

분자계의 Overlap Integral 의 계산의 Spherical Harmonics 전개방법의 응용

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

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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 CH₄, H₂O, NH₃, C₂H₆ 및 PH₃ 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 CH₄, H₂O, NH₃, C₂H₆ and PH₃ 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.

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

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.

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

여기에서 N 는 규격화상수이고 α 는 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 5 인 경우 ns np_σ 및 np_z 등의 Slater 원자궤도함수쌍에 대한 two center overlap integral이 Mulliken⁴ 등에 의하여 계계적이고 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 타원자좌표 (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

$$1 \leq \mu \leq \infty, 1 \leq \nu \leq 1 \text{ 및 } 0 \leq \phi \leq 2\pi \quad (5)$$

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

$n=3$ 및 5 인 Slater 원자궤도함수 np_z , nd_z , nd_σ 쌍사이의 two center overlap integral이 Jaffe⁵ 및 Liefer⁶ 등에 의하여 연구되었고 nd_σ 원자궤도

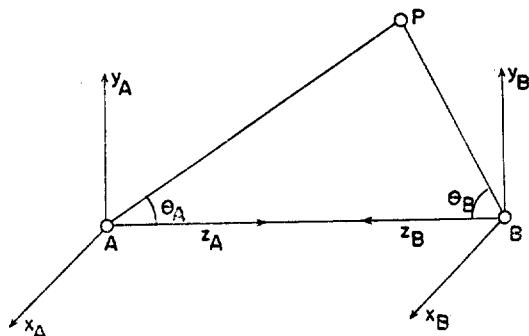


Fig. 1. The coordinate system for two center overlap integral of Mulliken.

함수쌍에까지 확장되었다.

s, p, d, f, g 및 h 원자궤도함수 사이의 two center overlap integral에 대한 일반식이 Lofthus에 의하여 유도되었다. Slater 원자궤도 함수에 대한 Mulliken의 two center overlap integral은 식(7)과 같이 기술할 수 있다⁷.

$$\begin{aligned} \langle \phi_A | \phi_B \rangle &= [p(1+t)]^{nA+1/2} [p(1-t)]^{nB+1/2} \\ &\times [(2n_A)! (2n_B)!]^{-1/2} \left\{ \int_1^\infty \int_{-1}^1 (\mu + \nu^{nA}) (\mu - \nu)^{nB} \right. \\ &\times \exp[-p(\mu + t\nu)] \theta_{IA}^{nA}(\mu, \nu) \theta_{IB}^{nB}(\mu, \nu) \\ &\left. \theta_{IB}^{nB}(\mu, \nu) d\mu d\nu \right\} \end{aligned} \quad (7)$$

여기에서

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

(8)이며 (8)식의 α 는 ϕ_A 의 slater 상수이고 β 는 ϕ_B 의 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 공통좌표상에⁸ 전개하는 방법 즉, spherical harmonics의 전개방법을 사용하여 two center overlap integral을 계산하는 방법을 발전시켰다.

2. Slater 원자궤도함수의 전개

Slater 원자궤도함수가 Fig. 2의 B 점에 위치

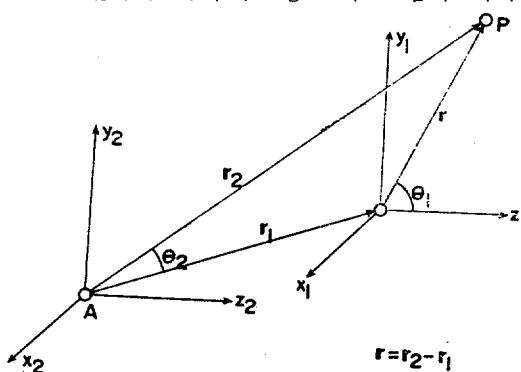


Fig. 2. The coordinate system for two center overlap integral of the expansion method.

한다고 가정하면 Moshinsky의 전개식^{9,10}을 사용하여 Spherical harmonics 부 및 지수파동함수 부를 기준점 A의 좌표상에 다음과 같이 전개할 수 있다.

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

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

여기에서 $\langle l_1 l_2 m_1 m_2 | l_1 l_2 l m \rangle$ 는 Clebsch-Gordan의 짹지음계수(coupling coefficient)이다.

