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A Comparison of Lobe and Cartesian Gaussian Basis Sets for Molecular Calculations

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Lobe gaussian and cartesian gaussian basis sets, of approximately minimal basis Slater accuracy, have been compared for molecular calculations. The basis sets were constructed so that they only differed in the representation of the angular dependence of the p function.

Calculation of total energy and several one-electron properties for a series of nine molecules shows that, for molecular calculations, the lobe and cartesian gaussian representations are equivalent.

Lobe- und cartesische Gauß-Basissätze mit näherungsweise der gleichen Genauigkeit wie minimale Slater-Basissätze wurden für den Fall von Rechnungen an Molekülen verglichen.

Die Basissätze wurden so konstruiert, daß sie nur in der Darstellung der Winkelabhängigkeit der p-Funktion voneinander abwichen.

Berechnungen der Gesamtenergie und verschiedener Einelektron-Eigenschaften einer Serie von neuen Molekülen zeigen, daß "Lobe"- und cartesische Gaußrepräsentationen für Rechnungen an Molekülen äquivalent sind.

Introduction

Since Boys [1] first pointed out the computational advantages in using gaussian functions for *ab initio* molecular orbital calculations, there has been a steady increase in the use of these functions so that currently most *ab initio* calculations on large molecules have employed gaussian basis sets in preference to Slater type orbitals (e.g. [2]). However during this time of renewed interest in gaussian functions, many different gaussian basis sets have appeared in the literature with little attempt to compare their accuracy in molecular calculations [3].

In the course of an investigation on the use of small gaussian basis sets that will give the same accuracy as a minimal basis set of Slater type orbitals (STO's) with substantial gains in computation time [4], we have found it necessary to compare the use of gaussian lobe functions and cartesian gaussian functions (spherical gaussians) for molecular calculations.

During the preparation of the results to be reported here, a report by Shih *etal.* [5] appeared in which the accuracy of lobe and cartesian gaussian bases for atomic calculations was investigated. Our work is an extension of the comparison of lobe and cartesian gaussians to molecular calculations where we seek to judge the ability of these two *atomic* basis sets to describe the molecular environment.

In keeping with the trend of using calculated one-electron properties as a more sensitive indication of the accuracy of a wavefunction [6], we have calculated the total energy and relevant one electron properties for several polyatomic molecules. The implications of these results will be discussed.

Basis Sets

The lobe (LG) and cartesian gaussian (CG) functions both employ the same radial function $\exp(-\alpha r^2)$ but have different angular functions. The CG may be directly compared with Slater type atomic orbitals in that the atomic function is obtained by combining the radial part with the appropriate spherical harmonic $Y_{lm}(\theta, \varphi)$

$$\varphi_{lm}^{\mathrm{CG}} = N_l r^l \exp(-\alpha r^2)\, Y_{lm}(\Theta, \varphi) \tag{1}$$

where

$$N_l = 2^{n+1}\, [(2n-1)!!]^{-\frac{1}{2}} \quad (2\pi)^{-\frac{1}{4}}\, \alpha^{\frac{2n+1}{4}}$$

$$(2n-1)!! = 1.\,3.\,\ldots\,(2n-1)\,.$$

The LG s-type function is of the same form as the s-type CG. The LG p-type function is obtained by placing pairs of s-type functions equidistant above and below the orbital centre [7]

$$\varphi_p^{\mathrm{LG}} = N\{\exp[-\alpha(r-R^0)^2] - \exp[-\alpha(r+R^0)^2]\} \tag{2}$$

where

R^0 = distance of the lobe from the orbital origin.

$$N = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} \left[2 - 2\exp\left(\frac{-\alpha R^2}{2}\right)\right]^{\frac{1}{2}}.$$

R = distance between the two lobes.

It has been shown [5, 8] that on substituting $R^0 = \gamma \alpha^{-\frac{1}{2}}$, where γ is an arbitrary constant, into Eq. (2) and expanding the function in a Taylor series one obtains in the limit, as γ approaches zero, the same expression as the corresponding CG. Shih *et al.* have pointed out that one needs to balance the value of γ so that it is small enough to allow only the first term of the Taylor series to be important but large enough to allow the molecular integrals to be calculated accurately. We have used the value of $\gamma = 0.03$ suggested by Whitten [8] and also used by Shih *et al.* [5], to obtain the lobe positions for the p type LG functions.

In keeping with our desire to produce small gaussian sets of minimal basis Slater accuracy we have used basis sets consisting of a 1*s* function, a 2*s* function and three 2*p* functions for each first row atom. We have used the contracted sets produced by Stewart [9] and have employed the usual scaling technique [3b] with exponents taken from Clementi and Raimondi [10]. As will be shown in a subsequent paper [4] we have found a five component 1*s* function, a three component 2*s* function, three component 2*p* functions for the heavy atoms, and a three component function for hydrogen, yield results which are very comparable with minimal basis Slater calculations [4, 11]. We will designate the heavy atom LG basis sets by [5, 3, 3] LG and the CG sets by [5, 3, 3] CG.

