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쌍극자모멘트 행렬요소를 계산하는 두가지 방법

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Two Method for Evaluation of the Dipole Moment Matrix Elements

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요 약. Spherical harmonic의 전개방법과 쌍극자모멘트의 행렬요소를 Mulliken의 overlap integral로 전환시키는 방법을 사용하여 쌍극자모멘트의 행렬요소를 계산하는 두가지 방법을 발전시켰다. 이 두 방법에 의하여 계산한 쌍극자모멘트행렬요소의 값은 서로 일치하였다.

ABSTRACT. Two methods for evaluation of the dipole moment matrix elements are developed, one using the expansion method for spherical harmonics and the other the transformation method of the dipole moment matrix elements into overlap intergrals for Mulliken.

The numerical values of the dipole moment matrix elements evaluated by two methods are in agreement with each other.

1. 서 론

쌍극자모멘트의 연산자(dipole moment operator)에 대한 양자역학적인 평균치(quantum mechanical expectation value)를 쌍극자모멘트의 행렬요소라고 부른다[1]. 쌍극자모멘트의 연산자는 전자에 대한 변위벡타(displacement vector)로서 공간좌표를 사용하여 다음과 같이 기술할 수 있다.

$$r=ix+jy+kz \qquad (1)$$

한개 이상의 전자를 가진 계의 경우 쌍극자모멘트의 연산자는 개개 전자의 쌍극자모멘트연산자의 합이며 LCAO, MO를 사용하면 분자궤도함수에 대한 쌍극자모멘트의 행렬요소는 식 (2)가 된다.

$$\langle\phi_i|\sum r_i|\phi_i\rangle=\sum_i\sum_\mu\sum_\nu C_{\mu i}C_{\nu i}\langle\phi_\mu|r_i|\phi_\nu\rangle \qquad (2)$$

여기에서 $\langle\phi_\mu|r_i|\phi_\nu\rangle$는 원자궤도함수에 대한 쌍극자모멘트의 행렬요소이다.

x, y 및 z축 방향의 쌍극자모멘트의 행렬요소는 쌍극자모멘트의 연산자 r를 x, y 및 z로 바꾸어주면 얻을 수 있다. 따라서 이들 쌍극자모멘트의 행렬요소는

$$\langle\phi_\mu|x|\phi_\nu\rangle,\ \langle\phi_\mu|y|\phi_\nu\rangle,\ \langle\phi_\mu|z|\phi_\nu\rangle \qquad (3)$$

이다.

쌍극자모멘트의 행렬요소를 계산할 수 있는 두 가지 방법을 본 연구에서 발전시켰다. 첫째 방법은 sphericeal harmonic의 전개방법[2]을 적용하여 쌍극자모멘트의 행렬요소를 계산하는 방법이며 둘째 방법은 쌍극자모멘트의 행렬요소를 Mulliken의 two center overlap integral[3]로 전환시켜서 쌍극자모멘트의 행렬요소를 계산하는 방법이다.

쌍극자모멘트의 행렬요소를 계산하기 위하여 좌표계에 있어서 기준점을 택하는 것이 필요하다[4].

2. SPHERICAL HARMONIC의 전개방법에 의한 쌍극자모멘트 행렬요소의 계산

Fig. 1에 나타난 것처럼 B점에 위치한 Slater 원자궤도함수[5]를 기준점 A에 대하여 전개하면 다음의 두 전개식을 얻을 수 있다[6].

$$
\begin{aligned}
|\phi_B\rangle &= Nr^l\exp(-\beta r)Y_{lm}(\theta\cdot\phi)\\
&= 4\pi N\sum_{l_1=0}^{l}\sum_{l_2=0}^{l}\sum_{m_1=-l_1}^{l_1}\sum_{m_2=-l_2}^{l_2}(-1)^{l_1}\delta(l_1+l_2,l)\\
&\quad\left\{\frac{4\pi(2l+1)!}{(2l_1+1)!(2l_2+1)!}\right\}^{\frac{1}{2}}\langle l_1l_2m_1m_2|l_1l_2lm\rangle\\
&\quad\sum_{n=0}^{\infty}b_n(r_1,r_2)\sum_{k=-n}^{n}Y_{nk}^*(\theta_1,\phi_1)Y_{l_1m_1}(\theta_1,\phi_1)\\
&\quad Y_{nk}(\theta_2,\phi_2)Y_{l_2m_2}(\theta_2,\phi_2) \qquad (4)
\end{aligned}
$$

$$
\begin{aligned}
|\phi_B'\rangle &= Nr^{l+1}\exp(-\beta r)Y_{lm}(\theta,\phi)\\
&= 4\pi N\sum_{l_1=0}^{l}\sum_{l_2=0}^{l}\sum_{m_1=-l_1}^{l}\sum_{m_2=-l_2}^{l_2}(-1)^{l_1}\delta(l_1+l_2,\delta)\\
&\quad\left\{\frac{4\pi(2l+1)!}{(2l_1+1)!(2l_2+1)}\right\}^{\frac{1}{2}}\langle l_1l_2m_1m_2|l_1l_2lm\rangle\\
&\quad\sum_{n=0}^{\infty}z_n(r_1,r_2)r_1^{l_1}r_2^{l_2}\sum_{k=-n}^{n}Y_{nk}^*(\theta_1,\phi_1)\\
&\quad Y_{l_1m_1}(\theta_1,\phi_1)Y_{nk}(\theta_2,\phi_2)Y_{l_2m_2}(\theta_2,\phi_2) \qquad (5)
\end{aligned}
$$

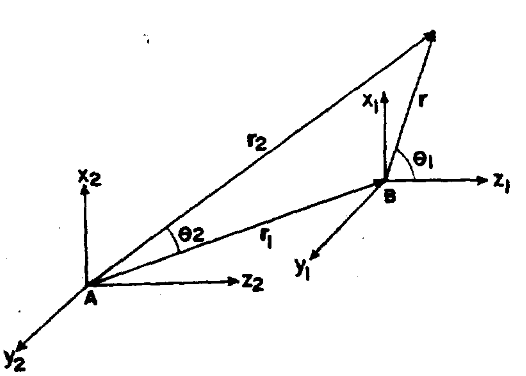

Fig. 1. The coordinate system. $r=r_2-r_1$

여기에서 $\langle l_1l_2m_1m_2|l_1l_2lm\rangle$는 Clebsch Gordan의 계수이며,

$$
\begin{aligned}
b(r_1,r_2) &= (r_>/r_<)^{1/2}I_{n+\frac{1}{2}}(\beta r_<)K_{n+\frac{3}{2}}(\beta r_>)\\
&\quad-(r_</r_>)^{1/2}I_{n-\frac{1}{2}}(\beta r_<)K_{n+\frac{1}{2}}(\beta r_>)\\
z(r_1,r_2) &= (1/r_1r_2)^{1/2}\{(r_1^2+r_2^2)I_{n+\frac{1}{2}}(\beta r_<)\\
&\quad K_{n+\frac{1}{2}}(\beta r_>)-\frac{2n}{(2n+1)}r_1r_2I_{n-\frac{1}{2}}(\beta r_<)\\
&\quad K_{n-\frac{1}{2}}(\beta r_>)-\frac{2(n+1)}{(2n+1)}r_1r_2I_{n+\frac{3}{2}}\\
&\quad(\beta r_<)K_{n+\frac{3}{2}}(\beta r_>)\}
\end{aligned}
$$

이다. 여기에서 $r_<$는 r_1과 r_2의 작게, $r_>$는 r_1과 r_2의 크게이고, I_n, K_n는 modified Bessel 함수이다.

