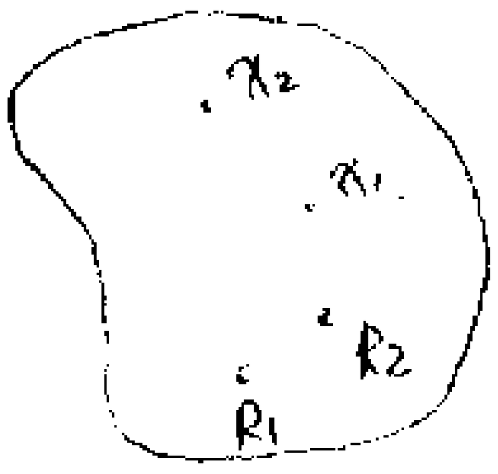
<2004. 9. 13. 월> 7.



→ 이 part를 사용하는 것이 Born-oppenheimer approximation. (nucleus의 wave function을 fix하고 전자의 wave function만 소거)

$$\Big[\sum_\alpha\left(-\frac{\hbar^2}{2M_\alpha}\nabla_{R_\alpha}^2\right)+\sum_i\left(-\frac{\hbar^2}{2m_i}\nabla_i^2\right)+\sum_\alpha\sum_i\frac{Z_\alpha(-e)}{4\pi\varepsilon_0|R_\alpha-r_i|}+\sum_i\sum_{j>i}\frac{(-e)^2}{4\pi\varepsilon_0|r_i-r_j|}$$

$$+\sum_\alpha\sum_{\beta>\alpha}\frac{Z_\alpha Z_\beta}{4\pi\varepsilon_0|R_\alpha-R_\beta|}\Big]f(x_1,x_2\cdots x_N,R_1,R_2\cdots)=Ef(x_1,x_2\cdots x_N,R_1,R_2\cdots)$$

$\Rightarrow \varepsilon(R_1,R_2\cdots R_\alpha)$

$\Downarrow$ 있어

$\psi(x_1,x_2\cdots x_N)\phi(R_1,R_2\cdots R_N)$

이를 seperation 하지 않고 풀 수 있어야 할 것...

일단 여기서는 nucleus가 seperation 된다고 생각하자 !!

