Ortho-normalized Slater-type Orbitals

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Orthogonalized Slater-type orbitals and Ortho-normalized Slater-type orbitals were derived from the conventional Slater-type orbitals (STO's) by use of the continuous orthonormalizing which is expanded from the Schmidt's orthogonalizing procedure. These orbitals have the merits which STO's have not, such as; they are *ortho*-normalized each other and have the same numbers of the radial nodes that the real hydrogenlike wave functions do, so that they must be a good basis functions of LCAO MO procedures, *i.e.*, the best approximate representation of SCF method.

Introduction

The calculation of the molecular energies, transition moments, bond strengths, and other physical and chemical quantities by the SCF (self-consistent field) method,[1-5] the MO (molecular orbital) is the LCAO (linear combination of atomic orbitals), in which AO's are called the "basis set" of MO.

Hydrogen-like atomic orbitals are rarely used as basis sets because the evaluation of the molecular integrals resulting from their use presents difficult mathematical problems.

One approach for simplifying the problem has been to substitute more manipulative mathematical functions for the hydrogen-like orbitals. The most frequently used mathematical expressions for the AO's are STO's (Slater-type orbitals)[6,7] or GTO's (Gaussian-type orbitals).[8,9]

The GTO's which are used to describe the atomic orbitals provide the theoretical chemist with the simplest form of function for evaluation, but bear more less resemblance to the hydrogenlike orbitals than STO's. Therefore, in order to achieve the same level of accuracy with a Gaussian basis set as with a Slater basis set, the three or more Gaussian functions must be used for the minimal basis which consists of the minimum number of atomic orbitals which are necessary to accommodate all the electrons of the system.[10,11]

To obtain orbital more similar to the hydrogenic orbital than STO's, the author orthogonalized and ortho-normalized the conventional STO's as follows; We can consider atom as a vector space and its AO's the component vectors in its vector space. Accordingly, putting $\chi_i = \eta_i$, the vector, χ_j orthogonal to χ_i must be given by the Schmidt's orthogonalizing process:

$$\chi_j = \eta_j - \frac{(\chi_i \mid \eta_j)}{(\chi_i \mid \chi_i)} \chi_i, \quad (j = i+1) \tag{1}$$

where $(\chi_i \mid \chi_i)$ is the dot product of vector χ_i which are equal to the overlap integrals between members of an orthogonal set of vector in all spaces, and η_j are the STO's[6,7] with the following algebraic form;

$$\eta_{nlm}(r, \theta, \phi) = ((2\zeta)^{2n+1}/(2n)!)^{\frac{1}{2}} r^{n-1} e^{-\zeta r} Y_{l,m}(\theta, \phi) \tag{2}$$

where ζ is Slater exponent which is either fixed or treated as a variational, and subscripts, n, l, m stand for quantum numbers.

One can extend the procedure of eq. (1) to the case of the system with n-atomic orbitals, and obtain the next equation:

$$\chi_1 = \eta_1$$
$$\chi_2 = \eta_2 - \frac{(\chi_1 \mid \eta_2)}{(\chi_1 \mid \chi_1)} \chi_1$$
$$\chi_3 = \eta_3 - \frac{(\chi_2 \mid \eta_3)}{(\chi_2 \mid \chi_2)} \chi_2 - \frac{(\chi_1 \mid \eta_3)}{(\chi_1 \mid \chi_1)} \chi_1$$

$$\chi_r = \eta_r - \frac{(\chi_{r-1} \mid \eta_r)}{(\chi_{r-1} \mid \chi_{r-1})} \chi_{r-1} - \cdots - \frac{(\chi_1 \mid \eta_r)}{(\chi_1 \mid \chi_1)} \chi_1 \tag{3}$$

where χ_r are the ortho-gonalized STO, $\chi_{nlm}(r, \theta, \varphi)$ and η_r stand for the $\eta_{nlm}(\gamma, \theta, \varphi)$ of Eq(2).

These χ_r and be normalized as follows[a];

$$\phi_r = \chi_r / (\langle \chi_r \mid \chi_r \rangle)^{\frac{1}{2}} \tag{4}$$

where ϕ_r denotes orthonormalized Slater-type orbital, $\phi_{nlm}(r, \theta, \varphi)$ with quantum numbers.

