

Multipole Expansion of Diatomic Overlap

1. The Method and Its Application to LiH, Li₂ and N₂

Othmar Steinhauser and Peter Schuster

Institut für Theoretische Chemie und Strahlenchemie der Universität Wien, Währinger Straße 17,
A-1090 Wien, Austria

A systematic extension of Ruedenberg's expansion formula is applied to evaluate two-electron integrals occurring in calculations on molecular structure. Minimum STO basis sets are used for all SCF-calculations within the framework of the MEDO-method (Multipole Expansion of Diatomic Overlap). The errors due to this approximation scheme are almost negligible compared to those introduced by the truncated basis set: LiH, Li₂ and N₂ are chosen as examples.

Key words: Two-electron integrals, approximation of \sim – Multiple expansion of diatomic overlap

1. Introduction

Large scale *ab initio* calculations on medium size molecules have become routine during the last decade. Despite their well known principal failures at the nuclei and at large distances, GTO's are applied most frequently in calculations on polyatomic molecules. In the case of basis sets with near Hartree-Fock quality the inadequate shape of a given single Gaussian lobe is certainly compensated by the huge number of functions applied. Additionally, there is good evidence from numerical calculations showing that STO and GTO basis sets converge indeed to the same limit of the independent particle model (see e.g. [1]). Small and medium size basis sets, as it is well known, are useful only for a qualitative discussion of molecular properties. Usually, energy values differ substantially from those at the Hartree-Fock limit and coincidence of numerical values for other properties is brought about by chance only in some rare cases.

Since the results of numerically accurate calculations using small or medium size basis sets are far off from the Hartree-Fock limit anyway, time-saving approximations within the frame of the numerical procedure seem to be well in place. The evaluation of two-electron integrals represents the most time-consuming step in *ab initio* calculations. Consequently, this is the appropriate part of the calculation,

where straightforward approximations have a chance to be effective. In GTO calculations the key problem is not the evaluation of the single two-electron integral, but the storage and handling of the huge number of numerical values. On the other hand, integral approximation procedures can help a lot in case of STO basis sets. Here the evaluation of multi-center two-electron integrals is the real bottleneck of the calculation. Therefore, we made an attempt to reactivate the systematic application of integral approximations in *ab initio* calculations using STO basis functions.

The first and crudest approximation of two-electron integrals consists in a systematic neglect of differential overlap (ZDO-approximation). However, straightforward incorporation into the *ab initio* MO-formalism leads to rather catastrophic results. Nevertheless, the ZDO-approximation scheme is an essential part of the so-called "semiempirical" methods [2-8]. Additionally, empirical parameters are introduced in order to compensate the brute force neglect of two-electron integrals. Later on, more elaborate approximations were proposed, but they also turned out to be too inaccurate for direct application to SCF-calculations. Two-term approximations like that of Mulliken [9] may serve as examples.

More recently, Harris and Rein [10], Cizek [11, 12] and Body [13] suggested different many-term expansions of diatomic overlap. These approximations were mainly tested by comparison of individual integrals and only occasionally applied to full SCF-calculations. In contrast to these papers we tried a more systematic approach to the whole problem of approximative SCF-calculations.

In two papers we present a systematic extension of Ruedenberg's [14] expansion formula. The procedure, characteristically called Multipole Expansion of Diatomic Overlap (MEDO), will be described in the first part. Additionally, SCF results for three diatomics LiH, Li₂ and N₂ will be reported. A forthcoming second part [15] will contain calculations on a series of other diatomic as well as polyatomic molecules. All results presented in these two papers have been obtained using minimal STO basis sets.

2. Multipole Expansion of Diatomic Overlap (MEDO)

Throughout this paper nuclear attraction and electron repulsion integrals are formulated as electrostatic interactions between charge distributions. Appropriately, we use the following notation for charge distributions:

$$\rho_r^{IJ}(v) = \chi_i^I(v)\chi_j^J(v) \quad v = 1, 2 \quad (1)$$

Here *I* and *J* denote the origins of the basis functions χ_i and χ_j . For the sake of clearness the double index (*ij*) is converted into a single index (*r*). Now, electron repulsion and nuclear attraction integrals can be written as follows:

$$\int \chi_i^A(1)\chi_j^B(1) \frac{1}{r_{12}} \chi_k^C(2)\chi_l^D(2) d\tau_1 d\tau_2 = \int \frac{\rho_s^{AB}(1)\rho_t^{CD}(2)}{r_{12}} d\tau_1 d\tau_2 \quad (2)$$

$$\int \chi_i^A(1) \frac{1}{r_{1c}} \chi_j^B(1) d\tau_1 = \int \frac{\rho_s^{AB}(1)}{r_{1c}} d\tau_1 \quad (3)$$