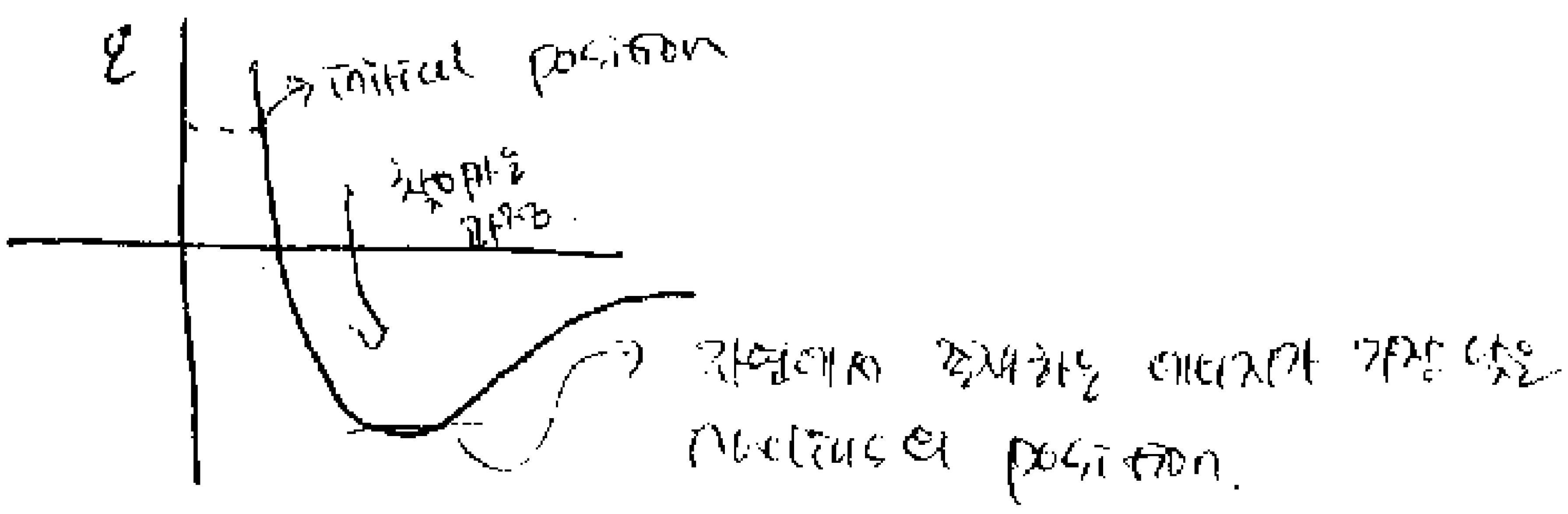
위의 식을

$$f_1\Big[\sum_\alpha\left(-\frac{\hbar^2}{2m_\alpha}\nabla_{R_\alpha}\right)\Big]\phi(R_1\cdots)+\phi(R_1\cdots)\Big[\sum_i\left(-\frac{\hbar^2}{2m_i}\nabla_i^2\right)+\varepsilon(R_1,R_2\cdots R_\alpha)\Big]f_1=\underset{\uparrow\,\text{const.}}{E}f_1\phi$$

$$\sum_\alpha\left(-\frac{\hbar^2}{2m_\alpha}\nabla_{R_\alpha}\right)+\sum_i\left(-\frac{\hbar^2}{2m_i}\nabla_i^2\right)+\varepsilon(R_1,R_2\cdots R_\alpha)=E$$

↳ 이 식을 만족하기 위해 좌변의 각 항이 const. 이어야 한다.

$$\Big[\sum-\frac{\hbar^2}{2m}\nabla_\alpha^2\Big]\phi=\varepsilon_1\phi_1\qquad\big[\varepsilon(R_1,R_2\cdots R_\alpha)\big]f_1=\varepsilon f_1$$



$$\sum\Big[-\frac{\hbar^2}{2m}\nabla_\alpha^2+\underline{\varepsilon(R_1,R_2\cdots R_N)}\Big]$$

이 potential은 solid 경우 vibration, gas [vibration, translation, rotation] mode 까지 포함된 값.

정리하면

$$\Big[\sum_i\left(-\frac{\hbar^2}{2m_i}\nabla_i^2\right)+\sum_\alpha\sum_i\frac{Z_\alpha(-e)}{4\pi\varepsilon_0|R_\alpha-r_i|}+\sum_i\sum_{j>i}\frac{(-e)^2}{4\pi\varepsilon_0|r_i-r_j|}+\sum_\alpha\sum_{\beta>\alpha}\frac{Z_\alpha Z_\beta}{4\pi\varepsilon_0|R_\alpha-R_\beta|}$$

$$f_1(x_1,x_2\cdots x_N)=\varepsilon f_1(x_1,x_2\cdots x_N)$$

$$\frac{1}{\sqrt{N!}}\det\overbrace{\begin{vmatrix}\phi_1(1)&\phi_2(1)&\phi_3(1)&\cdots&\phi_N(1)\\\phi_1(2)&\phi_2(2)&\phi_3(2)&\cdots&\phi_N(2)\\\vdots&&&&\\\phi_1(N)&\phi_2(N)&\phi_3(N)&\cdots&\phi_N(N)\end{vmatrix}}^{N개}\Bigg\}\,N개$$

