DAEHAN HWAHAK HWOEJEE
(Journal of the Korean Chemical Society)
Vol. 22, No. 3, 1978
Printed in Repubilc of Korea

분자계의 Orevlap Integral의 계산의 Spherical Harmonics 전개방법의 응용

安 商 雲*

호주 New South Wales 대학교 물리화학과

(1977. 12. 1 접수)

Application of the Expansion Method for Spherical Harmonics for Computation of Overlap Integnals in Molecular System

Sangwoon Ahn*

Department of Physical Chemistry, University of New South Wales, Sydeny, Australia

(Recived Dec. 1, 1977)

요 약. 두점 A와 B에 위치한 Slater 원자궤도함수의 spherical harmonics 부와 지름부를 기준점 A를 중심으로 전개하여 공통좌표상에 기술하였다.

이 Slater 원자궤도함수의 전개식을 사용하여 two center overlap integral의 기본식을 유도하였으며 이 기본식을 이용하여 CH_4, H_2O, NH_3, C_2H_6 및 PH_3 분자의 two center overlap integral을 계산하였을 때 이 값이 Mulliken의 값과 일치하였다.

ABSTRACT. Slater type orbitals, located at two different points A and B, are expressed in a common coordinate system by expanding the spherical harmonics and the radial part of these orbitals in terms of the reference point A.

Master formulas for two center overlap integrals are derived, using the general expansion formulas of slater type atomic orbitals. Two center overlap integrals for CH_4, H_2O, NH_3, C_2H_6 and PH_3 molecules are evaluated, using master formulas for two center overlap integrals.

The results are in agreement with those of two center overlap integrals of Mulliken.

1. 서 론

전자의 파동함수는 원자궤도함수를 사용하여 다음과 같이 기술할 수 있다.

$$\phi_{nlm}=R_{nl}(r)Y_{lm}(\theta,\phi) \tag{1}$$

여기에서 $R_{nl}(r)$은 지름파동함수이고 $Y_{lm}(\theta,\phi)$은 Spherical harmonic이다. 문제를 간단히 하기위하여 원자궤도함수로서 Slater 원자궤도함수[1,2]를 택하면 전자의 파동함수는 식(2)가 된다.

*Department of Chemistry, Joeonbuk National University, Jeonju, Korea

$$\phi_{nlm}=Nr^{n-1}\exp(-\alpha r)\ Y_{lm}(\theta,\phi) \quad (2)$$

여기에서 N는 규격화상수이고 α는 Slater 상수 ($\alpha=Z/n^*$)이다.

두 점 A 및 B에 위치한 두 원자궤도함수 ϕ_A 및 ϕ_B 사이의 two center overlap integral은 식(3)과 같이 정의된다.

$$S_{AB}=\int_0^\infty \phi_A^*\phi_B d\zeta=\langle\phi_A|\phi_B\rangle \quad (3)$$

n=1, 2, 3 및 5인 경우 ns np_σ 및 np_π 등의 Slater 원자궤도함수쌍에 대한 two center overlap integral이 Mulliken[4]등에 의하여 체계적이고 포괄적으로 연구되었고 이들 원자궤도함수쌍에 대하여 two center overlap integral의 기본식이 유도되었다. *Fig.* 1에 나타낸 것처럼 A 및 B에 위치한 Slater 원자궤도함수쌍에 대한 two center overlap integral을 계산하기 위하여 Mulliken 등은 Slater 원자궤도함수의 극좌표를 타원자표(Spheroidal coordinate)로 좌표 변환하였다.

$$\mu=(r_A+r_B)/R,\ \nu=(r_A-r_B)/R,\ \phi=\phi \quad (4)$$

여기에서 좌표한계(Coordinate limit)와 미분체적소는

$$1\le\mu\le\infty,\ 1\le\nu\le1 \text{ 및 } 0\le\phi\le2\pi \quad (5)$$

$$d\zeta=\left(\frac{R}{2}\right)^3(\mu^2-\nu^2)d\mu d\nu d\phi \quad (6)$$

n=3 및 5인 Slater 원자궤도함수 np_π, nd_π, nd_σ 쌍사이의 two center overlap integral이 Jaffe[5] 및 Liefer[6]등에 의하여 연구되었고 nd_σ 원자궤도함수쌍에까지 확장되었다.

s, p, d, f, g 및 h 원자궤도함수 사이의 two center overlap integral에 대한 일반식이 Lofthus에 의하여 유도되었다. Slater 원자궤도함수에 대한 Mulliken의 two center overlap integral은 식(7)과 같이 기술할 수 있다[7].

$$\langle\phi_A|\phi_B\rangle=[p(1+t)]^{nA+1/2}[p(1-t)]^{nB+1/2}[(2n_A)!(2n_B)!]^{-1/2}\left\{\int_1^\infty\int_{-1}^1(\mu+\nu^{nA})(\mu-\nu)^{nB}\exp[-p(\mu+t\nu)]\theta_{lA}^{mA}(\mu,\nu)\theta_{lA}^{mA}(\mu,\nu)\theta_{lB}^{mB}(\mu,\nu)d\mu d\nu\right\} \quad (7)$$

여기에서

$$p=(\alpha+\beta)R/2,\ t=(\alpha-\beta)/(\alpha+\beta)$$

(8)이며 (8)식의 α는 ϕ_A의 slater 상수이고 β는 ϕ_B의 Slater 상수이다.

Mulliken의 two center overlap integral에 있어서 두 원자의 중심을 잇는 선을 주축으로 정의하였고 두 원자의 중간점을 좌표의 기준점으로 택하였다(*Fig.* 1 참조).

본 연구에서는 Mulliken의 방법과 달리 식(15) 및 (16)에 기술한 것처럼 두 점에 위치한(*Fig.* 2 참조) Slater 원자궤도함수를 공통좌표상에[8] 전개하는 방법 즉, spherical harmonics의 전개방법을 사용하여 two center overlap integral을 계산하는 방법을 발전시켰다.

2. Slater 원자궤도함수의 전개

Slater 원자궤도함수가 *Fig.* 2의 B점에 위치

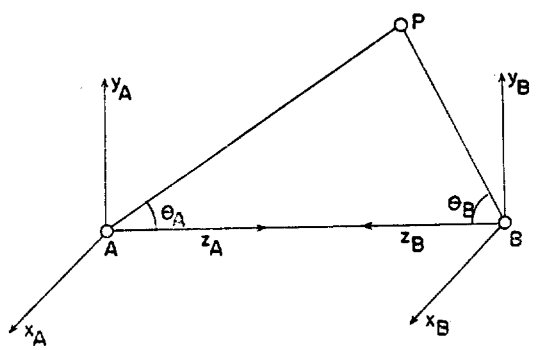

Fig. 1. The coordinate system for two center overlap integral of Mulliken.

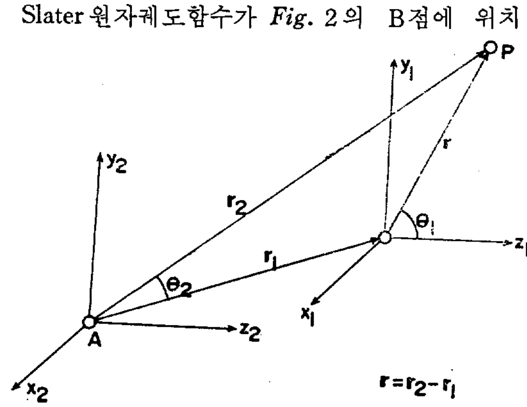

Fig. 2. The coordinate system for two center overlap integral of the expansion method.

