10. A. (Jr.) Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Willey, New York, 1961, pp. 117.
11. R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), **40**, 2474 (1964).
12. R.G. Parr, "The Quantum Theory of Molecular Electronic Structure," Benjamin, Amsterdam, 1964.
13. R.C. Bingham, M.J.S. Dewar, and D.H.Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).
14. A.G. Turner, "Molecular Orbital Theory," Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1974.
15. B.E. Conway and R.G. Barradas, *Electrochem. Acta*, **5**, 319 (1961).
16. A.S. Fouda, *J. Monätshefte für chemie*, in press.
17. V. Carassiti, F. Zucchi and G. Trabanelli, 3rd. European Symposium on Corrosion Inhibitors Annali Univ. Ferrara, *N.S., Sez.*, **5**, 525 (1971).
18. Z. Szklarska-Smialowska and M. Kaminski, *Corros. Sci.*, **13**, 1 (1973).

Ortho-normalized Gaussian Type Orbitals

Jong-Gi Jee

Department of Chemistry, Teacher's College, Kyungpook National University, Taegu 635

Received August 26, 1985

The conventional Gaussian type orbitals (GTO's) were generalized to have a regular form which is similar to the conventional Slater type orbitals (STO's). They were also orthogonalized and orthonormalized to have the same number of radial nodes that the hydrogenic orbitals have.

Introduction

Gaussian functions of the type of the next Eq.(1) and their linear combinations were first proposed by S.F. Boys as basis set orbitals in the calculation of ab-initio molecular orbitals.[1-3]

$$r^P \exp(-\alpha r_A^2)\, Y_l^{|m|}(\theta,\phi) \quad (1)$$

where $Y_l^{|m|}(\theta,\phi)$ are spherical harmonics, and $a>0$, P is integral, equal to or greater than 1, and is restricted to odd values for odd l, even values for even l. The virtue of these functions is the relatively simple closed analytic expression for the two-electron integrals in the three and four-centers cases, as well as for one and two-centers.

The Gaussian-type orbitals (GTO's) described in Eq.(1) do not contain same radial nodes that hydrogenic orbitals have. Therefore, author transformed Eq.(1) into the following form;

$$g_{nlm}(r) = N_r r^{n-1} e^{-\alpha r^2} \quad (2)$$

where N_r is the normalizing constant and n, l, and m stand for the usual quantum number. Normalizing Eq.(2) leads to the following equation.

$$g_{nlm}(r) = \left(\frac{2^{n+1}}{1\cdot3\cdot5\cdots(2n-1)}\right)^{\frac{1}{2}} \left((2\alpha)^{2n+1}/\pi\right)^{\frac{1}{4}} r^{n-1} e^{-\alpha r^2} \quad (3)$$

where $g_{nlm}(r)$ stand for the radial GTO's.

The combination of Eq.(3) and the real spherical harmonics, $Y_{lm\delta}^{real}(\theta,\phi)$, yields equation (4)

$$g_{nlm\delta}(r,\theta,\phi) = \left(2^{n+1}/1\cdot3\cdot5\cdots(2n-1)\right)^{\frac{1}{2}} \left((2\alpha)^{2n+1}/\pi\right)^{\frac{1}{4}} r^{n-1} e^{-\alpha r^2} Y_{lm\delta}^{real}(\theta,\phi) \quad (4)$$

where δ denotes zero, cosine and sine combination which the complex spherical harmonics are transformed into the real spherical harmonics according to its value zero, 1 and -1.[4] Eq.(4) is called to the generalized GTO's. The $g_{nlm\delta}(r,\theta,\phi)$ have the similar form with the Slater type orbitals (STO's) and are different only in the normalization constant and exponential term. $G_{nlm\delta}(r,\theta,\phi)$ do not have the radial nodes for the hydrogenic functions like STO's.[5,6]

