<2004. 9. 15. 수>

◉ 지난시간 정리

$$\int g_l^*(x_1 \cdots x_N)\, g_m(x_1 \cdots)\, dx_1 dx_2 = \delta_{lm}$$

basis set 고려하여도 $f(x_1, x_2 \cdots x_N) = \sum_{k=1}^{N} C_k\, g_k(x_1, x_2 \cdots x_N)$

$$\langle abc \cdots | \underbrace{\sum_i \left(-\frac{\hbar^2}{2m}\nabla_i^2\right)}_{①} + \underbrace{\sum_\alpha \sum_i \frac{g_\alpha(-1e)}{4\pi\varepsilon_0 |R_\alpha - r_i|}}_{②} + \underbrace{\sum_i \sum_{j>i} \left(\frac{e^2}{4\pi\varepsilon_0 |r_j - r_i|}\right)}_{③} + \underbrace{\sum_\alpha \sum_{\beta>\alpha} \left(\frac{g_\alpha g_\beta}{4\pi\varepsilon_0 (R_\alpha - R_\beta|}\right)}_{④} | abcd \cdots \rangle$$

$$= E \langle ab \cdots | ab \cdots \rangle$$

$$\sum_{i=a} \langle i | -\frac{\hbar^2}{2m}\nabla^2 | i \rangle + \sum_\alpha \sum \langle i | \frac{g_\alpha(-e)}{4\pi\varepsilon_0 |R_\alpha - r|} | i \rangle + \cdots + \sum_\alpha \sum_\beta \frac{g_\alpha g_\beta}{4\pi\varepsilon_0 |R_\alpha - R_\beta|}$$

· 가장 간단한 2개의 (전자) system 에 대해 고려해보자.

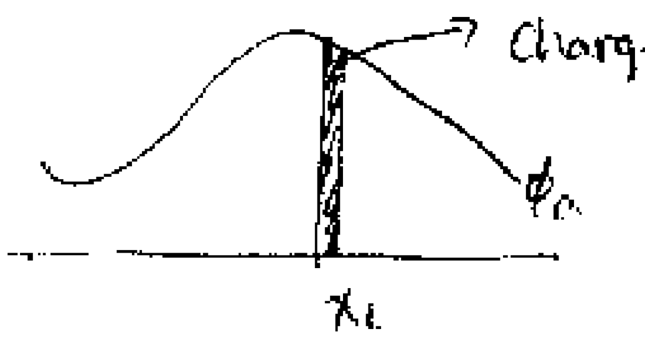
; 위의 식에 대해.

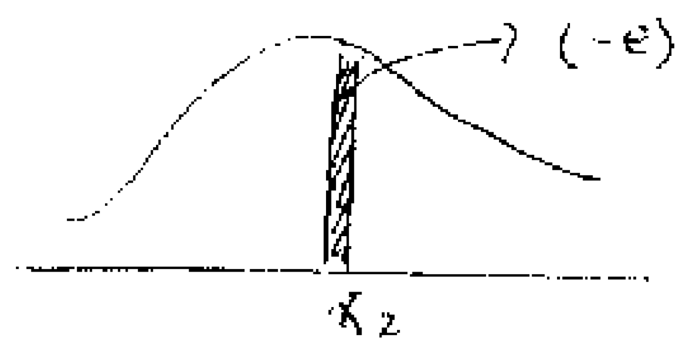
$x_1 \Rightarrow m \cdot g \cdot s$ 모두 포함한 것.