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

$$r \exp(-\beta r) = 4\pi \sum_{n=0}^{\infty} z_n(r_1 r_2) \sum_{h=-n}^n Y_{nh}^*(\theta_1, \phi_1) \\ Y_{nh}(\theta_2, \phi_2) \quad (12)$$

여기에서¹¹

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

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

여기에서 $r_<$ 는 r_1 과 r_2 의 작게, $r_>$ 는 r_1 과 r_2 의 크게이고 I_ν 및 K_ν 는 수정 Bessel 함수^{11,12}이다.

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

$$|\phi_B\rangle = N r^l \exp(-\beta r) Y_{lm}(\theta, \phi) \\ = 4\pi N \sum_{l_1=0}^l \sum_{l_2=0}^l \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} (-1)^{l_1} \delta(l_1 + l_2, l) \left\{ \frac{4\pi(2l+1)!}{(2l_1+1)!(2l_2+1)!} \right\}^{\frac{1}{2}} \langle l_1 l_2 m_1 m_2 | l_1 l_2 l m \rangle \\ |l_1 l_2 l m \rangle \sum_{n=0}^{\infty} b_n(r_1, r_2) r_1^{l_1} r_2^{l_2} \sum_{h=-n}^n Y_{nh}^*$$

$$(\theta_1, \phi_1) Y_{l_1 m_1}(\theta_1, \phi_1) Y_{nh}(\theta_2, \phi_2) Y_{l_2 m_2}(\theta_2, \phi_2) \quad (15)$$

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

3. Two Center Overlap Integral의 기본식

식 (15) 및 (16)을 사용하여 Fig. 2에 있어서 점 A에 위치한 Slater 원자궤도함수 ϕ_A 와 점 B에 위치한 ϕ_B 사이의 two center overlap integral의 일반식을 얻을 수 있다¹³.

$$\phi_A = Mr_2^n \exp(-\alpha r_2) Y_{l_3 m_3}(\theta_2, \phi_2) \quad (17)$$

여기에서 M 은 규격화상수이다.

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

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

n, l, l_2, l_3, l_4 및 m_1, m_2, m_3, m_4, h 및 n 에 대응하는 3-j symbols¹⁴를 식 (18)과 (19)에 넣어

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

여기에서 수정 Bessel 함수의 지름적분은 n 및 k 의 값에 따라 Table 2과 같이 정의하였다.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\begin{aligned}
\langle 3s | 2p_z \rangle &= \left(\frac{32}{45} \right)^{1/2} (\alpha/\beta)^{7/2} \cos\theta [W_1 - aV_0] \\
\langle 3p_x | 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_z | 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_r | 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_z \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 3p_z | 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 2p_y | 2p_z \rangle &= 4(\alpha/\beta)^{5/2} \sin^2\theta \cos\phi \sin\phi [V_2 - aZ_1] \\
\langle 3p_x | 2p_z \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_z \rangle &= \left(\frac{32}{45} \right)^{1/2} (\alpha/\beta)^{7/2} \sin\theta \cos\phi [W_1 - aV_0] \\
\langle 3p_y | 2p_z \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_z \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 \right. \\
&\quad \left. + \frac{5}{2} \cos\theta \sin\theta (\cos^2\phi - \sin^2\phi) [W_3 - aV_2]\} \\
\langle 3d_r | 2p_z \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_z \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 [\sin\phi - 4\sin^3\phi] [W_3 - aV_2]\} \\
\langle 3d_{x^2-y^2} | 2p_z \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 [\cos^3\phi - 3\cos\phi] [W_3 - aV_2]\} \\
\langle 2p_y | 2p_z \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) \right. \\
&\quad \left. + \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)\}
\end{aligned}$$

$$\{W^2 - aV_1\}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\langle 3p_z|3p_z \rangle = \left(\frac{8}{15}\right)^{1/2} (\alpha/\beta)^{7/2} \sin^2\theta \cos\phi \sin\phi (H_2 - aB_1)$$

