Quantum Chemistry.

H.W

textbook.

금 5:00 p.m 까지.

$E = \langle f | H | f \rangle$ ↳ ≠ Eigen States. ↳ a.b.c.d.

↓

Kinetic + interaction.

↓

전자사이

$$\sum_{i=1}^{4}\left(-\frac{\hbar^2}{2m}\nabla_i^2\right) + \sum_{i=1}^{4}\left(\frac{4e(-|e|)}{4\pi\varepsilon_0|r_i|}\right) + \sum_{i=1}^{4}\sum_{j>1}^{4}\left(\frac{e^2}{4\pi\varepsilon_0|r_i - r_j|}\right)$$

$$= \text{single body} \sum_{k=a}^{d} \langle k | \underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2 + \frac{4e(-e)}{4\pi\varepsilon_0|r|}\right]}_{h_1} | k \rangle + \sum_{k=a}^{d}\sum_{\substack{l>k \\ l=a}}^{d} [\ ]$$

$$\langle kl | \frac{e^2}{4\pi\varepsilon_0^2|r_1 - r_2|} | kl - lk \rangle$$

$\langle kl| \rightarrow \phi_k^*(1)\phi_l^*(2)$, $|kl\rangle \rightarrow \phi_k(1)\phi_l(2)$, $|lk\rangle \rightarrow \phi_l(1)\phi_k(2)$

$\rightarrow E_{kl}$, E^*_{kl}

$$\sum_{l=a} E_l^k + E_l^{Nl} + \sum_k\sum_{l>k}[J_{kl} - V_{kl}]$$

total E - ① K.E count

$$\underbrace{2E_a^* + E_b^*}_{\text{전자}} + \underbrace{2E_a^{Ne} + E_b^{Ne}}_{\text{neclens interaction}} + J_{aa} + 2J_{ab} - V_{ab}.$$

columb : e⁻사이 interaction. exchange spin이 같을때만.

ε_b —↑— b

ε_a —↑↓— a

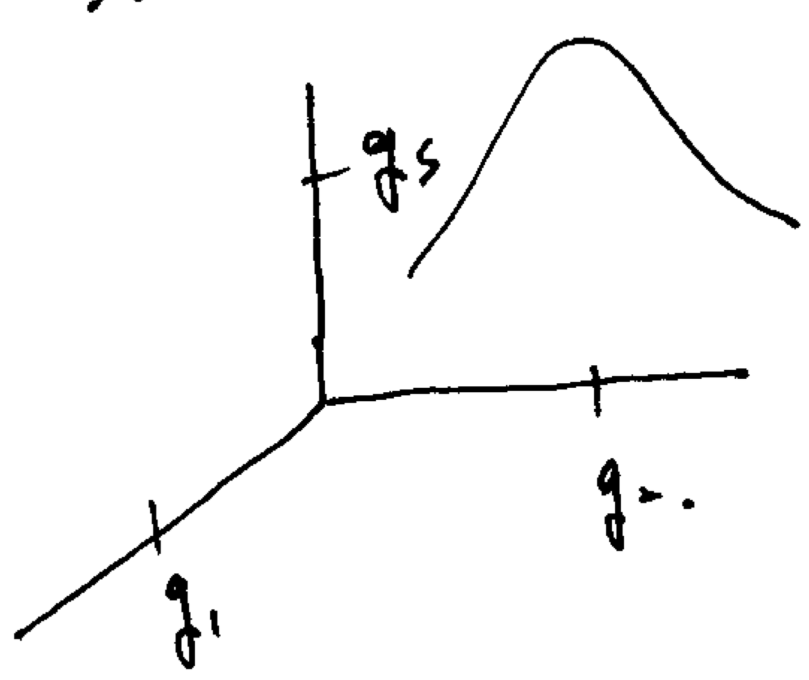
↓ Eigen Value.

