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분자의 사중극자모멘트의 계산 (제1보). 연산자법에 의한 사중극자모멘트행렬요소의 계산

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Calculation of the Molecular Quadrupole Moments (I). Calculation for the Quadrupole Moment Matrix Elements by Operator Technique

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요 약. 연산자법을 사중극자모멘트행렬요소를 계산하는데 응용하였다.

Spherical harmonics의 전개방법과 사중극자모멘트행렬요소를 Mulliken의 overlap integral로 전환시키는 방법을 사용하여 Slater 궤도함수쌍에 대한 사중극자모멘트행렬요소의 기본식을 유도하였다.

두 방법에 의하여 계산한 사중극자모멘트행렬요소의 값이 일치하였으며 바닥상태의 HCl 분자에 대하여 계산한 사중극자모멘트의 값이 Nesbet의 값과 일치하였다.

ABSTRACT. Operator technique has been applied for calculation of the quadrupole moment matrix elements. Master formulas for the quadrupole moment matrix elements for pairs of Slater type orbitals are derived, one using the expansion method for spherical harmonics and the other the transformed of the quadrupole moment matrix elements into overlap integrals for Mulliken. The numerical values of the quadrupole moment matrix elements evaluated by two methods are in agreement with each other and the calculated quadrupole moment for the ground state of HCl molecule is also in agreement with that of Nesbet.

1. 서 론

Fig. 1에 나타난 것처럼 원점에서 Z_1 및 Z_2 떨어진 점에 위치하는 전하 e_1 및 e_2로 인하여 임의의 점 P에 생기는 퍼텐셜에너지는 다음 식으로 기술할 수 있다.[1]

$$U=q\phi_0-\mu_\alpha F_\alpha-\frac{1}{3}\theta_{\alpha\beta}F'_{\alpha\beta}-\frac{1}{15}\Omega_{\alpha\beta\gamma}F''_{\alpha\beta\gamma} \quad (1)$$

여기에서

$$\left.\begin{aligned} q&=\sum_i e_i\\ \mu_\alpha&=\sum_i e_i r_i\\ \theta_{\alpha\beta}&=\frac{1}{2}\sum_i e_i(3r_{i\alpha}r_{i\beta}-r_i^2\delta_{\alpha\beta})\\ \Omega_{\alpha\beta\gamma}&=\frac{1}{2}\sum_i e_i[5r_{i\alpha}r_{i\beta}r_{i\gamma}\\ &\quad-(r_{i\alpha}\delta_{\beta\gamma}+r_{i\beta}\delta_{\gamma\alpha}+r_{i\gamma}\delta_{\alpha\beta})] \end{aligned}\right\} \quad (2)$$

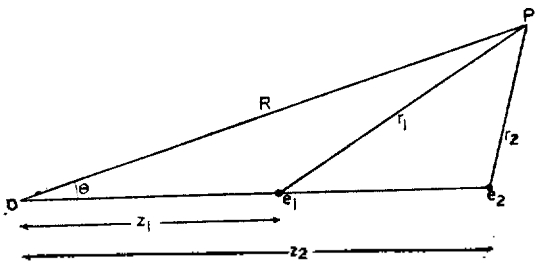

Fig. 1. The position of the arbitrary P relative to the origin 0 and the point charges e_1 and e_2.

이며 q, μ_α, $\theta_{\alpha\beta}$ 및 $\Omega_{\alpha\beta\gamma}$는 각각 계의 전하, 쌍극자모멘트, 사중극자모멘트 및 팔중극자모멘트를 나타낸다.

Spherical harmonics의 전개방법과 쌍극자모멘트행렬요소를 Mulliken의 overlap integral로 변환시키는 방법[2]에 의하여 쌍극자모멘트행렬요소를 계산하는 방법은 이미 보고 되었다.

사중극자모멘트는 전하에 대한 제이의 모멘트 (second moment)이며 9개의 성분을 가진 tensor이지만 이 tensor는 대칭이고 또 트레이스가 없으므로 (symmetrical and traceless) 일반적으로 다음의 5개의 독립적인 성분만을 가진다[3].

$$\left.\begin{aligned}&\theta_{\alpha\beta}=\theta_{\beta\alpha}\\&\theta_{\alpha\alpha}=\sum_{\alpha=x,y,z}\theta_{\alpha\alpha}=0\end{aligned}\right\}\quad(3)$$

$$\theta_{\alpha\beta}=\begin{Bmatrix}\theta_{xx} & \theta_{xy} & \theta_{xz}\\ \theta_{yx}=\theta_{xy} & \theta_{yy} & \theta_{yz}\\ \theta_{zx}=\theta_{xz} & \theta_{zy}=\theta_{yz} & \theta_{zz}=-\theta_{xx}-\theta_{yy}\end{Bmatrix}\quad(4)$$

그러나 $\alpha\neq\beta$이면 $\theta_{\alpha\beta}=0$가 되도록 서로 수직인 3개의 축 (x, y 및 z)을 택하는 것이 가능하며 이 경우 3개의 주 사중극자 모멘트 θ_{xx}, θ_{yy} 및 θ_{zz} 만이 남게된다[4].

$$\theta_{xx}=\frac{1}{2}\sum e_i[3x_i^2-r_i^2]\quad(5)$$

$$\theta_{yy}=\frac{1}{2}\sum e_i[3y_i^2-r_i^2]\quad(6)$$

$$\theta_{zz}=\frac{1}{2}\sum e_i[3z_i^2-r_i^2]\quad(7)$$

만일 전하의 분포가 연속적이라면 식 (5)～(7)에 있어서 전하의 합을 다음과 같이 전체 공간에 대한 전하밀도 $\rho(r)$의 적분으로 바꿀 수 있다.

$$\theta_{xx}=\frac{1}{2}\int(3x^2-r^2)\ \rho(r)dr\quad(8)$$

$$\theta_{yy}=\frac{1}{2}\int(3y^2-r^2)\ \rho(r)dr\quad(9)$$

$$\theta_{zz}=\frac{1}{2}\int(3z^2-r^2)\ \rho(r)\quad(10)$$

선형분자(대칭축으로서 z축을 가진 분자)의 경우

$$\theta_{zz}=-\frac{1}{2}\theta_{xx}=-\frac{1}{2}\theta_{yy}\quad(11)$$

이므로[5] 이들 분자는 하나의 사중극자모멘트만을 가진다.

양자역학적으로 분자의 사중극자모멘트를 계산하기 위하여 분자의 사중극자모멘트를 핵기여분(nuclear part of the quadrupole moment)과 전자기여분(electronic part of the quadrupole moment)으로 나누어 생각하는 것이 편리하다.

$$\left.\begin{aligned}\theta_{zz}&=\frac{1}{2}\sum_i e_i(3Z_i^2-R_i^2)\\&\quad+\frac{1}{2}\int(3z^2-r^2)\rho(r)dr\\ \theta_{xx}&=\frac{1}{2}\sum_i e_i(3X_i^2-R_i^2)\\&\quad+\frac{1}{2}\int(3x^2-r^2)\rho(r)dr\\ \theta_{yy}&=\frac{1}{2}\sum_i e_i(3Y_i^2-R_i^2)\\&\quad+\frac{1}{2}\int(3y^2-r^2)\rho(r)dr\end{aligned}\right\}\quad(12)$$

(12)식의 첫째 항이 사중극자모멘트의 핵기여분이며 기준점으로 부터 원자핵 까지의 거리 R_i의 성분 Z_i, X_i, 및 Y_i와 각 원자핵의 전하 e_i를 알 수 있으므로 사중극자모멘트의 핵기여분은 쉽게 계산할 수 있다.

(12)식의 둘째 항이 사중극자모멘트에 대한 전자기여분이며 분자내의 전자전하의 분포가 균일하므로 사중극자모멘트의 전자기여분은 전자전하밀도 $\rho(r)$의 분포로 부터

$$\rho(r)=-e\sum_i|\phi_i(r)|^2\quad(13)$$

계산할 수 있다.[6,7]

전자전하의 밀도를 계산하기 위하여 Slater 원

자궤도함수와 Gaussian orbitals 을 basis sets 로 사용하여 얻은 SCF 분자궤도함수가 사용되었다.[4]

근래에 Gaussian basis functions 을 사용한 ab initio SCF 계산, CNDO 계산[9,10] Refined Extended Hückel 계산[11]등에 의하여 전자전하의 밀도가 계산되었고 이로부터 분자의 사중극자모멘트의 전자기여분이 계산되었다.