STO's and GTO's differ in many respects. As is well known, any product of two Gaussian functions is just another Gaussian with different origin. This fundamental property of GTO's does not hold true for STO's. Therefore one is concerned with three- and four-center integrals, which in general cannot be evaluated by standard techniques. Usually, very expensive analytical or numerical integration techniques [16–26] have to be applied. The MEDO method avoids all these difficulties, because two-center charge distributions are approximated by a linear combination of one-center charge distributions:

$$\rho_s^{AB} = \sum_{p=1}^{n_{AB}} C_{s,p} \sigma_p \quad (4)$$

In principle, this expansion formula can be improved by adding more terms. In practice, however, one has to choose a compromise between efficiency and accuracy. Accordingly, we use a fixed set of one-center charge distributions $\{\sigma_p\}$ for a given pair of centers (A–B). The number of terms is denoted by n_{AB} . Further details about the choice of $\{\sigma_p\}$ will be given in Sect. 3.

Using the identities (2), (3) one can easily demonstrate how multicenter integrals are approximated within the framework of the MEDO method. Applying the expansion series (4) to two-electron integrals, we obtain the general formula:

$$\left\langle \chi_i^A \chi_j^B \left| \frac{1}{r_{12}} \right| \chi_k^C \chi_l^D \right\rangle = \sum_{p=1}^{n_{AB}} \sum_{q=1}^{n_{CD}} C_{s,p} C_{t,q} \left\langle \sigma_p \left| \frac{1}{r_{12}} \right| \sigma_q \right\rangle \quad (5)$$

A double sum will occur only if both ρ_s and ρ_t are two-center charge distributions. Further simplification is possible in case one charge distribution is of one-center type, e.g. ρ_t^{CC} :

$$\left\langle \chi_i^A \chi_j^B \left| \frac{1}{r_{12}} \right| \chi_k^C \chi_l^C \right\rangle = \sum_{p=1}^{n_{AB}} C_{s,p} \left\langle \sigma_p \left| \frac{1}{r_{12}} \right| \rho_t \right\rangle \quad (6)$$

A similar expression holds for nuclear attraction integrals:

$$\left\langle \chi_i^A \left| \frac{1}{r_{1C}} \right| \chi_j^B \right\rangle = \sum_{p=1}^{n_{AB}} C_{s,p} \left\langle \sigma_p \left| \frac{1}{r_{1C}} \right| \right\rangle \quad (7)$$

The three formulae (5) to (7) sum up all integral approximations used here. Nevertheless, we are still left with the problem how to calculate the expansion coefficients $\{C_{s,p}\}$. To our knowledge two different methods have been reported in the literature so far. Billingsley and Bloor [27, 28] used the procedure originally proposed by Harris and Rein [10]. They determined the coefficients $\{C_{s,p}\}$ by a system of linear equations, which was derived from exact reproduction of certain hybrid integrals. Newton *et al.* [29–31] evaluated the expansion coefficients by a “least-square-fit” technique. In contrast to these previous methods we decided to use another technique, originally proposed by Cizek [11, 12]. The coefficients $\{C_{s,p}\}$ are chosen such that all multipole moments of the given two-center charge

distributions are reproduced exactly up to a certain order. Thereby we obtain a system of linear equations:

$$\sum_{p=1}^{n_{AB}} C_{s,p} \int \sigma_p m_u d\tau = \int \rho_s m_u d\tau \quad (8)$$

$$m_u = x^i y^j z^k; \quad (u = 1, 2 \dots n_{AB})$$

Here i, j and k denote integers. Using the abbreviations $R_{pu} = \langle \sigma_p | m_u \rangle$, $S_{su} = \langle \rho_s | m_u \rangle$, system (8) can be rewritten as a matrix equation:

$$\mathbf{CR} = \mathbf{S} \quad (9)$$

Inversion of the one-center multipole matrix \mathbf{R} yields the final result:

$$\mathbf{C} = \mathbf{SR}^{-1} \quad (10)$$

In case the multipoles are appropriately selected – linear dependencies have to be avoided – the inversion of the matrix \mathbf{R} causes no numerical problems. Eq. (10) shows that the matrix of the expansion coefficients \mathbf{C} equals the product of two multipole matrices \mathbf{S} and \mathbf{R}^{-1} . The matrix elements $\{R_{p,u}\}$ and $\{S_{s,u}\}$ can be evaluated using standard formulae [32–35], which involve A- and B-functions only.