$$\varepsilon_a = E_a^K + E_a^{Ne} + J_{aa} + J_{ab} - V_{ab}.$$

$$\varepsilon_b = E_b^K + E_b^{Ne} + 2J_{ba} - V_{ba}.$$

3D

Basis - 잡을때 : 파울리 원리 생각하면서.



$$\boxed{\int g_i^* \cdot g_k = \delta_{ik}. \quad \text{이런 set 사용.}}$$

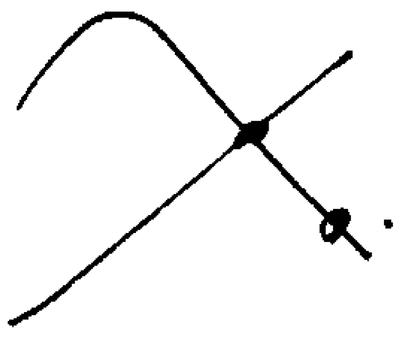
만족.

$$f(x_1 x_2 x_3) = \sum C_k g_k (x_1 x_2 x_3).$$

$\langle f |$

$$\int \sum_k C_k^* g_k^* \sum_l C_l E_k g_k \, dx_1 dx_2 dx_3.$$

$$= \sum_k E_k C_k^* C_k \geq E_0 \sum C_k^* C_k \geq E_0 \quad \text{Variation principle}$$



Constram 있을때.

$$E - \varepsilon\left[\sum_{i=a}\int \phi_i^*(x)\,\phi_i(x)\,dx - N\right] \quad ?$$

e^- 가진 E 구하는 operator.

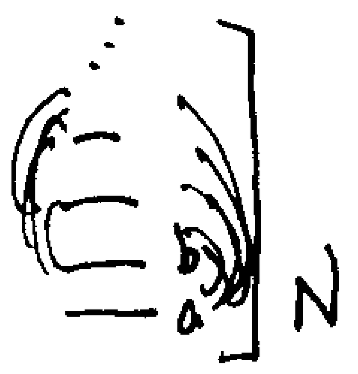
Clmb interaction.

ε_a.

$$\left[-\frac{\hbar}{2m}\nabla^2 + \sum_{\alpha}\frac{q_\alpha(-e)}{4\pi\varepsilon_0|R_\alpha - r|} + \sum_{j}\frac{e^2\phi^*(x)\left[(1-P)\,\phi_j^*(x)\right]dx}{4\pi\varepsilon_0|r_j - r|}\right]\phi_a(1) = \varepsilon\,\phi_a(1).$$

$$E = \langle \underbrace{ab\cdots\cdots}_{f} | \; H \; | \underbrace{abc\cdots}_{f} \rangle$$

$$= \sum \langle a | -\frac{\hbar^2}{2m}\nabla^2 + \sum_{\alpha} \frac{g_\alpha(-e)}{4\pi\varepsilon_0 |R_i - r|} | \alpha \rangle + \sum_{j=a} \sum_{\substack{j \geq i \\ j=a}} \langle ij | \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|} | ij - ji \rangle$$



$$f = \frac{1}{\sqrt{\ }} \det \begin{vmatrix} \phi a(1) \cancel{\phi_b(1)} \\ \phi a(N) \cancel{\phi_b(N)} \end{vmatrix}$$

a state 알고 싶다. 다 변수 함수 minimization.

각자 N개를 a. a*로. 나타내며, a로 편미분 하라.

b. c. d ⋯ 이것은 영향 안바꾸니⋯

a. a*은 independent.