본연구는 $\alpha \neq \beta$인 경우 $\theta_{\alpha\beta}=0$가 되도록 서로 수직인 좌표축을 택할 수 있는 분자에 대하여[13] 연산자법 (operator technique)에 의하여 Slater 궤도함수에 대한 사중극자행렬요소를 계산하는 새로운 방법을 발전시키기 위하여 시도되었다.

2. 연산자법에 의한 사중극자모멘트행렬요소의 계산

양자역학적으로 분자의 사중극자 모멘트 텐서는 그 분자에 대한 사중극자 모멘트 텐서 연산자의 기대값(expectation value)이다.

$$\theta_{zz}=-e\sum_i\langle\Psi_i|\frac{1}{2}(3z_i^2-r_i^2)|\Psi_i\rangle+\frac{1}{2}e\sum N_K(3Z_K^2-R_K^2) \qquad (14)$$

$$\theta_{xx}=-e\sum_i\langle\Psi_i|\frac{1}{2}(3x_i^2-r_i^2)|\Psi_i\rangle+\frac{1}{2}e\sum N_K(3X_K^2-R_K^2) \qquad (15)$$

$$\theta_{zz}=-e\sum_i\langle\Psi_i|\frac{1}{2}(3y_i^2-r_i^2)|\Psi_i\rangle+\frac{1}{2}e\sum N_K(3Y_K^2-R_K^2) \qquad (16)$$

여기에서 N_K는 K원자핵의 전하이고 Z_K, X_K, Y_K는 각각 원자핵 K의 x, y, z축 좌표이며 Ψ_i는 원자궤도함수를 basis function 으로 사용하여 얻은 분자궤도함수이다.

$$\Psi_i=\sum_i C_{\mu i}\phi_\mu \qquad (17)$$

따라서 x, y 및 z축 방향의 사중극자모멘트는 다음식으로 나타낼 수 있다.[12]

$$\theta_{zz}=-e\sum_i\sum_\mu\sum_\nu C_{\mu i}C_{\nu i}\langle\phi_\mu|\frac{1}{2}(3z_i^2-r_i^2)|\phi_\nu\rangle+\frac{1}{2}e\sum N_K(3Z_K^2-R_K^2) \qquad (18)$$

$$\theta_{xx}=-e\sum_i\sum_\mu\sum_\nu C_{\mu i}C_{\nu i}\langle\phi_\mu|\frac{1}{2}(3x_i^2-r_i^2)|\phi_\nu\rangle+\frac{1}{2}e\sum N_K(3X_K^2-R_K^2) \qquad (19)$$

$$\theta_{yy}=-e\sum_i\sum_\mu\sum_\nu C_{\mu i}C_{\nu i}\langle\phi_\mu|\frac{1}{2}(3y_j^2-r_i^2)|\phi_\nu\rangle+\frac{1}{2}e\sum N_K(3Y_K^2-R_K^2) \qquad (20)$$

여기에서 $\langle\phi_\mu|\frac{1}{2}(3z_i-r_i^2)|\phi_\nu\rangle$, $\langle\phi_\mu|\frac{1}{2}(3x_i^2-r_i^2)|\phi_\nu\rangle$ 및 $\langle\phi_\mu|\frac{1}{2}(3y_i^2-r_i^2)|\phi_\nu\rangle$을 x, y 및 z축 방향의 사중극자모멘트행렬요소라고 부른다.

Spherical Harmonics 의 전개 방법. Spherical harmonics 의 전개 방법에 의하여 사중극자모멘트행렬요소를 계산하기 위하여 사중극자모멘트 연산자를 spherical harmonics 의 꼴로 바꾸는 것이 편리하다.[14]

$$\hat{\theta}_{zz}=\frac{1}{2}(3z^2-r^2)=\left(\frac{4\pi}{5}\right)^{1/2}r^2Y_{20}(\theta,\phi) \qquad (21)$$

$$\begin{aligned}\hat{\theta}_{xx}&=\frac{1}{2}(3x^2-r^2)=-\frac{1}{2}(3z^2-r^2)+\frac{3}{2}(x^2-y^2)\\&=-\frac{1}{2}\left(\frac{4\pi}{5}\right)^{1/2}r^2Y_{20}(\theta,\phi)+\left(\frac{4\pi}{5}\right)^{1/2}r^2[Y_{2-2}(\theta,\phi)+Y_{22}(\theta,\phi)]\end{aligned} \qquad (22)$$

$$\begin{aligned}\hat{\theta}_{yy}&=\frac{1}{2}(3y^2-r^2)\\&=-\frac{1}{2}\left(\frac{4\pi}{5}\right)^{1/2}r^2Y_{20}(\theta,\phi)-\left(\frac{4\pi}{5}\right)^{1/2}r^2[Y_{2-2}(\theta,\phi)+Y_{22}(\theta,\phi)]\end{aligned} \qquad (23)$$

따라서 기준점 A에 있어서 (*Fig.* 2) x, y 및 z축 방향의 주 사중극자모멘트행렬요소는 다음 식으로 나타낼 수 있다.

$$\begin{aligned}\theta_{zz}&=\langle\phi_A|\hat{\theta}_{zz}|\phi_B\rangle\\&=C\langle\phi_A|r_2^2Y_{20}(\theta_2,\phi_2)|\phi_B\rangle\end{aligned} \qquad (24)$$

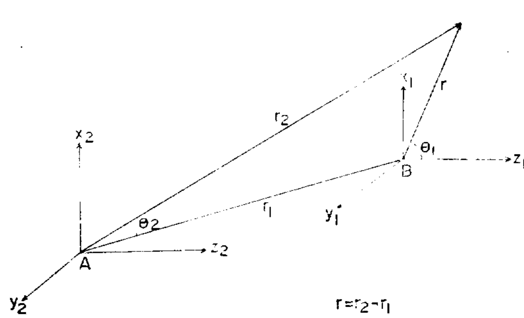

Fig. 2. The coordinate system for the two center integral.

$$\theta_{xx}=\langle\phi_A|\hat{\theta}_{xx}|\phi_B\rangle$$
$$=-\frac{1}{2}C\langle\phi_A|r_2{}^2Y_{20}(\theta_2,\phi_2)|\phi_B\rangle+C\langle\phi_A|r_2{}^2[Y_{2-2}(\theta_2,\phi_2)+Y_{22}(\theta_2,\phi_2)]|\phi_B\rangle$$
$$=-\frac{1}{2}C\langle\phi_A|r_2{}^2Y_{20}(\theta_2,\phi_2)|\phi_B\rangle+C\{\langle\phi_A|r_2{}^2Y_{2-2}(\theta_2,\phi_2)|\phi_B\rangle+\langle\phi_A|r_2{}^2Y_{22}(\theta_2,\phi_2)|\phi_B\rangle\} \qquad (25)$$

$$\theta_{yy}=\langle\phi_A|\hat{\theta}_{yy}|\phi_B\rangle$$
$$=-\frac{1}{2}C\langle\phi_A|r_2{}^2Y_{20}(\theta_2,\phi_2)|\phi_B\rangle-C\langle\phi_A|r_2{}^2[Y_{2-2}(\theta_2,\phi_2)+Y_{22}(\theta_2\phi_2)]|\phi_B\rangle$$
$$=-\frac{1}{2}C\langle\phi_A|r_2{}^2Y_{20}(\theta_2,\phi_2)|\phi_B\rangle-C\{\langle\phi_A|r_2{}^2Y_{2-2}(\theta_2,\phi_2)|\phi_B\rangle+\langle\phi_A|r_2{}^2Y_{22}(\theta_2,\phi_2)|\phi_B\rangle\} \qquad (26)$$

여기에서 $C=\left(\frac{4\pi}{5}\right)$이며 $\langle\phi_A|r_2{}^2Y_{2p}(\theta_2,\phi_2)|\phi_B\rangle$는 사중극자모멘트행렬요소의 허수꼴이다. 식(27)로 정의한 ϕ_A와 점 B에 위치한 ϕ_B를 기준점 A에 대하여 전개한 식을 사중극자모멘트행렬요소의 허수꼴에 넣어주면 사중극자모멘트행렬요소의 허수꼴에 대한 일반식을 얻을 수 있다.

