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On the Gaussian Basis Set Extended by Their Derivatives with Respect to Scale Factor

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Synopsis. There has been discussion with regard to the effect of the ζ value, which is a parameter adopted in the Gaussian exponent on the molecular orbital results calculated by use of a basis set extended by their derivatives with respect to ζ. These results are compared with the effect of polarization functions on the molecular orbital results.

In this work, the basis functions in ab initio MO calculations have been extended by their derivatives with respect to the scale factor, ζ, introduced into the Gaussian exponent, such as $e^{-\alpha(\zeta r)^2}$. For example, the ζ-derivative of s-type Gaussian function takes a 3s orbital form, $r^2e^{-\alpha(\zeta r)^2}$; that of a p-type Gaussian function takes a 4p orbital form, $(x,y,z)r^2e^{-\alpha(\zeta r)^2}$. The types of these derivatives are similar to those of functions included in either six-membered Gaussian d-orbitals or 10-membered Gaussian f-orbitals, which are frequently adopted as polarization functions. A comparison between the results calculated using a basis set augmented with derivatives and polarization functions is of great interest.

In this paper, for example, the first derivatives of the s-type Gaussian functions of hydrogen and the s,p-type Gaussian functions of oxygen for H_2O have been adopted; the effects of these derivatives on the total energy of H_2O are discussed. In comparison with these results, p- and d-type Gaussian functions have been applied as polarization functions referring to hydrogen and oxygen; the effects of these functions on the total energy are also discussed. The above-mentioned treatments have been performed for both the ground and electronic excited states of H_2O. The electronic excited states ($^1B_1$) of H_2O was calculated as a single excited configuration ($1b_1 \rightarrow 4a_1$).

Much discussion, by Nakatsuji et al.,$^{1)}$ has been presented concerning the derivative of the Hartree-Fock total energy of a molecule with respect to a parameter. The first derivative of the total energy with respect to a parameter, λ, is given as follows:

$$\begin{aligned}\frac{\partial E}{\partial\lambda}=&\sum_{pq}^{n}\sum_{i}^{\mathrm{occ}}c_{pi}c_{qi}\omega_i\frac{\partial(p|\hat{h}|q)}{\partial\lambda}\\&+\sum_{pq}^{n}\sum_{rs}^{n}\sum_{ij}^{\mathrm{occ}}c_{pi}c_{qi}c_{rj}c_{sj}\left\{\alpha_{ij}\frac{\partial(pq|rs)}{\partial\lambda}-\beta_{ij}\frac{\partial(pr|qs)}{\partial\lambda}\right\}\\&-2\sum_{pq}^{n}\sum_{ij}^{\mathrm{occ}}c_{pi}c_{qj}\frac{\partial(p|q)}{\partial\lambda}\varepsilon_{ji},\end{aligned}\tag{1}$$

where c_{pi} and c_{qi} are the coefficients of basis functions, χ_p and χ_q, in the i-th molecular orbital, and ω_i, α_{ij}, β_{ij} are coupling constants which are dependent on the electronic configuration. $(p|\hat{h}|q)$ and $(p|q)$ are one-electron integrals and $(pq|rs)$ denotes a two-electron integral. ε_{ji} is a Lagrangian multiplier.

If operator $\hat{h}$ is independent of parameter λ, Eq. 1 becomes more compact,

$$\partial E/\partial\lambda=4\sum_{i}^{\mathrm{occ}}\sum_{p}^{n}c_{pi}\sum_{q}^{n}\{(p'|\hat{F}_i|q)c_{qi}-\sum_{j}^{\mathrm{occ}}(p'|q)c_{qj}\varepsilon_{ji}\},\tag{2}$$

where p' represents $\partial\chi_p/\partial\lambda$; this term is the AO error defined by Nakatsuji et al.$^{1)}$

According to a theorem derived by Nakatsuji et al., the AO error is decreased by adding the derivatives $\{\partial\chi_p/\partial\lambda, \partial^2\chi_p/\partial\lambda^2...\}$ to the basis functions $\{\chi_p\}$.

Since ζ parameter introduced in this work has no relation to $\hat{h}$, it follows that the ζ-dependence of the total energy is decreased by considering the derivatives of Gaussian functions with respect to ζ.