한다고 가정하면 Moshinsky의 전개식[9,10]을 사용하여 Spherical harmonics부 및 지수파동함수부를 기준점 A의 좌표상에 다음과 같이 전개할 수 있다.

$$\phi_{nlm}=Nr^{n-1}\exp(-\beta r)Y_{lm}(\theta,\phi) \quad (9)$$

$$r^lY_{lm}(\theta,\phi)=\sum_{l_1=0}^{l}\sum_{l_2=0}^{l}\sum_{m_1=-l_1}^{l_1}\sum_{m_2=-l_2}^{l_2}(-1)^{l_1}\delta(l_1+l_2,l)\left\{\frac{4\pi(2l+1)!}{(2l_1+1)!(2l_2+1)!}\right\}^{\frac{1}{2}}\langle l_1l_2m_1m_2|l_1l_2lm\rangle r_1^{l_1}r_2^{l_2}Y_{l_1m_1}(\theta_1,\phi_1)Y_{l_2m_2}(\theta_2,\phi_2) \quad (10)$$

여기에서 $\langle l_12_2m_1m_2|l_1l_2lm\rangle$는 Clebsch-Gordan의 짝지음계수(coupling coefficient)이다.

$$\exp(-\beta r)=4\pi\sum_{n=0}^{\infty}b_n(r_1,r_2)\sum_{h=-n}^{n}Y_{nh}^*(\theta_1,\phi_1)Y_{nh}(\theta_2,\phi_2) \quad (11)$$

$$r\exp(-\beta r)=4\pi\sum_{n=0}^{\infty}z_n(r_1r_2)\sum_{h=-n}^{n}Y_{nh}^*(\theta_1,\phi_1)\cdot Y_{nh}(\theta_2\phi_2) \quad (12)$$

여기에서[11]

$$b_n(r_1,r_2)=(r_>/r_<)^{\frac{1}{2}}I_{n+\frac{1}{2}}(\beta r_<)K_{n+\frac{3}{2}}(\beta r_>)-(r_</r_>)^{\frac{1}{2}}I_{n-\frac{1}{2}}(\beta r_<)K_{n+\frac{1}{2}}(\beta r_>) \quad (13)$$

$$z_n(r_1,r_2)=\left(\frac{1}{r_1r_2}\right)^{\frac{1}{2}}\left\{(r_1^2+r_2^2)I_{n+\frac{1}{2}}(\beta r_<)K_{n+\frac{1}{2}}(\beta r_>)-\frac{2n}{2n+1}\gamma_1r_2I_{n-\frac{1}{2}}(\beta r_<)K_{n-\frac{1}{2}}(\beta r_>)+\frac{2(n+1)}{(2n+1)}r_1r_2I_{n+\frac{3}{2}}(\beta r_<)K_{n+\frac{3}{2}}(\beta r_>)\right\} \quad (14)$$

여기에서 $r_<$는 r_1과 r_2의 작게, $r_>$는 r_1과 r_2의 크게이고 I_ν 및 K_ν는 수정 Bessel 함수[11,12]이다.

Spherical harrmonics부와 지수파동함수부를 합하면 B점에 위치한 Slater 궤도함수에 대한 두개의 전개식(15), (16)을 얻을 수 있다.

$$|\phi_B\rangle=Nr^l\exp(-\beta r)Y_{lm}(\theta,\phi)=4\pi N\sum_{l_1=0}^{l}\sum_{l_2=0}^{l}\sum_{m_1=-l_1}^{l_1}\sum_{m_2=-l_2}^{l_2}(-1)^{l_1}\delta(l_1+l_2,l)\left\{\frac{4\pi(2l+1)!}{(2l_1+1)!(2l_2+1)!}\right\}^{\frac{1}{2}}\langle l_1l_2m_1m_2|l_1l_2lm\rangle\sum_{n=0}^{\infty}b_n(r_1,r_2)r_1^{l_1}r_2^{l_2}\sum_{h=-n}^{n}Y_{nh}^*(\theta_1,\phi_1)\,Y_{l_1m_1}(\theta_1,\phi_1)Y_{nh}(\theta_2,\phi_2)\,Y_{l_2m_2}(\theta_2\phi_2) \quad (15)$$

$$|\phi_B'\rangle=Nr^{l+1}\exp(-\beta r)Y_{lm}(\theta,\phi)=4\pi N\sum_{l_1=0}^{l}\sum_{l_2=0}^{l}\sum_{m_1=-l_1}^{l_1}\sum_{m_2=-l_2}^{l_2}(-1)^{l_1}\delta(l_1+l_2,l)\left\{\frac{4\pi(2l+1)!}{(2l_1+1)!\,(2l_2+1)!}\right\}^{\frac{1}{2}}\langle l_1l_2m_1m_2|l_1l_2lm\rangle\sum_{n=0}^{\infty}z_n(r_1,r_2)r_1^{l_1}r_2^{l_2}\sum_{h=-n}^{n}Y_{nh}^*(\theta_1,\phi_1)\,Y_{l_1m_1}(\theta_1,\phi_1)\,Y_{nh}(\theta_2\phi_2)\,Y_{l_2m_2}(\theta_2,\phi_2) \quad (16)$$

3. Two Center Overlap Integral의 기본식

식 (15) 및 (16)을 사용하여 *Fig.* 2에 있어서 점 A에 위치한 Slater 원자궤도함수 ϕ_A와 점 B에 위치한 ϕ_B 사이의 two center overlap integral의 일반식을 얻을 수 있다[13].

$$\phi_A=Mr_2^{\pi}\exp(-\alpha r_2)Y_{l3m3}(\theta_2,\phi_2) \quad (17)$$

여기에서 M는 규격화상수이다.

$$\langle\phi_A|\phi_B\rangle=4\pi NM\sum_{l_1=0}^{l}\sum_{l_2=0}^{l}\sum_{m_1=-l_1}^{l_1}\sum_{m_2=-l_2}^{l_2}\sum_{h=-n}^{n}\sum_{n=0}^{\infty}\sum_{l_4=|n-l_1|}^{n+l_1}\sum_{l_4=-m_4}^{m_4}(-1)^{l_2+h+m_3-m}\delta(l_1+l_2,l)(2l+1)(2n+1)\left\{\frac{(2l_3+1)(2l_4+1)(2l)!}{4\pi(2l_1)!(2l_2)!}\right\}^{\frac{1}{2}}r_1^{l_1}Y_{l_4m_4}^*(\theta_1,\phi_1)\int_0^{\infty}b_n(r_1r_2)r_2^{2+l_2+u}\exp(-\alpha r_2)dr_2\begin{pmatrix}l_1&l_2&l_k\\m_1&m_2&-m\end{pmatrix}\begin{pmatrix}n&l_1&l_4\\-h&m_1&m_4\end{pmatrix}\begin{pmatrix}l_3&n&l_2\\-m_3&h&m_2\end{pmatrix}\begin{pmatrix}l_3&n&l_2\\0&0&0\end{pmatrix}\begin{pmatrix}n&l_1&l_4\\0&0&0\end{pmatrix} \quad (18)$$

$$\langle\phi_A|\phi_B'\rangle=4\pi NM\sum_{l_1=0}^{l}\sum_{l_2=0}^{l}\sum_{m_2=-l_1}^{l_1}\sum_{m_1=-l_2}^{l_2}\sum_{h=-n}^{n}\sum_{n=0}^{\infty}\sum_{l_4=|n-l_1|}^{n+l_1}\sum_{l_4=-m_4}^{m_4}(-1)^{l_2+h+m_3-m}\delta(l_1+l_2,l)(2l+1)(2n+1)\left\{\frac{(2l_3+1)(2l_4+1)(2l)!}{4\pi(2l_1)!(2l_2)!}\right\}^{\frac{1}{2}}r_1^{l_1}Y_{l_4m_4}^*(\theta_1,\phi_1)\int_0^{\infty}z_n(r_1,r_2)\,r_2^{2+l+u}\exp(\alpha r_2)dr_2\begin{pmatrix}l_1&l_2&l_k\\m_1&m_2&-m\end{pmatrix}\begin{pmatrix}n&l_1&l_4\\-h&m_1&m_4\end{pmatrix}\begin{pmatrix}l_3&n&l_3\\-m_3&h&m_2\end{pmatrix}\begin{pmatrix}l_3&n&l_2\\0&0&0\end{pmatrix}\begin{pmatrix}nl_1l_4\\000\end{pmatrix} \quad (19)$$

n, l, l_2, l_3, l_4 및 m_1, m_2, m_3, m_4, h 및 n에 대응하는 3-j symbols[14]를 식(18)과 (19)에 넣어