$$\phi_A=Mr^{\kappa}\exp(-\alpha r_2)Y_{l_3m_3}(\theta_2,\phi_2) \qquad (27)$$
$$|\phi_B\rangle=Nr^K\exp(-\beta r)Y_{lm}(\theta,\phi)$$
$$=4\pi N\sum_{l_1=0}^{l}\sum_{l_2=0}^{l}\sum_{m_1}\sum_{m_2}(-1)^{l_1}\delta(l_1+l_2,l)\left\{\frac{4\pi(2l+1)!}{(2l_1+1)(2l_2+1)}\right\}^{1/2}$$
$$\langle l_1l_2m_1m_2|l_1l_2ml\rangle\sum_{n=0}^{\infty}f_n(r_1,r_2)r_1{}^{l_1}r_2{}^{l_2}\sum_{h=-n}^{n}Y_{nh}{}^*(\theta_1,\phi_1)\ Y_{l_1m_1}(\theta_1,\phi_1)\ Y_{nh}(\theta_2,\phi_2)Y_{l_2m_2}(\theta_2,\phi_2) \qquad (28)$$

여기에서 $K=l$이면 $f_n(r_1,r_2)=b_n(r_1,r_2)$이고 $K=l+1$이면 $f_n(r_1r_2)=z_n(r_1,r_2)$이며 $K=l+2$이면 $f_n(r_1,r_2)=h_n(r_1,r_2)$이다.[15,16]

$$\langle\phi_A|r_2{}^2Y_{2p}(\theta_2,\phi_2)|\phi_B\rangle=NM\sum_{l_1=0}^{l}\sum_{l_2=0}^{l}\sum_{n=0}^{\infty}\sum_{l_4}\sum_{l_5}\sum_{m_1}\sum_{m_2}\sum_{m_4}\sum_{m_5}\sum_{h}\delta(l_1+l_2,l)^{l_2-m+h+m_3+m_5}$$
$$r_1{}^{l_1}Y_{l_4m_4}{}^*(\theta_1,\phi_1)\int_0^{\infty}f_n(r_1,r_2)\,r_2{}^{l_2+\kappa+4}\exp(-\alpha r_2)dr_2(2l+1)(2n+1)(2l_5+1)$$
$$\left\{\frac{5(2l_3+1)(2l_4+1)(2l)!}{(2l_1)!\ (2l_2)!}\right\}^{1/2}\begin{pmatrix}l_1 & l_2 & l\\ m_1 & m_2 & -m\end{pmatrix}$$
$$\begin{pmatrix}n & l_1 & l_4\\ -h & m_1 & m_4\end{pmatrix}\begin{pmatrix}n & l_2 & l_5\\ h & m_2 & m_5\end{pmatrix}\begin{pmatrix}l_2 & 2 & l_5\\ -m_3 & p & m_5\end{pmatrix}\begin{pmatrix}n & l_1 & l_4\\ 0 & 0 & 0\end{pmatrix}$$
$$\begin{pmatrix}n & l_2 & l_5\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_3 & 2 & l_5\\ 0 & 0 & 0\end{pmatrix}$$

여기에서 $p=0$, 또는 ±2이다.

사중극자모멘트행렬요소의 허수꼴에 지름적분과 주어진 l_i, m_i, n, h 및 p에 대응하는 3-j symbol 값을 넣어주면 사중극자모멘트행렬요소의 기본식을 얻을 수 있다. 이 기본식은 *Table* 1에 나타내었다.

사중극자모멘트행렬요소를 Mulliken의 Overlap Integral로 전환시키는 방법. 사중극자모멘트 연산자를 spherical harmonics의 꼴로 바꾸고 사중극자모멘트행렬요소의 bra 벡타 $\langle\phi_A|$를

Table 1. Master formulas for the quadrupole moment moment matrix elements.

$$\langle|s|\hat{\theta}_{zz}|1s=2(\alpha/\beta)^{3/2}(2\cos^2\theta-\sin^2\theta)V_2/\beta^2$$

$$\langle 2s|\hat{\theta}_{zz}|1s\rangle=\left(\frac{4}{3}\right)^{1/2}(\alpha/\beta)^{5/2}(2\cos^2\theta-\sin^2\theta)W_2/\beta^2$$

$$\langle 2p_z|\hat{\theta}_{zz}|1s\rangle=\left(\frac{4}{5}\right)(\alpha/\beta)^{5/2}(2\cos\theta\ W_1+\frac{3}{2}(2\cos^3\theta-3\cos\theta\sin^2\theta)W_3)/\beta_2$$

$$\langle 3s|\hat{\theta}_{zz}|1s\rangle=\left(\frac{8}{45}\right)^{1/2}(\alpha/\beta)^{7/2}(2\cos^2\theta-\sin^2\theta)S_2/\beta^2$$

$$\langle 3p_z|\hat{\theta}_{zz}|1s\rangle=\left(\frac{32}{375}\right)^{1/2}(\alpha/\beta)^{7/2}(2\cos\theta\ S_1+\frac{3}{2}(2\cos^3\theta-3\cos\theta\sin^2\theta)S_3)/\beta^2$$

$$\langle 2p_x|\hat{\theta}_{zz}|1s\rangle=\left(\frac{4}{5}\right)(\alpha/\beta)^{5/2}\{2\sin\theta\cos\phi\ W_1-\frac{3}{2}(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi\ W_3\}/\beta^2$$

$$\langle 2p_y|\hat{\theta}_{zz}|1s\rangle=\left(\frac{4}{5}\right)(\alpha/\beta)^{5/2}\{2\sin\theta\sin\phi\ W_1+\frac{3}{2}(4\cos^2\theta\sin\theta-\sin^3\theta)\sin\phi\ W_3\}/\beta^2$$

$$\langle 3d_{z^2}|\hat{\theta}_{zz}|1s\rangle=\left(\frac{32}{225}\right)^{1/2}(\alpha/\beta)^{7/2}\{S_0+\frac{5}{7}(2\cos^2\theta-\sin^2\theta)S_2+\frac{9}{28}(35\cos^4\theta-3\cos^2\theta+3)S_4\}/\beta^2$$

$$\langle 3d_{xz}|\hat{\theta}_{zz}|1s\rangle=-\left(\frac{8}{147}\right)^{1/2}(\alpha/\beta)^{7/2}\{2\sin\theta\cos\theta\cos\phi\ S_2+3\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi\ S_4\}/\beta^2$$

$$\langle 2s|\hat{\theta}_{zz}|2s\rangle=\left(\frac{2}{3}\right)(\alpha/\beta)^{5/2}(2\cos^2\theta-\sin^2\theta)H_2/\beta^2$$

$$\langle 2p_z|\hat{\theta}_{zz}|2s\rangle=\left(\frac{48}{225}\right)^{1/2}(\alpha/\beta)^{5/2}\{2\cos\theta\ H_1+\frac{3}{2}(2\cos^3\theta-3\cos\theta\sin^2\theta)H_3\}/\beta^2$$

$$\langle 3s|\hat{\theta}_{zz}|2s\rangle=\left(\frac{8}{135}\right)^{1/2}(\alpha/\beta)^{7/2}(2\cos^2\theta-\sin^2\theta)I_2/\beta^2$$

$$\langle 3p_z|\hat{\theta}_{zz}|2s\rangle=\left(\frac{32}{1125}\right)^{1/2}(\alpha/\beta)^{7/2}\{2\cos\theta I_1+\frac{3}{2}(2\cos^2\theta-\sin^2\theta)I_3\}/\beta^2$$

$$\langle 2p_x|\hat{\theta}_{zz}|2s\rangle=\left(\frac{16}{75}\right)^{1/2}(\alpha/\beta)^{5/2}\{2\sin\theta\cos\phi\ H_1-\frac{3}{2}(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi\ H_3\}/\beta^2$$

$$\langle 2p_y|\hat{\theta}_{zz}|2s\rangle=\left(\frac{16}{75}\right)^{1/2}(\alpha/\beta)^{5/2}\{2\sin\theta\sin\phi\ H_1+\frac{3}{2}(4\cos^2\theta\sin\theta-\sin^3\theta)\sin\phi\ H_3\}/\beta^2$$

$$\langle 3p_x|\hat{\theta}_{zz}|2s\rangle=\left(\frac{32}{1125}\right)^{1/2}(\alpha/\beta)^{7/2}\{2\sin\theta\cos\phi\ I_1-\frac{3}{2}(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi I_3\}/\beta^2$$

$$\langle 3d_{z^2}|\hat{\theta}_{zz}|2s\rangle=\left(\frac{32}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\{I_0+\frac{5}{7}(2\cos^2\theta-\sin^2\theta)I_2+\frac{9}{28}(35\cos^4\theta-30\cos^2\theta+3)I_4\}/\beta^2$$

$$\langle 3d_{xz}|\hat{\theta}_{zz}|2s\rangle=-\left(\frac{8}{441}\right)^{1/2}(\alpha/\beta)^{7/2}\{2\sin\theta\cos\theta\cos\phi\ \ I_2+3\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi\ I_4\}/\beta^2$$

