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Calculation of NMR Chemical Shift for $5d^n$ Systems (I). Application of the Expansion Method for Spherical Harmonics for Computation of Overlap and Dipole Moment Matrix Elements

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The general formulas for SCF atomic orbita's $|5s>$ and $|6p>$ have been derived separately by expressing the spherical harmonics part in terms of the coordinate(r_1, r_2) of the reference point, and by translating the exponential part, $r^4 \exp(-\beta r)$, in terms of r_1 and r_2 and the modified Bessel functions. Master formulas for overlap and dipole moment matrix elements are derived. The computed values of overlap and dipole moment matrix elements for hyopthetical NO mole.ule are exactly in agreement with those for the previous methods.

1. Introduction

The first systematic and comprehensive study of two center overlap integrals was carried out, adopting Slater type atomic orbitals[1]. The evaluation of two center integrals has been performed using the spheroidal coordinate system[2]. In this spheroidal coordinate system, it is required to transform the spherical polar coordinate to the spheroidal coordinate for evaluation of two center integrals. Since two atoms must lie in one coordinate axis to evaluate two center integral in the spheroidal coordinate system[3], namely the z axis, this required, in general, a different coordinate transformation of each matrix element. To overcome the inconvenience of different coordinate transformations, the expansion method for spherical harmonics has been developed by Golding and Stubbs[4]. This method was applied to evaluate specific physical molecular properties such as dipole moments[5,6], quadrupole moments[7,8], polarizabilities[9,10] and NMR shifts in paramagnetic systems[11,12]. In the previous works[4,13], the expansion formulas for Slater type orbitals, $|1s>$, $|2p>$, $|3d>$, $|2s>$, $|3p>$, $|4d>$, $|3s>$, $|4p>$, $|5d>$, $|4s>$, and $|5p>$ have been derived to evaluate two center integrals for any pairs of those Slater type orbitals. However, it is required to derive the expansion formulas for SCF atomic orbitals[14] $|5s>$ and $|6p>$ to calculate the NMR chemical shift for SCF atomic orbitals $|5d>$.

The purpose of this work is to derive the general expansion formulas for SCF atomic orbitals $|5s>$ and $|6p>$ and to apply these formulas to obtain the analytical formulas for overlap and dipole moment matrix elements for any pairs of SCF atomic orbitals. We also compare the computed results obtained from the analytical formulas with those of Mulliken's method.

2. Derivation of the Expension Formulas for SCF Atomic Orbital $|5s<$ and $|6p>$

If a SCF atomic orbital is assumed to be located at the point B of Figure 1, the spherical harmonic part may be expressed in terms of the reference point A, using the following identities[15],

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

Where $< l_1 l_2 m_1 m_2 | l_1 l_2 l\ m>$ is Clebsch-Gordan coefficient.

The exponential part may also be translated into the following form

$$r^{K-l}\exp(-\beta r) = 4\pi \sum_{n=0}^{\infty} k_n(r_1, r_2) \sum_{h=-n}^{n} Y_{nh}^*(\theta_1, \phi_1)\, Y_{nh}(\theta_2, \phi_2) \quad (2)$$

because $|\phi_B> = Nr^K \exp(-\beta r)\, Y_{lm}(\theta, \phi)$ (3)

In equation (3), if $K=l$, $k_n(r_1, r_2) = b_n(r_1, r_2)^3$,
if $K=l+1$, $k_n(r_1, r_2) = z_n(r_1, r_2)^3$,
if $K=l+2$, $k_n(r_1, r_2) = h_n(r_1, r_2)^{13}$ and
if $K=l+3$, $k_n(r_1, r_2) = a_n(r_1, r_2)^{13}$

Where

$$a_n(r_1, r_2) = (r_< r_>)^{-\frac{1}{2}} \sum_{i=0}^{4} A_i I_{n-\frac{3}{2}+i}(\beta r_<)\ K_{n-\frac{3}{2}+i}(\beta r_>) \quad (4)$$

In this expression I_ν and K_ν are the modified Bessel functions and the coefficients, A_i, are as follows.