주어 two Center Overlap intègral의 기본식을 유도하였고 이를 *Table* 1에 기술하였다.

여기에서 수정 Bessel 함수의 지름적분은 n 및 k의 값에 따라 *Table* 2과 같이 정의하였다.

Table 1. Master formulas for the two center over lapintegrdls.*

$\langle 1s|1s\rangle=4(\alpha/\beta)^{3/2}T_0$

$\langle 2s|1s\rangle=(16/3)^{1/2}(\alpha/\beta)^{5/2}Z_0$

$\langle 2p_z|1s\rangle=4(\alpha/\beta)^{5/2}\cos\theta Z_1$

$\langle 2p_x|1s\rangle=4(\alpha/\beta)^{5/2}\sin\theta\cos\phi\ Z_1$

$\langle 2p_y|1s\rangle=4(\alpha/\beta)^{5/2}\sin\theta\sin\phi\ Z_1$

$\langle 3s|1s\rangle=\left(\frac{32}{45}\right)^{1/2}(\alpha/\beta)^{7/2}\ V_0$

$\langle 3p_x|1s\rangle=\left(\frac{32}{15}\right)^{1/2}(\alpha/\beta)^{7/2}\sin\theta\cos\phi\ V_1$

$\langle 3p_y|1s\rangle=\left(\frac{32}{15}\right)^{1/2}(\alpha/\beta)^{7/2}\sin\theta\sin\phi\ V_1$

$\langle 3d_{z^2}|1s\rangle=\left(\frac{8}{9}\right)^{1/2}(\alpha/\beta)^{7/2}(2\cos^2\theta-\sin^2\theta)\ V_2$

$\langle 3d_{xz}|1s\rangle=\left(\frac{32}{3}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\sin\theta\cos\phi\ V_2$

$\langle 3d_{yz}|1s\rangle=\left(\frac{23}{3}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\sin\theta\sin\phi\ V_2$

$\langle 3d_{xy}|1s\rangle=\left(\frac{32}{3}\right)^{1/2}(\alpha/\beta)^{7/2}\sin^2\theta\cos\phi\sin\phi\ V_2$

$\langle 3d_{x^2-y^2}|1s\rangle=\left(\frac{8}{3}\right)^{1/2}(\alpha/\theta)^{7/2}\sin^2\theta\ [\cos^2\phi-\sin^2\phi]\ V_2$

$\langle 1s|2s\rangle=4(\alpha/\beta)^{3/2}F_0$

$\langle 2p_z|2s\rangle=\left(\frac{4}{3}\right)(\alpha/\beta)^{5/2}\cos\theta\ C_1$

$\langle 2s|2s\rangle=\left(\frac{4}{3}\right)(\alpha/\beta)^{5/2}C_0$

$\langle 2p_x|2s\rangle=\left(\frac{16}{3}\right)^{1/2}(\alpha/\beta)^{5/2}\sin\theta\cos\phi\ C_1$

$\langle 2p_y|2s\rangle=\left(\frac{16}{3}\right)^{1/2}(\alpha/\beta)^{5/2}\sin\theta\sin\phi\ C_1$

$\langle 3p_x|2s\rangle=\left(\frac{32}{45}\right)^{1/2}(\alpha/\beta)^{7/2}\sin\theta\cos\phi\ B_1$

$\langle 3p_y|2s\rangle=\left(\frac{32}{45}\right)^{1/2}(\alpha/\beta)^{7/2}\sin\theta\sin\phi\ B_1$

$\langle 3d_{z^2}|2s\rangle=\left(\frac{32}{27}\right)^{1/2}(\alpha/\beta)^{7/2}(2\cos^2\theta-\sin^2\theta)\ B_2$

$\langle 3d_{xz}|2s\rangle=\left(\frac{32}{9}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\sin\theta\cos\phi\ B_2$

$\langle 3d_{yz}|2s\rangle=\left(\frac{32}{9}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\sin\theta\sin\phi\ B_2$

$\langle 3d_{x^2-y^2}|2s\rangle=\left(\frac{8}{9}\right)^{1/2}(\alpha/\beta)^{7/2}\sin^2\theta\ [\cos^2\phi-\sin^2\phi]\ B_2$

$\langle 3d_{xy}|2s\rangle=\left(\frac{32}{9}\right)^{1/2}(\alpha/\beta)^{7/2}\sin^2\theta\cos\phi\sin\phi\ B_2$

$\langle 2p_z|2p_z\rangle=\left(\frac{4}{3}\right)(\alpha/\beta)^{5/2}\ \{V_0+[2\cos^2\theta-\sin^2\theta]\ V_2-[1-(2\cos^2\theta-\sin^2\theta)]aZ_1\}$

$\langle 2p_x|2p_z\rangle=4(\alpha/\beta)^{5/2}\cos\theta\sin\theta\cos\phi\ [V_2-aZ_1]$

$\langle 2p_y|2p_z\rangle=4(\alpha/\beta)^{5/2}\cos\theta\sin\theta\sin\phi\ [V_2-aZ_1]$

$\langle 3s|2p_z\rangle=\left(\frac{32}{45}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\ [W_1-aV_0]$

$\langle 3p_z|2p_z\rangle=\left(\frac{32}{135}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{W_0+[2\cos^2\theta-\sin^2\theta]\ W_2-[1+(2\cos^2\theta-\sin^2\theta)]aV_1\}$

$\langle 3p_x|2p_z\rangle=\left(\frac{32}{15}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\ \sin\theta\ \cos\phi\ [W_2-aV_1]$

$\langle 3p_y|2p_z\rangle=\left(\frac{32}{15}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\ \sin\theta\ \sin\phi\ [W_2-aV_1]$

$\langle 3d_{z^2}|2p_z\rangle=\left(\frac{32}{225}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{3(2\cos^3\theta-3\cos\theta\sin^2\theta)\ W_3+2\cos\theta W_1-[2\cos\theta+3(2\cos^3\theta-3\cos\theta\ \sin^2\theta)]\ aV_2\}$

$\langle 3d_{xz}|2p_z\rangle=\left(\frac{288}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\sin\theta\ \cos\phi\ [W_1-aV_0]+(4\cos^3\theta\sin\theta-\sin^3\theta)\ \cos\phi\ [W_3-aV_2]\}$

$\langle 3d_{yz}|2p_z\rangle=\left(\frac{228}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\sin\theta\ \sin\phi\ [W_1-aV_0]+(4\cos^2\theta\ \sin\theta-\sin^3\theta)\ \sin\phi\ [W_3-aV_2]\}$