The general expression of the Gaussian function used in a basis set is as follows:

$$\chi(\zeta, r)=\sum_{i}d_ig_i(\zeta, r),\tag{3}$$

$$g_i(\zeta, r)=N_{lmn}x^ly^mz^n\exp\{-\alpha_i(\zeta r)^2\},$$

and

$$N_{lmn}=\left\{\frac{2^{2(l+m+n)+(3/2)}(\alpha_i\zeta^2)^{l+m+n+(3/2)}}{\pi^{3/2}(2l-1)!!\,(2m-1)!!\,(2n-1)!!}\right\}^{1/2}$$

This function is augmented by the following first derivative with respect to ζ:

$$\partial\chi/\partial\zeta=\sum_{i}d_i(\partial g_i/\partial\zeta),\tag{4}$$

and

$$\begin{aligned}\partial g_i/\partial\zeta=-(1/2\zeta)\,[&\{(2l+3)(2l+1)\}^{1/2}N_{l+2,m,n}\,x^{l+2}y^mz^n\\&+\{(2m+3)(2m+1)\}^{1/2}N_{l,m+2,n}\,x^ly^{m+2}z^n\\&+\{(2n+3)(2n+1)\}^{1/2}N_{l,m,n+2}\,x^ly^mz^{n+2}]\\&\times\exp\{-\alpha_i(\zeta r)^2\}.\end{aligned}$$

Computation

The energies of the ground and excited states of H_2O were calculated using Huzinaga/Dunning's (10s6p/5s)/[5s4p/3s] basis sets; severally augmented with their first derivatives with respect to ζ_{HS}, ζ_{OS}, and ζ_{OP} (scale factors for hydrogen s-type, oxygen s- and p-type functions, respectively). Except for the ζ in question, the other ζ values have been fixed at 1.00. Next, the total energy of H_2O was calculated using Huzinaga/Dunning's basis functions augmented with a polarization function. The p-type and d-type Gaussian functions were adopted as polarization functions for hydrogen and oxygen, respectively. The α and ζ values of the polarization functions were esti-

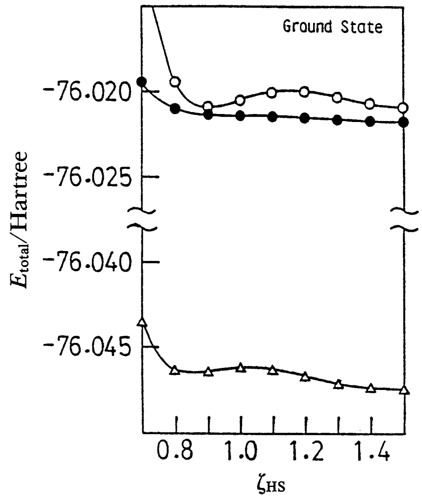

Fig. 1-A. Ground-state energy of H_2O vs. ζ_{HS} value. —●—: Results calculated with derivative. —○—: Results calculated without derivative. —△—: Results calculated with p-type polarization function.

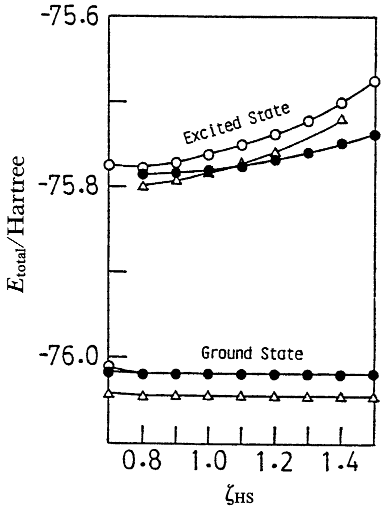

Fig. 1-B. Ground- and excited-state energies vs. ζ_{HS} value. —●—: Results calculated with derivative. —○—: Results calculated without derivative. —△—: Results calculated with p-type polarization function.

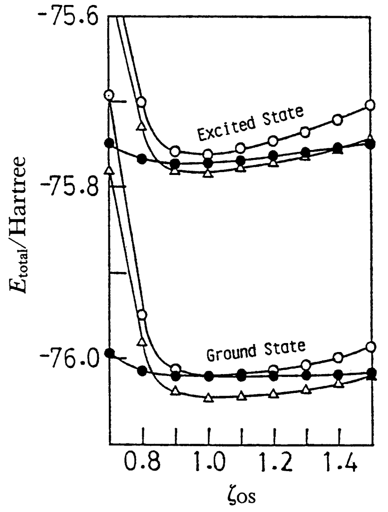

Fig. 2. Ground- and excited-state energies vs. ζ_{OS} value. —●—: Results calculated with derivative. —○—: Results calculated without derivative. —△—: Results calculated with d-type polarization function.