$$\langle 2p_z|\hat{\theta}_{zz}|2p_z\rangle=\left(\frac{4}{15}\right)(\alpha/\beta)^{5/2}\{2S_0+\frac{55}{14}(2\cos^2\theta-\sin^2\theta)+\frac{9}{14}(35\cos^4\theta-30\cos^2\theta+3)-2a[1+(2\cos^2\theta-\sin^2\theta)]$$
$$W_1-\frac{9}{14}a[3(2\cos^2\theta-\sin^2\theta)+(35\cos^4\theta-30\cos^2\theta+3)]W_3\}/\beta^2$$

$$\langle 3p_z|\hat{\theta}_{zz}|2p_z\rangle=\left(\frac{128}{3375}\right)^{1/2}(\alpha/\beta)^{7/2}\{2X_0+\frac{55}{14}(2\cos^2\theta-\sin^2\theta)\ X_2+\frac{9}{14}(35\cos^4\theta-30\cos^2\theta+3)X_4$$
$$-2[1+(2\cos^2\theta\quad-\sin^2\theta)]aS_1-\frac{9}{14}[3(2\cos^2\theta-\sin^2\theta)+(35\cos^4\theta-30\cos^2\theta+3)]aW_3\}/\beta^2$$

$$\langle 2p_x|\hat{\theta}_{zz}|2p_z\rangle=-\left(\frac{4}{5}\right)(\alpha/\beta)^{5/2}\frac{11}{7}\cos\theta\sin\theta\cos\phi\ S_2+\frac{15}{14}\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi\ S_4+\cos\theta\sin\theta\cos\phi\ aW_1$$
$$-\frac{3}{2}(4\cos^3\theta\sin\theta-\cos\theta\sin^3\theta)\cos\phi a\ W_3\}/\beta^2$$

$$\langle 3p_x|\hat{\theta}_{zz}|2p_z\rangle=-\left(\frac{32}{375}\right)^{1/2}(\alpha/\beta)^{7/2}\left\{\frac{11}{7}\cos\theta\ \sin\theta\cos\phi\ I_2+\frac{15}{14}\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi\ I_4+\cos\theta\sin\theta\cos\phi\ aH_1\right.$$
$$\left.-\frac{3}{2}(4\cos^3\theta\sin\theta-\cos\theta\sin^3\theta)\cos\phi\ aH_3\right\}/\beta^2$$

$$\langle 3d_{z^2}|\hat{\theta}_{zz}|2p_z\rangle=\left(\frac{32}{225}\right)^{1/2}(\alpha/\beta)^{7/2}\left\{\frac{11}{7}\cos\theta\ X_1+(2\cos^3\theta-3\cos\theta\sin^2\theta)X_3+\frac{5}{28}(63\cos^5\theta-70\cos^3\theta-15\cos\theta)X_5\right.$$
$$\left.-\cos\theta\ aS_0-\frac{5}{7}(2\cos^2\theta-\sin^2\theta)\cos aS_2-\frac{9}{28}(35\cos^4\theta-30\cos^2\theta+3)\cos\theta\ aS_4\right\}/\beta^2$$

$$\langle 3d_{xz}|\hat{\theta}_{zz}|2p_z\rangle=-\left(\frac{32}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\left\{\frac{3}{7}\sin\theta\cos\phi\ X_1+\frac{12}{5}(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi\ X_3+\frac{15}{14}\sin\theta\ (21\cos^4\theta\right.$$
$$-14\cos^2\theta+1)\cos^2\theta\sin\theta\cos\phi\ X_5-\frac{15}{7}\cos s\phi\ aS_2-\frac{45}{14}(4\cos^3\theta\sin\theta-\cos\theta\sin^3\theta)\cos\phi\ aS_4\}/\beta^2$$

$$\langle 2p_x|\hat{\theta}_{zz}|2p_x\rangle=\left(\frac{4}{15}\right)(\alpha/\beta)^{5/2}\left\{S_0-\frac{5}{14}[5(2\cos^2\theta-\sin^2\theta)-2\sin\theta\cos 2\phi]\ S_2+\frac{3}{28}[3(35\cos^4\theta-30\cos^2\theta+3)\right.$$
$$-5\sin^2\theta(7\cos^3\theta-3\cos\theta)\cos 2\phi]S_4-[1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{5}{7}\sin^2\theta\cos 2\phi]aW_1$$

$$+\frac{3}{28}[12(2\cos^2\theta-\sin^2\theta)-3(35\cos^4\theta-30\cos^2\theta+3)+5\sin^2\theta(7\cos^3\theta-3\cos\theta)\cos 2\phi)aW_3\Big\}\beta^2$$

$$\langle 3d_{zz}|\hat{\theta}_{zz}|2p_z\rangle=\left(\frac{32}{675}\right)^{1/2}(\alpha/\beta)^{7/2}\Big\{\frac{3}{7}\cos\theta X_1+\frac{4}{5}(2\cos^3\theta-3\cos\theta\sin^2\theta)X^3-\frac{5}{28}[(63\cos^5\theta-70\cos^3\theta+15\cos\theta)$$

$$-21\sin^2\theta(3\cos^3\theta-\cos\theta)\cos 2\phi)X_5-\Big[\frac{6}{7}\cos\theta-\frac{3}{7}(2\cos^3\theta-3\cos\theta\sin^2\theta)+\frac{15}{7}\cos\theta\sin^2\theta\cos 2\phi\Big]aS_2$$

$$-\Big[\frac{5}{7}(2\cos^3\theta-3\cos\theta\sin^2\theta)+\frac{15}{4}\sin^2\theta(3\cos^3\theta-\cos\theta)\cos^2\phi\, aS_4\Big\}/\beta^2$$

$$\langle 2p_y|\hat{\theta}_{zz}|2p_y\rangle=\left(\frac{4}{15}\right)(\alpha/\beta)^{5/2}\Big\{S_0-\frac{5}{14}[5(2\cos^2\theta-\sin^2\theta)+2\sin^2\theta\cos 2\phi]S_2+\frac{3}{28}[3(35\cos^4\theta-30\cos^2\theta+3)$$

$$+5\sin^2\theta(7\cos^3\theta-\cos\theta)\cos 2\phi]S_4-[1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{5}{7}\sin^2\theta\cos 2\phi\, aW_1$$

$$+\frac{3}{28}[12(2\cos^2\theta-\sin^2\theta)-3(35\cos^4\theta-30\cos^2\theta+3)-5\sin^2\theta(7\cos\theta-3\cos\theta)\cos 2\phi\, aW_3\}/\beta^2$$

$$\langle 3p_y|\hat{\theta}_{zz}|2p_y\rangle=\left(\frac{32}{375}\right)^{1/2}(\alpha/\beta)^{7/2}[X_0-\frac{5}{14}[5(2\cos^3\theta-\sin^2\theta)+2\sin^2\theta\cos\phi\}X_2+\frac{3}{28}[3(35\cos^4\theta-30\cos^2\theta+3)$$

$$+5\sin^2(7\cos^3\theta-3\cos\theta)\cos 2\phi)X_4-\Big[1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{5}{7}\sin^2\theta\cos 2\phi\Big]aS_1$$

$$+\frac{3}{38}[12(2\cos^2\theta-\sin^2\theta)-3(35\cos^4\theta-30\cos^2\theta+3)-5\sin^2\theta(7\cos^3\theta-3\cos\theta)\cos 2\phi)aS_3\}/\beta^2$$

$$\langle 3d_{yz}|\hat{\theta}_{zz}|2p_y\rangle=\left(\frac{32}{675}\right)(\alpha/\beta)^{7/2}\Big\{\frac{3}{7}\cos X_1+\frac{4}{5}(2\cos^3\theta-3\cos\theta\sin^2\theta)X_3-\frac{5}{28}(63\cos^5\theta-70\cos^3\theta+15\cos\theta)$$

$$+21\sin^2\theta(3\cos^3\theta-\cos\theta)\cos 2\phi)X_5-\frac{3}{7}[2\cos\theta-(2\cos^3\theta-3\cos\theta\sin^2\theta)-5\cos\theta\sin^2\theta\cos 2\phi]aS_2$$

$$-5[\frac{1}{7}(2\cos^3\theta-3\cos\theta\sin^2\theta)-\frac{3}{4}\sin^2\theta(3\cos^3\theta-\cos\theta)\cos 2\phi]aS_4\}/\beta^2$$

$$\langle 3s|\hat{\theta}_{zz}|3s\rangle=\left(\frac{4}{45}\right)(\alpha/\beta)^{7/2}(2\cos^2\theta-\sin^2\theta)Y_2$$