As the LG and CG basis sets chosen, only differ in their representation of the p-type function, one would expect molecular calculations involving these sets to highlight any deficiencies in the lobe representation.

Computer programs written by us were used for the LG and CG integral, SCF and one-electron property calculations. All programs have been thoroughly tested for speed and accuracy against other similar programs.

Results and Discussion

In an attempt to investigate the correspondence of the LG and CG basis sets in *all* regions of space, we have used the calculated wavefunctions to obtain one-electron properties that are sensitive to the region close to the nucleus (e.g. $\langle r^{-1} \rangle$, $\langle r^{-3} \rangle$), together with those that are more sensitive probes of the wavefunction away from the nucleus (e.g. $\langle r^2 \rangle$). The total energy is also reported although this is known to be a rather insensitive criterion of the wavefunction accuracy.

Calculations have been performed on the following series of nine common closed shell small molecules:

$$H_2O,\ NH_3,\ HF,\ HCN,\ H_2CO,\ CO,\ NOF,\ OF_2,\ O_3.$$

The latter four nonhydrogen containing molecules have been included in an attempt to ascertain whether the hydrogen representation has any unusual effect on the performance of the basis sets under discussion.

We have calculated $\langle r \rangle$, $\langle r^2 \rangle$, $\langle r^{-1} \rangle$, $\langle r^{-3} \rangle$, and the associated one-electron properties for each molecule using both basis sets and as the results show similar trends we felt it better to quote comparisons rather than actual values for each operator. We have therefore recorded in Table 1 maximum percentage difference and maximum absolute difference in each of the one electron properties, as calculated using the LG and CG basis sets, over the range of the nine molecules tested. The actual values of the one-electron properties calculated may be obtained from the authors. It should be noted that the values tabulated are the maximum differences found and in general the differences between the two basis sets were somewhat less than these tabulated values.

The total energies were found to differ in the 6th or 7th significant digit representing a maximum energy difference of $1 \times 10^{-4}\%$ which is quite insignificant

Table 1. Summary of the differences between LG basis and CG basis calculations

Property[b]	Maximum percentage difference	Maximum absolute difference
E total	0.001	0.0003 a.u.
ε_i	0.1	0.0003 a.u.
$\langle r \rangle$[a]	0.1	0.001 a.u.
μ		0.003 D.
$\langle r^{-1} \rangle$[a]	0.003	0.001 a.u.
σ^d av [c]		0.02 p.p.m.
$\langle r^{-3} \rangle$[a]	0.3	0.003 a.u.
eqQ[c]		0.005 M.Hz.
$\langle r^2 \rangle$[a]	0.2	0.007 a.u.
χ_{av}^d [d]		0.006[e]

[a] Electronic contribution only.

[b] Origins: H_2O, NH_3, HF – heavy atom;
NOF, OF_2, O_3 – central atom.

[c] Property calculated at N or O.

[d] Property calculated at the centre of mass.

[e] Units of 10^{-6} emu. mol^{-1}.

when one realizes that the basis sets employed here produce total energies which are some 0.5–0.6% from the Hartree-Fock limit. In looking at the actual integrals, it is found that generally the maximum difference in the one- and two-electron integrals is in the 4th or 5th significant digit with the LG values smaller. Hence it would seem that the self consistency procedure for obtaining the one electron orbital energies and total energy allows the differences in basic integral values to be partially averaged out.

For all molecules the individual orbital energies were found to differ by less than 0.1%.

Calculated values for $\langle z \rangle^e$ and dipole moment for each molecule also indicated that the difference between basis sets is small; the maximum relative difference in $\langle z \rangle$ being around 0.1% which corresponds to a maximum absolute difference of 0.003 *D* in the dipole moment. This small difference between basis sets is again quite insignificant when one notes the difficulty in calculating precise dipole moments even with large gaussian and STO basis sets.

We have also noted that these calculations mirror minimal basis Slater (MBS) calculations on dipole moment even to the poor dipole moment (c.f. experiment) for FNO and CO. This correspondence with MBS calculations will be reported in a future publication.

Because of the close similarity in total energy calculated with the basis sets, one would expect the electronic contributions to the potential at each atom to also be in close agreement. We found the difference in $\langle r^{-1} \rangle$ values occurred in the 5th or 6th significant figure with the LG values always the smaller.

Since the basis sets only differ in the representation of a *p* function, it would seem that near the nucleus, the LG *p* function is slightly inferior to the CG *p* function.