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

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

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

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

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

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

$$\begin{aligned}
\langle 3d_{yz} | 3p_y \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 \right. \\
&\quad \left. + \frac{5}{2} \cos\theta \sin^2\theta [H_3 - aB_2] \right\} \\
\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] \right. \\
&\quad \left. + \frac{5}{4} \sin^3\theta [3\sin\phi - 4\sin^3\phi] [H_3 - aB_2] \right\} \\
\langle 3d_{x,-z} | 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] \right. \\
&\quad \left. - \frac{4}{5} \sin^3\theta [3\sin\phi - 4\sin^3\phi] [W_3 - aV_2] \right\} \\
\langle 3s | d_x \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^2 V_0 \right\} \\
\langle 3d_{x,+} | 3d_x \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 \right. \\
&\quad \left. - \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) \right. \\
&\quad \left. + \frac{9}{28} (35\cos^4\theta - 30\cos^2\theta + 3) a^2 V_2] \right\} \\
\langle 3d_{xx} | 3d_x \rangle &= \left(\frac{64}{675} \right)^{1/2} (\alpha/\beta)^{7/2} \left\{ \frac{5}{7} \cos\theta \sin\theta \cos\phi [S_2 + a^2 V_0] + \frac{15}{14} \sin\theta (7\cos^3\theta - 3\cos\theta) \cos\phi [S_4 + a^2 V_2] \right. \\
&\quad \left. - 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 \right\} \\
\langle 3d_{yz} | 3d_x \rangle &= \left(\frac{64}{675} \right)^{1/2} (\alpha/\beta)^{7/2} \left\{ \frac{5}{7} \cos\theta \sin\theta \sin\phi [S_2 + a^2 V_0] + \frac{15}{14} \sin\theta (7\cos^3\theta - 3\cos\theta) \sin\phi [S_4 + a^2 V_2] \right. \\
&\quad \left. - 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 \right\} \\
\langle 3d_{xy} | 3d_x \rangle &= -\left(\frac{64}{1323} \right)^{1/2} (\alpha/\beta)^{7/2} \{ 2\sin\theta \cos\phi \sin\phi [S_2 + a^2 V_0] + \frac{3}{2} \sin^2\theta (7\cos^2\theta - 1) \cos\phi \sin\phi [S_4 + a^2 V_2] \right. \\
&\quad \left. + 2\sin^2\theta \cos\phi \sin\phi [1 + (7\cos^2\theta - 1)] aW_3 \right\} \\
\langle 3d_{x,-z} | 3d_x \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^2 V_0] + \frac{15}{28} \sin^2\theta (7\cos^2\theta - 1) [\cos^2\phi - \sin^2\phi] \right. \\
&\quad \left. [S_4 + a^2 V_2] + \frac{5}{7} \sin^2\theta [\cos^2\phi - \sin^2\phi] [1 + (7\cos^2\theta - 1)] aW_3 \right\} \\
\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 \right. \\
&\quad \left. - \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 \right. \\
&\quad \left. - \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) \right. \\
&\quad \left. (\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) \right. \\
&\quad \left. + \frac{15}{14} \sin^2\theta (7\cos^2\theta - 1) (\cos^2\phi - \sin^2\phi)] a^2 V_2 \right\} = \langle 3d_{yz} | 3d_{yz} \rangle \\
\langle 3d_{x,-z} | 3d_{xz} \rangle &= \left(\frac{8}{45} \right) (\alpha/\beta)^{7/2} \left\{ \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)] \right. \\
&\quad \left. 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 \right. \\
&\quad \left. + \frac{15}{7} [\cos\theta \sin\theta \cos\phi - \frac{1}{4} \sin\theta (7\cos^3\theta - 3\cos\phi) \cos\phi + \frac{7}{4} \sin^3\theta \cos\theta (\cos^3\phi - 3\cos\phi)] a^2 V_2 \right\} \\
\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. \\
&\quad \left. - 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 \right\}
\end{aligned}$$