$$\langle 3p_z|\hat{\theta}_{zz}|3s\rangle=\left(\frac{64}{16875}\right)^{1/2}(\alpha/\beta)^{7/2}[2\cos\theta Y_1+\frac{3}{2}(2\cos^3\theta-3\cos\theta\sin^2\theta)Y_3)/\beta^2$$

$$\langle 3p_x|\hat{\theta}_{zz}|3s\rangle=\left(\frac{64}{16875}\right)^{1/2}(\alpha/\beta)^{7/2}[2\sin\theta\cos\phi\, Y_1-\frac{3}{2}(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi\, Y_3]/\beta^2$$

$$\langle 3d_{z^2}|\hat{\theta}_{zz}|3s\rangle=\left(\frac{64}{10125}\right)^{1/2}(\alpha/\beta)^{7/2}\{Y_0+\frac{5}{7}(2\cos\theta-\sin^2\theta)Y_2+\frac{9}{28}(35\cos^4\theta-30\cos^2\theta+3)Y_4\}/\beta^2$$

$$\langle 3d_{xz}|\hat{\theta}_{zz}|3s\rangle=-\left(\frac{16}{6615}\right)^{1/2}(\alpha/\beta)^{7/2}[2\sin\theta\cos\theta\cos\phi\, Y_2+3\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi\, Y_4\Big\}/\beta^2$$

$$\langle 2p_z|\hat{\theta}_{zz}|3p_z\rangle=\left(\frac{128}{3375}\right)^{1/2}(\alpha/\beta)^{5/2}\Big\{2I_0+\frac{55}{14}(2\cos^2\theta-\sin^2\theta)I_2+\frac{9}{14}(35\cos^4\theta-30\cos^2\theta+3)I_4$$

$$-2a[1+(2\cos^2\theta-\sin^2\theta)]H_1-\frac{9}{14}[3(2\cos^2\theta-\sin^2\theta)+(35\cos^4\theta-30\cos^2\theta+3)]aH_3]/\beta^2$$

$$\langle 3p_z|\hat{\theta}_{zz}|3p_z\rangle=\left(\frac{8}{225}\right)(\alpha/\beta)^{7/2}\Big\{[2E_0+\frac{55}{14}(2\cos^2\theta-\sin^2\theta)E_2+\frac{9}{14}(35\cos^4\theta-30\cos^2\theta+3)E_4$$

$$-2[1+(2\cos^2\theta-\sin^2\theta)]aI_1-\frac{9}{14}[3(2\cos^2\theta-\sin^2\theta)+(35\cos^4\theta-30\cos^2\theta+3)]aI_3\Big\}\}/\beta^2$$

$$\langle 3p_x|\hat{\theta}_{zz}|3p_z\rangle=-\left(\frac{8}{75}\right)(\alpha/\beta)^{7/2}\Big\{\frac{11}{7}\cos\theta\sin\theta\cos\phi E_2+\frac{15}{14}\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi\, E_4+\cos\theta\sin\theta\cos\phi\, aI_1$$

$$-\frac{3}{2}(4\cos^3\theta\sin\theta-\cos\theta\sin^3\theta)\cos\phi\ aI_3\Big\}/\beta^2$$

$$\langle 3d_{z^2}|\hat{\theta}_{zz}|3p_z\rangle=\left(\frac{64}{3375}\right)^{1/2}(\alpha/\beta)^{7/2}\Big\{\frac{11}{7}\cos\theta E_1+(2\cos^3\theta-3\cos\theta\sin^2\theta)E_3+\frac{5}{28}(63\cos^5\theta-70\cos^3\theta+15\cos\theta)E_5$$

$$-\cos\theta\, aI_0-\frac{5}{7}(2\cos^2\theta-\sin^2\theta)\cos\theta\, aI_2-\frac{9}{28}(35\cos^4\theta-30\cos^2\theta+3)\cos\theta aI_4\Big\}/\beta^2$$

$$\langle 3d_{zz}|\hat{\theta}_{zz}|3p_z\rangle=-\left(\frac{64}{10125}\right)^{1/2}(\alpha/\beta)^{7/2}\Big\{\frac{3}{7}\sin\theta\cos\phi\,E_1+\frac{12}{5}(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi\,E_3$$

$$+\frac{15}{14}\sin\theta(21\cos^4\theta-14\cos^2\theta+1)\cos\phi\,E_5-\frac{15}{7}\cos^2\theta\sin\theta\cos\phi\,aI_2$$

$$-\frac{45}{14}(4\cos^3\theta\sin\theta-\cos\theta\sin^3\theta)\cos\phi\,Ia_4\Big\}/\beta^2$$

$$\langle 2p_z|\hat{\theta}_{zz}|3p_z\rangle=\left(\frac{32}{375}\right)^{1/2}(\alpha/\beta)^{5/2}\Big\{I_0-\frac{5}{14}\{5(2\cos^2\theta-\sin^2\theta)-2\sin^2\theta\cos 2\phi\}I_2+\frac{3}{28}\{3(35\cos^4\theta-30\cos^2\theta+3)$$

$$-5\sin^2\theta(7\cos^3\theta-3\cos\theta)\cos 2\phi\}I_4-\{1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{5}{7}\sin^2\theta\cos 2\phi\}aH_1$$

$$+\frac{3}{28}\{12(2\cos^2\theta-\sin^2\theta)-3(35\cos^4\theta-30\cos^2\theta+3)+5\sin^2\theta(7\cos^3\theta-3\cos\theta)\cos 2\phi\}aH_3\Big\}/\beta^2$$

$$\langle 3p_z|\hat{\theta}_{zz}|3p_z\rangle=\left(\frac{8}{75}\right)(\alpha/\beta)^{7/2}\Big\{E_0-\frac{5}{14}\{5(2\cos^2\theta-\sin^2\theta)-2\sin^2\theta\cos 2\phi\}E_2+\frac{3}{28}\{3(35\cos^4\theta-30\cos^2+3)$$

$$-5\sin^2\theta(7\cos^3-3\cos\theta)\cos 2\phi\}E_4-\{1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{5}{7}\sin^2\theta\cos 2\phi\}aI_1$$

$$+\frac{3}{28}\{12(2\cos^2\theta-\sin^2\theta)-3(35\cos^4\theta-30\cos^2\theta+3)+5\sin^2\theta(7\cos^3\theta-3\cos\theta)\cos 2\phi\}aI_3\Big\}/\beta^2$$

$$\langle 3d_{zz}|\hat{\theta}_{zz}|3p_z\rangle=\left(\frac{64}{10125}\right)^{1/2}(\alpha/\beta)^{7/2}\Big\{\frac{3}{7}\cos E_1+\frac{4}{5}(2\cos^3\theta-3\cos\theta\sin^2\theta)E_3-\frac{5}{28}\{(63\cos^5\theta-70\cos^3\theta+15\cos\theta)$$

$$-21\sin^2\theta(3\cos^3\theta-\cos\theta)\cos_2\phi\}E_5-\frac{3}{7}\{2\cos\theta-(2\cos^3\theta-3\cos\theta\sin^2\theta)+5\cos\theta\sin^2\theta\cos 2\phi\}aI_2$$

$$-\Big[\frac{5}{7}(2\cos^3\theta-3\cos\theta\sin^2\theta)+\frac{15}{4}\sin^2\theta\,(3\cos^3\theta-2\cos\theta\cos 2\phi\Big]aI_4\Big\}\}/\beta^2$$

$$\langle 2p_y|\hat{\theta}_{zz}|3p_y\rangle=\left(\frac{32}{375}\right)^{1/2}(\alpha/\beta)^{5/2}\Big\{I_0-\frac{5}{14}\{5(2\cos\theta-\sin^2\theta)+2\sin^2\theta\cos 2\phi\}I_2+\frac{3}{28}\{3(35\cos^4\theta-30\cos^2\theta+3)$$

$$+5\sin^2\theta(7\cos^3\theta-3\cos\theta)\cos^2\phi\}I_4-\{1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{5}{7}\sin^2\theta\cos 2\phi\}aH_1$$

$$+\frac{3}{28}\{12(2\cos^2\theta-\sin^2\theta)-3(35\cos^4\theta-30\cos^2\theta+3)-5\sin^2\theta\,(7\cos^3\theta-3\cos\theta)\cos 2\phi\,aH_3\Big\}/\beta^2$$