$\langle 3d_{xy}|2p_z\rangle=\left(\frac{32}{3}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\ \sin^2\theta\ \cos\phi\ \sin\phi\ [W_3-aV_2]$

$\langle 3d_{x^2-y^2}|2p_z\rangle=\left(\frac{8}{3}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\ \sin^2\theta\ [\cos^2\phi-\sin^2\phi]\ [W_3-aV_2]$

$\langle 2p_x|2p_x\rangle=\left(\frac{4}{3}\right)(\alpha/\beta)^{5/2}\ \{V_0-[\frac{1}{2}(2\cos^2\theta-\sin^2\theta)+\frac{3}{2}\sin^2\theta\ \ (\cos^2\phi-\sin 2\phi)]\ V_2-[1-\frac{1}{2}\ (2\cos^2\theta-\sin^2\theta)-\frac{3}{2}$
$\sin^2\theta\ (\cos^2\phi-\sin^2\phi)]aZ_1\}$

$\langle 3p_z|2p_x\rangle=\left(\frac{32}{15}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\ \sin\theta\ \cos\phi\ [W_2-aV_1]$

$\langle 2p_y|2p_x\rangle=4(\alpha/\beta)^{5/2}\sin^2\theta\ \cos\phi\ \sin\phi\ [V_2-aZ_1]$

$\langle 3p_x|2p_x\rangle=\left(\frac{32}{135}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{W_0-\frac{1}{2}\ (2\cos^2\theta-\sin^2\theta)W_2-[1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)]\ aV_1+\frac{3}{2}\sin^2\theta\ (\cos^2\phi-\sin^2\phi)$
$[W_2-aV_1]\}$

$\langle 3s|2p_x\rangle=\left(\frac{32}{45}\right)^{1/2}(\alpha/\beta)^{7/2}\sin\theta\ \cos\phi\ [W_1-aV_0]$

$\langle 3p_y|2p_x\rangle=\left(\frac{32}{15}\right)^{1/2}(\alpha/\beta)^{7/2}\sin^2\theta\ \cos\phi\ \sin\phi\ [W_2-aV_1]$

$\langle 3d_{xz}|2p_x\rangle=\left(\frac{32}{75}\right)^{1/2}(\alpha/\beta)^{7/2}\ [\cos\theta W_1-\frac{1}{2}(2\cos^3\theta-3\cos\theta\ \sin^2\theta)W_3-[\cos\theta-\frac{1}{2}\ (2\cos^3\theta-3\cos\theta\ \sin^2\theta)]aV_2$
$+\frac{5}{2}\cos\theta\ \sin\theta\ (\cos^2\phi-\sin^2\phi)\ [W_3-aV_2]\}$

$\langle 3d_{z^2}|2p_x\rangle=\left(\frac{32}{225}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{-\sin\theta\ \cos\phi\ [W_1-aV_0]+\frac{3}{2}[4\cos^2\theta\ \sin\theta-\sin^3\theta]\ \cos\phi\ [W_3-aV_2]\}$

$\langle 3d_{xy}|2p_x\rangle=\left(\frac{32}{75}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\sin\theta\ \sin\phi\ [W_1-aV_0]-\frac{1}{4}[4\cos^2\theta\ \sin\theta-\sin^3\theta]\ \sin\phi\ [W_3-aV_2]+\frac{5}{4}\sin^3\theta$
$[3\sin\phi-4\sin^3\phi][W_3-aV_2]\}$

$\langle 3d_{x^2-y^2}|2p_x\rangle=\left(\frac{32}{75}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\sin\theta\ \cos\phi\ [W_1-aV_0]-\frac{1}{4}\ [4\cos^2\theta\ \sin\theta-\sin^3\theta]\cos\phi\ [W_3-aV_2]-\frac{5}{4}\sin^3\theta$
$[4\cos^3\phi-3\cos\phi]\ [W_3-aV_2]\}$

$\langle 2p_y|2p_y\rangle=\left(\frac{4}{3}\right)(\alpha/\beta)^{5/2}\ \{V_0-\left[\frac{1}{2}\ (2\cos^2\theta-\sin^2\theta)-\frac{3}{2}\sin^2\theta\ (\cos^2\phi-\sin^2\phi)\right]\ V^2-[1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)$
$+\frac{3}{2}\sin^2\theta\ (\cos^2\phi-\sin^2\phi)]\ aZ_1\}$

$\langle 3s|2p_y\rangle=\left(\frac{32}{45}\right)^{1/2}(\alpha/\beta)^{7/2}\sin\theta\ \sin\phi\ [W_1-aV_0]$

$\langle 3p_x|2p_y\rangle=\left(\frac{32}{15}\right)^{1/2}(\alpha/\beta)^{7/2}\sin^2\theta\ \cos\phi\ \sin\phi\ [W_2-aV_1]$

$\langle 3p_z|2p_y\rangle=\left(\frac{32}{15}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\sin\theta\ \sin\phi\ [W_2-aV_1]$

$\langle 3p_y|2p_y\rangle=\left(\frac{32}{135}\right)^{1/2}(\alpha/\beta)^{7/2}\{W_0-\frac{1}{2}\ (2\cos^2\theta-\sin^2\theta)W_2-[1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)]\ aV_1-\frac{3}{2}\sin^2\theta\ (\cos^2\phi-\sin^2\phi)$

$$(W^2-aV_1)\}$$

$$\langle 3d_{yz}|2p_y\rangle=\left(\frac{32}{75}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\cos\theta W_1-\frac{1}{2}\ (2\cos^3\theta-3\cos\theta\ \sin^3\theta)W_3-(\cos\theta-\frac{1}{2}(2\cos^3\theta-3\cos\theta\ \sin^2\theta))aV_2$$
$$-\left(\frac{5}{2}\right)\cos\theta\ \sin^2\theta\ (\cos^2\phi-\sin^2\phi)\ (W_3-aV_2)\}$$

$$\langle 3d_{z^2}|2p_y\rangle=-\left(\frac{32}{225}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\sin\theta\ \sin\phi\ (W_1-aV_0)-(4\cos^2\theta\ \sin\theta-\sin^3\theta)\ \sin\phi\ (W_3-aV_2)\}$$

$$\langle 3d_{xy}|2p_y\rangle=\left(\frac{32}{75}\right)(\alpha/\beta)^{7/2}\ \{\sin\theta\ \cos\phi\ (W_1-aV_0)\ -\frac{1}{4}\ (4\cos^2\theta\sin\theta-\sin^3\theta)\ (W_3-aV_2)$$
$$+\frac{5}{4}\ \sin^3\theta\ (4\cos^3\phi-3\cos\phi)(W_3-aV_2)\}$$

$$\langle 3d_{x^2-y^2}|2p_y\rangle=-\left(\frac{32}{75}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\sin\theta\ \sin\phi\ (W_1-aV_0)-\frac{1}{4}(4\cos^2\theta\ \sin\theta-\sin^3\theta)\sin\phi\ (W_3-aV_2)$$
$$-\frac{5}{4}\ \sin^3\theta\ (3\sin\phi-4\sin^3\phi)(W_3-aV_2)\}$$

$$\langle 3s|3p_z\rangle=\left(\frac{64}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\ (H_1-aB_0)$$

$$\langle 3p_z|3p_z\rangle=\left(\frac{8}{45}\right)(\alpha/\beta)^{7/2}\ \{H_0+(2\cos^2\theta-\sin^2\theta))H_2-(1+(2\cos^2\theta-\sin^2\theta))\ aB_1\}$$