3. Choice of One-Center Charge Distributions

Obviously, efficiency and accuracy of the MEDO approximation depend strongly on two types of quantities: the expansion coefficients $\{C_{s,p}\}$ and the set of one-center charge distributions $\{\sigma_p\}$. In the previous section we described the procedure to determine the expansion coefficients. Now we turn to the problem how to find an appropriate set of one-center charge distributions (OC's). Bearing in mind that our basic assumption was to use a fixed set of OC's for a given pair of centers (A–B), we start with a minimal basis ($1s_A, 2s_A, \dots, 2pz_A$) of five STO's located on center A. Accounting for symmetry properties 15 distinct pairwise products of STO's can be formed: $\sigma_1 = 1s_A 1s_A$, $\sigma_2 = 2s_A 1s_A$, $\sigma_3 = 2s_A 2s_A \dots \sigma_{15} = 2pz_A 2pz_A$. In the same way we obtain for center B: $\sigma_{16} = 1s_B 1s_B \dots \sigma_{30} = 2pz_B 2pz_B$. Thus a preliminary set of 30 OC's results.

Now we are still left with the problem how to choose the exponents for the individual STO's. For practical purposes it is useful to distinguish four cases:

- a) The functions are located on a hydrogen nucleus. In this case the same exponent $\alpha = 1.0$ is used for all five functions ($1s_H \dots 2pz_H$).
- b) The center of the five functions coincides with a nucleus of atomic number 2 to 6 (He, Li, Be, B, C). In that case exponents determined by Slater rules are used. For atoms with higher atomic numbers (N, O and F) the orbital exponents derived from Slater rules were found to be inadequate for the expansion of two-electron integrals. Especially, the $1s$ -functions are too steep for this purpose. Consequently, the OC's are contracted too much in the regions close to the centers and therefore the interatomic regions are described rather poorly. We tried to avoid this problem in the following stepwise approach.

- c) The exponents of the $2p$ -functions for N, O and F have been reduced to the Slater value for carbon $\alpha_{2p} = 1.625$. Furthermore, optimization procedures done for a number of diatomic molecules showed that the uniform exponents $\alpha_{1s} = \alpha_{2s} = 0.8$ yield an appropriate description of SCF-results for molecules containing N, O or F. Calculations on polyatomic molecules confirmed this fact and it seemed that such a crude choice of uniform exponents is quite sufficient.
- d) For a given pair of centers (A–B) it may occur that the atomic number of the nucleus A varies between 2 and 6, whereas the atomic number of nucleus B falls in the range 7 to 9, or the other way round. In this case the rules given in c) are applied likewise to both centers A, B.

A priori one cannot assume that the preliminary set of OC's is already sufficient for the numerical demands we have in mind. In order to check the reliability of this set, SCF-calculations on several diatomics were carried out. These test calculations discovered an important fact: the calculated force constants showed that the expansion used is not able to reproduce integrals equally well at different internuclear distances. This deficiency indicates that the preliminary set of OC's describes only the regions close by the centers. Contributions from the interatomic regions are neglected too much.

In principle there are two possibilities to achieve a better description of interatomic regions. One approach uses additional OC's, which are located *between* the centers. Such an improvement of the preliminary set causes one important difficulty. The total number of basic OC's becomes a quadratic function, instead of increasing linearly with the numbers of centers. According to our initial ideas such an increase is undesirable and would destroy the economic arguments in favor of the MEDO expansion.