$$A_0 = \frac{4n(n-1)}{(2n+1)(2n-1)}\ r_<^2 r_>^2)$$

$$A_1 = -\frac{4n}{(2n+1)}(r_<^3 r_> + r_< r_>^3)$$

$$A_2 = \left(r_<^4 + r_>^4 + \frac{2(8n^2+8n-5)}{(2n+3)(2n-1)} r_<^2 r_>^2\right)$$

$$A_3 = -\frac{4(n+1)}{(2n+1)}(r_<^3 r_> + r_< r_>^3)$$

$$A_4 = \frac{4(n+1)(n+2)}{(2n+1)(2n+3)} r_<^2 r_>^2$$

If equation (4) is differentiated with respect to β, we may obtain the expansion formula for $r^4 \exp(-\beta r)$ as given by

$$-\frac{\partial}{\partial\beta}[r^3\exp(-\beta r)] = -4\pi\sum_{n=0}^{\infty}\frac{\partial}{\partial\beta}[a_n(r_1, r_2)] \sum_{h=-n}^{n} Y_{nh}^*(\theta_1, \phi_1)\, Y_{nh}(\theta_2, \phi_2) = 4\pi\sum_{n=0}^{\infty} d_n(r_1, r_2) \sum_{h=-n}^{n} Y_{nh}^* (\theta_1, \phi_1)\ Y_{nh}(\theta_2, \phi_2) \quad (5)$$

Where

$$d_n(r_1, r_2) = (r_< r_>)^{-\frac{1}{2}} \sum_{i=0}^{5} D_i I_{n-\frac{5}{2}+i} (\beta r_<) K_{n-\frac{5}{2}+i}(\beta r_>) \quad (6)$$

Where

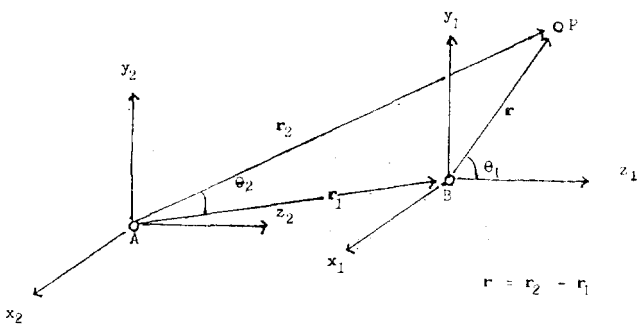

Figure 1. The coordinate system for two center integral of the expansion method.

$$D_0 = \frac{4n(n-1)}{(2n+1)(2n-1)} r_<^2 r_>^3$$

$$D_1 = -\frac{4n}{(2n+1)}\left(\frac{(3n-2)}{(2n-1)} r_<^3 r_>^2 + r_< r_>^4\right)$$

$$D_2 = \left(\frac{(6n+1)}{(2n+1)} r_<^4 r_> + \frac{2(24n^3+32n^2-8n-5)}{(2n+3)(2n+1)(2n-1)} r_<^2 r_>^3 + r_>^5\right)$$

$$D_3 = -\left(r_<^5 + \frac{2(24n^3+40n^2-11)}{(2n+3)(2n+1)(2n-1)} r_<^3 r_>^2 + \frac{(6n+5)}{(2n+1)} r_< r_>^4\right)$$

$$D_4 = \frac{4(n+1)}{(2n+1)}\left(r_<^4 r_> + \frac{(3n+5)}{(2n+3)} r_<^2 r_>^3\right)$$

$$D_5 = -\frac{4(n+1)(n+2)}{(2n+1)(2n+3)} r_<^3 r_>^2$$

Therefore

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

3. Overlap Matrix Elements

Combining the SCF atomic orbital located at the point A with the SCF atomic orbital which is expressed in a common coordinate system represented by equation (7) gives the general formula for overlap matrix element.

$$<\phi_A|\phi_B> = 4\pi NM \sum_{l_3=0}^{l}\sum_{l_4=0}^{l}\sum_{m_3=-l_3}^{l_3}\sum_{m_4=-l_4}^{l_4}\sum_{n=0}^{\infty}\sum_{h=-n}^{n}\sum_{l_3=|n-l_1|}^{n+l_1}\sum_{m_3=-l_3}^{l_3} (-1)^{l_2+h+m_3-m}\, \delta(l_1+l_2,\ l)\,(2l+1)\,(2n+1) \left\{\frac{(2l_3+1)(2l_4+1)(2l)!}{4\pi(2l_1)!\,(2l_2)!}\right\}^{\frac{1}{2}} r_1^{l_1} Y_{l_4 m_4}^*(\theta_1, \phi_1) \int_0^{\infty} d_n(r_1, r_2)\, r_2^{2+l_2+U} \exp(-\beta r_2) dr_2 \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & -m \end{pmatrix}\begin{pmatrix} n & l_1 & l_4 \\ -h & m_1 & m_4 \end{pmatrix}\begin{pmatrix} l_3 & n & l_2 \\ -m_3 & h & m_2 \end{pmatrix} \begin{pmatrix} l_3 & n & l_2 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} n & l_1 & l_4 \\ 0 & 0 & 0 \end{pmatrix} \quad (8)$$

Where $|\phi_A> = Mr^U \exp(-\beta r_2)\, Y_{l_3 m_3}(\theta_2, \phi_2)$

Substitution of the numerical values of 3-j symbols[16] for the specified n, l, m, h, l_i and m_i and the radial integrals into equation (8) leads to master formulas of two center overlap matrix elements listed in Table 2.