$$\langle 3p_x|3p_z\rangle=\left(\frac{64}{225}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\ \sin\theta\ \cos\phi\ (H_2-aB_1)$$

$$\langle 3p_y|3p_z\rangle=\left(\frac{64}{225}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\ \sin\theta\ \sin\phi\ (H_2-aB_1)$$

$$\langle 3d_{z^2}|3p_z\rangle=\left(\frac{64}{3375}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{2\cos\theta\ H_1+3\ (2\cos^3\theta-3\cos\theta\sin^2\theta)\ H_3-(2\cos\theta+3(2\cos^3\theta-3\cos\theta\ \sin^2\theta))\ aB_2\}$$

$$\langle 3d_{xz}|3p_z\rangle=\left(\frac{64}{1125}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\sin\theta\ \cos\phi\ (H_1-aB_0)+(4\cos^2\theta\ \sin\theta-\sin^3\theta)\ \cos\phi\ (H_3-aB_2)\}$$

$$\langle 3d_{yz}|3p_z\rangle=\left(\frac{64}{1125}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\sin\theta\ \sin\phi\ (H_1-aB_0)+(4\cos^2\theta\ \sin\theta-\sin^3\theta)\ \sin\phi\ (H_3-aB_2)\}$$

$$\langle 3d_{xy}|3p_z\rangle=\left(\frac{64}{45}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\sin^2\theta\ \cos\phi\ \sin\phi\ (H_3-aB_2)$$

$$\langle 3d_{x^2-y^2}|3p_z\rangle=\left(\frac{16}{45}\right)^{1/2}(\alpha/\beta)^{7/2}\cos\theta\ \sin^2\theta\ (\cos^2\phi-\sin^2\phi)\ (H_3-aB_2)$$

$$\langle 3s|3p_x\rangle=\left(\frac{64}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\sin\theta\ \cos\phi\ (H_2-aB_1)$$

$$\langle 3p_y|3p_x\rangle=\left(\frac{8}{15}\right)(\alpha/\beta)^{7/2}\sin^2\theta\ \cos\phi\ \sin\phi\ (H_2-aB_1)$$

$$\langle 3d_{z^2}|3p_x\rangle=-\left(\frac{64}{3375}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\sin\theta\ \cos\phi\ (H_1-aB_0)-(4\ \cos^2\theta\ \sin\theta-\sin^3\theta)\ \cos\phi\ (H_3-aB_2)\}$$

$$\langle 3d_{xz}|3p_x\rangle=\left(\frac{64}{1125}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\cos\theta\ H_1-\frac{1}{2}\ (2\cos^3\theta-3\cos\theta\ \sin^2\theta)H_3-(\cos\theta-\frac{1}{2}\ (2\cos^3\theta-3\cos\theta\ \sin^2\theta))\ aB_2$$
$$+\frac{5}{2}\ \cos\theta\ \sin^2\theta\ (H_3-aB_2)\}$$

$$\langle 3d_{xy}|3p_x\rangle=\left(\frac{64}{1164}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\sin\theta\ \sin\phi\ (H_1-aB_0)-\frac{1}{4}(4\cos^2\theta\ \sin\theta-\sin^3\theta)\ \sin\phi\ (H_3-aB_2)$$
$$-\frac{5}{4}\ \sin^3\theta\ (4\cos^3\phi-3\cos\phi)\ (H_3-aB_2)\}$$

$$\langle 3s|3p_y\rangle=\left(\frac{64}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\sin\theta\ \sin\phi\ (H_2-aB_1)$$

$$\langle 3p_y|3p_y\rangle=\left(\frac{8}{45}\right)(\alpha/\beta)^{7/2}\ \{H_0-\frac{1}{2}\ (2\cos^2\theta-\sin^2\theta)H_2-(1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta))aB_1-\frac{3}{2}\sin^2\theta\ (\cos^2\phi-\sin^2\phi)$$
$$(H_2-aB_1)\}=\langle 3p_x|3p_x\rangle$$

$$\langle 3d_{z^2}|3p_y\rangle=-\left(\frac{64}{3375}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\sin\theta\ \sin\phi\ (H_1-aB_0)\ -(4\cos^2\theta\ \sin\theta-\sin^3\theta)\ \sin\phi\ (H_3-aB_2)\}$$

$$\langle 3d_{yz}|3p_z\rangle=\left(\frac{64}{1125}\right)^{1/2}(\alpha/\beta)^{7/2}\ [\cos\theta\ H_1-\frac{1}{2}\ (2\cos^3\theta-3\cos\theta\ \sin^2\theta)H_3-(\cos\theta-\frac{1}{2}\ (2\cos^3\theta-3\cos\theta\ \sin\theta))\ aB_2$$
$$+\frac{5}{2}\cos\theta\ \sin^2\theta\ [H_3-aB_2]\}$$

$$\langle 3d_{xy}|3p_y\rangle=\left(\frac{64}{1125}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\sin\theta\ \cos\phi\ [H_1-aB_0]-\frac{1}{4}\ [4\cos^2\theta\ \sin\theta-\sin^3\theta]\ \cos\phi\ [H_3-aB_2]$$
$$+\frac{5}{4}\sin^3\theta\ [3\sin\phi-4\sin^3\phi]\ [H_3-aB_2]\}$$

$$\langle 3d_{x^2-y^2}|3p_y\rangle=-\left(\frac{32}{75}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\sin\theta\ \sin\phi\ [W_1-aV_0]-\frac{1}{4}\ [4\cos^2\theta\ \sin\theta-\sin^3\theta)\ \sin\phi\ [W_3-aV_2]$$
$$-\frac{4}{5}\sin^3\theta\ [3\sin\phi-4\sin^3\phi]\ [W_3-aV_2]\}$$

$$\langle 3s|d_{z^2}\rangle=\left(\frac{64}{405}\right)^{1/2}(\alpha/\beta)^{7/2}\ \left\{\frac{1}{2}\ (2\cos^2\theta-\sin^2\theta)S_2-\frac{3}{2}\ [1+(2\cos^2\theta-\sin^2\theta)]\ aW_1+\frac{1}{2}\ (2\cos^2\theta-\sin^2\theta)\ a^2V_0\right\}$$

$$\langle 3d_{z^2}|3d_{z^2}\rangle=\left(\frac{8}{45}\right)(\alpha/\beta)^{7/2}\ [S_0+\frac{2}{7}\ (2\cos^2\theta-\sin^2\theta)\ S_2+\frac{9}{28}\ (35\cos^4\theta-30\cos^2\theta+3)\ S_4-\frac{4}{3}\ [1+(2\cos^2\theta-\sin^2\theta)]aW_1$$
$$-\frac{3}{7}\ \{3(2\cos^2\theta-\sin^2\theta)+(35\cos^4\theta-30\cos^2\theta+3))\ aW_3+[1+\frac{5}{7}\ (2\cos^2\theta-\sin^2\theta)$$
$$+\frac{9}{28}\ (35\cos^4\theta-30\cos^2\theta+3)\ a^2V_2\}$$

$$\langle 3d_{xz}|3d_{z^2}\rangle=\left(\frac{64}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\{\frac{5}{7}\cos\theta\ \sin\theta\ \cos\phi\ [S_2+a^2V_0]+\frac{15}{14}\sin\theta\{7\cos^3\theta-3\cos\theta]\ \cos\phi\ [S_4+a^2V_2]$$
$$-2\cos\theta\ \sin\theta\ \sin\phi\ aW_1-\frac{2}{7}\ [5\cos\theta\ \sin\theta\ \sin\phi+8\sin\theta\ (7\cos^3\theta-3\cos\theta)\ \cos\phi]aW_3\}$$