Alternatively one can use OC's with *reduced* orbital exponents. Again these additional OC's are located at the centers, but they are flatter and therefore allow a better description of interatomic regions. Practically, these additional OC's can be built up from four additional STO's ($2s_1, 2px_1, 2py_1, 2pz_1$). Again all symmetry allowed products are taken. The exponents ($\alpha_{2s_1}, \alpha_{2px_1} \cdots \alpha_{2pz_1}$) are determined by multiplying the previously used exponents ($\alpha_{2s_0} \cdots \alpha_{2pz_0}$) by a uniform factor k . In test calculations $k = 0.8$ was found to be a reasonable choice. The uniform value $k = 0.8$ has been used for all molecules reported in this and the forthcoming paper.

The use of additional OC's of the kind described above does not alter the simplicity and efficiency of the MEDO expansion in any respect. The only noticeable economic result consists in a slight increase of the factors C_1 and C_2 in formulae (11) and (12) respectively. The extended set, composed of preliminary and additional OC's, will be called a standard set. This set represents a reasonable compromise between integral accuracy and numerical efforts. Furthermore, the standard set allows a balanced description of two-center charge distributions and consequently of multi-center integrals. We did not investigate the question of uniqueness, however. Most probably, many sets of OC's may work for the approximation of two-electron integrals equally well.

It should be mentioned here that the standard set of OC's is purely additive with respect to the number of centers. Assuming that the number of centers equals the number of atoms in the molecule, the total number of OC's is a linear function of the number of atoms:

$$N_{\text{OC}} = C_1 N_{\text{atom}} \quad (11)$$

From Eq. (11) we see immediately that the total number of Coulomb integrals $\langle \sigma_p | \sigma_q \rangle$ is a quadratic function of N_{atom} :

$$N_{\text{Coul}} = C_2 N_{\text{atom}} (N_{\text{atom}} + 1) / 2 \quad (12)$$

The total number of expansion coefficients $\{C_{s,p}\}$ similarly spans a quadratic manifold:

$$N_{\text{cof}} = C_3 N_{\text{basis}} (N_{\text{basis}} + 1) / 2 \quad (13)$$

The symbol N_{basis} denotes the size of the molecular basis set.

Summing up the previous arguments we arrive at the final conclusion: Within the framework of the MEDO method three- and four-center integrals are approximated by a linear combination of Coulomb integrals. Thus the huge number of two-electron integrals – this number rises with N_{basis}^4 – can be split up into sums over two quadratic manifolds, the expansion coefficients $\{C_{s,p}\}$ and the Coulomb integrals $\langle \sigma_p | \sigma_q \rangle$. Obviously, this advantage of an integral approximation procedure becomes more and more important with increasing size of the molecules considered. Furthermore, the Coulomb integrals required belong to the simplest class of two-electron integrals. Corresponding formulae [32] involve elementary functions only.

4. Comparison of SCF-Results obtained with and without the MEDO Approximation

So far, we have shown how multicenter integrals can be approximated in a simple and consistent way. The next step would be to analyze critically the accuracy obtained for various types of nuclear attraction or electron repulsion integrals. On the other hand, the values of basic interest are the final SCF-results. The evaluation of integrals is only one part of the whole SCF procedure. Furthermore, it is quite obvious that a direct comparison of SCF-results will show all systematic and unsystematic errors introduced by the MEDO approximation. Therefore we omitted the tedious task of analyzing the huge number of basic integrals and turned to a direct comparison of SCF calculations with and without integral approximations.

The three diatomic molecules LiH, Li₂ and N₂ have been selected for a critical test of the MEDO method. In order to avoid discrepancies caused by different geometries or basis sets, we have used quite the same geometries and basis sets as reported in Ref. [36]. Additionally, the exponents of the basis functions were determined by Slater rules. In Table 1 orbital energies, overlap populations, dipole moments and atomic charges are listed. For LiH and N₂ orbital energies of near Hartree-Fock quality are given too. Thus errors due to the truncation of the basis set can be figured out.