The radial integrals involving the modified Bessel functions are evaluated in elsewhere[17]. We denote the radial integrals, depending on n and K as represented in Table 1.

4. Dipole Moment Matrix Elements

If a LCAO MO is used, the dipole moment matrix element for molecular orbitals is given by

$$<\Psi_i|\Sigma_i r_i|\Psi_i> = \Sigma_i\Sigma_u\Sigma_v C_{ui} C_{vi} <\phi_u|r_i|\phi_v> \quad (9)$$

Where $<\phi_u|r_i|\phi_v>$ is called the dipole moment matrix

TABLE 1: Definition of the Radial Part Integrals

K	$\int_0^\infty d_n(r_1,r_2)r_2\exp(-\alpha r_2)dr_2$	n			
		0	1	2	3
2	E_n	E_0			
3	F_n	F_0	F_1		
4	G_n	G_0	G_1	G_2	
5	H_n	H_0	H_1	H_2	H_3
6	I_n	I_0	I_1	I_2	I_3
7	J_n	J_0	J_1	J_2	J_3

TABLE 2: Master Formulas for Two Center Overlap Matrix Elements

$$<1s\ |\ 5s> = (32/14175)^{\frac{1}{2}}(\alpha/\beta)^{\frac{3}{2}}E_0$$
$$<2s\ |\ 5s> = (32/42525)^{\frac{1}{2}}(\alpha/\beta)^{\frac{6}{2}}F_0$$
$$<2p_z\ |\ 5s> = (32/14175)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}\cos\theta\ F_1$$
$$<2p_x\ |\ 5s> = (32/14175)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}\sin\theta\ \cos\phi\ F_1$$
$$<2p_y\ |\ 5s> = (32/14175)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}\sin\theta\ \sin\phi\ F_1$$
$$<3s\ |\ 5s> = (8/135)(1/35)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}\ G_0$$
$$<3p_z\ |\ 5s> = (8/45)(1/105)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}\cos\theta\ G_1$$
$$<3p_x\ |\ 5s> = (8/45)(1/105)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}\sin\theta\ \cos\phi\ G_1$$
$$<3p_y\ |\ 5s> = (8/45)(1/105)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}\sin\theta\ \sin\phi\ G_1$$
$$<3d_{z^2}\ |\ 5s> = (4/135)(1/7)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(2\cos^2\theta-\sin^2\theta)\ G_2$$
$$<3d_{xz}\ |\ 5s> = (8/45)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}\cos\theta\ \sin\theta\ \cos\phi\ G_2$$
$$<3d_{yz}\ |\ 5s> = (8/45)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}\cos\theta\ \sin\theta\ \sin\phi\ G_2$$
$$<3d_{xy}\ |\ 5s> = (8/45)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}\sin^2\theta\ \sin\phi\ \cos\phi\ G_2$$
$$<3d_{x^2-y^2}\ |\ 5s> = (2/45)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}\sin^2\theta\ (\cos^2\phi-\sin^2\phi)\ G_2$$
$$<4s\ |\ 5s> = (4/945)(2/5)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}\ H_0$$
$$<4p_z\ |\ 5s> = (4/315)\ (2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}\cos\theta\ H_1$$
$$<4p_x\ |\ 5s> = (4/315)(2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}\sin\theta\ \cos\phi\ H_1$$
$$<4p_y\ |\ 5s> = (4/315)(2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}\sin\theta\ \sin\phi\ H_1$$
$$<5s\ |\ 5s> = (8/14175)(\alpha/\beta)^{\frac{11}{2}}I_0$$
$$<5p_z\ |\ 5s> = (8/14175)(3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}\cos\theta\ I_1$$
$$<5p_x\ |\ 5s> = (8/14175)(3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}\sin\theta\ \cos\phi\ I_1$$
$$<5p_y\ |\ 5s> = (8/14175)(3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}\sin\theta\ \sin\phi\ I_1$$

element in terms of the atomic orbitals. The dipole moment matrix elements along the x, y and z axes can be obtained by replacing the dipole moment operator r by x, y and z.