$$\langle 3d_{yz}|3d_{z^2}\rangle=\left(\frac{64}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{\frac{5}{7}\cos\theta\ \sin\theta\ \sin\phi\ [S_2+a^2V_0]+\frac{15}{14}\sin\theta\ (7\cos^3\theta-3\cos\theta)\ \sin\phi\ [S_4+a^2V_2]$$
$$-2\cos\theta\ \sin\theta\sin\phi\ aW_1-\frac{2}{7}\ [5\cos\theta\ \sin\theta\ \sin\phi+8\sin\theta\ (7\cos^3\theta-3\cos\theta)\ \sin\phi]aW_3\}$$

$$\langle 3d_{xy}|3d_{z^2}\rangle=-\left(\frac{64}{1323}\right)^{1/2}(\alpha/\beta)^{7/2}\ \{2\sin\theta\ \cos\phi\ \sin\phi\ [S_2+a^2V_0]+\frac{3}{2}\sin^2\theta\ [7\cos^2\theta-1]\ \cos\phi\ \sin\phi\ [S_4+a^2V_2]$$
$$+2\sin^2\theta\ \cos\phi\ \sin\phi\ [1+(7\cos^2\theta-1)]\ aW_3\}$$

$$\langle 3d_{x^2-y^2}|3d_{z^2}\rangle=-\left(\frac{64}{1323}\right)^{1/2}(\alpha/\beta)^{7/2}\ \left\{\frac{5}{7}\sin^2\theta\ [\cos^2\phi-\sin^2\phi]\ [S_2+a^2V_0]+\frac{15}{28}\sin^2\theta\ (7\cos^2\theta-1)\ (\cos^2\phi-\sin^2\phi)\right.$$
$$[S_4+a^2V_2]+\frac{5}{7}\sin^2\theta\ [\cos^2\phi-\sin^2\phi]\ [1+(7\cos^2\theta-1)]\ aW_3\}$$

$$\langle 3d_{xz}|3d_{xz}\rangle=\left(\frac{8}{45}\right)(\alpha/\beta)^{7/2}\ \{S_0+\frac{5}{7}\ (2\cos^2\theta-\sin^2\theta)+\frac{3}{2}\sin^2\theta\ (\cos^2\phi-\sin^2\phi)\ S_2+\frac{3}{14}\ [5\sin^2\theta\ (7\cos^2\theta-1)(\cos^2\phi$$
$$-\sin^2\phi)-(35\cos^4\theta-30\cos^2\theta+3)]\ S_4-[2+\frac{1}{2}\ (2\cos^2\theta-\sin^2\theta)+\frac{3}{2}\sin^2\theta\ (\cos^2\phi-\sin^2\phi)]\ aW_1$$
$$-\frac{3}{14}\ [(2\cos^2\theta-\sin^2\theta)-2\ (35\cos^4\theta-30\cos^2\theta+3)+5\sin^2\theta\ (\cos^2\phi-\sin^2\phi)+10\sin^2\theta\ (7\cos^2\theta-1)$$
$$(\cos^2\phi-\sin^2\phi)]aW_3+[1+\frac{5}{7}\ (2\cos^2\theta-\sin^2\theta)-\frac{3}{14}\ (35\cos^4\theta-30\cos^2\theta+3)+\frac{15}{14}\sin^2\theta(\cos^2\phi-\sin^2\phi)$$
$$+\frac{15}{14}\sin^2\theta\ (7\cos^2\theta-1)\ (\cos^2\phi-\sin^2\phi)]\ a^2V_2\}=\langle 3d_{yz}|3d_{yz}\rangle$$

$$\langle 3d_{x^2-y^2}|3d_{xz}\rangle=\left(\frac{8}{45}\right)(\alpha/\beta)^{7/2}\ [\frac{15}{7}\cos\theta\ \sin\theta\ \cos\phi\ S_2-\frac{15}{28}[\sin\theta(7\cos^3\theta-1)\ \cos\phi-7\sin^3\theta\ \cos\theta\ (4\cos^3\phi-3\cos\phi)]$$
$$S_4-3\cos\theta\ \sin\theta\ \cos\phi\ aW_1-3\ [\cos\theta\ \sin\theta\ \cos\phi+\frac{5}{2}\sin^3\theta\ \cos\theta\ (4\cos^3\phi-3\cos\phi)\ aW_3$$
$$+\frac{15}{7}[\cos\theta\ \sin\theta\cos\phi-\frac{1}{4}\sin\theta(7\cos^3\theta-3\cos\theta)\ \cos\phi+\frac{7}{4}\sin^3\theta\ \cos\theta\ (\cos^3\phi-3\cos\phi)]a^2V_2\}$$

$$\langle 3d_{xy}|3d_{xz}\rangle=\frac{8}{45}\ (\alpha/\beta)^{7/2}\left\{\frac{15}{7}\cos\theta\ \sin\theta\ \sin\phi\ S_2-\frac{15}{28}[\sin\theta\ (7\cos^3\theta-3\cos\theta)\ \sin\phi-7\sin^3\theta\ \cos\theta\ (3\sin\phi-4\sin^3\phi)]\ S_4\right.$$
$$-3\cos\theta\ \sin\theta\ \sin\phi\ aW_1-3[\cos\theta\ \sin\theta\ \sin\phi+\frac{5}{2}\sin^3\theta\ \cos\theta\ (3\sin\phi-4\sin^3\phi)]aW_3$$

$$+\frac{15}{7}\left[\cos\theta\ \sin\theta\ \sin\phi-\frac{1}{4}\ \sin\theta\ (7\cos^3\theta-3\cos\theta)\sin\phi+\frac{7}{4}\ \sin^3\theta\ \cos\theta\ (3\sin\phi-4\sin^3\phi)\right]a^2V_2\Big\}$$

$$\langle 3d_{xy}|3d_{yz}\rangle=\left(\frac{8}{45}\right)(\alpha/\beta)^{7/2}\Big\{\frac{15}{7}\cos\theta\ \sin\theta\ \cos\phi\ S_2-\frac{15}{28}\left[\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi-7\sin^3\theta\ \cos\theta\ (4\cos^3\phi-3\cos\phi)\right]S_4$$

$$-3\cos\theta\ \sin\theta\ \cos\phi\ aW_1-3\left[\cos\theta\ \sin\theta\ \cos\phi+\frac{5}{2}\ \sin^3\theta\ \cos\theta\ (4\cos^3\phi-3\cos\phi)\right]aW_3$$

$$+\frac{15}{7}\left[\cos\theta\ \sin\theta\ \cos\phi-\frac{1}{4}\ \sin\theta\ (7\cos^3\theta-3\cos\theta)\cos\phi-\frac{7}{4}\ \sin^3\theta\ \cos\theta\ (4\cos^3\phi-3\cos\phi)\right]a^2V_2\Big\}$$

$$\langle 3d_{x^2-y^2}|3d_{yz}\rangle=\left(\frac{8}{45}\right)(\alpha/\beta)^{7/2}\Big\{-\frac{15}{7}\cos\theta\ \sin\theta\ \sin\phi\ S_2+\frac{15}{28}\left[\sin\theta\ (7\cos^3\theta-3\cos\theta)\ \sin\phi+7\sin^3\theta\ (3\sin\phi-4\sin^3\phi)\right]S_4$$

$$+3\cos\theta\ \sin\theta\ \sin\phi\ aW_1+3\left[\cos\theta\ \sin\theta\ \sin\phi-\frac{5}{2}\sin^2\theta\ \cos\theta\ (3\sin\phi-4\sin^3\phi)\right]aW_3$$

$$-\frac{15}{7}\left[\cos\theta\ \sin\theta\ \sin\phi-\frac{1}{4}\ \sin\theta\ (7\cos^3\theta-3\cos\theta)\ \sin\phi-\frac{7}{4}\ \sin^3\theta\ \cos\theta\ (3\sin\phi-4\sin^3\phi)\right]a^2\ V_2\Big\}$$

where $a=\beta r$ and α is the Slater constont for the atomic orbital in bra vector and β that for atomic orbital in ket vector.