$$\langle 3p_y|\hat{\theta}_{zz}|3p_y\rangle=\left(\frac{8}{75}\right)(\alpha/\beta)^{7/2}\Big\{E_0-\frac{5}{14}\{5(2\cos^2\theta-\sin^2\theta)+2\sin^2\theta\cos 2\phi\}E_2+\frac{3}{28}\{3(35\cos^4\theta-30\cos^2\theta+3)$$

$$+5\sin^2\theta(7\cos^3\theta-3\cos\theta)\cos_2\phi\}E_4-\{1-\frac{1}{2}(2\cos^2\theta-\sin^2\theta)-\frac{5}{7}\sin^2\theta\cos 2\phi\}aI_1$$

$$+\frac{3}{28}\{12(2\cos^2\theta-\sin^2\theta)-3(35\cos^4\theta-30\cos^2\theta+3)-5\sin^2\theta(7\cos^2\theta-3\cos\theta)\cos 2\phi\}aI_3\Big\}/\beta^2$$

$$\langle 3d_{yz}|\hat{\theta}_{zz}|3p_y\rangle=\left(\frac{64}{10125}\right)^{1/2}(\alpha/\beta)^{7/2}\Big\{\frac{3}{7}\cos\theta E_1+\frac{4}{5}(2\cos^3\theta-3\cos\theta\sin^2\theta)E_3-\frac{5}{28}\{(63\cos^5\theta-70\cos^3\theta+15\cos\theta)$$

$$+21\sin^2\theta(3\cos^3\theta-\cos\theta)\cos 2\phi\}E_5-\frac{3}{7}\{2\cos\theta-(2\cos^3\theta-3\cos\theta\sin^2\theta)$$

$$-5\cos\theta\sin^2\theta\cos 2\phi\}aI_2-5\Big\{\frac{1}{7}(2\cos^3\theta-3\cos\theta\sin^2\theta)-\frac{3}{4}\sin^2\theta(3\cos^3\theta-\cos\theta)\cos 2\phi\}aI_4\Big\}/\beta^2$$

$$\langle 1s|\hat{\theta}_{\alpha\alpha}|1s\rangle=2\sqrt{6}\,(\alpha/\beta)^{3/2}\sin^2\theta\cos 2\phi\,V_2/\beta^2$$

$$\langle 2s|\hat{\theta}_{\alpha\alpha}|2s\rangle=\left(\frac{8}{3}\right)(\alpha/\beta)^{5/2}\sin^2\theta\cos 2\phi\,H_2/\beta^2$$

$$\langle 2s|\hat{\theta}_{\alpha\alpha}|1s\rangle=2\sqrt{2}\,(\alpha/\beta)^{5/2}\sin^2\theta\cos 2\phi\,W_2/\beta^2$$

$$\langle 2p_z|\hat{\theta}_{\alpha\alpha}|1s\rangle=2\sqrt{6}\,(\alpha/\beta)^{5/2}\cos\theta\sin^2\theta\cos 2\phi\,W_3/\beta^2$$

$$\langle 2p_z|\hat{\theta}_{\alpha\alpha}|2s\rangle=2\sqrt{2}\,(\alpha/\beta)^{5/2}\cos\theta\sin^2\theta\cos 2\phi\,H_3/\beta^2$$

$$\langle 2p_x|\hat{\theta}_{\alpha\alpha}|1s\rangle=\left(\frac{24}{25}\right)^{1/2}(\alpha/\beta)^{5/2}\{2\sin\theta\cos\phi\,W_1+\frac{1}{2}\{5\sin^2\theta\cos 3\phi-(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi\}W_3\Big\}/\beta^2$$

$$\langle 2p_x|\hat{\theta}_{\alpha\alpha}|2s\rangle=\left(\frac{8}{25}\right)(\alpha/\beta)^{5/2}\Big\{2\sin\theta\cos\phi\,H_1+\frac{1}{2}\{5\sin^2\theta\cos 3\phi-(4\cos^2\theta\sin\theta-\sin^3\theta)\cos\phi\}H_3\Big\}/\beta_2$$

$$\langle 2s|\hat{\theta}_{\alpha\alpha}|2p_z\rangle=2\sqrt{2}\,(\alpha/\beta)^{5/2}\{\cos\theta\sin^2\theta\cos 2\phi\{S_3-aW_3\}\}/\beta_2$$

$$\langle 3s|\hat{\theta}_{\alpha\alpha}|2p_z\rangle=\left(\frac{16}{15}\right)^{1/2}(\alpha/\beta)^{7/2}\{\cos\theta\sin^2\theta\cos 2\phi\,\{X_3-aS_3\}\}/\beta^2$$

$$\langle 2p_z|\hat{\theta}_{\alpha\alpha}|2p_z\rangle=\left(\frac{24}{49}\right)^{1/2}(\alpha/\beta)^{5/2}\{\sin^2\cos 2\phi\,S_2-\sin^2\theta(7\cos^2\theta-1)\cos 2\phi\,S_4-\sqrt{7}\cos\theta\sin^2\theta\cos 2\phi\,aW_3\}/\beta^2$$

$$\langle 2p_x|\hat{\theta}_{\alpha\alpha}|2p_z\rangle=\left(\frac{24}{49}\right)^{1/2}(\alpha/\beta)^{7/2}\{2\cos\theta\sin\theta\cos\phi\,S_2+\frac{1}{2}[7\sin^2\theta\cos\theta\cos 3\phi-\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi]S_4$$
$$-\frac{14}{5}\cos\theta\sin\theta\cos\phi\,aW_1-\frac{1}{2}\{7\sin^3\theta\cos\theta\cos 3\phi-\frac{8}{5}\cos\theta\sin\theta\cos\phi-\sin\theta(7\cos^3\theta-3\cos\theta)$$
$$\cdot\cos\phi\,aW_3\}/\beta^2$$

$$\langle 3s|\hat{\theta}_{\alpha\alpha}|3p_z\rangle=\left(\frac{32}{225}\right)^{1/2}(\alpha/\beta)^{7/2}\{\cos\theta\sin^2\theta\cos 2\phi[E_3-aI_3]\}/\beta^2$$

$$\langle 2p_z|\hat{\theta}_{\alpha\alpha}|3p_z\rangle=\left(\frac{16}{245}\right)^{1/2}(\alpha/\beta)^{5/2}\{\sin^2\theta\cos 2\phi\,I_2+\sin^2\theta(7\cos^2\theta-1)\cos 2\phi\,I_4-\sqrt{7}\cos\theta\sin^2\theta\cos 2\phi\,aH_3\}/\beta^2$$

$$\langle 3p_z|\hat{\theta}_{\alpha\alpha}|3p_z\rangle=\left(\frac{32}{3675}\right)^{1/2}(\alpha/\beta)^{7/2}\{\sin^2\theta\cos 2\phi\,E_2+\sin^2\theta(7\cos^2\theta-1)\cos 2\phi\,E_4-\sqrt{7}\cos\theta\sin^2\theta\cos 2\phi\,aI_3\}/\beta^2$$

$$\langle 3p_x|\hat{\theta}_{\alpha\alpha}|3p_z\rangle=\left(\frac{32}{3675}\right)^{1/2}(\alpha/\beta)^{7/2}\{2\cos\theta\sin\theta\cos\phi E_2+\frac{1}{7}[7\sin^2\theta\cos\theta\cos 3\phi-\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi\}E_4$$
$$-\frac{14}{5}\cos\theta\sin\theta\cos\phi\,aI_1-\frac{1}{2}[7\sin^3\theta\cos\theta\cos 3\phi-\frac{8}{5}\cos\theta\sin\theta\cos\phi$$
$$-\sin\theta(7\cos^3\theta-3\cos\theta)\cos\phi\}aI_3\}/\beta^2$$

$$\langle 2p_x|\hat{\theta}_{\alpha\alpha}|2p_x\rangle=\left(\frac{8}{25}\right)^{1/2}(\alpha/\beta)^{5/2}\{2S_0-[2(\cos^2\theta-\sin^2\theta)+\frac{66}{7}\sin^2\theta\cos 2\phi)S_2+\frac{1}{28}[3(35\cos^4\theta-30\cos^2\theta+3)$$
$$-10\sin^2\theta(7\cos^2\theta-1)\cos\phi\}S_4-[2-(2\cos^2\theta-\sin^2\theta)+6\sin^2\theta\cos 2\phi]aW_1$$
$$-\frac{1}{7}[1-\frac{3}{4}(35\cos^4\theta-30\cos^2\theta+3)+24\sin 2\theta\cos^2\phi-5\sin^2\theta(7\cos^2\theta-1)\cos 2\phi)]aW_3/\beta^2$$