Spherical harmonic의 전개방법에 의하여 쌍극자모멘트의 행렬요소를 계산하기 위하여 쌍극자모멘트의 연산자를 spherical harmonics꼴로 나타내는 것이 필요하다.

$$
\begin{aligned}
x &= (2\pi/3)^{1/2}r[Y_{1-1}(\theta,\phi)-Y_{11}(\theta,\phi)]\\
y &= (2\pi/3)^{1/2}ir[Y_{1-1}(\theta,\phi)+Y_{11}(\theta,\phi)]\\
z &= (4\pi/3)^{1/2}rY_{10}(\theta,\phi) \qquad (6)
\end{aligned}
$$

방정식 (3)에 (6)을 치환하면 x, y 및 z축 방향의 쌍극자모멘트의 행렬요소는 다음이 된다.

$$
\begin{aligned}
\langle\phi_A|x|\phi_B\rangle &= (2\pi/3)^{1/2}\langle\phi_A|r_2[Y_{1-1}(\theta_2,\phi_2)\\
&\quad-Y_{11}(\theta_2,\phi_2)]|\phi_B\rangle\\
&= (2\pi/3)^{1/2}\{\langle\phi_A|r_2Y_{1-1}(\theta_2,\phi_2)|\phi_B\rangle\\
&\quad-\langle\phi_A|r_2Y_{11}(\theta_2,\phi_2)|\phi_B\rangle\} \qquad (7)
\end{aligned}
$$

$$
\begin{aligned}
\langle\phi_A|y|\phi_B\rangle &= (2\pi/3)^{1/2}i\{\langle\phi_A|r_2Y_{1-1}(\theta_2,\phi_2|\phi_B\rangle\\
&\quad-\langle\phi_A|r_2Y_{11}(\theta_2,\phi_2)|\phi_B\rangle\} \qquad (8)
\end{aligned}
$$

$$
\langle\phi_A|z|\phi_B\rangle = (3\pi/4)^{1/2}\langle\phi_A|r_2Y_{10}(\theta_2,\phi_2)|\phi_B\rangle \qquad (9)
$$

여기에서 $\langle\phi_A|r_2Y_{1P}(\theta_1\phi_2)\phi_B\rangle$는 A점을 기준으로 잡았을 때 쌍극자모멘트행렬요소의 허수꼴(imaginary form)이다(*Fig.* 1 참조).

Slater 원자궤도함수의 두개의 전개식(방정식

(4) 및 (5))을 쌍극자모멘트행렬요소의 허수꼴에 치환하면 쌍극자모멘트의 행렬요소에 대한 일반식을 얻을 수 있다.

$$\langle\phi_A|r_2Y_{1P}(\theta_2,\phi_2)|\phi_B\rangle=NM\sum_{l_1=0}^{l}\sum_{l_2=0}^{l}\sum_{n=0}^{\infty}\sum_{l_4}\sum_{l_5}\sum_{m_1}\sum_{m_2}\sum_{m_4}\sum_{m_5}\sum_{K}\delta(l_1+l_2,l)(-1)^{l_2-m+K+m_3+m_5}r_1^{l_1}Y(\theta_1,\phi_1)\int_0^\infty b_n(r_1,r_2)r_2^{l_2+3+n}\exp(-\alpha r_2)(2l+1)(2n+1)(2l_5+1)\left\{3(2l_3+1)(2l_4+1)\frac{(2l)!}{(2l_1)!(2l_2)!}\right\}^{1/2}\begin{pmatrix}l_1 & l_2 & l\\ m_1 & m_2 & -m\end{pmatrix}\begin{pmatrix}n & l_1 & l_4\\ -K & m_1 & m_4\end{pmatrix}\begin{pmatrix}n & l_2 & l_5\\ K & m_2 & m_5\end{pmatrix}\begin{pmatrix}l_3 & 1 & l_5\\ -m_3 & P & -m_5\end{pmatrix}\begin{pmatrix}n & l_1 & l_4\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}n & l_2 & l_5\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_3 & 1 & l_5\\ 0 & 0 & 0\end{pmatrix} \quad (10)$$

여기에서 $\phi_A=Mr_2^{n}\exp(-\alpha r_2)Y_{l_3m_3}(\theta_2,\phi_2)$ 및 $P=\pm1$, 또는 0임.

$$\langle\phi_A|r_2Y_{1P}(\theta_2,\phi_2)|\phi_B'\rangle=NM\sum_{l_1=0}^{l}\sum_{l_2=0}^{l}\sum_{n=0}^{\infty}\sum_{l_4}\sum_{l_5}\sum_{m_1}\sum_{m_3}\sum_{m_4}\sum_{m_5}\sum_{K}\delta(l_1+l_2,\delta)(-1)^{l_2-m+K+m_3+m_5}r_1^{l_1}Y^*_{l_1m_1}(\theta_1,\phi_1)\int_0^\infty z_n(r_1,r_2)r_2^{l_2+3+n}\exp(-\alpha r_2)dr_2\,(2l+1)(2n+1)(2l_5+1)\left\{3(2l_3+1)(2l_4+1)\frac{(2l)!}{(2l_1)!(2l_2)!}\right\}^{1/2}\begin{pmatrix}l_1 & l_2 & l\\ m_1 & m_2 & -m\end{pmatrix}\begin{pmatrix}n & l_1 & l_4\\ -K & m_1 & m_4\end{pmatrix}\begin{pmatrix}n & l_2 & l_5\\ K & m_2 & m_5\end{pmatrix}\begin{pmatrix}l_3 & 1 & l_5\\ -m_3 & P & -m_5\end{pmatrix}\begin{pmatrix}n & l_1 & l_4\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}n & l_2 & l_5\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_3 & 1 & l_5\\ 0 & 0 & 0\end{pmatrix} \quad (11)$$

여기에서 $\phi_A=Mr_2^{n}\exp(-\alpha r_2)Y_{l_3m_3}(\theta_2,\phi_2)$ 및 $P=\pm1$, 또는 0임.

쌍극자모멘트행렬요수의 허수꼴의 일반식에 지름적분(radial part integral)과 주어진 $l_1, l_2, l_3, l_4, l_5, m_1, m_2, m_3, m_4, m_5$ 및 P에 대응하는 3-j symbol 및 Clebsch Gordan 계수의 값을 넣어준 후 쌍극자모멘트의 행렬요소의 허수꼴을 실수꼴로 바꾸면 *Table* 1에 주어진 쌍극자모멘트의 행렬 요소의 식을 얻을 수 있다.