Results and Discussion

The results calculated from the eqs. (2), (3) and (4) were listed in Table 1 and 2. Comparing $\chi_{nlm}(r, \theta, \phi)$ and $\phi(r, \theta, \varphi)$ with the real hydrogenlike wave function, $\psi_{nlmd}(r, \theta, \varphi)$,[13] we may recognize that thir type is the same form as $\psi_{nlmd}(r, \theta, \varphi)$, so that they have the same numbers of their radial node, $n - (l + 1)$. Therefore they are a good representation of the SCF method mentioned above but the conventional *STO's*, $\eta_{nlm}(r, \theta, \varphi)$[14] have no radial nodes for the orbitals; *2s, 3s, 3p, 4s, 4p, 4d, 5s* etc. So they are not a good description of the SCF method.

Also two of $\eta_{nlmd}(r, \theta, \varphi)$ which are different from each other only in their n quantum number are not orthogonal, but the $\chi_{nlmd}(r, \theta, \varphi)$ are orthogonal, so that the 465 overlap integrals between any two orbitals of 31 $\chi_{nlmd}(r, \theta, \varphi)$'s with only one different value among n, l, m and δ go to zero, and in the case of $\phi_{nlmd}(r, \theta, \varphi)$, those integrals have only unit or zero value as they are orthonormal each other by the next equation.

$$\langle \phi_{nlmd}^{(r,\theta,\varphi)} \mid \phi_{n'l'm'd'}^{(r,\theta,\varphi)} \rangle > \delta_{nlmd, n'l'm'd'} \tag{5}$$

where $\phi_{nlmd}(r, \theta, \varphi)$ and $\phi_{n'l'm'd'}(r, \theta, \varphi)$ belong to the same atom (center) of the molecule. If the subscripts have the same value respectively, $\delta_{nlmd, n'l'm'd'}$ has unit value and if not, it has zero value.

As an example, if we will consider the overlap integrals, $(2p_z \mid 2p_z)$ and $(2p_z \mid 2p_y)$, we shall obtain very easily unit from the former and zero from the latter repectively. Eventually, we have