위 식에 대해 정리하면

$$= \frac{1}{\sqrt{2}} \Big[\underbrace{\langle a | -\frac{\hbar^2}{2m}\nabla_1^2 | a \rangle + \langle b | -\frac{\hbar^2}{2m}\nabla_1^2 | b \rangle}_{\int \phi_b^*(1)\left(-\frac{\hbar^2}{2m}\nabla_1^2\right)\phi_b(1)\,dx_1} + \underbrace{\langle a | -\frac{\hbar^2}{2m}\nabla_2^2 | a \rangle + \langle b | -\frac{\hbar^2}{2m}\nabla_2^2 | b \rangle}_{\phi_b^*(2)\left(-\frac{\hbar^2}{2m}\nabla_2^2\right)\phi_b(2)\,dx_2}$$

따라서 general 하게 정리하면

$$= \langle a | -\frac{\hbar^2}{2m}\nabla^2 | a \rangle + \langle b | -\frac{\hbar^2}{2m}\nabla^2 | b \rangle$$

$$= \underline{\underline{\sum_{i=a}^{b} \langle \overset{\to \phi_i}{i} | -\frac{\hbar^2}{2m}\nabla | i \rangle}}$$

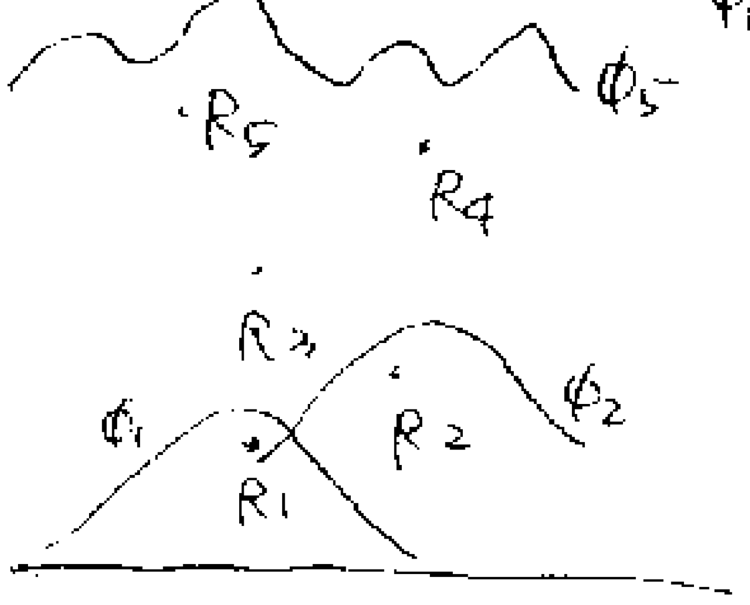
(kinetic 값은 many body와 상관없는 값이 된다)

ii) nucleus - electron interaction.

$$\underbrace{\langle ab | \frac{g_\alpha(-e)}{4\pi\varepsilon_0 |r_1|} | ab \rangle}_{\frac{1}{\sqrt{2}}\int \left(\phi_a^*(1)\phi_b^*(2) - \phi_b^*(1)\phi_a^*(2)\right)\left(\frac{g_\alpha(-e)}{4\pi\varepsilon_0|r_1|}\right)\frac{1}{\sqrt{2}}\left(\phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2)\right)dx_1 dx_2} + \langle ab | + \frac{g_\alpha(-e)}{4\pi\varepsilon_0 |r_2|} | ab \rangle$$

$$= \langle a | + \frac{g_\alpha e}{4\pi\varepsilon_0 |r|} | a \rangle + \langle b | + \frac{g_\alpha e}{4\pi\varepsilon_0 |r|} | b \rangle$$

$$= \sum_{i=a}^{b} \langle i | \frac{g_\alpha(-e)}{4\pi\varepsilon_0 |r_i|} | i \rangle$$



각 전자의 state ϕ을 N개까지 결정하는 것이 우리의 목적.
(ϕ 한개에는 전자가 spin의 2개씩 들어간다)

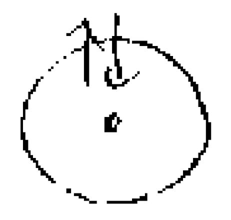
앞의 식을 Hamiltonian으로 고려하여 정리하면.

$$hf = \varepsilon f \qquad \int f^*(x_1, x_2 \cdots x_N)\, h\, f(x_1, x_2 \cdots x_N)\, dx_1 dx_2 \cdots dx_N$$

$$\hat{\varepsilon} = \langle f | h | f \rangle = \langle f | \varepsilon | f \rangle$$ → 실제 실험에서 측정되는 값을 평균치를 구하는 것이다.