Table 1. The dipole moment matrix elements derived by the expansion method for spherical harmonics.

$$\langle 1s|z|1s\rangle=4(\alpha/\beta)^{3/2}\cos\theta Z_1/\beta$$
$$\langle 1s|z|1s\rangle=4(\alpha/\beta)^{3/2}\sin\theta\cos\phi Z_1/\beta$$
$$\langle 1s|y|1s\rangle=4(\alpha/\beta)^{3/2}\sin\theta\sin\phi Z_1/\beta$$
$$\langle 2s|z|1s\rangle=\left(\frac{16}{3}\right)^{1/2}(\alpha/\beta)^{5/2}\cos\theta V_1/\beta$$
$$\langle 2s|x|1s\rangle=\left(\frac{16}{3}\right)^{1/2}(\alpha/\beta)^{5/2}\sin\theta\cos\phi V_1/\beta$$
$$\langle 2s|y|1s\rangle=\left(\frac{16}{3}\right)^{1/2}(\alpha/\beta)^{5/2}\sin\theta\sin\phi V_1/\beta$$
$$\langle 2p_z|z|1s\rangle=\left(\frac{4}{3}\right)(\alpha/\beta)^{5/2}\{V_0+(2\cos^2\theta-\sin^2\theta)V_2\}/\beta$$
$$\langle 2p_x|x|1s\rangle=\left(\frac{4}{3}\right)(\alpha/\beta)^{5/2}\left\{V_0-\left[\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{3}{2}\sin^2\theta\cos2\phi\right]V_2\right\}/\beta$$
$$\langle 2p_y|y|1s\rangle=\left(\frac{4}{3}\right)(\alpha/\beta)^{5/2}\left\{V_0-\left[\frac{1}{2}(2\cos^2\theta-\sin^2\theta)+\frac{3}{2}\sin^2\theta\cos2\phi\right]V_2\right\}/\beta$$
$$\langle 2p_x|x|1s\rangle=\sqrt{8}(\alpha/\beta)^{5/2}\cos\theta\sin\theta\cos\phi V_2/\beta=\langle 2p_x|z|1s\rangle$$
$$\langle 2p_z|y|1s\rangle=\sqrt{8}(\alpha/\beta)^{5/2}\cos\theta\sin\theta\sin\phi V_2/\beta=\langle 2p_y|z|1s\rangle$$
$$\langle 2s|z|2s\rangle=\left(\frac{4}{3}\right)(\alpha/\beta)^{5/2}\cos\theta B_1/\beta$$
$$\langle 2s|x|2s\rangle=\left(\frac{4}{3}\right)(\alpha/\beta)^{5/2}\sin\theta\cos\phi B_1/\beta$$
$$\langle 2s|y|2s\rangle=\left(\frac{4}{3}\right)(\alpha/\beta)^{5/2}\sin\theta\sin\phi B_1/\beta$$
$$\langle 2p_z|z|2s\rangle=\left(\frac{16}{27}\right)^{1/2}(\alpha/\beta)^{5/2}\{B_0+(2\cos^2\theta-\sin^2\theta)B_2\}/\beta$$
$$\langle 2p_z|x|2s\rangle=\left(\frac{8}{3}\right)^{1/2}(\alpha/\beta)^{5/2}\cos\theta\sin\theta\cos\phi B_2/\beta=\langle 2p_x|z|2s\rangle$$

$\langle 2p_z|y|2s\rangle=\left(\frac{8}{3}\right)^{1/2}(\alpha/\beta)^{5/2}\cos\theta\sin\theta\sin\phi B_2/\beta=\langle 2p_y|z|2s\rangle$

$\langle 3s|z|2s\rangle=\left(\frac{32}{135}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta H_1/\beta$

$\langle 3p_z|z|2s\rangle=\left(\frac{32}{405}\right)^{1/2}(\alpha/\beta)^{7/2}\{H_0+(2\cos^2\theta-\sin^2\theta)H_2\}/\beta$

$\langle 3p_x|z|2s\rangle=\left(\frac{32}{135}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\sin\theta\cos\phi H_2/\beta=\langle 3p_z|x|2s\rangle$

$\langle 3p_y|z|2s\rangle=\left(\frac{32}{135}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\sin\theta\sin\phi H_2/\beta=\langle 3p_z|y|2s\rangle$

$\langle 2p_x|x|2s\rangle=\left(\frac{16}{27}\right)^{1/2}(\alpha/\beta)^{5/2}\left\{B_0-\left[\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{3}{2}\sin^2\theta\cos2\phi\right]B_2\right\}/\beta$

$\langle 2p_y|y|2s\rangle=\left(\frac{16}{27}\right)^{1/2}(\alpha/\beta)^{5/2}\left\{B_0-\left[\frac{1}{2}(2\cos^2\theta-\sin^2\theta)+\frac{3}{2}\sin^2\theta\cos2\phi\right]B_2\right\}/\beta$

$\langle 3p_x|x|2s\rangle=\left(\frac{32}{405}\right)^{1/2}(\alpha/\beta)^{7/2}\left\{H_0-\left[\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{3}{2}\sin^2\theta\cos2\phi\right]H_2\right\}/\beta$

$\langle 3p_y|y|2s\rangle=\left(\frac{32}{405}\right)^{1/2}(\alpha/\beta)^{7/2}\left\{H_0-\left[\frac{1}{2}(2\cos^2\theta-\sin^2\theta)+\frac{3}{2}\sin^2\theta\cos2\phi\right]H_2\right\}/\beta$

$\langle 3dz^2|z|2s\rangle=\left(\frac{32}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\left\{2\cos\theta H_1+\frac{3}{2}(2\cos^3\theta-3\sin^2\theta\cos\theta)H_3\right\}/\beta$

$\langle 3d_{xz}|z|2s\rangle=\left(\frac{32}{2025}\right)^{1/2}(\alpha/\beta)^{7/2}\{\sin\theta\cos\phi H_1-(4\cos^2\theta-\sin^3\theta)\cos\phi H_3\}/\beta$

$\langle 3d_{yz}|z|2s\rangle=\left(\frac{32}{2025}\right)^{1/2}(\alpha/\beta^{7/2}\{\sin\theta\sin\phi H_1-(4\cos^2\theta-\sin^3\theta)\sin\phi H_3\}/\beta$

$\langle 3d_{xz}|x|2s\rangle=\left(\frac{32}{2025}\right)^{1/2}(\alpha/\beta)^{7/2}\left\{H_1-\left[\frac{3}{2}(2\cos^3\theta-3\sin^2\theta\cos\theta)+\frac{15}{2}\cos\theta\sin\theta\cos2\phi\right]H_3\right\}/\beta$

$\langle 3d_{yz}|y|2s\rangle=\left(\frac{32}{2025}\right)^{1/2}(\alpha/\beta)^{7/2}\left\{H_1-\left[\frac{3}{2}(2\cos^3\theta-3\cos\theta\sin\theta)-\frac{15}{2}\cos\theta\sin\theta\cos2\phi\right]H_3\right\}/\beta$

$\langle 3d_{x^2-y^2}|x|2s\rangle=\left(\frac{32}{225}\right)^{1/2}(\alpha/\beta)^{7/2}\left\{\sin\theta\cos\phi H_1-\left[\frac{1}{4}(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi+\frac{5}{4}\sin^3\theta\cos3\phi\right]H_3\right\}/\beta$