It was also noticeable that the absolute difference in the $\langle r^{-1} \rangle$ values at the heavy nuclei were greater than at hydrogen due presumably to the higher nuclear charge on the heavy atom accentuating any slight changes in the representation of the electron distribution.

The computed values of the electric field gradient tensor $\boldsymbol{q}$ (which is directly proportional to $\langle r^{-3} \rangle$) again show the difference between the basis sets is in the 4th or 5th significant figure. This corresponds to a maximum absolute difference of 0.003 a.u. in the field gradient and a maximum difference of 0.005 MHz in the calculated heavy atom nuclear quadrupole coupling constants.

As the field gradient has shown to be a sensitive probe of the electron density in the vicinity of the nucleus, the above small differences between the two basis sets would allow one to conclude that the representation around the nucleus is essentially the same with either type of *p* function.

Neumann and Moskowitz [6] have suggested, on the basis of accurate calculations on H_2O, H_2CO and CO, that the operator r^2 is a rather insensitive test of the accuracy of the wavefunction. However it does give a means of comparing the wavefunctions, from the two basis sets, in the region away from the nucleus.

Our results for $\langle r^2 \rangle$ once again show the small difference in the two basis sets with the LG basis producing wavefunctions which are slightly more diffuse than those given by the CG basis. The relative differences in $\langle r^2 \rangle$ values are less than

0.10% which is quite small in view of the fluctuations in calculated $\langle r^2 \rangle$ even with large basis sets [6]. This differences in $\langle r^2 \rangle$ would mean a difference of 0.006[1] in the average diamagnetic susceptibility χ^d_{av}.

Conclusion

We have shown that the differences in calculated molecular properties using (i) cartesian gaussians and (ii) gaussian lobe functions scaled to the cartesian gaussians (using the formula $R^0 = 0.03\,\alpha^{-\frac{1}{2}}$ where R^0 is the distance of the lobe from the nuclear centre and α is the gaussian exponent) as basis sets, are quite small. The basis sets used were of approximately minimal Slater accuracy and only differed in the representation of the p-type function. By surveying the regions close to the nucleus (with $\langle r^{-1} \rangle$ and $\langle r^{-3} \rangle$) and those further out (with $\langle r^2 \rangle$) we have shown that the two basis sets are essentially the same for molecular calculations.

It is our conclusion that the representation of a p orbital with a gaussian lobe function obtained using the above formula is, for molecular calculations, the same as that with the corresponding cartesian gaussian. We find, with our computer programs, calculations emplyoing LG basis sets are very slightly faster than those with CG basis sets.

References

1. Boys, S. F.: Proc. Roy. Soc. (London) A **200**, 542 (1950).
2. a) Buenker, R. J., Whitten, J. L., Petke, J. D.: J. chem. Physics **49**, 2261 (1968).
   b) Peyerimhoff, S. D., Buenker, R. J.: Theoret. chim. Acta (Berl.) **19**, 1 (1970).
   c) Demuynch, J., Veillard, A.: Chem. Physics Letters **6**, 204 (1970).
   d) Robin, M. B., Basch, H., Knebler, N. A., Wiberg, K. B., Ellison, G. B.: J. chem. Physics **51**, 45 (1969).
3. a) Dunning, T. H.: J. chem. Physics **53**, 2823 (1970).
   b) O-ohata, K., Taketa, H., Huzinaga, S.: J. physic. Soc. Japan **21**, 2306 (1966).
   c) Stewart, R. F.: J. chem. Physics **50**, 2485 (1969).
   d) Ditchfield, W., Hehre, W. J., Pople, J. A.: J. chem. Physics **52**, 5001 (1970).
4. Brown, R. D., Burden, F. R., Hart, B. T.: To be published.
5. Shih, S., Buenker, R. J., Peyerimhoff, S. D., Wirsam, B.: Theoret. chim. Acta (Berl.) **18**, 277 (1970).
6. a) Neumann, D. B., Moskowitz, J. W.: J. chem. Physics **49**, 2056 (1968).
   b) — — J. chem. Physics **50**, 2216 (1969).
   c) Aung, S., Pitzer, R. M., Chan, S. J.: J. chem. Physics **49**, 2071 (1968).
7. Whitten, J. L.: J. chem. Physics **44**, 359 (1966).
8. Petke, J. D., Whitten, J. L., Douglas, A. W.: J. chem. Physics **51**, 256 (1969).
9. Stewart, R. F.: J. chem. Physics **52**, 431 (1970).
10. Clementi, E., Raimondi, D. L.: J. chem. Physics **38**, 2686 (1963).
11. Klessinger, M.: Theoret. chim. Acta (Berl.) **15**, 353 (1969).

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[1] In units of 10^{-6} emu. mol^{-1}.