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Least-Squares Gaussian Expansions of Atomic Orbitals

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New Gaussian basis sets, which are derived from the method of least-squares, are presented for the first row atoms.

The Least-Squares Procedure

One of the simplest ways of obtaining Gaussian expansions of atomic orbitals is the method of a least-squares fit to Slater-type functions or Hartree-Fock functions. This method has been employed by Boys and Shavitt [1] in a non-simultaneous adjustment of coefficient and exponential parameters in blocks. Other workers [2] have determined the coefficients and exponents independently and Stewart [3] has recently reported small Gaussian expansions by a full matrix method for 1*s* orbitals through to 5*g* orbitals. Our basis sets for the first row atoms were obtained by simultaneously fitting both the coefficients and exponential parameters to Slater-type functions and Hartree-Fock functions by using a least-squares criterion and the Fletcher-Powell [4] minimization procedure. This allows additional flexibility to the functional form of the orbital. The exponents for the Slater functions were taken as those obtained from molecular optimizations.

The Size of the Basis Set

Various workers [5] have considered the question of determining the relative number of *s*- and *p*- Gaussian type functions needed to give minimal Slater basis accuracy in molecular calculations. It has been found that 5 or 6*s*-functions and 4 or 5*p*-functions are required for this desired accuracy. With this in mind, we have determined the atomic orbitals of the first row atoms in terms of 5-*s* Gaussian and 5-*p* Gaussian functions, except hydrogen where a 4*s* expansion is included.

The Gaussian Function Employed

In both atomic and molecular calculations Gaussian lobe functions give results of equivalent accuracy [6] as the Cartesian Gaussian functions provided the exponents (α) of the lobe function and the distance the lobe is placed from the nucleus (R) are related by the expression [7]

$$R = \gamma \alpha^{-\frac{1}{2}} \tag{1}$$

where γ is a constant, taken as 0.030.

The Tables

The tabulations include the orbital expansion vectors, the exponential parameters, the lobe distances (where appropriate) and the mean-square error. The contents are shown in the following Table 1.

Table 1. Least-squares Gaussian expansions of Slater-type functions

Atom	Range of ζ_{1s}	Range of ζ_{2s}	Range of ζ_{2p}
H	1.00–1.50	—	—
He	1.6875	—	—
Li	2.6865	0.6372	—
Be	3.6847	0.9562	—
B	4.6794–4.7194	1.33825–1.37825	1.21055–1.25055
C	5.6726–5.7126	1.6028–1.6428	1.63805–1.79805
N	6.6652–6.7052	1.9236–1.9639	1.9170–2.1370
O	7.6680–7.6580	2.2461–2,2861	2.22625–2.35625
F	8.6501–8.6901	2.5639–2.6039	2.54985–2.66985
Ne	9.6421	2.8792	2.8792

Table 2. Least-squares Gaussian expansions of Hartree-Fock functions

Atom	*State*
C, O	^3P, ^1D, ^1S
N	^4S, ^2D, ^2P
F	^2P

The present tabulation is available upon request to the authors.

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References

1. Boys, S. F., Shavitt, I.: Proc. Roy. Soc. (London) A **254**, 487 (1960).
2. Reeves, C. M., Fletcher, R.: J. chem. Physics **42**, 4073 (1965).
   O-Öhata, K., Taketa, H., Huzinaga, S.: J. physic. Soc. Japan **21**, 2306 (1966).
3. Stewart, R. F.: J. chem. Physics **52**, 431 (1970).
4. Fletcher, R., Powell, M. J. D.: Compt. J. **6**, 163 (1963).
5. See for example, Hornback, C. J.: Ph. D. Thesis Case Institute of Technology (1967).
6. Shih, S. *et al.*: Theoret. chim. Acta (Berl.) **18**, 277 (1970).
   Brown, R. D., Burden, F. R., Hart, B. T.: Theoret. chim. Acta (Berl.) **25**, 49 (1972).
7. Petke, J. D., Whitten, J. L., Douglas, A. W.: J. chem. Physics **51**, 256 (1969).

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