$\langle 3d_{xy}|y|2s\rangle=\left(\frac{32}{225}\right)^{1/2}(\alpha/\beta)^{7/2}\left\{\sin\theta\sin\phi H_1-\left[\frac{1}{4}(4\cos^2\theta\sin\theta-\sin^3\theta)\sin\phi+\frac{5}{4}\sin^3\theta\sin3\phi\right]H_3\right\}/\beta$

$\langle 2p_z|z|2p_z\rangle=\left(\frac{4}{3}\right)(\alpha/\beta)^{5/2}\left\{\frac{9}{5}\cos\theta W_1+\frac{3}{5}(2\cos^2\theta-3\cos\theta\sin^2\theta)W_3-a\left[V_0-\left(\frac{4}{5}\cos\theta+\frac{3}{5}(2\cos^2\theta-3\cos\theta\sin^2\theta)\right)V_2\right]\right\}/\beta$

$\langle 2p_x|z|2p_x\rangle=\left(\frac{4}{5}\right)(\alpha/\beta)^{5/2}\left\{\sin\theta\cos\phi W_1+(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi W_3-a(\sin\theta\cos\phi+(4\cos^2\theta\sin^2\theta-\sin^3\theta)\cos\phi)V_2\right\}/\beta$

$\langle 3s|z|2p_z\rangle=\left(\frac{32}{405}\right)^{1/2}(\alpha/\beta)^{7/2}\{S_0+(2\cos^2\theta-\sin^2\theta)S_2-a(1+(2\cos^2\theta-\sin^2\theta))W_1\}/\beta$

$\langle 3p_z|z|2p_z\rangle=\left(\frac{32}{135}\right)^{1/2}(\alpha/\beta)^{7/2}\left\{\frac{9}{5}\cos\theta S_1+\frac{3}{5}(2\cos^3\theta-3\cos\theta\sin^2\theta)S_3-a\left[W_0-\left(\frac{4}{5}\cos\theta+\frac{3}{5}(2\cos^3\theta-3\cos\theta\sin^2\theta)\right)\right.\right.$

$\left.\left.W_2\right]\right\}/\beta$

$\langle 2p_x|x|2p_z\rangle=\left(\frac{4}{5}\right)(\alpha/\beta)^{5/2}\left\{\cos\theta W_1-\left[\frac{1}{2}(2\cos^3\theta-3\cos\theta\sin^2\theta)+\frac{5}{2}\cos\theta\sin^2\theta\cos2\phi\right]W_3-\frac{5}{6}a\cos\theta V_0\right.$

$\left.+a\left[\frac{1}{3}\cos\theta+\frac{1}{2}(2\cos^3\theta-3\cos\theta\sin^2\theta)+\frac{5}{2}\cos\theta\sin^2\theta\cos2\phi\right]V_2\right\}/\beta$

$\langle 3p_x|x|2p_z\rangle=\left(\frac{32}{375}\right)^{1/2}(\alpha/\beta)^{7/2}\left\{\cos\theta S_1-\left[\frac{1}{2}(2\cos^3\theta-3\sin\theta\sin^2\theta)+\frac{5}{2}\cos\theta\sin^2\theta\cos2\phi\right]S_3-\frac{5}{6}a\cos\theta W_0\right.$

$\left.+a\left[\frac{1}{3}\cos\theta+\frac{1}{2}(2\cos^3\theta-3\cos\theta\sin^2\theta)+\frac{5}{2}\cos\theta\sin^2\theta\cos2\phi\right]W_2\right\}/\beta$

$\langle 3p_y|y|2p_z\rangle=\left(\frac{32}{375}\right)^{1/2}(\alpha/\beta)^{7/2}\left\{\cos\theta S_1-\left[\frac{1}{2}(\cos^3\theta-3\cos\theta\sin^2\theta)-\frac{5}{2}\cos\theta\sin^2\theta\cos2\phi\right]S_3-\frac{5}{6}a\cos\theta W_0\right.$

$\left.+a\left[\frac{1}{3}\cos\theta+\frac{1}{2}(2\cos^3\theta-3\mathrm{coc}\theta\sin^2\theta)-\frac{5}{2}\cos\theta\sin^2\theta\cos2\phi\right]W_2\right\}/\beta$

$$\langle 3d_{z^2}|z|2p_z\rangle=\left(\frac{32}{2035}\right)^{1/2}(\alpha/\beta)^{7/2}\{2S_0+\frac{55}{14}(2\cos^2\theta-\sin^2\theta)S_2+\frac{9}{14}(35\cos^4\theta-30\cos^2\theta+3)S_4$$
$$-a(2+2(2\cos^2\theta-\sin^2\theta))W_1-a[\frac{27}{14}(2\cos^2\theta-\sin^2\theta)+\frac{9}{14}35\cos^4\theta-30\cos^2\theta+3)]W_3\}/\beta$$

$$\langle 3d_{xz}|z|2p_z\rangle=\left(\frac{16}{2025}\right)^{1/2}(\alpha/\beta)^{7/2}\{S_0+[\frac{5}{7}(2\cos^2\theta-\sin^2\theta)+\frac{15}{14}\sin^2\theta\cos2\phi]S_2-[\frac{3}{14}(35\cos^4\theta-30\cos^2\theta+3)S_4$$
$$-\frac{45}{14}\sin^2\theta(7\cos^2\theta-1)\cos2\phi]S_4-a(1+(2\cos^2\theta-\sin^2\theta))W_1+[\frac{9}{14}(\cos^2\theta-\sin^2\theta)$$
$$+\frac{3}{14}(35\cos^4\theta-30\cos^2\theta+3)-\frac{45}{14}\sin^2\theta(7\cos^2\theta-1)\cos2\phi)]aW_3\}/\beta$$

$$\langle 2p_x|x|2p_x\rangle=\left(\frac{4}{15}\right)(\alpha/\beta)^{5/2}\{9\sin\theta\cos2\phi W_1-[\frac{9}{4}(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi-\frac{15}{4\sqrt{2}}\sin^3\theta\cos3\phi]W_3-5\sin\theta\cos\phi aV_0$$
$$-[\frac{3}{2}\sin\theta\cos\phi-9(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi+\frac{15}{4\sqrt{2}}\sin^3\theta\cos3\phi]aV_2\}/\beta$$

$$\langle 3s|x|2p_x\rangle=\left(\frac{32}{405}\right)^{1/2}(\alpha/\beta)^{7/2}\{S_0-[\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{3}{2}\sin^2\theta\cos2\phi]S_2-[1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)+\frac{3}{2}\sin^2\theta\cos2\phi]$$
$$aW_1\}/\beta$$

$$\langle 2s|x|2p_x\rangle=\left(\frac{16}{27}\right)^{1/2}(\alpha/\beta)^{5/2}\{W_0-[\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{3}{2}\sin^2\theta\cos2\phi]W_2-[1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)$$
$$+\frac{3}{2}\sin^2\theta\cos2\phi]aV_1\}/\beta$$

$$\langle 3p_x|x|2p_x\rangle=\left(\frac{16}{3375}\right)^{1/2}(\alpha/\beta)^{7/2}\{9\sin\theta\cos\phi S_1-[\frac{9}{4}(\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi-\frac{15}{4\sqrt{2}}\sin^3\theta\cos3\phi]S_3-5\sin\theta\cos\phi aW_0$$
$$-[\frac{3}{2}\sin\theta\cos\phi-\frac{9}{4}(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi-\frac{15}{4\sqrt{2}}\sin^3\theta\cos3\phi]aW_2\}/\beta$$