$$\begin{aligned}
 & + \frac{15}{7} [\cos\theta \sin\theta \sin\phi - \frac{1}{4} \sin\theta (7\cos^3\theta - 3\cos\theta) \sin\phi + \frac{7}{4} \sin^3\theta \cos\theta (3\sin\phi - 4\sin^3\phi)] a^2 V_2 \\
 \langle 3d_{x^2-y^2} | 3d_{z^2} \rangle = & \left(\frac{8}{45} \right) (\alpha/\beta)^{7/2} \left\{ \frac{15}{7} \cos\theta \sin\theta \cos\phi S_2 - \frac{15}{28} [\sin\theta (7\cos^3\theta - 3\cos\theta) \cos\phi - 7\sin^3\theta \cos\theta (4\cos^3\phi - 3\cos\phi)] S_4 \right. \\
 & - 3\cos\theta \sin\theta \cos\phi a W_1 - 3 [\cos\theta \sin\theta \cos\phi + \frac{5}{2} \sin^3\theta \cos\theta (4\cos^3\phi - 3\cos\phi)] a W_3 \\
 & \left. + \frac{15}{7} [\cos\theta \sin\theta \cos\phi - \frac{1}{4} \sin\theta (7\cos^3\theta - 3\cos\theta) \cos\phi - \frac{7}{4} \sin^3\theta \cos\theta (4\cos^3\phi - 3\cos\phi)] a^2 V_2 \right\} \\
 \langle 3d_{x^2-y^2} | 3d_{xy} \rangle = & \left(\frac{8}{45} \right) (\alpha/\beta)^{7/2} \left\{ -\frac{15}{7} \cos\theta \sin\theta \sin\phi S_2 + \frac{15}{28} [\sin\theta (7\cos^3\theta - 3\cos\theta) \sin\phi + 7\sin^3\theta (3\sin\phi - 4\sin^3\phi)] S_4 \right. \\
 & + 3\cos\theta \sin\theta \sin\phi a W_1 + 3 [\cos\theta \sin\theta \sin\phi - \frac{5}{2} \sin^2\theta \cos\theta (3\sin\phi - 4\sin^3\phi)] a W_3 \\
 & \left. - \frac{15}{7} [\cos\theta \sin\theta \sin\phi - \frac{1}{4} \sin\theta (7\cos^3\theta - 3\cos\theta) \sin\phi - \frac{7}{4} \sin^3\theta \cos\theta (3\sin\phi - 4\sin^3\phi)] a^2 V_2 \right\}
 \end{aligned}$$

where $a = \beta r$ and α is the Slater constant 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 CH₄, H₂O, NH₃, C₂H₆, 및 PH₃ 분자의 two center overlap inte-

gral 을 계산하는데 적용하였다. 이미 설명한 spherical harmonics의 전개 방법을 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 CH₄ molecule.*

Overlap integral	Expansion method	Mulliken	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 H₂O 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 NH₃ Molecule.

Overlap integral	Expansion method	Mulliken	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 C₂H₆ molecule.

Overlap integral	Expansion method	Mulliken	Overlap Integral	Expansion method	Mulliken
$\langle 1s_{c1} H_1 \rangle$	0.064357	0.064352	$\langle 2p_{xc1} H_5 \rangle$	0.03348	0.033425
$\langle 1s_{c1} H_4 \rangle$	0.005852	0.00550	$\langle 2p_{yc1} H_1 \rangle$	0	0
$\langle 2s_{c1} H_1 \rangle$	0.512176	0.512156	$\langle 2p_{yc1} H_2 \rangle$	0.395521	0.396080
$\langle 2s_{c1} H_4 \rangle$	0.114967	0.114941	$\langle 2p_{yc1} H_3 \rangle$	-0.395521	-0.395555
$\langle 2p_{zc1} H_1 \rangle$	-0.162806	-0.162779	$\langle 2p_{yc1} H_5 \rangle$	-0.057899	-0.057898
$\langle 2p_{zc1} H_4 \rangle$	0.123236	0.123204	$\langle 2p_{yc1} H_6 \rangle$	0.057899	0.057898
$\langle 2p_{zc1} H_1 \rangle$	0.456708	0.456706	$\langle 2p_{xc2} H_1 \rangle$	0.066856	-0.033425
$\langle 2p_{zc1} H_2 \rangle$	-0.228354	-0.228345	$\langle 2p_{xc2} H_4 \rangle$	0.456708	0.456706
$\langle 2p_{zc1} H_3 \rangle$	-0.228354	-0.228345	$\langle 2p_{xc2} H_2 \rangle$	-0.033428	0.066854
$\langle 2p_{xc1} H_4 \rangle$	0.066856	0.066854	$\langle 2p_{xc5} H_5 \rangle$	0.22835	0.228345
$\langle 2p_{yc1} H_2 \rangle$	0.057899	0.057718	$\langle 2p_{yc2} H_5 \rangle$	-0.395521	-0.395535
$\langle 2p_{yc1} H_3 \rangle$	-0.057899	-0.057898	$\langle 2p_{yc2} H_6 \rangle$	0.395521	0.395535
$\langle 2p_{xc1} H_6 \rangle$	0.033428	0.033425	$\langle 2p_{xc2} H_3 \rangle$	-0.033428	-0.033425
$\langle 2p_{zc1} H_6 \rangle$	0.228354	0.228345	$\langle 2p_{zc2} H_1 \rangle$	-0.123236	-0.123204

Table 7. Two center overlap integrals for pH₃ molecule.