Accordingly, author orthogonalize and normalize the $g_{nlm\delta}(r,\theta,\phi)$ as follows; one can consider atom as a vector space and its atomic orbitals (AO's) as the component vector in its vector space.[6] Putting g_k equal to $g_{nlm\delta}(r,\theta,\phi)$ in Eq.(4), we may obtain the next equation by using the Schmidt's orthorgonalizing process for vectors.[4,7]

$$g_1^\circ = g_1$$

$$g_2^\circ = g_2 - \frac{(g_1^\circ/g_2)}{(g_1^\circ/g_1^\circ)} g_1^\circ$$

$$g_3^\circ = g_3 - \frac{(g_2^\circ/g_3)}{(g_2^\circ/g_2^\circ)} g_2^\circ - \frac{(g_1^\circ/g_3)}{(g_1^\circ/g_1^\circ)} g_1^\circ$$

....

$$g_k^\circ = g_k - \frac{(g_k^\circ/g_k)}{(g_{k-1}^\circ/g_{k-1}^\circ)} g_{k-1}^\circ \cdots - \frac{(g_1^\circ/g_k)}{(g_1^\circ/g_1^\circ)} g_1^\circ \quad (5)$$

where g_k° are the orthogonalized GTO, $g_{nlm\delta}^\circ(r,\theta,\phi)$ and (g_k°/g_k) denotes the dot product, overlap integral between g_k° and g_k.

Then, these g_k° can be normalized as follows;[8]

$$g_k^\ominus = g_k^\circ / (g_k^\circ/g_k^\circ) \quad (6)$$

where $g_k^\ominus$ denotes orthonormalized GTO, $g_{nlm\delta}^\ominus(r,\theta,\phi)$.

Results and Discussion

The result calculated from Eq.(4) was listed in Table 1. Comparing $g_{nlm\delta}(r,\theta,\phi)$, in Table 1 with the conventional STO's

Table 1. Caussian type orbitals ($g_{nlm\delta}(r,\theta,\phi)$)

n	l	m	δ	designation	function
1	0	0	0	1s	$(1/3\pi)^{\frac{1}{2}}((2\alpha)^3/\pi)^{\frac{1}{4}}e^{-\alpha r^2}$
2	0	0	0	2s	$(2/15\pi)^{\frac{1}{2}}((2\alpha)^5/\pi)^{\frac{1}{4}}r\ e^{-\alpha r^2}$
2	1	0	0	$2p_z$	$(2/5\pi)^{\frac{1}{2}}((2\alpha)^5/\pi)^{\frac{1}{4}}r\ e^{-\alpha r^2}\cos\theta$
2	1	±1	1	$2p_x$	$(2/5\pi)^{\frac{1}{2}}((2\alpha)^5/\pi)^{\frac{1}{4}}r\ e^{-\alpha r^2}\sin\theta\cos\phi$
2	1	±1	−1	$2p_y$	$(2/5\pi)^{\frac{1}{2}}((2\alpha)^5/\pi)^{\frac{1}{4}}r\ e^{-\alpha r^2}\sin\theta\sin\phi$
3	0	0	0	3s	$(4/105\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}$
3	1	0	0	$3p_z$	$(4/35\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}\cos\theta$
3	1	±1	−1	$3p_x$	$(4/35\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}\sin\theta\cos\phi$
3	1	±1	1	$3p_y$	$(4/35\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}\sin\theta\sin\phi$
3	2	0	0	$3d_{z^2}$	$(1/21\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}(3\cos^2\theta-1)$
3	2	±1	1	$3d_{xz}$	$(1/7\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}\sin(2\theta)\cos\phi$
3	2	±1	−1	$3d_{yz}$	$(1/7\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}\sin(2\theta)\sin\phi$
3	2	±2	1	$3d_{x^2-y^2}$	$(1/7\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}\sin^2\theta\cos(2\phi)$
3	2	±2	−1	$3d_{xy}$	$(1/7\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}\sin^2\theta\sin(2\theta)$
4	0	0	0	4s	$(8/945\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}$
4	1	0	0	$4p_z$	$(8/315\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\cos\theta$
4	1	±1	1	$4p_x$	$(8/315\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin\theta\cos\phi$
4	1	±1	−1	$4p_y$	$(8/315\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin\theta\sin\phi$
4	2	0	0	$4d_{z^2}$	$(2/189\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}(3\cos^2\theta-1)$