$$\langle 3d_{z^2}|x|2p_x\rangle=\left(\frac{32}{2025}\right)^{1/2}(\alpha/\beta)^{7/2}\{-S_0+[\frac{15}{7}\sin^2\theta\cos2\phi-\frac{25}{28}(2\cos^2\theta-\sin^2\theta)]S_2-[\frac{9}{56}(35\cos^4\theta-30\cos^2\theta+3)$$
$$+\frac{45}{28}(7\cos^2\theta-1)\cos2\phi]S_4+[1-\frac{1}{4}(2\cos^2\theta-\sin^2\theta)-\frac{3}{\sqrt{2}}\sin^2\theta\cos2\phi]aW_1-[\frac{9}{14}(2\cos^2\theta$$
$$-\sin^2\theta)-\frac{9}{56}(35\cos^4\theta\quad-30\cos^2\theta+3)-\frac{3}{7}\sin^2\theta\cos2\phi+\frac{45}{28}\sin^2\theta(7\cos^2\theta-1)\cos2\phi]aW_3\}/\beta$$

$$\langle 3d_{xz}|x|2p_x\rangle=\left(\frac{32}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\{\frac{45}{7}\cos\theta\sin\theta\cos\phi S_2-\frac{15}{2}\sin^3\theta\cos\theta\cos3\phi S_3-\frac{45}{56}\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi S_4-3\cos\theta$$
$$\sin\theta\sin\phi aW_1-[\frac{45}{7}\cos\theta\sin\theta\cos\phi-\frac{45}{56}\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi-\frac{15}{2}\sin^3\theta\cos\theta\cos3\phi]aW_3\}/\beta$$

$$\langle 3d_{x^2-y^2}|x|2p_x\rangle=\left(\frac{8}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\{S_0-\frac{5}{7}(2\cos^2\theta-\sin^2\theta)S_2+\frac{3}{56}(35\cos^4\theta-30\cos^2\theta+3)S_4-a[1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)$$
$$-3\cos^2\theta\cos2\phi]W_1-[\frac{3}{14}(2\cos^2\theta-\sin^2\theta)-\frac{3}{56}(35\cos^4\theta-30\cos^2\theta+3)-3\sin^2\theta\cos2\phi+\frac{15}{4}\sin^4\theta\cos4\phi]aW_3\}/\beta$$

$$\langle 2p_y|y|2p_y\rangle=\left(\frac{4}{15}\right)(\alpha/\beta)^{5/2}\{9\sin\theta\sin\phi W_1-[\frac{9}{4}(4\cos^2\theta\sin\theta-3\sin^3\theta)\sin\phi+\frac{15}{4\sqrt{2}}\sin^3\theta\sin3\phi]W_3-5\sin\theta\sin\phi aV_0$$
$$-[\frac{3}{2}\sin\phi-\frac{9}{4}(4\sin^2\theta\sin\theta-\sin^3\theta)\sin\phi+\frac{15}{4\sqrt{2}}\sin^3\theta\sin3\phi]aV_2\}/\beta$$

$$\langle 2s|y|2p_y\rangle=\left(\frac{16}{27}\right)^{1/2}(\alpha/\beta)^{5/2}\{W_0-[\frac{1}{2}(\cos^2\theta-\sin^2\theta)+\frac{3}{2}\sin^2\theta\cos2\phi]W_2-[1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{3}{2}\sin^2\theta\cos2\phi]$$
$$aV_1\}/\beta$$

$$\langle 3s|y|2p_y\rangle=\left(\frac{32}{405}\right)^{1/2}(\alpha/\beta)^{7/2}\{S_0-[\frac{1}{2}(2\cos^2\theta-\sin^2\theta)+\frac{3}{2}\sin^2\theta\cos2\phi]S_2-[1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{3}{2}\sin^2\theta\cos2\phi]$$
$$aW_1\}/\beta$$

$$\langle 3p_y|y|2p_y\rangle=\left(\frac{16}{3375}\right)^{1/2}(\alpha/\beta)^{7/2}\{9\sin\theta\sin\phi S_1-[\frac{9}{4}(4\cos^2\theta\sin\theta-\sin^3\theta)\sin\phi-\frac{15}{4\sqrt{2}}\sin^3\theta\sin3\phi]S_3-5\sin\theta\sin\phi aW_0$$

$$-\left[\frac{3}{2}\sin\theta\sin\phi-\frac{9}{4}(4\cos^2\theta\sin\theta-\sin^3\theta)\sin\phi+\frac{15}{4\sqrt{2}}\sin^3\theta\sin 3\phi\right]aW_2\Big\}/\beta$$

$$\langle 3d_{z^2}|y|2p_y\rangle=\left(\frac{32}{2025}\right)^{1/2}(\alpha/\beta)^{7/2}\Big\{-S_0+\left(\frac{15}{7}\sin^2\theta\sin2\phi-\frac{25}{28}(2\cos^2\theta-\sin^2\theta)\right)\Big]S_2-\Big[\frac{9}{56}(35\cos^4\theta-30\cos^2\theta+3)$$

$$+\frac{45}{28}\sin^2\theta(7\cos^2\theta-1)\sin2\phi\Big]S_4+\left[1-\frac{1}{4}(2\cos^2\theta-\sin^2\theta)-\frac{3}{\sqrt{2}}\sin^2\theta\sin 2\phi\right]aW_1-\Big[\frac{9}{14}(2\cos^2\theta-\sin^2\theta)$$

$$-\frac{9}{56}(35\cos^4\theta-30\cos^2\theta+3)-\frac{3}{7}\sin^2\theta\sin 2\phi+\frac{45}{28}\sin^2\theta(7\cos^2\theta-1)\sin2\phi\Big]aW_3\Big\}/\beta$$

$$\langle 3d_{yz}|y|2p_y\rangle=\left(\frac{32}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\Big\{\frac{45}{7}\cos\theta\sin\theta\sin\phi S_2-\frac{15}{2}\sin^3\theta\cos\theta\sin3\phi S_4-\frac{45}{56}\sin\theta(7\cos^3\theta-3\cos\theta)\sin\phi S_4-3\cos\theta\sin\theta$$

$$\sin\phi aW_1-\left[\frac{45}{7}\cos\theta\sin\theta\sin\phi-\frac{45}{56}\sin\theta(7\cos^3\theta-3\cos\theta)\sin\phi-\frac{15}{2}\cos^3\theta\cos\theta\sin3\phi\right]aW_3\Big\}/\beta$$

$$\langle 3d_{xy}|y|2p_y\rangle=\left(\frac{8}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\Big\{S_0-\frac{5}{7}(2\cos^2\theta-\sin^2\theta)S_2+\frac{3}{56}(35\cos^4\theta-30\cos^2\theta+3)S_4-\Big[1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)$$

$$-3\sin^2\theta\sin2\phi\Big]aW_1-\left[\frac{3}{14}(2\cos^2\theta-\sin^2\theta)-\frac{3}{56}(35\cos^4\theta-30\cos^2\theta+3)-3\sin^2\theta\sin2\phi+\frac{15}{4}\sin^4\theta\cos4\phi\right]aW_3\Big\}/\beta$$