In this paper, the dipole moment operators are expressed in spherical harmonics form,[16] for convenience, namely

$$x=(2/3)^{\frac{1}{2}}r\{Y_{1-1}(\theta,\ \phi)-Y_{11}(\theta,\ \phi)\}$$
$$y=(2/3)^{\frac{1}{2}}r\{Y_{1-1}(\theta,\phi)+Y_{11}(\theta,\ \phi)$$
$$z=(4/3)^{\frac{1}{2}}rY_{10}(\theta,\phi) \qquad (10)$$

To represent the dipole moment matrix elements in analytical forms, the dipole moment operators must be expressed in terms of the coordinate system of the reference point. If an arbitrary point is taken as the reference point, the dipole moment operator may be represented in the general form,

$$r_3Y_{1P}(\theta_3,\ \phi_3)=r_2Y_{1P}(\theta_2,\ \phi_2)+RY_{1P}(\theta_2,\ \phi_2) \qquad (11)$$

Where $P=0$ or ±1.

Combining the general form of the dipole moment operator with the expansion formulas for SCF orbitals gives the general formula for the imaginary form of the dipole moment matrix element.

$$<\phi_A|r_3Y_{1P}(\theta_3,\ \phi_3)|\phi_B>=<\phi_A|r_2Y_{1P}(\theta_2,\phi_2)|\phi_B>+RY_{1P}(\theta_2,\ \phi_2)<\phi_A|\phi_B> \qquad (12)$$

Where the first part is the imaginary form of the dipole moment matrix element when point A in Figure 1 is taken as a reference point. The general formula is given by

$$\begin{aligned}&<\phi_A|r_2Y_{1P}(\theta_2,\phi_2)|\phi_B>\\&=NM\sum_{l_1=0}^{l}\sum_{l_2=0}^{l}\sum_{m_1=-l_1}^{l_1}\sum_{m_2=-l_2}^{l_2}\sum_{l_4=|n-l_1|}^{n+l_1}\sum_{l_5=|n-l_2|}^{n+l_2}\sum_{m_4=-l_4}^{l_4}\sum_{m_5=-l_5}^{l_5}\sum_{n=0}^{\infty}\sum_{h=-n}^{n}\\&\delta(l_1+l_2,\ l)\,(-1)^{l_2-m+h+m_3+m_5}\,r_1^{l_1}Y^*_{l_4m_4}(\theta_1,\ \phi_1)\\&\int_0^\infty d_n(r_1,\ r_2)\,r_2^{l_2+U+3}\exp(-\beta r)\,dr_2(2l+1)\\&(2n+1)\,(2l_5+1)\left\{\frac{3(2l_3+1)\,(2l_4+1)\,(2l)\,!}{(2l_1)\,!\,(2l_2)\,!}\right\}^{\frac{1}{2}}\\&\begin{pmatrix}l_1 & l_2 & l\\ m_1 & m_2 & -m\end{pmatrix}\begin{pmatrix}n & l_1 & l_4\\ -h & m_1 & m_4\end{pmatrix}\begin{pmatrix}n & l_2 & l_5\\ h & m_2 & m_5\end{pmatrix}\begin{pmatrix}l_3 & 1 & l_5\\ -m_3 & P & -m_5\end{pmatrix}\\&\begin{pmatrix}n & l_1 & l_4\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}n & l_2 & l_5\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_3 & 1 & l_5\\ 0 & 0 & 0\end{pmatrix}\end{aligned} \qquad (13)$$

Substituting the numerical values of the 3-j symbols for the specified n,l,m,h,P,l_i and m_i and the radial integrals gives the imaginary form of the dipole moment matrix elements. The dipole moment matrix elements may be obtained by transforming the imaginary form of the dipole moment matrix elements into the real form. The dipole moment matrix elements between pairs of SCF orbitals centered at two different atoms are listed in appendix.

5. Results and Discussion

For a hypothetical NO molecule, the calculated overlap integrals using the analytical formulas listed in Table 2 are represented in Table 3 with Mulliken's results. As shown in Table 3, the numerical values of two center overlap integrals is exactly in agreement with those for Mulliken's method.

As shown in Table 4, the numerical values of the dipole moment matrix elements evaluated using the analytical formulas listed in Appendix are also exactly in agreement with those of the transformation method of the dipole moment matrix element into overlap matrix elements[5].