Table 1. Continued

n	l	m	δ	designation	function
4	2	±1	1	$4d_{xz}$	$(2/63\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin(2\theta)\cos\phi$
4	2	±1	−1	$4d_{yz}$	$(2/63\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin(2\theta)\cos\phi$
4	2	±2	1	$4d_{x^2-y^2}$	$(2/63\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin^2\theta\cos(2\phi)$
4	2	±2	−1	$4d_{xy}$	$(2/63\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin^2\theta\sin(2\theta)$
4	3	0	0	$4f_{z^3}$	$(1/135\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}(5\cos^3\theta-3\cos\theta)$
4	3	±1	1	$4f_{xz^2}$	$(1/180\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}(5\cos^2\theta-1)\sin\theta\cos\phi$
4	3	±1	−1	$4f_{yz^2}$	$(1/180\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}(5\cos^2\theta-1)\sin\theta\sin\phi$
4	3	±2	1	$4f_{z(x^2-y^2)}$	$(1/18\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{2}}r^3e^{-\alpha r^2}\sin^2\theta\cos\theta(\cos^2\phi-\sin^2\phi)$
4	3	±2	−1	$4f_{xyz}$	$(1/18\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin^2\theta\cos\theta\sin\phi\cos\phi$
4	3	±3	1	$4f_{x^3}$	$(1/108\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin^3\theta\cos\phi(\cos^2\phi-3\sin^2\phi)$
4	3	±3	−1	$4f_{y^3}$	$(1/108\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin^3\theta\sin\phi(\sin^2\phi-3\cos^2\phi)$
5	0	0	0	5s	$(1/650\pi)^{\frac{1}{2}}((2\alpha)^{11}/\pi)^{\frac{1}{4}}r^4e^{-\alpha r^2}$

Table 2. Orthogonalized Gaussian type orbitals ($g^{\circ}_{nlm\delta}(r,\theta,\phi)$)

n	l	m	δ	designation	function
1	0	0	0	1s	$(1/3\pi)^{\frac{1}{2}}((2\alpha)^3/\pi)^{\frac{1}{4}}e^{-\alpha r^2}$
2	0	0	0	2s	$(2/15\pi)^{\frac{1}{2}}((2\alpha)^5/\pi)^{\frac{1}{4}}(r-\sqrt{1/2\pi\alpha})e^{-\alpha r^2}$
2	1	0	0	$2p_z$	$(2/5\pi)^{\frac{1}{2}}((2\alpha)^5/\pi)^{\frac{1}{4}}r\ e^{-\alpha r^2}\cos\theta$
2	1	±1	1	$2p_x$	$(2/5\pi)^{\frac{1}{2}}((2\alpha)^5/\pi)^{\frac{1}{4}}r\ e^{-\alpha r^2}\sin\theta\cos\phi$
2	1	±1	−1	$2p_y$	$(2/5\pi)^{\frac{1}{2}}((2\alpha)^5/\pi)^{\frac{1}{4}}r\ e^{-\alpha r^2}\sin\theta\sin\phi$
3	0	0	0	3s	$(4/105\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}((r^2-(1/\pi-2)\sqrt{\pi/2\alpha}\ r-(\pi-4)/4\alpha(\pi-2))\cdot e^{-\alpha r^2}$
3	1	0	0	$3p_z$	$(4/35\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r(r-\sqrt{2/\pi\alpha})e^{-\alpha r^2}\cos\theta$
3	1	±1	1	$3p_x$	$(4/35\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r(r-\sqrt{2/\pi\alpha})e^{-\alpha r^2}\sin\theta\cos\phi$
3	1	±1	−1	$3p_y$	$(4/35\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r(r-\sqrt{2/\pi\alpha})e^{-\alpha r^2}\sin\theta\sin\phi$
3	2	0	0	$3d_{z^2}$	$(1/21\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r^2((3\cos^2\theta-(\pi/2)-1))e^{-\alpha r^2}$
3	2	±1	1	$3d_{xz}$	$(1/7\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}\sin(2\theta)\cos\phi$
3	2	±1	−1	$3d_{yz}$	$(1/7\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}\sin(2\theta)\sin\phi$
3	2	±2	1	$3d_{x^2-y^2}$	$(1/7\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{2}}r^2e^{-\alpha r^2}\sin^2\theta\cos(2\phi)$
3	2	±2	−1	$3d_{xy}$	$(1/7\pi)^{\frac{1}{2}}((2\alpha)^7/\pi)^{\frac{1}{2}}r^2e^{-\alpha r^2}\sin^2\theta\sin(2\phi)$
4	0	0	0	4s	$(8/945\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{2}}((r^3-1/\sqrt{2\pi\alpha}(4\cos^2\theta+12)r^2-(28/\alpha)r-(1/4\alpha\sqrt{2\pi\alpha}))e^{-\alpha r^2}$
4	1	0	0	$4p_z$	$(8/315\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r((r^2-(1/3\pi-8)\sqrt{2\pi/\alpha}\ r-(9\pi-32/4\alpha(3\pi-8)))e^{-\alpha r^2}\cos\theta$
4	1	±1	1	$4p_x$	$(8/315\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r((r^2-(1/3\pi-8)\sqrt{2\pi/\alpha}\ r-(9\pi-32/4\alpha(3\pi-8)))e^{-\alpha r^2}\sin\theta\cos\phi$
4	1	±1	−1	$4p_y$	$(8/315\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r((r^2-(1/3\pi-8)\sqrt{2\pi/\alpha}\ r-(9\pi-32/4\alpha(3\pi-8)))e^{-\alpha r^2}\sin\theta\sin\phi$
4	2	0	0	$4d_{z^2}$	$(2/189\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^2((r-(4/3)\sqrt{2/\pi\alpha}))e^{-\alpha r^2}(3\cos^2\theta-1)$
4	2	±1	1	$4d_{xz}$	$(2/63\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^2((r-(4/3)\sqrt{2/\pi\alpha}))e^{-\alpha r^2}\sin(2\theta)\cos\phi$
4	2	±1	−1	$4d_{yz}$	$(2/63\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^2((r-(4/3)\sqrt{2/\pi\alpha}))e^{-\alpha r^2}\sin(2\theta)\sin\phi$
4	2	±2	1	$4d_{x^2-y^2}$	$(2/63\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^2((r-(4/3)\sqrt{2/\pi\alpha}))e^{-\alpha r^2}\sin^2\theta\cos(2\phi)$
4	2	±2	−1	$4d_{xy}$	$(2/63\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^2((r-(4/3)\sqrt{2/\pi\alpha}))e^{-\alpha r^2}\sin^2\theta\sin(2\phi)$