$$\langle 2p_x|\hat{\theta}_{\alpha\alpha}|3p_x\rangle=\left(\frac{16}{1125}\right)^{1/2}(\alpha/\beta)^{5/2}\{2I_0-[2(2\cos^2\theta-\sin^2\theta)+\frac{66}{7}\sin^2\theta\cos 2\phi\}I_2+\frac{1}{28}[3(35\cos^4\theta-30\cos^2\theta+3)$$
$$-10\sin^2\theta(7\cos^2-1)\cos 2\phi\}I_4-[2-(2\cos^2\theta-\sin^2\theta)+6\sin^2\theta\cos 2\phi\}aH_1$$
$$-\frac{1}{7}[1-\frac{3}{4}(35\cos^4\theta-30\cos^2\theta+3)+24\sin^2\theta\cos 2\phi-5\sin^2\theta(7\cos^2\theta-1)\cos 2\phi\}aH_3\}/\beta^2$$

$$\langle 3p_x|\hat{\theta}_{\alpha\alpha}|3p_x\rangle=\left(\frac{32}{16875}\right)^{1/2}(\alpha/\beta)^{7/2}\{2E_0-[2(2\cos^2\theta-\sin^2\theta)+\frac{66}{7}\sin^2\theta\cos 2\phi]E_2+\frac{1}{28}[3(35\cos^4\theta-30\cos^2\theta+3)$$
$$-10\sin^2\theta(7\cos^2\theta-1)\cos 2\phi]E_4-[2-(2\cos^2\theta-\sin^2\theta)+6\sin^2\theta\cos 2\phi]aI_1$$
$$-\frac{1}{7}[1-\frac{3}{4}(35\cos^4\theta-30\cos^2\theta+3]+24\sin^2\theta\cos 2\phi-5\sin^2\theta(7\cos^2\theta-1)\cos 2\phi)aI_3\}/\beta^2$$

$$\langle 2p_y|\hat{\theta}_{\alpha\alpha}|2p_y\rangle=\left(\frac{8}{25}\right)^{1/2}(\alpha/\beta)^{5/2}\{-2S_0+[2(2\cos^2\theta-\sin^2\theta)-\frac{66}{7}\sin^2\cos 2\phi)S_2-\frac{1}{28}[3(35\cos^4\theta-30\cos^2\theta+3)$$
$$+10\sin^2\theta(7\cos^2\theta-1)\cos 2\phi]S_4+[2-(2\cos\theta-\sin^2\theta)-6\sin^2\theta\cos 2\phi)aW_1$$
$$+\frac{1}{7}[1-\frac{3}{4}(35\cos^4\theta-30\cos^2\theta+3)-24\sin^2\theta\cos 2\phi+5\sin^2(7\cos^2\theta-1)\cos 2\phi)aW_3\}/\beta^2$$

$$\langle 3p_y|\hat{\theta}_{\alpha\alpha}|3p_y\rangle=\left(\frac{32}{16875}\right)^{1/2}(\alpha/\beta)^{7/2}[-2E_0+[2(2\cos^2-\sin^2\theta)-\frac{66}{7}\sin^2\theta\cos 2\phi]E_2-\frac{1}{28}[3(35\cos^4\theta-30\cos^2\theta+3)$$
$$+10\sin^2\theta(7\cos^2\theta-1)\cos 2\phi]E_4+[2-(2\cos^2\theta-\sin^2\theta)-6\sin^2\theta\cos_2\phi)aI_1$$
$$+\frac{1}{7}[1-\frac{3}{4}(35\cos^4\theta-30\cos^2\theta+3)-24\sin^2\theta\cos 2\phi+5\sin^2\theta(7\cos^2\theta-1)\cos 2\phi]aI_3\}/\beta^2$$

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where $\hat{\theta}_{\alpha\alpha}=\left(\frac{4\pi}{5}\right)^{1/2}r^2[Y_{2-2}(\theta_2,\ \phi_2)+Y_{22}(\theta_2,\ \phi_2)]$

Table 2. The transformed part of the quadrupole moment matrix elements into overlap integrals for Mülliken.

$\langle 1s|\hat{\theta}_{zz}=\left(\frac{9}{2}\right)^{1/2}/\alpha^2\ \langle 3d_{z^2}|$

$\langle 2s|\hat{\theta}_{zz}\sqrt{21}/\alpha^2\langle 4d_{z^2}|$

$\langle 2p_z|\hat{\theta}_{zz}=\frac{1}{\alpha^2}\left\{\sqrt{21}\langle 4s|+\left(\frac{84}{5}\right)^{1/2}\langle 4f_{z^3}|\right\}$

$\langle 2p_x|\hat{\theta}_{zz}=\frac{1}{\alpha^2}\left\{\left(\frac{21}{5}\right)^{1/2}\langle 4p_x|-\left(\frac{36}{5}\right)^{1/2}\langle 4f_{xz^2}|\right\}$

$\langle 2p_y|\hat{\theta}_{zz}=\frac{1}{\alpha^2}\left\{\left(\frac{21}{5}\right)^{1/2}\langle 4p_y|-\left(\frac{36}{5}\right)^{1/2}\langle 4f_{yz^2}|\right\}$

$\langle 3s|\hat{\theta}_{zz}=3\sqrt{7}/\alpha^2\langle 5d_{z^2}|$

$\langle 3p_z|\hat{\theta}_{zz}=\frac{3}{\alpha^2}\left\{2\left(\frac{7}{5}\right)^{1/2}\langle 5p_z|+3\left(\frac{3}{5}\right)^{1/2}\langle 5f_{z^3}|\right\}$

$\langle 3p_x|\hat{\theta}_{zz}=\frac{3}{\alpha^2}\left\{-\left(\frac{7}{5}\right)^{1/2}\langle 5p_x|+3\left(\frac{2}{5}\right)^{1/2}\langle 5f_{xz}|\right\}$

$\langle 3p_y|\hat{\theta}_{zz}=\frac{3}{\alpha^2}\left\{-\left(\frac{7}{5}\right)^{1/2}\langle 5p_y|+3\left(\frac{2}{5}\right)^{1/2}\langle 5f_{yz^2}\right\}$

$\langle 3d_{z^2}|\hat{\theta}_{zz}=\frac{1}{\alpha^2}\left\{3\sqrt{7}\langle 5s|+6\left(\frac{7}{5}\right)^{\frac{1}{2}}\langle 5d_{z^2}|+18\left(\frac{1}{7}\right)^{\frac{1}{2}}\right.$

$\left.\langle 5f_{z^4}|\right\}$

$\langle 3d_{xz}|\hat{\theta}_{zz}=\frac{1}{\alpha^2}\left\{3\left(\frac{5}{7}\right)^{1/2}\langle 5d_{xz}|+3\left(\frac{30}{7}\right)^{1/2}\langle 5f_{xz^3}|\right\}$

$\langle 3d_{yz}|\hat{\theta}_{zz}=\frac{1}{\alpha^2}\left\{3\left(\frac{5}{7}\right)^{1/2}\langle 5d_{yz}|+3\left(\frac{30}{7}\right)^{1/2}\langle 5f_{yz^3}|\right\}$

$\langle 3d_{xy}|\hat{\theta}_{zz}=\frac{3}{\alpha^2}\left\{-2\left(\frac{5}{7}\right)^{1/2}\langle 5d_{xy}|+\left(\frac{30}{7}\right)^{1/2}\langle 5f_{xyz^2}|\right\}$

$\langle 3d_{x^2-y^2}|\hat{\theta}_{zz}=\frac{3}{\alpha^2}\left\{-2\left(\frac{5}{7}\right)^{1/2}\langle 5d_{x^2-y^2}|+\left(\frac{30}{7}\right)^{1/2}\langle 5f_{z^2-y^2}|\right\}$

$\langle 1s|\hat{\theta}_{\alpha\alpha}=\left(\frac{9}{2}\right)^{1/2}/\alpha^2\langle 3d_{x^2-y^2}|$

$\langle 2s|\hat{\theta}_{\alpha\alpha}=\sqrt{21}/\alpha^2\langle 4d_{x^2-y^2}|$

$\langle 3s|\hat{\theta}_{\alpha\alpha}=3\sqrt{7}/\alpha^2\langle 5d_{x^2-y^2}|$

$\langle 2p_z|\hat{\theta}_{\alpha\alpha}=\sqrt{9}/\alpha^2\langle 4f_{z(x^2-y^2)}|$

$\langle 2p_x|\hat{\theta}_{\alpha\alpha}=3\sqrt{3}/\alpha^2\langle 4f_{x(x^2-y^2)}|+3\left(\frac{18}{5}\right)^{1/2}$