TABLE 1: Orthogonalized Slater-type Orbitals $(\chi_{nlm\delta})^*$

n	ℓ	m	δ	Designation	Function
1	0	0	0	$1s$	$(\zeta^3/\pi)^{1/2}e^{-\zeta r}$
2	0	0	0	$2s$	$(\zeta^5/12\pi)^{1/2}(2\zeta r-1)e^{-\zeta r}$
2	1	0	0	$2p_z$	$(\zeta^5/\pi)^{1/2}re^{-\zeta r}\cos\theta$
2	1	±1	1	$2p_x$	$(\zeta^5/\pi)^{1/2}re^{-\zeta r}\sin\theta\cos\phi$
2	1	±1	-1	$2p_y$	$(\zeta^5/\pi)^{1/2}re^{-\zeta r}\sin\theta\sin\phi$
3	0	0	0	$3s$	$(\zeta^7/90\pi)^{1/2}(2\zeta^2r^2-4\zeta r+1)e^{-\zeta r}$
3	1	0	0	$3p_z$	$(\zeta^7/30\pi)^{1/2}r(2\zeta-3)e^{-\zeta r}\cos\theta$
3	1	±1	1	$3p_x$	$(\zeta^7/30\pi)^{1/2}r(2\zeta r-3)e^{-\zeta r}\sin\theta\cos\phi$
3	1	±1	-1	$3p_y$	$(\zeta^7/30\pi)^{1/2}r(2\zeta r-3)e^{-\zeta r}\sin\theta\sin\phi$
3	2	0	0	$3d_{z^2}$	$(\zeta^7/8\pi)^{1/2}r^2e^{-\zeta r}(2\cos^2\theta-\pi)$
3	2	±1	1	$3d_{xz}$	$(2\zeta^7/3\pi)^{1/2}r^2e^{-\zeta r}\sin\theta\cos\theta\cos\phi$
3	2	±1	-1	$3d_{yz}$	$(2\zeta^7/3\pi)^{1/2}r^2e^{-\zeta r}\sin\theta\cos\theta\sin\phi$
3	2	±2	1	$3d_{x^2-y^2}$	$(\zeta^7/6\pi)^{1/2}r^2e^{-\zeta r}\sin^2\theta(\cos^2\phi-\sin^2\phi)$
3	2	±2	-1	$3d_{xy}$	$(2\zeta^7/3\pi)^{1/2}r^2e^{-\zeta r}\sin^2\theta\sin\phi\cos\phi$
4	0	0	0	$4s$	$(\zeta^9/5040\pi)^{1/2}(4\zeta^3r^3-18\zeta^2r^2+18\zeta r-3)e^{-\zeta r}$
4	1	0	0	$4p_z$	$(\zeta^9/105\pi)^{1/2}r(\zeta^2r^2-4\zeta r+3)e^{-\zeta r}\cos\theta$
4	1	±1	1	$4p_x$	$(\zeta^9/105\pi)^{1/2}r(\zeta^2r^2-4\zeta r+3)e^{-\zeta r}\sin\theta\cos\phi$
4	1	±1	-1	$4p_y$	$(\zeta^9/105\pi)^{1/2}r(\zeta^2r^2-4\zeta r+3)e^{-\zeta r}\sin\theta\sin\phi$
4	2	0	0	$4d_{z^2}$	$(\zeta^9/448\pi)^{1/2}r^2(2\zeta r-5)e^{-\zeta r}(2\cos^2\theta-\pi)$
4	2	±1	1	$4d_{xz}$	$(\zeta^9/84\pi)^{1/2}r^2(2\zeta r-5)e^{-\zeta r}\sin\theta\cos\theta\cos\phi$
4	2	±1	-1	$4d_{yz}$	$(\zeta^9/84\pi)^{1/2}r^2(2\zeta r-5)e^{-\zeta r}\sin\theta\cos\theta\sin\phi$
4	2	±2	1	$4d_{x^2-y^2}$	$(\zeta^9/336\pi)^{1/2}r^2(2\zeta r-5)e^{-\zeta r}\sin^2\theta(\cos^2\phi-\sin^2\phi)$
4	2	±2	-1	$4d_{xy}$	$(\zeta^9/84\pi)^{1/2}r^2(2\zeta r-5)e^{-\zeta r}\sin^2\theta\sin\phi\cos\phi$
4	3	0	0	$4f_{z^3}$	$(5\zeta^9/576)^{1/2}r^3e^{-\zeta r}\cos\theta(4\cos^2\theta-3)$
4	3	±1	1	$4f_{xz^2}$	$(5\zeta^9/384\pi)^{1/2}r^3e^{-\zeta r}\sin\theta\cos\phi(4\cos^2\theta-1)$
4	3	±1	-1	$4f_{yz^2}$	$(5\zeta^9/384\pi)^{1/2}r^3e^{-\zeta r}\sin\theta\sin\phi(4\cos^2\theta-1)$
4	3	±2	1	$4f_{z(x^2-y^2)}$	$(\zeta^9/12\pi)^{1/2}r^3e^{-\zeta r}\sin^2\theta\cos\theta(\cos^2\phi-\sin^2\phi)$
4	3	±2	-1	$4f_{xyz}$	$(\zeta^9/3\pi)^{1/2}r^3e^{-\zeta r}\sin^2\theta\cos\theta\sin\phi\cos\phi$
4	3	±3	1	$4f_{x^3}$	$(\zeta^9/72\pi)^{1/2}r^3e^{-\zeta r}\sin^3\theta\cos\phi(\cos^2\phi-3\sin^2\phi)$
4	3	±3	-1	$4f_{y^3}$	$(\zeta^9/72\pi)^{1/2}r^3e^{-\zeta r}\sin^3\theta\sin\phi(\sin^2\phi-3\cos^2\phi)$
5	0	0	0	$5s$	$(\zeta^{11}/28350\pi)^{1/2}(2\zeta^4r^4-16\zeta^3r^3+36\zeta^2r^2-24\zeta r+3)$ $\times e^{-\zeta r}$

*δ value; 0.1 and -1 stand for having zero, cosine and sine combination in the transformation of the complex wave functions into the real functions.