Table 2. Continued

n	l	m	δ	function	designation
4	3	0	0	$4f_{z^3}$	$(1/135\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3(5\cos^2\theta-15/4)e^{-\alpha r^2}\cos\theta$
4	3	±1	1	$4f_{xz^2}$	$(1/180\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3(5\cos^2\theta-5/4)e^{-\alpha r^2}\sin\theta\cos\phi$
4	3	±1	−1	$4f_{yz^2}$	$(1/180\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3(5\cos^2\theta-5/4)e^{-\alpha r^2}\sin\theta\sin\phi$
4	3	±2	1	$4f_{z(x^2-y^2)}$	$(1/18\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin^2\theta\cos\theta(\cos^2\phi-\sin^2\phi)$
4	3	±2	−1	$4f_{xyz}$	$(1/18\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin^2\theta\cos\theta\sin\phi\cos\phi$
4	3	±3	1	$4f_{x^3}$	$(1/108\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin^3\theta\cos\phi(\cos^2\phi-3\sin^2\phi)$
4	3	±3	−1	$4f_{y^3}$	$(1/108\pi)^{\frac{1}{2}}((2\alpha)^9/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin^3\theta\sin\phi(\sin^2\phi-3\cos^2\phi)$
5	0	0	0	5s	$(1/650\pi)^{\frac{1}{2}}((2\alpha)^{11}/\pi)^{\frac{1}{4}}((r^4-3/5(3\cos^2\theta-1)\sqrt{\pi/2\alpha}\ r^3$ $-(4/5\alpha)(3\cos^2\theta-1)r^2+(5/\alpha)\sqrt{\pi/2\alpha}\ r+15/32\alpha))e^{-\alpha r^2}$