$$\int \frac{1}{\sqrt{2}} \Big(\underbrace{\phi_a(1)^* \phi_b^*(2)}_{A} - \underbrace{\phi_a^*(2)\phi_b^*(1)}_{B}\Big) \left[\frac{e^2}{4\pi\varepsilon_0 |r_2 - r_1|}\right] \frac{1}{\sqrt{2}} \Big(\underbrace{\phi_a(1)\phi_b(2)}_{C} - \underbrace{\phi_a(2)\phi_b(1)}_{D}\Big)\, dx_1 dx_2$$

$$\frac{1}{2}\left[\frac{e^2}{4\pi\varepsilon_0}\frac{\phi_a^*(1)\phi_a(1)\phi_b^*(1)\phi_b(1)+\phi_a^*(2)\phi_a(2)\phi_b^*(2)\phi_b(2)}{|r_2-r_1|}\right]dx_1dx_2$$

$$=\int\frac{e^2}{4\pi\varepsilon_0}\frac{\phi_a^*(1)\phi_a(1)\phi_b^*(1)\phi_b(1)}{|r_2-r_1|}dx_1dx_2$$ ↳ Coulomb Repulsion





$$\int -\frac{1}{2}\left[\frac{e^2}{4\pi\varepsilon_0|r_2-r_1|}\phi_a^*(1)\phi_b(1)\phi_b^*(2)\phi_a(2)+\phi_a^*(2)\phi_b(2)\phi_b^*(1)\phi_a(1)\right]dx_1dx_2$$

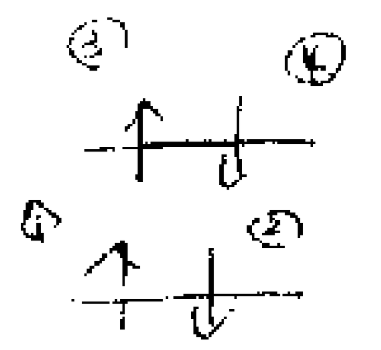
$$=-\left[\frac{e^2}{4\pi\varepsilon_0|r_2-r_1|}\phi_a^*(1)\phi_b(1)\phi_b^*(2)\phi_a(2)\right]dx_1dx_2$$ ↳ Exchange (many-body 물질에서 magnetic properties 부여해줌?)

⇓ $\phi_a(1)=\phi(r_1)\alpha$, $\phi_b(1)=\phi(r_1)\beta$ } 스핀을 고려하여 정리하면

$$\Rightarrow -\left[\frac{e^2}{4\pi\varepsilon_0|r_2-r_1|}\phi^*(r_1)\alpha^*(1)\phi(r_1)\alpha(1)\phi^*(r_2)\alpha^*(2)\phi(r_2)\beta(2)\right]dr_1ds_1dr_2ds_2.$$

정리 $\int\alpha^*(x)\beta(x)dx=0$, $\int\alpha^*(x)\alpha(x)dx=1$ 이므로.

위의 식처럼 될 경우 exchange $E=0$. ← spin이 같을 때는 성립할 수 없다.



①② = 0
①③ ≠ 0
①④ ?

• ③번 항을 정리하자.

$$\sum_{i=a}\sum_{j>i}\langle ij|\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|ij\rangle-\sum_i\sum_{j>i}\langle ij|\frac{e^2}{4\pi\varepsilon_0|r_2-r_1|}|ji\rangle$$

$$\int\frac{e^2\phi_i^*(1)\phi_i(1)\phi_j^*(2)\phi_j(2)\,dx_1dx_2}{4\pi\varepsilon_0|r_2-r_1|}$$ ↳ Coulomb

$$\int\frac{e^2\phi_i^*(1)\phi_j(1)\phi_j^*(2)\phi_i(2)}{4\pi\varepsilon_0|r_2-r_1|}dx_1dx_2$$ ↳ exchange (overlap 없다면 이것은 없어지는가?)

$$=\frac{1}{2}\left[\sum_{i=a}\sum_{j=a}\langle ij|\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|ij\rangle-\sum_i\sum_{j=a}\langle ij|\frac{e^2}{4\pi\varepsilon_0|r_2-r_1|}|ji\rangle\right].$$

∴ 결국 이 많은 state 중에 E를 minimize 할 수 있는 값을 어떻게 찾을 것인가가 양자역학의 중요한 문제!