Overlap integral	Expansion method	Mulliken	Overlap 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
$\langle 2p_{zp} H_1 \rangle$	0.025217	0.025214	$\langle 2p_{yp} H_2 \rangle$	0.021839	0.021834
$\langle 2p_{yp} H_3 \rangle$	-0.021838	-0.021834	$\langle 3d_{x^2-p^2} H_2 \rangle$	-0.169746	-0.169744
$\langle 3s_p H_1 \rangle$	0.444464	0.444440	$\langle 3d_{x^2-p^2} H_3 \rangle$	-0.169746	-0.169744
$\langle 3p_{zp} H_3 \rangle$	0.278324	0.278303	$\langle 3d_{z^2} H_1 \rangle$	-0.025220	-0.025246
$\langle 3p_{zp} H_1 \rangle$	0.431048	0.431039	$\langle 3d_{y^2} H_1 \rangle$	0	0
$\langle 3p_{zp} H_2 \rangle$	-0.215524	-0.215525	$\langle 3d_{y^2} H_2 \rangle$	0.294010	0.293990
$\langle 3p_{zp} H_3 \rangle$	-0.215524	-0.215525	$\langle 3d_{xy} H_3 \rangle$	-0.294010	-0.293990
$\langle 3p_{yp} H_1 \rangle$	0	0	$\langle 3d_{xz-y^2} H_1 \rangle$	0.262891	0.262897
$\langle 3p_{yp} H_2 \rangle$	0.073299	0.373280	$\langle 3d_{xz-y^2} H_2 \rangle$	-0.131445	-0.131441

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

CH₄ 분자. Palke 및 Lipscomb¹⁵이 사용한 CH₄ 분자의 기하학적인 구조를 택하여 CH₄ 분자의 Slater 원자궤도함수에 대한 two center overlap integral을 계산하였다 (Table 3).

H₂O 분자. O-H 결합길이가 0.958 Å이고 H-O-H 결합각이 104.5°인 H₂O 분자¹⁶의 two center overlap integral을 계산하였다 (Table 4).

NH₃ 분자. NH₃ 분자의 two center overlap integral을 Palke 및 Lipscomb¹⁵의 평형구조를 택하여 계산하였다 (Table 5).

C₂H₆ 분자. Palke 및 Lipscomb¹⁵의 C₂H₆ 분자의 평형구조를 택하여 two center overlap integral을 계산하였다 (Table 6).

PH₃ 분자. Boyd 및 Lipscomb¹⁷의 평형구조를 택하여 PH₃ 분자의 two center overlap integral을 계산하였다 (Table 7).

5. 고찰

Table 3~7에 나타난 것처럼 spherical harmonics의 전개방법을 적용하여 계산한 two center overlap integral의 값이 Mulliken의 two center overlap integral의 값과 소수점이하 네째 자리까지 완전히 일치하였다. Mulliken의 방법에서는 Fig. 1에 나타난 것처럼 A 및 B 점이 동일

평면 (One coordinate plane)¹⁸상에 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_z, d_{xz}, 및 d_{yz} 원자궤도함수의 Euler transformation matrix는 대단히 복잡하여¹⁸ 적합한 Euler 각을 택해야 된다는 어려운 문제가 따른다. 그러나 spherical harmonics의 전개방법에 의하면 두점 A와 B가 동일 평면상에 위치하지 않을 경우에도 기준점 A로부터 B 점의 방향이 θ₁ 및 φ₁에 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 B 점에 위치한 Slater 원자궤도함수를 기준점 A의 좌표와 일치하도록 전개하는 것만이 필요하다. 뿐만 아니라 전이원소차물에 대한 group overlap integral^{19,20}을 계산하고자 할 때 Mulliken의 방법에서는 금속의 온의 좌표를 리간드의 좌표로 좌표변환해야하며 d_{xy}, d_{yz}, d_{xz} 및 d_{x^2-y^2} 궤도함수를 d_{z^2} 원자궤도함수로 고쳐야만 two center overlap integral을 계산할 수 있다.

그러나 spherical harmonics 전개 방법에서는 리간드의 좌표를 금속이온의 좌표로 좌표변환하면 어떤 원자궤도함수사이의 two center overlap integral을 계산할 수 있는 이점이 있다²².

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