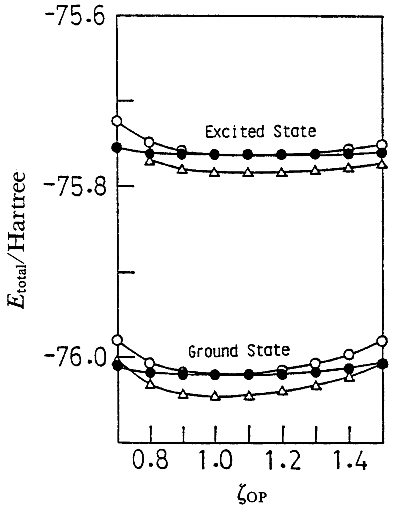

Fig. 3. Ground- and excited-state energies vs. ζ_{OP} value. —●—: Results calculated with derivative. —○—: Results calculated without derivative. —△—: Results calculated with d-type polarization function.

mated to be 1.00.

The electronic excited state ($^1B_1$) of H_2O was calculated by means of a generalized coupling operator method, proposed by Hirao and Nakatsuji[2] and modified by Ishikawa.[3]

In the calculations we adopted the following structure of H_2O: R_{OH}=1.80 Bohr[a] and ∠HOH=105° (used by Ishikawa[3]).

The calculations were performed using the HITAC M-680H System at the Computer Center of the University of Tokyo.

Results and Discussion

The ζ-dependence of the total energy of H_2O are indicated in Figs. 1 to 3 (the values calculated with and without the first derivatives are marked with black and white spots and the results calculated with polarization functions are indicated by white triangles). It should be noted that the total energies given in Fig. 1-A are ploted with a scale greater than those in other figures.

Regarding the result for the ground state of H_2O calculated without derivatives, two energy-minimum points were found at ζ_{HS}=0.9 and 1.5. The total energies, however, are −76.02090 Hartree.[b] The minimum point at ζ_{HS}=0.9 disappeared upon introducing the derivatives. The total energy calculated with derivatives at optimum $\zeta_{HS}(\zeta_{HS}^{op})$=1.5 is −76.02178 Hartree. The total energies of the ground states at

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[a] 1 Bohr=0.529177×10^{-10}m.

[b] 1 Hartree=2.62550×10^6 J mol^{-1}.

optimum ζ_{OS} and ζ_{OP} are as follows: −76.02056 Hartree at $\zeta_{\mathrm{OS}}^{\mathrm{op}}$ and $\zeta_{\mathrm{OP}}^{\mathrm{op}}=1.0$ in results without derivatives; −76.02118 at $\zeta_{\mathrm{OS}}^{\mathrm{op}}=1.0$ and −76.02172 Hartree at $\zeta_{\mathrm{OP}}^{\mathrm{op}}=1.0$ in results with derivatives.

The optimum ζ values for excited states are in the region 0.8 to 1.1. The energies of the excited states at optimum ζ values are as follows: −75.77686 at $\zeta_{\mathrm{HS}}^{\mathrm{op}}=0.8$, at −75.76151 at $\zeta_{\mathrm{OS}}^{\mathrm{op}}=1.0$ and −75.76191 Hartree at $\zeta_{\mathrm{OP}}^{\mathrm{op}}=1.1$ in results without derivatives; −75.78511 at $\zeta_{\mathrm{HS}}^{\mathrm{op}}=0.8$, −75.77225 at $\zeta_{\mathrm{OS}}^{\mathrm{op}}=0.9$, and −75.76336 Hartree at $\zeta_{\mathrm{OP}}^{\mathrm{op}}=0.9$ in results with derivatives.

The total energies of the ground states calculated with a polarization function at the optimum ζ value are as follows: −76.04747 at $\zeta_{\mathrm{HS}}^{\mathrm{op}}=1.5$, −76.04638 Hartree at $\zeta_{\mathrm{OS}}^{\mathrm{op}}$ and $\zeta_{\mathrm{OP}}^{\mathrm{op}}=1.0$. The total energies of the excited states calculated with a polarization function at optimum ζ values are as follows: −75.80078 at $\zeta_{\mathrm{HS}}^{\mathrm{op}}=0.8$, −75.78409 at $\zeta_{\mathrm{OS}}^{\mathrm{op}}=1.0$, and −75.78445 Hartree at $\zeta_{\mathrm{OP}}^{\mathrm{op}}=1.1$.