*Author omitted the subscript "1" of the polar and azimuthal angles in master formulas for two center overlap integrals.

Table 2(A). Definition of the radial part integrals.

K	$\int_0^\infty z_n(r_1,r_2)r_2^K\ \exp(-\alpha r_2)dr_2$	n				
		0	1	2	3	4
2	T_n	T_0				
3	Z_n	Z_0	Z_1			
4	V_n	V_0	V_1	V_2		
5	W_n	W_0	W_1	W_2	W_3	
6	S_n	S_0	S_1	S_2	S_3	S_4
7	X_n	X_0	X_1	X_2	X_3	X_4

The above radial integrals were integrated elsewhere.[21]

Table 2(B). Definition of the radial part integrals.

K	$\int_0^\infty z_n(r_1,r_2)r_2^K\ \exp(-\alpha r_2)dr_2$	n				
		0	1	2	3	4
2	F_n	F_0				
3	C_n	C_0	C_1			
4	B_n	B_0	B_1	B_2		
5	H_n	H_0	H_1	H_2	H_3	
6	I_n	I_0	I_1	I_2	I_3	I_4
7	E_n	E_0	E_1	E_2	E_3	E_4

The above radial integrals were integrated elsewhere.[21]

4. Two Center Overlap Integral의 계산에 기본식의 응용

Table 1에 제시한 기본식을 CH_4, H_2O, NH_3, C_2H_6, 및 PH_3 분자의 two center overlap integral을 계산하는데 적용하였다. 이미 설명한 spherical harmonics의 전개방법을 사용하여 계산한 two center overlap integral의 값을 Mulliken의 방법에 의하여 계산한 값과 함께 *Table* 3~7에 제시하였다. 여기에서 각 원자궤

Table 3. Two center overlap integrals for CH_4 molecule. *

Overlap integral	Expansion method	Mullliken	Overlap integral	Expansion method	Mulliken
$\langle 1s_c \| H \rangle$	0. 065569	0. 065557	$\langle 2p_{xc} \| H \rangle$	0. 281441	0. 281426
$\langle 2s_c \| H \rangle$	0. 516917	0. 516870	$\langle 2p_{yc} \| H \rangle$	0. 281441	0. 281426
$\langle 2p_{zc} \| H \rangle$	0. 281441	0. 281426	$\langle H \| H' \rangle$	0. 183255	0. 183259

* H indicates 1s atomic orbital of hydrogen atom.

Table 4. Overlap integral for H_2O molecule.

Overlap integral	Expansion method	Mulliken	Overlap integral	Expansion method	Mulliken
$\langle 2s_0 \| H \rangle$	0. 479005	0. 479010	$\langle 2p_{y0} \| H \rangle$	0. 302555	0. 302546
$\langle 2p_{z0} \| H \rangle$	0. 234263	0. 234279	$\langle 2p_{x0} \| H \rangle$	0	0

Table 5. Overlap integrals for NH_3 Molecule.

Overlap integral	Expansion method	Mulliben	Overlap integral	Expansion method	Mulliken
$\langle 2s_N \| H_1 \rangle$	0. 503457	0. 503426	$\langle 2p_{xN} \| H_1 \rangle$	0. 403210	0. 403250
$\langle 1s_N \| H_1 \rangle$	0. 061166	0. 061159	$\langle 2p_{xN} \| H_2 \rangle$	−0. 20165	−0. 201605
$\langle 2p_{zN} \| H_1 \rangle$		0. 163422	$\langle 2p_{yN} \| H_1 \rangle$	0	0
$\langle 2p_{yN} \| H_2 \rangle$	0. 34190	0. 349157	$\langle 2p_{yN} \| H_3 \rangle$	−0. 349190	−0. 349190

Table 6. Overlap integrals for C_2H_6 molecule.

Overlap integral	Expansion method	Mulliken	Overlap Integral	Expansion method	Mulliken
$\langle 1s_{c_1} \| H_1 \rangle$	0. 064357	0. 064352	$\langle 2p_{xc_1} \| H_5 \rangle$	0. 03348	0. 033425
$\langle 1s_{c_1} \| H_4 \rangle$	0. 005852	0. 00550	$\langle 2p_{yc_1} \| H_1 \rangle$	0	0
$\langle 2s_{c_1} \| H_1 \rangle$	0. 512176	0. 512156	$\langle 2p_{yc_1} \| H_2 \rangle$	0. 395521	0. 396080
$\langle 2s_{c_1} \| H_4 \rangle$	0. 114967	0. 114941	$\langle 2p_{yc_1} \| H_3 \rangle$	−0. 395521	−0. 395555
$\langle 2p_{xc_1} \| H_1 \rangle$	−0. 162806	−0. 162779	$\langle 2p_{yc_1} \| H_5 \rangle$	−0. 057899	−0. 057898
$\langle 2p_{zc_1} \| H_4 \rangle$	0. 123236	0. 123204	$\langle 2p_{yc_1} \| H_6 \rangle$	0. 057899	0. 057898
$\langle 2p_{xc_1} \| H_1 \rangle$	0. 456708	0. 456706	$\langle 2p_{xc_1} \| H_1 \rangle$	0. 066856	−0. 033425
$\langle 2p_{xc_1} \| H_2 \rangle$	−0. 228354	−0. 228345	$\langle 2p_{zc_2} \| H_4 \rangle$	0. 456708	0. 456706
$\langle 2p_{xc_1} \| H_3 \rangle$	−0. 228354	−0. 228345	$\langle 2p_{xc_1} \| H_2 \rangle$	−0. 033428	0. 066854
$\langle 2p_{xc_1} , H_4 \rangle$	0. 066856	0. 066854	$\langle 2p_{xc_5} \| H_5 \rangle$	0. 22835	0. 228345
$\langle 2p_{yc_2} \| H_2 \rangle$	0. 057899	0. 057718	$\langle 2p_{yc_2} \| H_5 \rangle$	−0. 395521	−0. 395535
$\langle 2p_{yc_2} \| H_3 \rangle$	−0. 057899	−0. 057898	$\langle 2p_{yc_2} \| H_6 \rangle$	0. 395521	0. 395535
$\langle 2p_{zc_2} \| H_6 \rangle$	0. 033428	0. 033425	$\langle 2p_{xc_2} \| H_3 \rangle$	−0. 033428	−0. 033425
$\langle 2p_{xc_2} \| H_6 \rangle$	0. 228354	0. 228345	$\langle 2p_{zc_2} \| H_1 \rangle$	−0. 123236	−0. 123204

Table 7. Two center overlap integrals for pH_3 molecule.