TABLE 3: The Numerical Values of Two Center Overlap Integrals for a Hypothetical NO Molecule ($\alpha=1.950$, $\beta=2.275$ and $r=1.50$Å)

Overlap integral	Numerical value	
	This method	Mulliken's method
$<1s\ \|\ 5s>$	0.264763	0.264763
$<2s\ \|\ 5s>$	0.402010	0.402010
$<2p_z\ \|\ 5s>$	0.259706	0.259706
$<3s\ \|\ 5s>$	0.504653	0.504653
$<3p_z\ \|\ 5s>$	0.377752	0.377752
$<4s\ \|\ 5s>$	0.570577	0.570577
$<4p_z\ \|\ 5s>$	0.480267	0.480267
$<5s\ \|\ 5s>$	0.601650	0.601650
$<5p_z\ \|\ 5s>$	0.557729	0.557729

TABLE 4: The Num rical Results for the Dipole Moment Matrix Elements and the Corresponding Transfromed Overlap Integrals (α=1.950, β=2.275 and r=1.50 Å)

Dipole moment matrix elements	Numerical value	Transformed overlap integrals	Numerical value
$\langle 1s \mid z \mid 5s\rangle$	0.070480	$(1/\alpha)\langle 2p_z \mid 5s\rangle$	0.070480
$\langle 2s \mid z \mid 5s\rangle$	0.162092	$(2/5)^{\frac{1}{2}}(1/\alpha)\langle 3p_z \mid 5s\rangle$	0.162092
$\langle 3s \mid z \mid 5s\rangle$	0.281560	$(14/3)^{\frac{1}{2}}(1/\alpha)\langle 4p_z \mid 5s\rangle$	0.281560
$\langle 4s \mid z \mid 5s\rangle$	0.414514	$(15/2)^{\frac{1}{2}}(1/\alpha)\langle 5p_z \mid 5s\rangle$	0.414514
$\langle 5s \mid z \mid 5s\rangle$	0.543160	$(11)^{\frac{1}{2}}(1/\alpha)\langle 6p_z \mid 5s\rangle$	0.543160
$\langle 2p_z \mid z \mid 5s\rangle$	0.255091	$(5/2)^{\frac{1}{2}}(1/\alpha)\langle 3s \mid 5s\rangle + (2)^{\frac{1}{2}}(1/\alpha)\langle 3d_{z^2} \mid 5s\rangle$	0.255091
$\langle 3p_z \mid z \mid 5s\rangle$	0.417419	$(14/3)^{\frac{1}{2}}(1/\alpha)\langle 4s \mid 5\rangle + (56/15)^{\frac{1}{2}}(1/\alpha)\langle 4d_{z^2} \mid 5s\rangle$	0.417419
$\langle 4p_z \mid z \mid 5s\rangle$	0.594937	$(15/2)^{\frac{1}{2}}(1/\alpha)\langle 5s \mid 5s\rangle + (6)^{\frac{1}{2}}(1/\alpha)\langle 5d_{z^2} \mid 5s\rangle$	0.594937
$\langle 5p_z \mid z \mid 5s\rangle$	0.768339	$(11)^{\frac{1}{2}}(1/\alpha)\langle 6s \mid 5s\rangle + (44/5)^{\frac{1}{2}}(1/\alpha)\langle 6d_{z^2} \mid 5s\rangle$	0.768339

Such results indicate that we may evaluate two center integrals such as the overlap and the dipole moment matrix elements for any pairs of SCF orbital $|5s\rangle$, $|6p\rangle$ without coordinate transformations into spheroidal coordinate. We have evaluated the hyperfine integrals for $4d^x$ systems[19] and calculated the NMR chemical shift for a $4d^1$ system in a strong crystal field environment of octahedral and tetragonal symmetries[20,21].

To calculate the NMR chemical shift and the hyperfine interaction tensor components for $5d^1$ systems, the expansion formula for $r^4\exp(-\beta r)$ is required.

Therefore, this work may be applied to calculate the two center overlap and dipole moment matrix elements for second and third series of transition metal complexes. As mentioned in the previous paragraph, the expansion formula for SCF orbitals $|5s\rangle$ and $|6p\rangle$ can be used to calculate the NMR chemical shift and the hyperfine interaction tensor components for $5d^x$ system.