TABLE 2: Orthonormalized Slater-type Orbitals $(\phi_{nlm\delta})^*$

n	ℓ	m	δ	Designation	Function
1	0	0	0	$1s$	$(2\zeta)^{1/2}e^{-\zeta r}$
2	0	0	0	$2s$	$(2\zeta)^{1/2}(2\zeta r-1)e^{-\zeta r}$
2	1	0	0	$2p_z$	$(8\zeta^3/\pi)^{1/2}re^{-\zeta r}\cos\theta$
2	1	±1	1	$2p_x$	$(8\zeta^3/\pi^2)^{1/2}re^{-\zeta r}\sin\theta\cos\phi$
2	1	±1	-1	$2p_y$	$(8\zeta^3/\pi^2)^{1/2}re^{-\zeta r}\sin\theta\sin\phi$
3	0	0	0	$3s$	$(2\zeta)^{1/2}(2\zeta^2r^2-4\zeta r+1)e^{-\zeta r}$
3	1	0	0	$3p_z$	$(8\zeta^3/3\pi)^{1/2}r(2\zeta r-3)e^{-\zeta r}\cos\theta$
3	1	±1	1	$3p_x$	$(8\zeta^3/3\pi^2)^{1/2}r(2\zeta r-3)e^{-\zeta r}\sin\theta\cos\phi$
3	1	±1	-1	$3p_y$	$(8\zeta^3/3\pi^2)^{1/2}r(2\zeta r-3)e^{-\zeta r}\sin\theta\sin\phi$
3	2	0	0	$3d_{z^2}$	$(8\zeta^5/(9\pi-6\pi^2))^{1/2}r^2e^{-\zeta r}(2\cos^2\theta-\pi)$
3	2	±1	1	$3d_{xz}$	$(32\zeta^5/3\pi^2)^{1/2}r^2e^{-\zeta r}\sin\theta\cos\theta\cos\phi$
3	2	±1	-1	$3d_{yz}$	$(32\zeta^5/3\pi^2)^{1/2}r^2e^{-\zeta r}\sin\theta\cos\theta\sin\phi$
3	2	±2	1	$3d_{x^2-y^2}$	$(32\zeta^5/9\pi^2)^{1/2}r^2e^{-\zeta r}\sin^2\theta(\cos^2\phi-\sin^2\phi)$
3	2	±2	-1	$3d_{xy}$	$(128\zeta^5/9\pi^2)^{1/2}r^2e^{-\zeta r}\sin^2\theta\sin\phi\cos\phi$
4	0	0	0	$3s$	$(2\zeta/9)^{1/2}(4\zeta^3r^3-18\zeta^2r^2+18\zeta r-3)e^{-\zeta r}$
4	1	0	0	$3p_z$	$(16\zeta^3/3\pi)^{1/2}r(\zeta^2r^2-4\zeta r+3)e^{-\zeta r}\cos\theta$
4	1	±1	1	$4p_x$	$(16\zeta^3/3\pi^2)^{1/2}r(\zeta^2r^2-4\zeta r+3)e^{-\zeta r}\sin\theta\cos\phi$
4	1	±1	-1	$4p_y$	$(16\zeta^3/3\pi^2)^{1/2}r(\zeta^2r^2-4\zeta r+3)e^{-\zeta r}\sin\theta\sin\phi$
4	2	0	0	$4d_{z^2}$	$(8\zeta^5/(45\pi-30\pi^2))^{1/2}r^2(2\zeta r-5)e^{-\zeta r}(2\cos^2\theta-\pi)$
4	2	±1	1	$4d_{xz}$	$(32\zeta^9/15\pi^2)^{1/2}r^2(2\zeta r-5)e^{-\zeta r}\sin\theta\cos\theta\cos\phi$
4	2	±1	-1	$4d_{yz}$	$(32\zeta^9/15\pi^2)^{1/2}r^2(2\zeta r-5)e^{-\zeta r}\sin\theta\cos\theta\sin\phi$
4	2	±2	1	$4d_{x^2-y^2}$	$(32\zeta^9/45\pi^2)^{1/2}r^2(2\zeta r-5)e^{-\zeta r}\sin^2\theta(\cos^2\phi-\sin^2\phi)$