Overlap integrdl	Expansion method	Mulliken	Overldp integral	Expansion method	Mulliken
$\langle 1s_p \| H_1 \rangle$	0.007522	0.007521	$\langle 2p_{zp} \| H_2 \rangle$	−0.012609	−0.012607
$\langle 2s_p \| H_2 \rangle$	0.061072	0.061064	$\langle 2p_{zp} \| H_3 \rangle$	−0.012609	−0.012607
$\langle 2p_{zp} \| H_1 \rangle$	0.016282	0.016280	$\langle 2p_{yp} \| H_1 \rangle$	0	0
$\langle 2p_{xp} \| H_1 \rangle$	0.025217	0.025214	$\langle 2p_{yp} \| H_2 \rangle$	0.021839	0.021834
$\langle 2p_{yp} \| H_3 \rangle$	−0.021838	−0.021834	$\langle 3d_{xzp} \| H_2 \rangle$	−0.169746	−0.169744
$\langle 3s_p \| H_1 \rangle$	0.444464	0.444440	$\langle 3d_{xzp} \| H_3 \rangle$	−0.169746	−0.169744
$\langle 3p_{zp} \| H_3 \rangle$	0.278324	0.278303	$\langle 3d_{z^2p} \| H_1 \rangle$	−0.025220	−0.025246
$\langle 3p_{xp} \| H_1 \rangle$	0.431048	0.431039	$\langle 3d_{yzp} \| H_1 \rangle$	0	0
$\langle 3p_{xp} \| H_2 \rangle$	−0.215524	−0.215525	$\langle 3d_{yzp} \| H_2 \rangle$	0.294010	0.293990
$\langle 3p_{xp} \| H_3 \rangle$	−0.215524	−0.215525	$\langle 3d_{yzp} \| H_3 \rangle$	−0.294010	−0.293990
$\langle 3p_{yp} \| H_1 \rangle$	0	0	$\langle 3d_{x^2-y^2} \| H_1 \rangle$	0.262891	0.262897
$\langle 3p_{yp} \| H_2 \rangle$	0.073299	0.373280	$\langle 3d_{x^2-y^2} \| H_2 \rangle$	−0.131445	−0.131441

도함수의 Slater 상수는 Palke 및 Lipscomb의 최적치(Optimum value)[15]를 사용하였다.

CH_4 분자. Palke 및 Lipscomb[15]이 사용한 CH_4 분자의 기하학적인 구조를 택하여 CH_4분자의 Slater 원자궤도함수에 대한 two center overlap integral을 계산하였다(*Table* 3).

H_2O 분자. O-H 결합길이가 0.958Å이고 H-O-H결합각이 104.5°인 H_2O분자[16]의 two center overlap integral을 계산하였다(*Table* 4).

NH_3 분자. NH_3 분자의 two center overlap integral을 Palke 및 Lipscomb[15]의 평형구조를 택하여 계산하였다(*Table* 5).

C_2H_6분자. Palke 및 Lipscomb[15]의 C_2H_6분자의 평형구조를 택하여 two center overlap integral을 계산하였다(*Table* 6).

PH_3분자. Boyd 및 Lipscomb[17]의 평형구조를 택하여 PH_3분자의 two center overlap integral을 계산하였다(*Table* 7).

5. 고 찰

Table 3~7에 나타난 것처럼 spherical harmonics의 전개방법을 적용하여 계산한 two center overlap integral의 값이 Mulliken의 two cente overlap integral의 값과 소수점이하 네째 자리까지 완전히 일치하였다. Mulliken의 방법에서는 *Fig.* 1에 나타난 것처럼 A 및 B점이 동일 평면(One coordinate plane)[18]상에 위치하여야만 two center overlap integral을 계산할 수 있다. 그렇지 않으면 Euler 변환(Euler transformation)에 의하여 두점이 동일평면상에 위치하도록 좌표변환을 해야만 two center overlap integral을 계산할 수 있다. 동일평면상에 위치하지 않은 p_π, d_π, 및 d_σ 원자궤도함수의 Euler transformation matrix는 대단히 복잡하며[18] 적합한 Euler각을 택해야 된다는 어려운 문제가 따른다. 그러나 spherical harmonics의 전개방법에 의하면 두점 A와 B가 동일 평면상에 위치하지 않을 경우에도 기준점 A로부터 B점의 방향이 θ_1 및 ϕ_1에 의하여 결정되므로 *Table* 2의 기본식을 사용하여 쉽게 two center overlap integral을 계산할 수 있다. Mulliken의 방법은 두점 A 및 B에 위치한 Slater 원자궤도함수의 극좌표를 타원좌표로 좌표변환을 해야한다. 그러나 spherical harmonics의 전개방법에서는 극좌표의 좌표변환이 필요없으며 B점에 위치한 Slater 원자궤도함수를 기준점 A의 좌표와 일치하도록 전개하는 것만이 필요하다. 뿐만아니라 전이원소착물에 대한 group overlap integral[19,20]을 계산하고저할 때 Mulliken의 방법에서는 금속의온의 좌표를 리간드의 좌표로 좌표변환해야하며 d_{zy}, d_{yz}, d_{xy} 및 $d_{x^2-y^2}$ 궤도함수를 d_{z^2} 원자궤도함수로 고쳐야만 two center overlap integral을 계산할 수 있다.

그러나 spherical harmonics 전개방법에서는 리간드의 좌표를 금속이온의 좌표로 좌표변환하면 어떤 원자궤도함수사이의 two center overlap integral을 계산할 수 있는 이점이 있다[22].

감 사

본 연구의 일부는 호주 New South Wales 대학교의 물리화학과에서 행해졌으며 본 연구를 지도하여주신 호주 New South Wales의 대학교 물리화학과과장 Prof. R. M. Golding에 감사하는 바이다.

REFERENCE

1. C. J. Slater, *Phys. Revs.*, **36**, 57 (1930).
2. C. Zener, *Phys. Revs.*, **36**, 51 (1930).
3. S. P. McGlynn, L. C. Vanquickenborne, M. Kinoshita and D. G. Carroll, "Intraduction to Appliedquentum Chemistry", p. 41, Halt, Reinhart and Winston, (1972).
4. R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).
5. H. H. Jaffe, *J. Chem. Phys.*, **21**, 258 (1953).
6. L. Leifer, F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **28**, 364 (1958)
7. A. Loftus, *Mol. Phys.*, **5**, 105 (962).
8. J. R. Macdonald and R. M. Golding, *Mol, Phys.*, **31**, 289 (1975).
9. M. Moshinsky *Nuclear Phys.*, **13**, 104 (1959).
10. L. Stubbs and R. M. Golding, *Proc. Roy. Soc.* in press.
11. L. Stubbs. unpublished Thesis(Honor degree, University of New South Wales, 1973)
12. M. R. Spiegel, "Mathematical Handbook," McGraw Hill, 1968.
13. A. R. Edmond, "Angular Momentum Quantum Mechanics", P. 63, Princeton, 1957.
14. M. Rotenbeg, "The 3-*j* and 6-*j* Symbols", Cambridge, 1959.
15. W. E. Palke and W. N. Lipscomb *J. Amer. Chem. Soc.*, **88**, 2384 (1966).
16. L. F. Sutton, Interatomic Distances Special Publication 11, The Chemical Society, London (1958).
17. D. B. Boyd and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 910 (1967).
18. Reference (3) P. 59
19. H. D. Bedon, S. M. Hornar and S. Y. Tyree, Jr., *Inorg. Chem.*, **3**, 647 (1964).
20. C. J. Ballhansen and H. B. Gray, "Molecul orbital Theory", P. 101, 1964.
21. S. Ahn, unpublished thesis (Ph. D. Univesity of N. S. W, 1977)
22. S. Ahn, *Progress of Chem. and Chem. Industry*, **17**, 392 (1977).