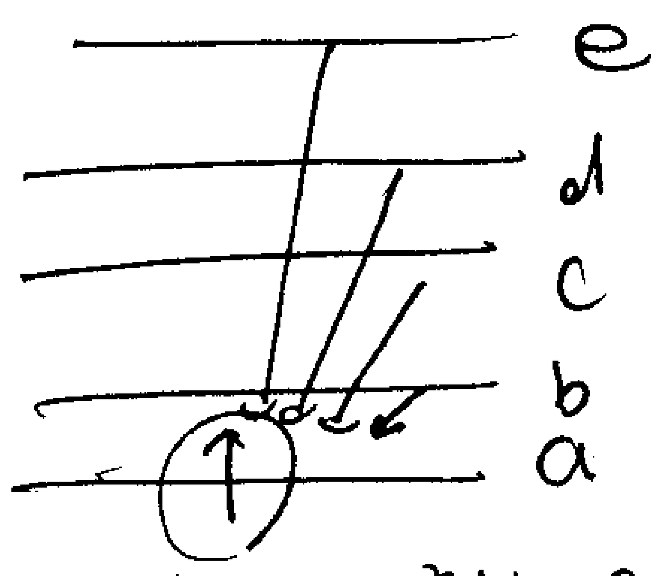
$$\int \phi a^*(x)\left(-\frac{\hbar^2}{2m}\nabla^2\right)\phi a(x)\,dx + \langle a | \sum_{\alpha} \sum \frac{g_a(-e)}{4\pi\varepsilon_0 |R_a - r|} | \alpha \rangle .$$

$$\frac{\partial E(a.b.\cdots)}{\partial \phi a^*(X)} \Rightarrow \frac{\hbar^2}{-2m}\nabla^2 \phi a. + \sum_{\alpha} \frac{g_\alpha(-e)}{4\pi\varepsilon_0 |R_a - r|}\phi a(1). + \sum_j \frac{\left[\int \phi_j^*(2)\phi_j(2)\,dx\right]}{4\pi\varepsilon |r_2 - r|}\phi a(1)$$

$$\frac{\partial ABC}{\partial} = BC\frac{\partial ABC}{\partial A} + \cdots$$

$$\sum_{j>i} \int_{x_1}\int_{x_2} \frac{e^2 \phi_j^*(2)\phi_j(2)\,\phi_a^*(1)\phi_a(1)}{4\pi\varepsilon_0 |r_2 - r_1|}\,dx_1\,dx_2$$

$$\int_{x_1}\left[\sum_j \int \frac{e^2 \phi_j^*(2)\phi_j\,dx_2}{4\pi\varepsilon_0 |r_2 - r_1|}\right]dx.$$



다른 것에 받는 Coulomb effect는?

last term. 편미분

$$\boxed{\phi_j(2)\phi a(1)\,dx_2 = P.}$$

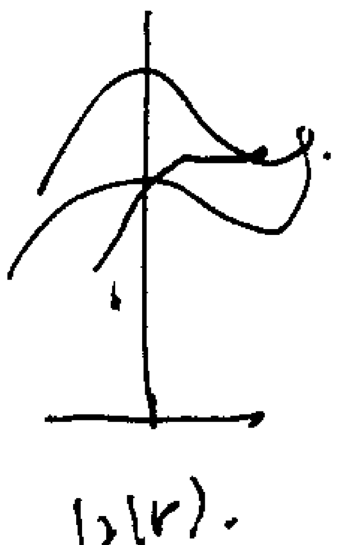
$$\left[\int_{x_2}\sum_j \frac{e^2 \phi_a^*(1)\phi_j(1)\phi a(2)\phi_j^*(2)}{4\pi\varepsilon_0 |r_2 - r_1|}\,dx_2\right] dx_1$$

$$\parallel$$

$$e^2 \phi^*(2)\,P$$

$$\frac{\partial E}{\partial \phi a^*} = \int \Big[-\frac{\hbar^2}{2m}\nabla^2 + \sum_{\alpha} \frac{g_a(-e)}{4\pi\varepsilon_0 |R_a - r|} + \sum_j \int \frac{e^2 \phi_j^*(x)\phi_j(x)\,dx}{4\pi\varepsilon_0 |r_j - r|} - \sum_j \int \frac{e^2 \phi_j^*(x) P \phi_j(x)}{4\pi\varepsilon_0 |r_j - r|}dx$$

$$\phi a(x_1)\Big)\,dx_1 = 0.$$



N state 전자 $\int \rho(r)\,dr = \int \sum \phi a^*(r)\phi a(r)\,dr = N.$

$\rho(r).$