$dx\,dy\,dz\,ds.$

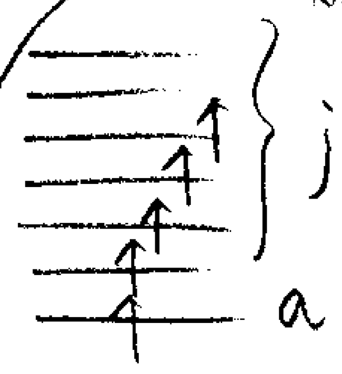
$dr_2\,ds_2$

h

$$h = \left[\left(-\frac{\hbar^2}{2m}\nabla^2\right) + \sum\left[\frac{-e^2 Z}{4\pi\varepsilon_0 |R_a - r|}\right] + \sum_j\left[\int \frac{\phi_j^*(x_2)[1-P]\phi_j(x_2)\,dx_2}{4\pi\varepsilon_0 |r_2 - r|}\right]\right] \phi_a(\ ) = \varepsilon_a \phi_a(x)$$

$= \varepsilon \sum_{k=1}^{N} C_k b_k$

K.E



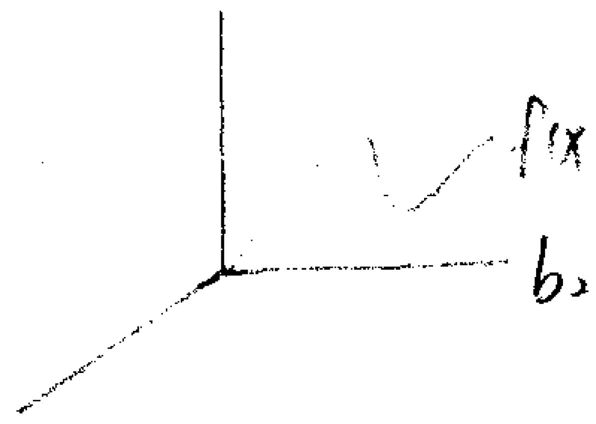
j

a

nucleus

n개의 미지수

basis 도입 (dimension에 대해)



$f(x, x_2)$

$b_2(x, x_2)$

Basis ↑, 더 정확한 E 추정

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

$$\sqrt{(x_\alpha - x)^2 + (y_\alpha - y)^2 + (z_\alpha - z)^2}$$

columb

exchange operator

a 전자들이 생김

전자 자리할 수 있는 state.

$\sum C_k \phi_k^{\#}(x)$ ⇐ state.

1s

2s

2p

$\therefore \int \phi_k^{*\#}(x)\,\phi_\ell^{\#}(x)\,dx = \delta_{\ell k}$

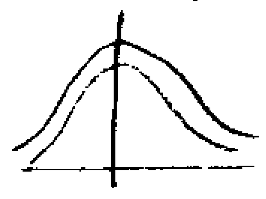
$\phi_1^{\alpha_1}$: $C_{2px}^{\alpha_1}\phi_{2px}^{\alpha_1} + C_{2py}^{\alpha_1}\phi_{2py}^{\alpha_1} + C_{2pz}^{\alpha_1}\phi_{2pz}^{\alpha_1} + C_{2px}^{\alpha_2}\phi_{2px}^{\alpha_2} + C_{2py}^{\alpha_2}\phi_{2py}^{\alpha_2} + C_{2pz}^{\alpha_2}\phi_{2pz}^{\alpha_2}$

$$\sqrt{(x_2 - x)^2 + (y_2 - y)^2 + (z_2 - z)^2}$$

Pople Basis set

도입 후 계수만 결정하면 된다

$\underbrace{\sum_k C_k e^{-\alpha r^2}}_{\text{fitting}}$



1s $\sum_k^K (e^{-\alpha r})$ 각 term 곱하기 $(x^k y^m z^\ell)$

$\sum C_k e^{-\alpha(r-r_2)\cdot(x-x_a)(y-y_a)}$

$$= \varepsilon \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

$$\det \begin{pmatrix} h_{11} - \varepsilon_{11} & h_{12} \\ h_{21} & h_{22} - \varepsilon\varepsilon_{22} \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$\phi_1 = C_1 b_1 + C_2 b_2$

$\phi_2 = C_1' b_1 + C_2' b_2$

$|C_1|^2 + |C_2|^2 = 0 \leftarrow \int \phi_k^*(x)\phi_k(x)\,dx = 1$

$C_1 = 2C_2$ …… 구하기

$\varepsilon = \varepsilon_1, \varepsilon_2$

기대

$$(h_{11} - \varepsilon\varepsilon_{11})(h_{22} - \varepsilon\varepsilon_{22}) - h_{12}h_{21} = 0$$

$$\varepsilon^2(\varepsilon_{11}\varepsilon_{22}) - \varepsilon(h_{11}S_{22} + h_{22}S_{11}) + h_{11}h_{22} - h_{12}h_{21} = 0$$

$$\therefore \varepsilon_{1,2} = \frac{(h_{11}S_{22} + h_{22}S_{11}) \mp \sqrt{(h_{11}S_{22} + h_{22}S_{11})^2 - 4S_{11}S_{22}(h_{11}h_{22} - h_{12}h_{21})}}{2(S_{11}S_{22})}$$

$\therefore \varepsilon_2 =$ 〃

1p의 첫번째 line 식 $h_1 h_2$ 오를때.

$\varepsilon_1(0)$ $\varepsilon_1(0)$

$\phi_1(0)$ $\phi_2(0)$ $\phi_3(0)\cdots$ $\phi_n(0)$ $\longrightarrow$ $\varepsilon_1(1)$ $\varepsilon_1(1)$ $\phi_1(1)$ $\phi_2(1)\cdots$ $\longrightarrow$ $\varepsilon(k)\,\varepsilon(k)$ $\phi_k(k)\,\phi(k)$ $|\varepsilon_i^k-\varepsilon_i^{k+1}|<10^{-8}$

self-constent Approxima.

$$\begin{pmatrix}1\\0\\0\\1\end{pmatrix}\begin{pmatrix}0\\1\\1\\0\end{pmatrix}\begin{pmatrix}0\\0\\1\\0\end{pmatrix}\cdots\cdots\begin{pmatrix}0\\0\\0\\\vdots\\1\end{pmatrix}\longrightarrow\begin{pmatrix}\frac{1}{\sqrt{5}}\\\sqrt{4}\\0\\0\end{pmatrix}\begin{pmatrix}\frac{3}{\sqrt{10}}\\\frac{1}{\sqrt{10}}\\\vdots\end{pmatrix}\longrightarrow\begin{pmatrix}c_1(k)\\c_2(k)\\\vdots\end{pmatrix}\begin{pmatrix}\ \\ \ \end{pmatrix}$$