APPENDIX: Master Formulas for Dipole Moment MatrixElements

$\langle 1s \mid z \mid 5s\rangle = (32/14175)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\cos\theta\ F_1$

$\langle 2s \mid z \mid 5s\rangle = (32/42525)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}(1/\beta)\cos\theta\ G_1$

$\langle 2p_z \mid z \mid 5s\rangle = (4/135)(2/7)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}(1/\beta)\{G_0+(2\cos^2\theta-\sin^2\theta)\ G_2\}$

$\langle 2p_x \mid z \mid 5s\rangle = (4/45)(2/7)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}(1/\beta)\cos\theta\sin\theta\cos\phi\ G_2$

$\langle 2p_y \mid z \mid 5s\rangle = (4/45)(2/7)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}(1/\beta)\cos\theta\sin\theta\sin\phi\ G_2$

$\langle 3s \mid z \mid 5s\rangle = (8/135)(1/35)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\cos\theta\ H_1$

$\langle 3p_z \mid z \mid 5s\rangle = (8/135)(1/105)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\{H_0+(2\cos^2\theta-\sin^2\theta)\ H_2\}$

$\langle 3p_x \mid z \mid 5s\rangle = (8/45)(1/105)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\cos\theta\sin\theta\cos\phi\ H_2$

$\langle 3p_y \mid z \mid 5s\rangle = (8/45)(1/105)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\cos\theta\sin\theta\sin\phi\ H_2$

$\langle 3d_{z^2} \mid z \mid 5s\rangle = (4/675)(1/7)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\cos\theta\{4H_1+3(2\cos^2\theta-3\sin^2\theta)\ H_3\}$

$\langle 3d_{xz} \mid z \mid 5s\rangle = (8/225)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\sin\theta\cos\phi\{H_1+(4\cos^2\theta-\sin^2\theta)\ H_3\}$

$\langle 3d_{yz} \mid z \mid 5s\rangle = (8/225)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\sin\theta\sin\phi\{H_1+(4\cos^2\theta-\sin^2\theta)\ H_3\}$

$\langle 3d_{xy} \mid z \mid 5s\rangle = (8/45)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\cos\theta\sin^2\theta\sin\phi\cos\phi\ H_3$

$\langle 3d_{x^2-y^2} \mid z \mid 5s\rangle = (4/45)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\cos\theta\sin^2\theta(\cos^2\phi-\sin^2\phi)\ H_3$

$\langle 4s \mid z \mid 5s\rangle = (4/945)(2/5)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\cos\theta\ I_1$

$\langle 4p_z \mid z \mid 5s\rangle = (4/945)(2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\{I_0+(2\cos^2\theta-\sin^2\theta)\ I_2\}$

$\langle 4p_x \mid z \mid 5s\rangle = (4/315)(2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\cos\theta\sin\theta\cos\phi\ I_2$

$\langle 4p_y \mid z \mid 5s\rangle = (4/315)(2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\cos\theta\sin\theta\sin\phi\ I_2$

$\langle 5s \mid z \mid 5s\rangle = (8/14175)(\alpha/\beta)^{\frac{11}{2}}(1/\beta)\cos\theta\ J_1$

$\langle 5p_z \mid z \mid 5s\rangle = (8/14175)(1/3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}(1/\beta)\{J_0+(2\cos^2\theta-\sin^2\theta)\ J_2\}$

$\langle 5p_x \mid z \mid 5s\rangle = (8/14175)(3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}(1/\beta)\cos\theta\sin\theta\cos\phi\ J_2$

$\langle 5p_y \mid z \mid 5s\rangle = (8/14175)(3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}(1/\beta)\cos\theta\sin\theta\sin\phi\ J_2$

$\langle 1s \mid x \mid 5s\rangle = (32/14175)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\sin\theta\cos\phi\ F_1$

$\langle 2s \mid z \mid 5s\rangle = (32/42525)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}(1/\beta)\sin\theta\cos\phi\ G_1$

$\langle 2p_x \mid x \mid 5s\rangle = (32/14175)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}(1/\beta)\cos\theta\sin\theta\cos\phi\ G_2$

$\langle 2p_z \mid x \mid 5s\rangle = (2/135)(2/7)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}(1/\beta)\ [G_0-[(2\cos^2\theta-\sin^2\theta)-3\sin^2\theta(\cos^2\phi-\sin^2\phi)]\ G_2]$

$\langle 2p_y \mid x \mid 5s\rangle = (32/14175)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}(1/\beta)\sin^2\theta\sin\phi\cos\phi\ G_2$

$\langle 3s \mid x \mid 5s\rangle = (8/135)(1/35)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\sin\theta\cos\phi\ H_1$

$\langle 3p_z \mid x \mid 5s\rangle = (8/45)(1/105)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\cos\theta\sin\theta\cos\phi\ H_2$

$\langle 3p_x \mid x \mid 5s\rangle = (4/135)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\ \{H_0-[(2\cos^2\theta-\sin^2\theta)-3\sin^2\theta(\cos^2\phi-\sin^2\phi)]\ H_2\}$