4	2	±2	−1	$4\,d_{xy}$	$(128\zeta^5/45\pi^2)^{\frac12}r^2(2\zeta r-5)\zeta^{-\zeta r/}sin^2\theta\ sin\phi\ cos\phi$
4	3	0	0	$4\,f_{z^3}$	$(16\zeta^7/45\pi)^{\frac12}r^3e^{-\zeta r/}cos\theta(4cos^2\theta-3)$
4	3	±1	1	$4\,f_{xz^2}$	$(16\zeta^7/45\pi^2)^{\frac12}r^3e^{-\zeta r/}sin\theta(4cos^2\theta-1)cos\phi$
4	3	±1	−1	$4\,f_{yz^2}$	$(16\zeta^7/45\pi^2)^{\frac12}r^3e^{-\zeta r/}sin\theta(4cos^2\theta-1)sin\phi$
4	3	±2	1	$4\,f_{z(x^2-y^2)}$	$(128\zeta^7/45\pi^2)^{\frac12}r^3e^{-\zeta r/}sin^2\theta\ cos\theta(cos^2\phi-sin^2\phi)$
4	3	±2	−1	$4\,f_{xyz}$	$(512\zeta^7/45\pi^2)^{\frac12}r^3e^{-\zeta r/}sin^2\theta\ cos\theta\ sin\phi\ cos\phi$
4	3	±3	1	$4\,f_{x^3}$	$(128\zeta^7/225\pi^2)^{\frac12}r^3e^{-\zeta r/}sin^3\theta\ cos\phi(cos^2\phi-3sin^2\phi)$
4	3	±3	−1	$4\,f_{y^3}$	$(128\zeta^7/225\pi^2)^{\frac12}r^3e^{-\zeta r/}sin^3\theta\ sin\phi(sin^2\phi-3cos^2\phi)$
5	0	0	0	$5\,s$	$(2\zeta/9)^{\frac12}(2\zeta^4r^4-16\zeta^3r^3+36\zeta^2r^2-24\zeta r+3)e^{-\zeta r/}$

*d value; 0.1 and −1 stand for having zero, cosine and sine combination in the transformation of the complex wave functions into the real functions.

improved the conventional STO's and obtained the orthonormalized STO's which are closest in form to the hydrogenic orbitals. These new orbitals, $\chi_{nlmd}(r,\ \theta,\ \phi)$ shall be extensively utilized in LCAO-MO procedures in the near future.

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The Pressure Effect on the Ionization of m-chloroanilinium Ion in Sodiumacetate Buffer Solution

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The dissociation constants(K)of *m*-chloroanilinium ion in water-ethanol mixture, where the volume percentage of water is 89.5%, were evaluated by UV-spectroscopic method at 20~50°C, up to 1500 bars with changing ionic strength from 0.04 to 0.10 mol kg^{-1} by use of acetate buffer. K values enhance with increasing ionic strength and temperature, but decrease with elevating pressure. From K values, we obtained the partial molar volume change and some other thermodynamic parameters. From the values of enthalpy, entropy and isoequilibrium temperature (649 K), we concluded that the dissociation of m-chloroanilinium ion mentioned above is controlled by enthalpy.

Introduction

To observe the more direct phenomena of the solution, one must measure the effect of pressure on the volumes of different concentrations because pressure is the conjugated thermodynamic variable of volume which is more direct and visual parameter than entropy conjugated to temperature.

The influence of pressure on the ionization of some substituted anilinium ions had already been studied.[1] But m-chloroanilinium ion has not been done, so the authors measured its optical coefficients up to 1500 bars at several pH's and temperatures in water-ethanol mixture.

To extend the study to ionization reaction of some similar types, let us consider the next equation.

$$RNH_3^+ + H_2O \rightleftharpoons RNH_2 + H_3O^+ \qquad (1)$$
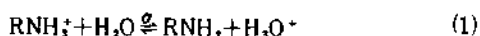
where RNH_3^+ stands for anilinium ion from aniline(RNH_2) in an acidic solution.

Putting the degree of dissociation of eq. (1) α, one can write the optical density of the buffer solution containing the anilinium ion, A as follows:

$$A = (1-\alpha)A_{RNH_3^+} + \alpha A_{RNH_2} \qquad (2)$$

where $A_{RNH_3^+}$ and A_{RNH_2} are the absorbance of the RNH_3^+ and RNH_2 respectively.

From the eq's.(1) and (2), we simplified the dissociation constant, K of anilinium ion to be the exact relationship.[2-4]

$$K = \frac{\alpha}{1-\alpha}\ \frac{\gamma_{RNH_2}\gamma_{H_2O}+m_{H_3O^+}}{\gamma_{RNH_3^+}} \qquad (3)$$

where the γ_i denotes activity coefficients of chemical species, i and $m_{H_3O^+}$ represents the molality of hydronium ions, by