Table 3. Ortho-normalized Gaussian type orbitals ($g^{\ominus}_{nlm\delta}(r,\theta,\phi)$)

n	l	m	δ	designation	function
1	0	0	0	1s	$\sqrt{2}(2\alpha/\pi)^{\frac{1}{4}}e^{-\alpha r^2}$
2	0	0	0	2s	$2(2\alpha/\pi-2)^{\frac{1}{2}}(2\pi\alpha)^{\frac{1}{4}}(r-\sqrt{1/2\pi\alpha})e^{-\alpha r^2}$
2	1	0	0	$2p_z$	$4(\alpha/\pi)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r\ e^{-\alpha r^2}\cos\theta$
2	1	±1	1	$2p_x$	$4/\pi(\alpha)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r\ e^{-\alpha r^2}\sin\theta\cos\phi$
2	1	±1	−1	$2p_y$	$4/\pi(\alpha)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r\ e^{-\alpha r^2}\sin\theta\sin\phi$
3	0	0	0	3s	$4\alpha(\pi-2/\pi-3)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}((r^2-(1/\pi-2)\sqrt{\pi/2\alpha}\ r-(\pi-4/4\alpha(\pi-2)))e^{-\alpha r^2}$
3	1	0	0	$3p_z$	$8\alpha(1/3\pi-8)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r(r-\sqrt{2/\pi\alpha})e^{-\alpha r^2}\cos\theta$
3	1	±1	1	$3p_x$	$8\alpha(1/\pi(3\pi-8))^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r(r-\sqrt{2/\pi\alpha})e^{-\alpha r^2}\sin\theta\cos\phi$
3	1	±1	−1	$3p_y$	$8\alpha(1/\pi(3\pi-8))^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r(r-\sqrt{2/\pi\alpha})e^{-\alpha r^2}\sin\theta\sin\phi$
3	2	0	0	$3d_{z^2}$	$16\alpha(1/3\pi(2\pi^2-4\pi+11))^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^2((3\cos^2\theta-(\pi/2)-1))e^{-\alpha r^2}$
3	2	±1	1	$3d_{xz}$	$8\alpha/\pi(1/3)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}\sin(2\theta)\cos\phi$
3	2	±1	−1	$3d_{yz}$	$8\alpha/\pi(1/3)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}\sin(2\theta)\sin\phi$
3	2	±2	1	$3d_{x^2-y^2}$	$16\alpha/3\pi(2\alpha/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}\sin^2\theta\cos(2\phi)$
3	2	±2	−1	$3d_{xy}$	$16\alpha/3\pi(2\alpha/\pi)^{\frac{1}{4}}r^2e^{-\alpha r^2}\sin^2\theta\sin(2\phi)$
4	0	0	0	4s	$8\alpha(\alpha/56\alpha+21715\sqrt{2\pi\alpha}+578)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}((r^3-(1/\sqrt{2\pi\alpha})(4\cos^2\theta+12)\ r^2-(28/\alpha)r-1/4\alpha\sqrt{2\pi r}))e^{-\alpha r^2}$
4	1	0	0	$4p_z$	$8\alpha(2\alpha(3\pi-8)/\pi(9\pi-28))^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r((r^2-(1/3\pi-8)\sqrt{2\pi/\alpha}\ r-(9\pi-32)/4\alpha(3\pi-8))e^{-\alpha r^2}\cos\theta$
4	1	±1	1	$4p_x$	$8\alpha/\pi(2\alpha(3\pi-8)/9\pi-28))^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r((r^2-(1/3\pi-8)\sqrt{2\pi/\alpha}\ r-(9\pi-32)/4\alpha(3\pi-8))e^{-\alpha r^2}\sin\theta\cos\phi$