$\langle 3p_y \mid x \mid 5s\rangle = (8/45)(1/105)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\sin^2\theta\sin\phi\cos\phi\ H_2$

$\langle 3d_{z^2} \mid x \mid 5s\rangle = (4/1575)(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\sin\theta\cos\phi\{3(4\cos^2\theta-\sin^2\theta)\ H_3-2H_1\}$

$\langle 3d_{xz} \mid x \mid 5s\rangle = (4/675)(3/7)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\cos\theta\ \{2H_1-[(2\cos^2\theta-3\sin^2\theta)-5\sin^2\theta(\cos^2\phi-\sin^2\phi)]\ H_3\}$

$\langle 3d_{yz} \mid x \mid 5s\rangle = (8/45)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\cos\theta\sin^2\theta\sin\phi\cos\phi\ H_3$

$\langle 3d_{xy} \mid x \mid 5s\rangle = (2/225)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\sin\theta\sin\phi\ \{4H_1+[5\sin\theta(3-2\sin^2\phi)-(4\cos^2\theta-\sin^2\theta)]\ H_3\}$

$\langle 3d_{x^2-y^2} \mid x \mid 5s\rangle = (2/225)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\sin\theta\cos\phi\ \{4H_1+[5\sin\theta(3-4\sin^2\phi)-(4\cos^2\theta-\sin^2\theta)]\ H_3\}$

$\langle 4s \mid x \mid 5s\rangle = (4/945)(2/5)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\sin\theta\cos\phi\ I_1$

$\langle 4p_x \mid x \mid 5s\rangle = (4/315)(2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\cos\theta\sin\theta\cos\phi\ I_2$

$\langle 4p_z \mid x \mid 5s\rangle = (2/945)(2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\{I_0-[(\cos^2\theta-\sin^2\theta)-3\sin^2\theta(\cos^2\phi-\sin^2\phi)]\ I_2\}$

$\langle 4p_y \mid x \mid 5s\rangle = (4/315)(2/14)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\sin^2\theta\sin\phi\cos\phi\ I_2$

$\langle 5s \mid x \mid 5s\rangle = (8/14175)(\alpha/\beta)^{\frac{11}{2}}(1/\beta)\sin\theta\cos\phi\ J_1$

$\langle 5p_z \mid x \mid 5s\rangle = (8/14175)(3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}(1/\beta)\cos\theta\sin\theta\cos\phi\ J_2$

$\langle 5p_x \mid x \mid 5s\rangle = (4/14175)(1/3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}(1/\beta)\ \{J_0-[(2\cos^2\theta-\sin^2\theta)-3\sin^2\theta(\cos^2\phi-\sin^2\phi)]J_2\}$

$\langle 5p_y \mid x \mid 5s\rangle = (8/14175)(3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}(1/\beta)\sin^2\theta\sin\phi\cos\phi\ J_2$

$\langle 1s \mid y \mid 5s\rangle = (32/14175)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\sin\theta\sin\phi\ F_1$

$\langle 2s \mid y \mid 5s\rangle = (32/42525)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}(1/\beta)\sin\theta\sin\phi\ G_1$

$\langle 2p_x \mid y \mid 5s\rangle = (32/14175)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}(1/\beta)\cos\theta\sin\theta\sin\phi\ G_2$

$\langle 2p_z \mid y \mid 5s\rangle = (32/14175)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}(1/\beta)\sin^2\theta\sin\theta\cos\phi\ G_2$

$\langle 2p_y \mid y \mid 5s\rangle = (2/135)(2/7)^{\frac{1}{2}}(\alpha/\beta)^{\frac{5}{2}}(1/\beta)\ \{G_0-[(2\cos^2\theta-\sin^2\theta)+3\sin^2\theta(\cos^2\phi-\sin^2\phi)]\ G_2\}$

$\langle 3s \mid y \mid 5s\rangle = (8/135)(1/35)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\sin\theta\sin\phi\ H_1$

$\langle 3p_z \mid y \mid 5s\rangle = (8/45)(1/105)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\cos\theta\sin\theta\sin\phi\ H_2$