$/\alpha^2\langle 4p_x|-\left(\frac{9}{5}\right)^{1/2}/\alpha^2\langle 4f_{xz^2}|$

$\langle 2p_y|\hat{\theta}_{\alpha\alpha}=3\sqrt{3}/\alpha^2\langle 4f_{y(x^2-y^2)}|+3\left(\frac{18}{5}\right)^{1/2}$

$/\alpha^2\langle 4p_y|-\left(\frac{9}{5}\right)^{1/2}/\alpha^2\langle 4f_{yz^2}|$

$\langle 3p_z|\hat{\theta}_{\alpha\alpha}=3\sqrt{3}/\alpha^2\langle 5f_{z(x^2-y^2)}|$

$\langle 3p_x|\hat{\theta}_{\alpha\alpha}=9/\alpha^2\langle 5f_{x(x^2-y^2)}|+3\left(\frac{42}{5}\right)^{\frac{1}{2}}\langle 5p_x|-3\left(\frac{3}{5}\right)^{\frac{1}{2}}\langle 5f_{xz^2}|$

$\langle 3p_y|\hat{\theta}_{\alpha\alpha}=9/\alpha^2\langle f_{y(x^2-y^2)}|+3\left(\frac{42}{5}\right)^{\frac{1}{2}}\langle 5p_y|-3\left(\frac{3}{5}\right)^{\frac{1}{2}}\langle 5f_{yz^2}|$

where $\hat{\theta}_{\alpha\alpha}=\left(\frac{4\pi}{5}\right)^{1/2}[Y_{2-2}(\theta,\phi)+Y_{22}(\theta,\phi)]$

Slater 원자궤도함수로 치환하면 사중극자모멘트행렬요소에 대한 다음과 같은 일반식을 얻을 수 있다.

$$\langle\phi_A|\frac{1}{2}(3z^2-r^2)|\phi_B\rangle=$$
$$NC\langle r^{l+2}\exp(-\alpha r)Y_{lm}(\theta,\phi)Y_{20}(\theta,\phi)|\phi_B\rangle \quad (30)$$

$$\langle\phi_A|\frac{1}{2}(3x^2-r)|\phi_B\rangle=$$
$$-\frac{1}{2}NC\langle r^{l+2}\exp(-\alpha r)Y_{lm}(\theta,\phi)Y_{20}(\theta,\phi)|\phi_B\rangle$$
$$+NC\{\langle r^{l+2}\exp(-\alpha r)Y_{lm}(\theta,\phi)Y_{2-2}(\theta,\phi)|\phi_B\rangle$$
$$+\langle r^{l+2}\exp(-\alpha r)Y_{lm}(\theta,\phi)Y_{22}(\theta,\phi)|\phi_B\rangle\} \quad (31)$$

$$\langle\phi_A|\frac{1}{2}(3y^2-r^2)|\phi_B\rangle=$$
$$-\frac{1}{2}NC\langle r^{l+2}\exp(-\alpha r)Y_{lm}(\theta,\phi)Y_{20}(\theta,\phi)|\phi_B\rangle$$
$$-NC\{r^{l+2}\exp(-\alpha r)Y_{lm}(\theta,\phi)Y_{2-2}(\theta,\phi)\rangle$$
$$+\langle r^{l+2}\exp(-\alpha r)Y_{lm}(\theta,\phi)Y_{22}(\theta,\phi)|\phi_B\rangle\} \quad (32)$$

방정식 (26), (27) 및 (28)의 overlap integral을 일반식으로 바꾸면 다음이 된다.[27]

$$\langle r^{l+2}\exp(-\alpha r)Y_{lm}(\theta,\phi)Y_{2p}(\theta,\phi)|\phi_B\rangle$$
$$=\sum_{l'=|l-2|}^{l+2}\sum_{l'=-m'}^{m'}\left[\frac{(2l+1)5(2l'+1)}{4\pi}\right]^{1/2}$$
$$(-1)^m\begin{pmatrix} l & 2 & l' \\ -m & p & m' \end{pmatrix}\begin{pmatrix} l & 2 & l' \\ 0 & 0 & 0 \end{pmatrix}$$
$$\langle r^{l+2}\exp(-\alpha r)Y^*_{l'm'}(\theta,\phi)|\phi_B\rangle \quad (33)$$

여기에서 $p=0$ 또는 ± 2임.

주어진 l, m, l', m' 및 p 에 대응하는 3-j symbols의 값을 방정식 (29)에 대입하여 얻은 overlap integral의 일반식을 방정식 (26)~(28)에 치환하여 주면 x, y 및 z 축방향의 주 사중극자모멘트행렬요소에 대한 전환 overlap integral을 얻을 수 있다. 사중극자모멘트행렬요소를 overlap integral로 전환시킨 부분 (transformed part of the quadrupole moment matrix element), $\langle\phi_A|\theta_{\alpha\alpha}$을 *Table* 2에 나타내었다.

3. 결과 및 고찰

Table 1 및 2에 기술한 기본식을 사용하여 가상적인 NO 분자의 Slater 원자궤도함수에 대하여 사중극자모멘트행렬요소를 계산하여 *Table* 3에,

Table 3. The calculated values of the quadrupole moment matrix elements for a hypothetical No molecule whose Slater constants are 1.95 (N) and 2.275 (0), respectively (r=1.5Å).

Quadrupole moment matrix	Expansion method	Transformed overlap integral	Mulliken
$\langle 1s \vert \hat{\theta}_{zz} \vert 1s \rangle$	0.025197	$\left(\frac{9}{2}\right)^{1/2}/\alpha^2\langle 3d_{z^2} \vert 1s \rangle$	0.0251934
$\langle 2s \vert \hat{\theta}_{zz} \vert 1s \rangle$	0.079984	$(21)^{1/2}/\alpha^2\langle 4d_{z^2} \vert 1s \rangle$	0.079898
$\langle 1s \vert \hat{\theta}_{zz} \vert 2p^z \rangle$	−0.025422	$\left(\frac{9}{2}\right)^{1/2}/\alpha^2\langle 3d_z^2 \vert 2p_z \rangle$	−0.025452
$\langle 1s \vert \hat{\theta}_{zz} \vert 2s \rangle$	0.029510	$\left(\frac{9}{2}\right)^{1/2}\langle 3d_{z^2} \vert 2s \rangle$	0.029568
$\langle 2s \vert \hat{\theta}_{zz} \vert 2s \rangle$	0.090842	$(21)^{1/2}/\alpha^2\langle 4d_{z^2} \vert 2s \rangle$	0.090995
$\langle 2s \vert \hat{\theta}_{zz} \vert 2p_z \rangle$	−0.0561235	$(21)^{1/2}/\alpha^2\langle 4d_z \vert 2p_z \rangle$	−0.056590

나타내었다. *Table* 3에 나타난것 처럼 사중극자 모멘트 연산자를 spherical harmonics 꼴로 바꾼 다음 spherical harmonics의 전개방법에 의하여 계산한 사중극자모멘트행렬요소의 값이 사중극자모멘트행렬요소를 Mulliken의 overlap integral로 변환시킨 사중극자모멘트행렬요소의 전환 overlap integral의 값과 소수점이하 네째 자리까지 일치하였다.

사중극자모멘트연산자를 spherical harmonics 꼴로 바꾼 다음 연산자법에 의하여 분자의 사중극자모멘트는 *Table* 1 및 2에 주어진 기본식을 사용하여 각 원자궤도함수에 대한 사중극자모멘트행렬요소를 계산하고 분자궤도함수의 basis sets에 대한 사중극자모멘트행렬요소의 값을 방정식 (18)～(21)에 넣어주므로서 간단히 계산할 수 있다.

이상의 연산자법은 간단한 분자의 사중극자모멘트를 계산하는데 사용되었으며[18] Nesbet[19]의 Hartree Fock 분자궤도함수를 사용하고 본 연구의 연산자법에 의하여 바닥상태의 HCl 분자에 대한 사중극자모멘트를 계산하였을때 본 연구의 방법에 의하여 얻은 사중극자 모멘트의 값이 3.457×10^{-26} esu cm^2 전자전하밀도의 계산으로부터 얻은 꼭같은 분자궤도 함수에 대한 Nesbet의 값 3.46×10^{-26} esu cm^{2}과 일치하였다. 이상의 연산자법에 의한 사중극자모멘트행렬요소의 계산은 전자전하밀도의 분포로부터 또는 Bloor 및 Maksic[12]의 방법에 의한 계산과 달리 많은 전산시간을 필요로 하지 않으며 소형 전자계산기를 사용하여 계산할 수 있다는 잇점이 있다.

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