$$\langle 3s|z|3p_z\rangle=\left(\frac{8}{45}\right)(\alpha/\beta)^{7/2}\{I_0+(2\cos^2\theta-\sin^2\theta)I_2-a(1+(2\cos^2\theta-\sin^2\theta))H_1\}/\beta$$

$$\langle 3p_z|z|3p_z\rangle=\left(\frac{8}{45}\right)(\alpha/\beta)^{7/2}\Big\{\frac{9}{5}\cos\theta I_1+\frac{3}{5}(2\cos^3\theta-3\cos\theta\sin^2\theta)I_3-a\Big[H_0-\left(\frac{4}{5}\cos\theta+\frac{3}{5}(2\cos^3\theta-3\cos\theta\sin^2\theta)H_2\right)\Big\}/\beta$$

$$\langle 3d_{z^2}|z|3p_z\rangle=\left(\frac{64}{30375}\right)^{1/2}(\alpha/\beta)^{7/2}\Big\{2I_0+\frac{55}{14}(2\cos^2\theta-\sin^2\theta)I_2+\frac{9}{14}(35\cos^4\theta-30\cos^2\theta+3)I_4$$

$$-a(2+2(2\cos^2\theta-\sin^2\theta))H_1-a\left[\frac{27}{14}(2\cos^2\theta-\sin^2\theta)+\frac{9}{14}(35\cos^4\theta-30\cos^2\theta+3)\right]H_3\Big\}/\beta$$

$$\langle 3p_x|x|3p_x\rangle=\left(\frac{32}{50625}\right)^{1/2}(\alpha/\beta)^{7/2}\Big\{9\sin\theta\cos\phi I_1-\left[\frac{9}{4}(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi-\frac{15}{4\sqrt{2}}\sin^3\theta\cos3\phi\right]I_3-5\sin\theta\cos\phi H_0$$

$$-\left[\frac{3}{2}\sin\theta\cos\phi-\frac{9}{4}(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi+\frac{15}{4\sqrt{2}}\sin^3\theta\cos3\phi\right]H_3\Big\}/\beta$$

$$\langle 3d_{z^2}|x|3p_x\rangle=\left(\frac{64}{50625}\right)^{1/2}(\alpha/\beta)^{7/2}\Big\{-I_0+\left[\frac{15}{7}\sin^2\theta\cos2\phi-\frac{25}{28}(2\cos^2\theta-\sin^2\theta)\right]I_2-\Big[\frac{9}{56}(35\cos^4\theta-30\cos^2\theta+3)+\frac{45}{28}$$

$$\sin^2\theta(7\cos^2\theta-1)\cos2\phi\Big]I_4+\left[1-\frac{1}{4}(2\cos^2\theta-\sin^2\theta)-\frac{3}{\sqrt{2}}\sin^2\theta\cos 2\phi\right]aH_1$$

$$-\left[\frac{9}{14}(2\cos^2\theta-\sin^2\theta)-\frac{9}{56}(35\cos^4\theta-30\cos^2\cos\theta+3)-\frac{3}{7}\sin^2\theta\cos2\phi+\frac{45}{28}\sin^2\theta(7\cos^2\theta-1)\cos2\phi\right]aH_3\Big\}/\beta$$

$$\langle 3d_{xz}|x|3p_x\rangle=\left(\frac{64}{10125}\right)^{1/2}(\alpha/\beta)^{7/2}\Big\{\frac{45}{7}\cos\theta\sin\theta\cos\phi I_2-\frac{15}{2}\sin^3\theta\cos3\phi I_4-\frac{45}{56}\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi I_4$$

$$-\left[\frac{54}{7}\cos\theta\sin\theta\ \ \cos\phi-\frac{45}{56}\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi-\frac{15}{2}\sin^3\theta\cos\theta\cos3\phi\right]aH_3-3\cos\theta\sin\theta\cos\phi aH_1\Big\}/\beta$$

$$\langle 3d_{x^2-y^2}|x|3P_x\rangle=\left(\frac{16}{10125}\right)^{1/2}(\alpha/\beta)^{7/2}\Big\{I_0-\frac{5}{7}(2\cos^2\theta-\sin^2\theta)I_2+\frac{3}{56}(35\cos^4\theta-30\cos^2\theta+3)I_4-\Big[1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)$$

$$-3\sin^2\theta\cos 2\phi\Big]aH_1-\left[\frac{3}{14}(2\cos^2\theta-\sin^2\theta)-\frac{3}{56}(35\cos^4\theta-30\cos^2\theta+3)-3\sin^2\theta\cos2\phi+\frac{15}{4}\sin^4\theta\cos4\phi\right]H_3\Big\}/\beta$$

Where α is the Slater constant for atomic orbital in bra vector which is chosen as the reference point and β the Slater constant for atomic orbital in Ket vector. The alphabets that are used to represent the radial part integrals of the general expansion formulas were defined in the previous report.[2]

3. 쌍극자모멘트의 행렬요소를 MULLIKEN 의 OVERLAP INTEGRAL로 전환시키는 방법

이미 설명한 것처럼 원자궤도함수에 대한 쌍극자모멘트의 행렬요소는 다음 식으로 기술할 수 있다.

$$\langle\phi_\mu|r|\phi_\nu\rangle \tag{12}$$

x, y 및 z 축 방향의 쌍극자모멘트의 행렬요소를 spherical harmonics 꼴로 바꾸고 쌍극자모멘트의 bra 벡타(bra vector, $\langle\phi_\mu|$)를 Slater 궤도함수로 치환하면 쌍극자모멘트의 행렬요소에 대한

식을 다음과 같이 얻을 수 있다.

$$\langle\phi_\mu|x|\phi_\nu\rangle = NK\{\langle r^{l+1}\exp(-\alpha r)Y_{lm}(\theta,\phi) Y_{1-1}(\theta,\phi)\phi_\nu\rangle + \langle r^{l+1}\exp(-\alpha r)Y_{lm}(\theta,\phi) Y_{11}(\theta,\phi)|\phi_\nu\rangle \tag{13}$$

$$\langle\phi_\mu|y|\phi_\nu\rangle = NKi\{\langle r^{l+1}\exp(-\alpha r)Y_{lm}(\theta,\phi) Y_{1-1}(\theta\cdot\phi)|\phi_\nu\rangle + \langle r^{l+1}\exp(-\alpha r)Y_{lm}(\theta,\phi) Y_{1-1}(\theta,\phi)|\phi_\nu\rangle \tag{14}$$

$$\langle\phi_\mu|z|\phi_\nu\rangle = NK'\langle r^{l+1}\exp(-\alpha r)Y_{lm}(\theta,\phi) Y_{10}(\theta,\phi)|\phi_\nu\rangle \tag{15}$$

여기에서 $K=(2\pi/3)^{1/2}$, 그리고 $K'=(4\pi/3)^{1/2}$ 임.