The $\zeta_{\mathrm{HS}}^{\mathrm{op}}$ values (=1.5) calculated with and without derivatives for the ground state of H_2O coincides with Dunning's report,[4] in which the optimum ζ_{HS} is 1.49 under the following structure: $R_{\mathrm{OH}}=1.8111$ Bohr, ∠HOH=104°27′, and total energy is −76.0207 Hartree. For other references, Pople et al. reported that the optimum valence shell scale factors of the 4-31G basis functions for H_2O are $\zeta'_{\mathrm{H}}=1.27$, $\zeta''_{\mathrm{H}}=1.25$ and $\zeta'_{\mathrm{O}}=0.98$, $\zeta''_{\mathrm{O}}=0.97$,[5] and those of LEMAO[c] 6G are $\zeta_{\mathrm{H}}=1.505$, $\zeta_{\mathrm{O}}=0.976$ ($E_{\mathrm{total}}=-75.99181$ Hartree).[6]

The decrease in the ζ-dependence of the total energy by introducing derivatives is quite obvious from the fact that the curve is very flat, as indicated by Nakatsuji's theorem. However, by adding the derivatives of the basis functions, there is little effect on the total energy of ground state at optimum ζ value. These stabilized energies are 0.00088, 0.00062, and 0.00115 Hartree at $\zeta_{\mathrm{HS}}^{\mathrm{op}}=1.5$, $\zeta_{\mathrm{OS}}^{\mathrm{op}}=1.0$, and $\zeta_{\mathrm{OP}}^{\mathrm{op}}=1.0$. It can be considered that stabilization of the total energies at other ζ values is caused by the flattness of the curves related to the derivatives.

On the other hand, by adding the polarization functions to the basic functions, the stabilization energies are about 0.025 Hartree in all cases; the shapes of curves (E_{total} vs. ζ value) are similar to those calculated without derivatives (the optimum ζ values are equal to those of cases without derivatives).

The stabilization energies of the excited state ($^1B_1$) calculated with derivatives are under 0.01 Hartree at the optimum ζ value, which is less than half of stabilization energies (about 0.023 Hartree) referring to the polarization functions.

The derivative of an s-type Gaussian function takes the 3s orbital form, $r^2e^{-\alpha(\zeta r)^2}=(x^2+y^2+z^2)e^{-\alpha(\zeta r)^2}$, and that of a p-type Gaussian function takes the 4p orbital form, $xr^2e^{-\alpha(\zeta r)^2}=(x^3+xy^2+xz^2)e^{-\alpha(\zeta r)^2}$, $yr^2e^{-\alpha(\zeta r)^2}=(yx^2+y^3+yz^2)e^{-\alpha(\zeta r)^2}$, and $zr^2e^{-\alpha(\zeta r)^2}=(zx^2+zy^2+z^3)e^{-\alpha(\zeta r)^2}$. These derivatives have little effect on the total energy of the ground state of H_2O. Probably, this fact indicates that the Huzinaga/Dunning basis functions used in this work are sufficient as s- and p-types basis set for expression of ground state of H_2O. Otherwise, it seems that those results have been obtained by reason of following fact: the exponent of the derivative is equal to that of the original function.

The derivative of the s-type Gaussian function includes three terms of d(6)-type Gaussian functions; those of the p-type Gaussian functions include nine terms of the f(10)-type Gaussian function (as indicated above). If these three or nine terms are employed separately, they probably contribute to a stabilization of the total energy in the same way as do polarization functions.

By adding the derivatives to the basis functions, the total energies of the excited state are stabilized by about 0.01 Hartree. In contrast to the case of the ground state, these results indicate that Huzinaga/Dunning's s- and p-type basis functions are not sufficient for expressing the electronic excted state of H_2O.

When the derivatives are introduced to the basis functions of oxygen there is little variance in the ground-state energy in the ζ_{OS} (or ζ_{OP}) region of 0.8 to 1.2. It may be of interest to note in this connection that the square root of the ratio between the Huzinaga/Dunning Gaussian exponents of nitrogen and oxygen, $(\alpha_{i\mathrm{N}}/\alpha_{i\mathrm{O}})^{1/2}$ (=0.87), and the value between fluorine and oxygen, $(\alpha_{i\mathrm{F}}/\alpha_{i\mathrm{O}})^{1/2}$ (=1.14), are comparable to the region (0.8—1.2) described above; also, the coeffents of the Gaussian functions for these different atoms almost coinside with one another. In other words, it would seem that the basis set of oxygen augmented with their derivatives may be used instead of the basis set for nitrogen or fluorine in a molecule. The examination of this question will be studied in the future.

References

1) H. Nakatsuji, K. Kanda, and T. Yonezawa, *Chem. Phys. Lett.*, **75**, 340 (1980); H. Nakatsuji, T. Hayakawa, and M. Hada, *Chem. Phys. Lett.*, **80**, 94 (1981).

2) K. Hirao and H. Nakatsuji, *J. Chem. Phys.*, **59**, 1457 (1973).

3) Y. Ishikawa, *Chem. Phys. Lett.*, **37**, 597 (1976).

4) T. H. Dunning, Jr., *J. Chem. Phys.*, **55**, 716 (1971).

5) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

6) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **53**, 932 (1970).

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[c] LEMAO: Least Energy Minimal Atomic Orbital.