4	1	±1	−1	$4p_y$	$8\alpha/\pi(2\alpha(3\pi-8)/9\pi-28))^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r((r^2-(1/3\pi-8)\sqrt{2\pi/\alpha}\ r-(9\pi-32)/4\alpha(3\pi-8))e^{-\alpha r^2}\sin\theta\sin\phi$
4	2	0	0	$4d_{z^2}$	$32\alpha(3\alpha/11(45\pi-128))^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^2((r-(4/3)\sqrt{2/\pi\alpha}))e^{-\alpha r^2}(\cos^2\theta-1)$
4	2	±1	1	$4d_{xz}$	$16\alpha(3\alpha/\pi(45\pi-128))^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^2((r-(4/3)\sqrt{2/\pi\alpha}))e^{-\alpha r^2}\sin(2\theta)\cos\phi$
4	2	±1	−1	$4d_{yz}$	$16\alpha(3\alpha/\pi(45\pi-128))^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^2((r-(4/3)\sqrt{2/\pi\alpha}))e^{-\alpha r^2}\sin(2\theta)\sin\phi$
4	2	±2	1	$4d_{x^2-y^2}$	$32\alpha(\alpha/\pi(45\pi-128))^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^2((r-(4/3)\sqrt{2/\pi\alpha}))e^{-\alpha r^2}\sin^2\theta\cos(2\phi)$
4	2	±2	−1	$4d_{xy}$	$32\alpha(\alpha/\pi(45\pi-128))^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^2((r-(4/3)\sqrt{2/\pi\alpha}))e^{-\alpha r^2}\sin^2\theta\sin(2\phi)$
4	3	0	0	$4f_{z^3}$	$16\alpha/5(2\alpha/15)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^3(5\cos^2\theta-15/4)e^{-\alpha r^2}\cos\theta$
4	3	±1	1	$4f_{xz^2}$	$64\alpha/15(\alpha/5\pi)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^3(5\cos^2\theta-5/4)e^{-\alpha r^2}\sin\theta\cos\phi$
4	3	±1	−1	$4f_{yz^2}$	$64\alpha/15(\alpha/5\pi)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^3(5\cos^2\theta-5/4)e^{-\alpha r^2}\sin\theta\sin\phi$
4	3	±2	1	$4f_{z(x^2-y^2)}$	$32\alpha/\pi(\alpha/15)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin^2\theta\cos\theta(\cos^2\phi-\sin^2\phi)$
4	3	±2	−1	$4f_{xyz}$	$64\alpha/\pi(\alpha/15)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin^2\theta\cos\theta\sin\phi\cos\phi$
4	3	±3	1	$4f_{x^3}$	$32\alpha/5(2\alpha/3)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin^3\theta\cos\phi(\cos^2\phi-3\sin^2\phi)$
4	3	±3	−1	$4f_{y^3}$	$32\alpha/5(2\alpha/3)^{\frac{1}{2}}(2\alpha/\pi)^{\frac{1}{4}}r^3e^{-\alpha r^2}\sin^3\theta\sin\phi(\sin^2\phi-3\cos^2\phi)$
5	0	0	0	5s	$(5/7\pi^2-3\pi)^{\frac{1}{2}}\alpha^2(2\alpha/\pi)^{\frac{1}{4}}((r^4-3/5(3\cos^2\theta-1)\sqrt{\pi/2\alpha}\ r^3-4/5\alpha(3\cos^2\theta-1)r^2$ $+(5/\alpha)\sqrt{\pi/2\alpha}\ r+15/32\alpha^2))e^{-\alpha r^2}$