방정식 (13), (14),및 (15)로 나타낸 overlap integral을 일반식으로 바꾸면 다음이 된다.[7,8]

$$\langle r^{l+1}\exp(-\alpha r)Y_{lm}(\theta,\phi)Y_{1P}(\theta,\phi)|\phi_\nu\rangle = \sum_{l'=|l-1|}^{|l+1|}\sum_{l'=-m'}^{m'}\left[\frac{(2l+1)3(2l'+1)}{4\pi}\right]^{1/2}(-1)^m\begin{pmatrix} l & 1 & l' \\ -m & P & m'\end{pmatrix}\begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0\end{pmatrix}\langle r^{l+1}\exp(-\alpha r)Y_{l'm'}(\theta,\phi)|\phi_\nu\rangle \tag{16}$$

여기에서 $P=\pm 1$, 또는 0임.

주어진 l, m, l', m' 및 P에 대응하는 3-j symbol의 값을 방정식(16)에 대입하여 얻은 Overlap integral의 일반식을 방정식 (13), (14) 및 (15)에 치환하여 주면 x, y 및 z축 방향의 쌍극자모멘트 행렬요소에 대한 전환 overlap integral (transformed overlap integral)을 얻을 수 있다.

쌍극자모멘트 행렬요소를 overlap integral로 전환시킨 부분(transformed part of dipole moment matrix element), $\langle\phi_\mu|r$, 을 *Table* 2에 나타내었다. Ket vector, $|\phi_\nu\rangle$에 쌍극자모멘트의 overap integral로 전환부분을 연산해 주면 쌍극자모멘트의 전환 overlap integral을 얻을수 있다.

보기로서 $\langle 3d_{z^2}|z|2p_z\rangle$의 overlap integral로 전환부분, $\langle 3d_{z^2}|z$를 $|2p_z\rangle$에 연산해 주면 다음과 같이 $\langle 3d_{z^2}|z|2p_z\rangle$의 전환 overlap integral을 얻을 수 있다.

$$\langle 3d_{z^2}|z|2p_z\rangle = 1/\alpha\left\{\left(\frac{56}{15}\right)^{1/2}\langle 4p|2p_z\rangle + \left(\frac{18}{5}\right)^{1/2}\langle 4f_{z^3}|2p_z\rangle\right\}$$

Table 2. The transformed part of the dipole moment matrix elements.

$\langle 1s\|z = 1/\alpha < 2p_z\|$	$\langle 1s\|x = 1/\alpha < 2p_x\|$
$\langle 2s\|z = \left(\frac{5}{2}\right)^{1/2}/\alpha < 3P_z\|$	$\langle 2s\|x = \left(\frac{5}{2}\right)^{1/2}/\alpha < 3p_x\|$
$\langle 2p_z\|z = \left(\frac{5}{2}\right)^{1/2}/\alpha < 3s\| + \left(\frac{1}{2}\right)^{1/2}/\alpha < 3d_{z^2}\|$	$\langle 2p_z\|x = \left(\frac{3}{2}\right)^{1/2}/\alpha < 3d_{xz}\|$
$\langle 2p_x\|z = \left(\frac{3}{2}\right)^{1/2}/\alpha < 3d_{xz}\|$	$\langle 2p_x\|x = 1/\alpha\left\{\left(\frac{5}{2}\right)^{1/2} < 3s\| - \frac{1}{\sqrt{2}} < 3d_{z^2}\| + \left(\frac{3}{4}\right)^{1/2} < 3d_{x^2-y^2}\|\right\}$
$\langle 2p_y\|z = \left(\frac{3}{2}\right)^{1/2}/\alpha < 3d_{yz}\|$	$\langle 3s\|x = \left(\frac{14}{3}\right)^{1/2}/\alpha < 4p_x\|$
$\langle 3s\|z = \left(\frac{14}{3}\right)^{1/2}/\alpha < 4p_z\|$	$\langle 3p_z\|x = \left(\frac{14}{5}\right)^{1/2}/\alpha < 4d_{xz}\|$
$\langle 3p_z\|z = \left(\frac{14}{3}\right)^{1/2}/\alpha < 4s\| + \left(\frac{56}{15}\right)^{1/2}/\alpha < 4d_{z^2}\|$	$\langle 3p_x\|x = 1/\alpha\left\{\left(\frac{14}{3}\right)^{1/2} < 4s\| - \left(\frac{14}{15}\right)^{1/2} < 4d_{z^2}\| + \left(\frac{14}{5}\right)^{1/2} < 4d_{x^2-y^2}\|\right\}$
$\langle 3p_x\|z = \left(\frac{14}{5}\right)^{1/2}/\alpha < 4d_{xz}\|$	$\langle 3d_{z^2}\|x = 1/\alpha\left\{-\left(\frac{14}{15}\right)^{1/2} < 4p_x\| + \left(\frac{12}{5}\right)^{1/2} < 4f_{xz^2}\|\right\}$
$\langle 3p_y\|z = \left(\frac{14}{5}\right)^{1/2}/\alpha < 4d_{yz}\|$	$\langle 3d_{xz}\|x = 1/\alpha\left\{\left(\frac{14}{5}\right)^{1/2} < 4p_z\| - \left(\frac{6}{5}\right)^{1/2} < 4f_{z^3}\| + \sqrt{2} < 4f_{z(x^2-y^2)}\|\right\}$
$\langle 3d_{z^2}\|z = \left(\frac{56}{15}\right)^{1/2}/\alpha < 4p_z\| + \left(\frac{18}{5}\right)^{1/2}/\alpha < 4f_{z^3}\|$	
$\langle 3d_{xz}\|z = \left(\frac{14}{5}\right)^{1/2}/\alpha < 4p_x\| + \left(\frac{16}{5}\right)^{1/2}/\alpha < 4f_{xz^2}\|$	
$\langle 3d_{yz}\|z = \left(\frac{14}{5}\right)^{1/2}/\alpha < 4p_y\| + \left(\frac{16}{5}\right)^{1/2}/\alpha < 4f_{yz^2}\|$	
$\langle d_{x^2-y^2}\|z = \sqrt{2}/\alpha < 4f_{z(x^2-y)}\|$	
$\langle 3d_{xy}\|z = \sqrt{2}/\alpha < 4f_{xyz}\|$	

$$\langle 3d_{x^2-y^2}|x = 1/\alpha\left\{\left(\frac{14}{5}\right)^{1/2}\langle 4p_x| - \left(\frac{1}{5}\right)^{1/2}\langle 4f_{xz^2}| + \sqrt{3}\langle 4f_{x(x^2-y^2)}|\right\}$$

$$\langle 3d_{xy}|x = 1/\alpha\left\{\left(\frac{14}{5}\right)^{1/2}\langle 4p_y| - \left(\frac{1}{5}\right)^{1/2}\langle 4f_{yz^2}| + \sqrt{3}\langle 4f_{y(x^2-z^2)}|\right\}$$

$$\langle 1s|y = 1/\alpha\langle 2p_y|$$

$$\langle 2s|y = \left(\frac{5}{2}\right)^{1/2}/\alpha\langle 3p_y|$$

$$\langle 2p_z|y = \left(\frac{3}{2}\right)^{1/2}/\alpha\langle 3d_{yz}|$$

$$\langle 2p_y|y = 1/\alpha\left\{\left(\frac{5}{2}\right)^{1/2}\langle 3s| - \left(\frac{1}{2}\right)^{1/2}\langle 3d_{z^2}| - \left(\frac{3}{2}\right)^{1/2}\langle 3d_{x^2-y}|\right\}$$

