rho(r_1)} \underbrace{\phi_j(x_2)}_{\rho(r_2)} \frac{e^2}{4\pi\epsilon_0 (r_1 - r_2)} \phi_i(x_1) \phi_j(x_2)\, d^3x_1 d^3x_2$

(3) $-\sum \sum \int \phi_i^*(x_1) \phi_j(x_2) \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|} \phi_j(x_1) \phi_i(x_2)\, d^3x_1 d^3x_2$ $\rho(r_2, \rho_1)$ $\rho(r_1, r_2)$

이 term은 (HF)로서 있는 DFT에서는 새로이 포함되어 있음 ← *correlation ion.

(exact orbital) $+ E^{CI} - E^{ref}$ (reference orbital)

$$\rho(r) = \sum_{i=1}^{N} \phi_i^*(r) \phi_i(r). \quad // \quad \rho(r_1 r_2) = \sum_{i=1}^{N} \phi_i^*(r_2) \phi_i(r_1).$$

coloumb

$$\sum_{i=1}^{N} \left[\sum_{\alpha} \int \frac{\rho(e)\, \phi_i^*(r) \phi_i(r)}{4\pi\epsilon_0 |R_a - r|} d^3r \right]$$

basis set

$\rho(r_1 r_2) = \sum_{i=1}^{N} \phi_i^*(r) \phi_i(o)$ → if exact orbital

$$\int \left[-\frac{\hbar^2}{2m} \nabla^2 \rho(r_1 r_2) \right]_{r_2 = r} d^3r + \sum_{\alpha} \int \frac{q_a (-e) \rho(r)}{4\pi\epsilon_0 |R_a - r|} d^3r + \frac{1}{2} \int \frac{(-e)\rho(r_1) \rho(r_2)(-e)}{4\pi\epsilon_0 |r_1 - r_2|} d^3r_1 d^3r_2$$

K.E　쿨롱 attraction　쿨롱 repulsion

$$-\frac{1}{4} \int \frac{(-e)\rho_1(r_1 r_2)\, \rho_2(r_2 \rho_1)(-e)}{4\pi\epsilon_0 |r_1 - r_2|} d^3r_1 d^3r_2 + \sum_{\alpha} \sum_{\beta} \frac{q_a q_\beta}{4\pi\epsilon_0 |R_a - R_\beta|}$$

exact.　핵사이 repulsion

density matrix functional theory

$$\rho(r_1 r_2) \rightarrow \rho\left(\frac{r_1 + r_2}{2} \right)$$

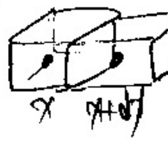
free electron

모사) K.E만 P.E 없이.

해) plane wave → 에너지 띠 구성

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + 0 \right] \phi(r_i) = E \phi_i(r)$$

⇓



PBC (Periodic Boundary Condition)

모든 system은 boundary 있음

전범위까지 확대하여 solution 구해 . 유한된 범위에서 사용 가능

sol) $\phi(x) = C_1 e^{i\sqrt{\frac{2mE}{\hbar^2}}x} + C_2 e^{\cdots}$

$= C_1 e^{i\frac{\cdots}{\hbar}(x + L)}$

$$\phi(x, t) = C_1 e^{\left(\sqrt{\frac{2mE}{\hbar^2}} x - \frac{E}{\hbar} t \right)}$$