$\eta_{nlm\sigma}(r,\theta,\phi)$,[9] we may realize that their type is the same except the parts of the normalization constants and exponents and they do not have the same radial nodes that the hydrogenic wave functions, $\Psi_{nlm\sigma}(r,\theta,\phi)$[10] have *i.e.* they have no radial nodes for the orbitals; 2s, 3s, 3p, 4s, 4p, 4d, 5s etc. Therefore, they are not a good description of the self-consistent field (SCF) method.[11,12]

Author has orthonormalized the conventional STO's.[4] But their analytic expression for the two-electron integrals in the two, three, and four-centers cases are very complex so that author has generalized and orthonormalized the conventional GTO's by using of Eq.(5) and (6). The orthogonalized GTO and orthonormalized GTO are listed in Table 2 and 3, respectively.

These GTO's have the same radial nodes and the same nodal numbers, $n-(l+1)$ that the hydrogenic orbitals, $\Psi_{nlm\sigma}(r,\theta,\phi)$, have. Therefore they are another good representations of the SCF and have very simple analytic expression for the integrals mentioned above.

Also two of $g^{\circ}_{nlm\sigma}(r,\theta,\phi)$ which are different from each other only in their quantum numbers, are orthogonal, so that the 465 overlap integrals between any two orbitals of 31 $g^{\circ}_{nlm\sigma}(r,\theta,\phi)$ with only one different value among n,l,m and σ go to zero, and in the case of $g^{\ominus}_{nlm\sigma}(r,\theta,\phi)$, those integrals have only unit or zero value because they are orthonormalized from each other by the next equation.

$$(g^{\ominus}_{nlm\sigma}(r,\theta,\phi)/g^{\ominus}_{n'l'm'\sigma'}(r,\theta,\phi))=\delta_{nlm\sigma}\delta_{n'l'm'\sigma'} \qquad (7)$$

where $g^{\ominus}_{nlm\sigma}(r,\theta,\phi)$ and $g^{\ominus}_{n'l'm'\sigma'}(r,\theta,\phi)$ are located at the same center in the molecule, and $\delta_{nlm\sigma}$ represents Kronecker delta.

Eventually, author has generalized the conventional GTO's which have no regular form for each atomic orbital with legal quantum numbers to obtain the $g^{\circ}_{nlm\sigma}(r,\theta,\phi)$ and $g^{\ominus}_{nlm\sigma}(r,\theta,\phi)$ which are the closest in the GTO's form to the hydrogenic orbitals.

These new GTO's shall be intensively utilized in ab-initio MO procedures in the near future because of their regular atomic orbital form and simple analytic representation of the integrals which must be evaluated in the ab-initio molecular orbital calculation. These integrals based on the orthonormalized Gaussian type orbitals, $g^{\ominus}_{nlm\sigma}(r,\theta,\phi)$ shall have been determined in the series of our following papers.

Reference

1. S.F. Boys, *Proc. Roy. Soc.*, (London) **200**, 542 (1950).
2. L.C. Allen, *J. Chem. Phys.*, **31**, 736 (1959).
3. L.C. Allen, *ibid*, **37**, 200 (1960).
4. J-G. Jee, *Bull. Korean Chem. Soc.*, **6**, 264 (1985).
5. J.C. Slater, *Phys. Rev.*, **36**, 57 (1930).
6. E. Clementi and D.L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).
7. I.G. Csizmadia, Progress in theoretical organic chemistry Vol. 1. P. 15. (Elsevier Scientific Pub. Comp. Amsterdam-Oxford-New York 1976).
8. Ref. 7, P. 17.
9. Ref. 7, P. 313, Table XII-2.
10. Ira N. Levine, Quantum Chemistry 3rd Ed. P 124, Table 6.2 (Allyn and Bacon, Inc. Boston London Sydney 1983).
11. C.C.J. Roothaan, *Revs. Modern Phys.*, **32**, 179 (1960).
12. L.C. Allen, *J. Chem. Phys.*, **34**, 1156 (1961).

Preparation and Properties of $Co_{9-x}M_xS_8$(M = Ni, Rh, Ru, and Fe)

Kwan Kim

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151

Received September 28, 1985

Samples with the nominal composition of $Co_{9-x}M_xS_8$(M = Ni, Rh, Ru, and Fe) were prepared, and their magnetic properties were measured. X-ray diffraction analysis showed that small amount of the elements Ni, Rh, and Fe could be incorporated into Co_9S_8 forming a homogeneous π-phase, whereas the Ru-incorporated sample could not be prepared in a single phase. The lattice parameter was observed to increase as other elements were incorporated into Co_9S_8. Samples incorporated with the elements of Ni, Rh, and Ru showed Pauli-paramagnetism while the Fe-incorporated sample exhibited weak ferromagnetism. The values of magnetic susceptibility for the Ni, Rh, Ru-incorporated samples were nearly the same as that of pure Co_9S_8.

Introduction

The nature of the cobalt present in sulfided cobalt molybdate catalysts has been the subject of several studies.[1-3] An early study by de Beer *et al.*[4] indicated that the sulfur content present in sulfided cobalt molybdate catalysts corresponded to the value anticipated for a composition of Co_9S_8 and MoS_2. However, since the actual catalysts were amorphous, direct evidence for the existence of those phases by the X-ray diffraction patterns of the catalysts was not found. In fact, if Co_9S_8 is one of the necessary component in hydrodesulfurization (HDS) catalysts, slight modification of Co_9S_8 by the chemical substitution of cobalt with other elements may result in enhancement of the catalytic activities of the catalysts that can be caused by the possible changes in the cell size as well as in the energy levels of Co_9S_8.

Following the above implications, we have prepared members of the Co-M-S system with a nominal composition