↓ experimental value.

① He atom.



$Z_a = 2$.

$\begin{cases} \phi_a = \phi(r)\alpha \to \text{spin}\uparrow \\ \phi_b = \phi(r)\beta \to \text{spin}\downarrow \end{cases}$

전항

$$\left[\sum_{i=1}^{2} -\frac{\hbar^2}{2m}\nabla_i^2 + \sum_i^{2} \frac{(Ze)(-e)}{4\pi\varepsilon_0|r_i|} + \frac{(-e)^2}{4\pi\varepsilon_0|r_1 - r_2|} \right] \frac{\det}{\sqrt{2!}} \begin{pmatrix} \phi_a(1) & \phi_b(1) \\ \phi_b(2) & \phi_b(2) \end{pmatrix}$$

↑ 전자의 mass는 동일하므로

우항

$$[\qquad] \frac{1}{\sqrt{2}}(\phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2)) = \varepsilon \frac{\det}{\sqrt{2!}} \begin{pmatrix} \phi_a(1) & \phi_b(1) \\ \phi_a(2) & \phi_b(2) \end{pmatrix}$$

이 값을 구하는 것이 목표이다

양변을 complex conjugation 하여 적분해준다.

$$\int \left[\frac{1}{\sqrt{2}}(\phi_a^*(1)\phi_b^*(2) - \phi_b^*(1)\phi_a^*(2)) [\qquad] \frac{1}{\sqrt{2}}(\phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2)) \right] dx_1 dx_2$$

$$= \varepsilon \left(\int \_\_^* \, \varepsilon \, \_\_ \, dx_1 dx_2 \right)$$

i) kinetic E만 고려하면

원식 $\langle ab | -\frac{\hbar^2}{2m}\nabla_1^2 | ab \rangle + \langle ab | -\frac{\hbar^2}{2m}\nabla_2^2 | ab \rangle$

$$\int \frac{1}{\sqrt{2}}(\underset{①}{\phi_a^*(1)\phi_b^*(2)} - \underset{②}{\phi_b^*(1)\phi_a^*(2)}) \left(-\frac{\hbar^2}{2m}\nabla_1^2\right) \frac{1}{\sqrt{2}}(\underset{③}{\phi_a(1)\phi_b(2)} - \underset{④}{\phi_b(1)\phi_a(2)}) dx_1 dx_2$$

① - ③ ; $\frac{1}{2}\left[\int \phi_a^*(1)\left(-\frac{\hbar^2}{2m}\nabla_1^2\right)\phi_a(1)dx_1 \underbrace{\int \phi_b^*(2)\phi_b(2)dx_2}_{\text{"1"}} \right.$

$$= \frac{1}{2}\langle a | -\frac{\hbar^2}{2m}\nabla_1^2 | b \rangle$$

① - ④ ; $\frac{1}{2}\int \phi_a^*(1)\left(-\frac{\hbar^2}{2m}\nabla_1^2\right)\phi_a(1)dx_1 + \int \phi_b^*(1)\left(-\frac{\hbar^2}{2m}\nabla_1^2\right)\phi_b(1)dx_1 \int \phi_a^*(2)\phi_b(2)dx_1$

$$= \frac{1}{2}\langle a | -\cancel{\frac{\hbar^2}{2m}}\nabla_1^2 | a \rangle + \underline{\underline{\langle b | -\frac{\hbar^2}{2m}\nabla_1^2 | b \rangle}}$$