$\langle 3p_x \mid y \mid 5s\rangle = (8/45)(1/105)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\sin^2\theta\sin\phi\cos\phi\ H_2$

$$\langle 3p_y \mid y \mid 5s\rangle = (4/135)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\ \{H_0-[(2\cos^2\theta-\sin^2\theta)+3\sin^2\theta(\cos^2\phi-\sin^2\phi)]\ H_2\}$$

$$\langle 3d_{xz} \mid y \mid 5s\rangle = (4/1575)(\alpha/\beta)^{\frac{7}{2}}\ (1/\beta)\ \sin\theta\ \sin\phi\ \{3(4\cos^2\theta-\sin^2\theta)\ H_3-2H_1\}$$

$$\langle 3d_{zz} \mid y \mid 5s\rangle = (8/45)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\ \cos\theta\sin^2\theta\sin\ \phi\ \cos\phi\ H_3$$

$$\langle 3d_{yz} \mid y \mid 5s\rangle = (4/675)(3/7)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\ \cos\theta\ \{2H_1+[(2\cos^2\theta-3\sin^2\theta)-5\sin^2\theta(\cos^2\phi-\sin^2\phi)]\ H_3\}$$

$$\langle 3d_{xy} \mid y \mid 5s\rangle = (2/225)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\ \sin\phi\ \cos\phi\ \{[5\sin\theta(4\cos^2\phi-3)+(4\cos^2\theta-\sin^2\theta)]H_3-4H_1\}$$

$$\langle 3d_{x^2-y^2} \mid y \mid 5s\rangle = (2/225)(1/21)^{\frac{1}{2}}(\alpha/\beta)^{\frac{7}{2}}(1/\beta)\ \sin\theta\ \sin\phi\ \{[5\sin\theta(3-4\sin^2\phi)+(4\cos^2\theta-\sin^2\theta)]\ H_3-4H_1\}$$

$$\langle 4s \mid y \mid 5s\rangle = (4/945)(2/5)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\ \sin\theta\ \sin\phi\ I_1$$

$$\langle 4p_z \mid y \mid 5s\rangle = (4/315)(2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\ \cos\theta\ \sin\theta\ \sin\phi\ I_2$$

$$\langle 4p_x \mid y \mid 5s\rangle = (4/315)(2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\ \sin^2\theta\ \sin\phi\ \cos\phi\ I_2$$

$$\langle 4p_y \mid y \mid 5s\rangle = (2/945)(2/15)^{\frac{1}{2}}(\alpha/\beta)^{\frac{9}{2}}(1/\beta)\ \{I_0-[(2\cos^2\theta-\sin^2\theta)+3\sin^2\theta(\cos^2\phi-\sin^2\phi)]\ I_2\}$$

$$\langle 5s \mid y \mid 5s\rangle = (8/14175)(\alpha/\beta)^{\frac{11}{2}}(1/\beta)\ \sin\theta\ \sin\phi\ J_1$$

$$\langle 5p_z \mid y \mid 5s\rangle = (8/14175)(3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}(1/\beta)\ \cos\theta\ \sin\theta\ \cos\phi\ J_2$$

$$\langle 5p_x \mid y \mid 5s\rangle = (8/14175)(3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}(1/\beta)\ \sin^2\theta\ \sin\phi\ \cos\phi\ J_2$$

$$\langle 5p_y \mid y \mid 5s\rangle = (4/14175)(1/3)^{\frac{1}{2}}(\alpha/\beta)^{\frac{11}{2}}(1/\beta)\ \{J_0-[(2\cos^2\theta-\sin^2\theta)+3\sin^2\theta(\cos^2\phi-\sin^2\phi)]\ J_2\}$$

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The Crystal and Molecular Structure of Phlorizin Dihydrate

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The crystal structure of phlorizin, a β-D-glucopyranoside of a flavonoid dihydrochalcone phloretin, has been determined by single crystal diffraction methods using diffractometer data obtained by the ω–2θ scan technique with Cu Kα radiation from a crystal with space group symmetry $P2_12_12_1$ and unit cell parameters a=4.9094 (2), b=19.109 (1), c = 23.275 (4) Å. The structure was solved by direct methods and refined by full-matrix least-squares to a final R = 0.047 for the 1697 observed reflections. The dihydrochalcone moiety is flat and fully extended. The glucose ring has the $^4C_1$ chair conformation and the conformation of the primary alcohol group is *gauche-gauche*. The crystal packing is dominated by an extensive hydrogen bonding pattern. There are one strong and two weak intramolecular hydrogen bonds in the phlorizin molecule.

Introduction

Some of the flavonoid dihydrochalcones and their saccharide derivatives display an intensely sweet taste and have potential use for the nonnutritive sweetners, while the corresponding flavanones are usually bitter compounds.[1-3] Little is known about the conformational characteristics of the flavonoid dihydrochalcones themselves and their modes of linkage to the saccharides. Phlorizin, 2-β-D-glucopyranoside of phloretin, is a sweet compound with bitter aftertaste.