$$\langle 3s|y = \left(\frac{14}{3}\right)^{1/2}/\alpha\langle 4p_y|$$

$$\langle 3p_z|y = \left(\frac{14}{5}\right)^{1/2}/\alpha\langle 4d_{yz}|$$

$$\langle 3p_y|y = 1/\alpha\left\{\left(\frac{14}{3}\right)^{1/2}\langle 4s| - \left(\frac{14}{15}\right)^{1/2}\langle 4d_{z^2}| - \left(\frac{14}{5}\right)^{1/2}\langle 4d_{x^2-y^2}|\right\}$$

$$\langle 3d_{z^2}|y = 1/\alpha\left\{-\left(\frac{14}{15}\right)^{1/2}\langle 4p_y| + \left(\frac{12}{5}\right)^{1/2}\langle 4f_{yz^2}|\right\}$$

$$\langle 3d_{yz}|y = 1/\alpha\left\{\left(\frac{14}{5}\right)^{1/2}\langle 4p_z| - \left(\frac{6}{5}\right)^{1/2}\langle 4f_{z^3}| - \sqrt{2}\langle 4f_{z(x^2-y^2)}|\right\}$$

$$\langle 3d_{xy}|y = 1/\alpha\left\{\left(\frac{14}{5}\right)^{1/2}\langle 4p_x| - \left(\frac{1}{5}\right)^{1/2}\langle 4f_{xz^2}| - \sqrt{3}\langle 4f_{x(x^2-y^2)}|\right\}$$

4. 쌍극자모멘트의 행렬요소를 계산하는 두 방법의 비교

몇 개의 쌍극자모멘트의 행렬요소를 spherieal harmonic의 전개방법을 사용하여 계산하였고, 이에 대응하는 전환 overlap integral을 Mulliken의 overlap integral의 기본식을 써서 계산하여 *Table* 3에 나타내었다.

Table 3의 보기에 나타난 것처럼 spherical harmonics의 전개방법을 사용하여 계산한 쌍극자모멘트의 값이 Mulliken의 방법에 의하여 계산한전환 overlap intergral의 값과 일치한다.

주양자수 $n\geq 4$인 Slater 원자궤도함수에 대하여 spherical harmonic의 전개방법에 의하여 계산한 쌍극자모멘트의 행렬요소가 rounding error 때문에 너무 큰 값을 가진다[9]. 그러나 쌍극자모멘트의 행렬요소를 Mulliken의 overlap integral로 전환시킨 다음 쌍극자모멘트의 행렬요소를 계산해도 $n\geq 4$인 Slater orbital에 대해서 정확한 쌍극자모멘트의 행렬요소의 값을 얻을 수

Table 3(a) The numerical results for the dipole moment matrix elements and the corresponding transformed overlap integrals ($r=1.5$Å).

Dipole moment matrix elements	Numerical value	Transformed overlap integral	Numerical value
$\langle 1s\|z\|1s\rangle$	0.0783740	$\frac{1}{\alpha}\langle 1s\|2p_z\rangle$	0.0783740
$\langle 2s\|z\|2s\rangle$	0.3064773	$\left(\frac{5}{2}\right)^{1/2}/\alpha\langle 2s\|3p_z\rangle$	0.3064774
$\langle 2s\|z\|1s\rangle$	0.2036565	$\left(\frac{5}{2}\right)^{1/2}/\alpha\langle 1s\|3p_z\rangle$	0.2036565
$\langle 1s\|z\|2s\rangle$	0.1260920	$\frac{1}{\alpha}\langle 2s\|2p_z\rangle$	0.1260920
$\langle 2s\|z\|3p_z\rangle$	−0.2396521	$\left(\frac{5}{2}\right)^{1/2}/\alpha\langle 2p_z\|3p_z\rangle$	−0.2396519
$\langle 2p_z\|z\|2p_z\rangle$	0.3573951	$\left(\frac{5}{2}\right)^{1/2}/\alpha\left\{\langle 2p_z\|3s\rangle + \frac{2}{\sqrt{5}}\langle 2p_z\|3d_{z^2}\rangle\right\}$	−0.3573949
$\langle 2p_x\|z\|2p_x\rangle$	0.1422311	$\left(\frac{3}{2}\right)^{1/2}/\alpha\langle 2p_x\|3d_{xz}\rangle$	0.1423310

Calculation of the above dipole moment matrix elements are carried out for a hypothetical molecule of NO whose Slater constants for the oxygen and nitrogen atoms are 2,275(α) and 1.625(β) respectively. The oxygen atom is chosen as the point *A* of *Fig.* 1.

Table 3(b). The numerical results for the dipale moment matrix elements and the corresponding transformed everlap integrals.

The dipole moment matrix element	Numerical Value	The transformed overlap integral	Numerical value	r(Å)
$\langle 3s\|z\|2s\rangle$*	0.9978	$\left(\frac{14}{3}\right)^{1/2}/\alpha\ \langle p_z\|2s\rangle$	0.9978	2.13
$\langle 3s\|z\|2p_z\rangle$*	−0.2997	$\left(\frac{14}{3}\right)^{1/2}/\alpha\ \langle 2p_z\|4p_z\rangle$	−0.2997	〃
$\langle 3p_z\|z\|2s\rangle$*	1.5390	$\left(\frac{14}{3}\right)^{1/2}/\alpha\ \langle 4s\|2s\rangle + (56/15)^{1/2}/\alpha\langle 4d_z^2\|2s\rangle$	1.5390	〃
$\langle 3p_y\|z\|2p_y\rangle$*	0.4907	$\left(\frac{14}{3}\right)^{1/2}/\alpha\ \langle 4d_z\|2p_y\rangle$	0.4907	〃
$\langle 5s\|z\|2s\rangle$**	1.1881	$\left(\frac{15}{2}\right)^{1/2}/\alpha\langle 5p_z\|2s\rangle$	1.1881	2.25
$\langle 5s\|z\|2p_z\rangle$**	−0.1486	$\left(\frac{15}{2}\right)^{1/2}/\alpha\ \langle 5p_z\|2p_z\rangle$	−0.1486	〃

* The dipole moment matrix elements for Mg-C bond whose Slater constants for Mg and C are 1.1025 and 1.625, repectively; **The dipole moment matrix elements for Cd-C bond whose Slater constants for Cd and C are 1.10 and 1.625, respectively.

있기는 하지만[9] Euler transformation matrix[10]를 사용하여 주어진 분자에 있어서 원자의 좌표계를 쌍극자모멘트의 방향으로 좌표변환하는 것이 필요하며 좌표변환이 복잡하기 때문에 때로는 오차를 유발시킬 수도 있다. Spherical harmonics의 전개방법에 의한 쌍극자모멘트의 행렬요소를 계산하는 방법은 간단한 분자[11] 및 전이원소의 R-diimine 착물[12]의 쌍극자모멘트, 그리고 간단한 분자의 편극률텐서[13]를 계산하는데 사용하였으며 쌍극자모멘트의 행렬요소를 Mulliken의 overlap integral로 전환시키는 방법은 mercapto-β-diketone의 전이원소착물 및 [Se-SalenN(R′)R]$_2$M(II)착물[14]의 쌍극자모멘트를 계산하는데 적용하였다.

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