Table 1. Comparison of SCF-results for LiH, Li₂ and N₂

	LiH			Li ₂			N ₂						
	SCF	SCF ^b	SCF	SCF	SCF ^b	SCF	SCF	SCF ^a	SCF				
	MEDO ^a	MEDO ^a	MEDO ^a	MEDO ^a	MEDO ^a	MEDO ^a	MEDO ^a	MEDO ^a	MEDO ^a				
Orbital energies (a.u.)													
1σ	-2.4457	-2.4470	-2.4453	1σ _g	-2.4267	-2.4267	1σ _g	-15.703	-15.722	-15.6820			
2σ	-0.3013	-0.3035	-0.3017	1σ _u	-2.4267	-2.4265	1σ _u	-15.698	-15.720	-15.6783			
3σ	0.0166	0.0167	0.0196	2σ _g	-0.1783	-0.1789	2σ _g	-1.39	-1.45	-1.47			
Atomic Li	0.31	0.31		2σ _u	0.0286	0.0291	2σ _u	-0.78	-0.73	-0.78			
charges H	-0.31	-0.31		3σ _g	0.0918	0.0917	1π _g , 1π̄ _g	-0.57	-0.58	-0.615			
(e ₀)				3σ _u	0.3652	0.3579	3σ _g	-0.55	-0.54	-0.635			
Mulliken Overlap populations				2s	0.91	0.91	2s	1.83	1.74				
	0.28	0.28		pz	0.09	0.09	pz	1.17	1.26				
H 1s	1.31	1.31					px, py	1.00	1.00				
Dipole moment	6.40	6.41	6.00 ^d										

^a This work.

^b Values taken from Ref. [36].

^c Values taken from Ref. [38], [39], [40] respectively.

^d Value taken from Ref. [41].

Table 2. Total energies, minimum geometries and harmonic force constants for LiH, Li₂ and N₂

		LiH	Li ₂	N ₂
Total energy at experimental geometry (a.u.)	SCF-MEDO ^a	-7.96	-14.84	-108.56
	SCF ^b	-7.97	-14.84	-108.57
	SCF-HFL ^c	-7.99	-14.87	-108.99
	EXP ^d	-8.07	-14.99	-109.59
Minimum geometries (Å)	SCF-MEDO ^a	1.630	2.877	1.116
	SCF ^b	1.615	2.828	1.104
	SCF-HFL ^c	1.605	2.783	1.065
	EXP ^d	1.595	2.672	1.098
Harmonic force constants (mdyn/Å)	SCF-MEDO ^a	1.180	0.2385	32.51
	SCF ^b	1.201	0.2347	36.42
	SCF-HFL ^c	1.066	0.2198	30.73
	EXP ^d	1.026	0.2552	22.94

^a This work.

^b Values taken from Ref. [37].

^c Values taken from Ref. [38], [39], [40] respectively.

^d Experimental values taken from Ref. [37].

Most integral approximations suffer from the inability to yield a sufficient integral accuracy for a longer range of interatomic distances. It was our principal aim to develop an approximation scheme which produces a sufficient accuracy at least in the harmonic region. Therefore we calculated the total energy of each molecule for five different points around the energy minimum. Then polynomials of third degree were fitted to these five energy values. From this fit minimum geometries and harmonic force constants were derived. Results are summarized in Table 2. In order to yield a critical comparison, corresponding values taken from the literature are listed too. For each molecule and each property four values are given. The first row contains values obtained by the MEDO method, whereas the second row corresponds to SCF calculations using no integral approximations [37]. Thus the errors introduced by the MEDO approximation can be figured out directly. The values given in the third row are taken from SCF calculations of near Hartree-Fock quality [38, 39, 40]. Finally, experimental values are listed in order to complete the story.

5. Discussion

From the numerical point of view the method of integral approximation chosen here seems to be very satisfactory. All errors introduced thereby are by far smaller than those resulting from the use of unsaturated, minimum basis sets. Since the results of minimum basis set SCF calculations are usually far off from the Hartree-Fock limit anyway, the approximations proposed do not introduce any serious decrease in reliability. In case of LiH and Li₂ the results of SCF- and SCF-MEDO calculations are almost completely identical. However, a slight reduction of accuracy can be observed for molecules with more electrons in the valance shell. N₂

may be regarded as an illustrative example. Nevertheless, even in this critical case total energies, orbital energies and eigenvectors are fairly reproduced. No errors larger than 10% of absolute value were found. For short we did not present the eigenvectors here, but the results of Mulliken's overlap population analysis are listed.

Furthermore, equilibrium geometries and force constants are reproduced in good agreement with results obtained without any integral approximations. As stated above, this point is extremely important and represents a critical test for the applicability of a given approximation scheme to general calculations on molecules. Most methods proposed so far turned out to be useful only within a very small range of internuclear distances and therefore failed to give correct energy minima and force constants. As expected the SCF force constants differ substantially from experimental values.

Finally, we want to stress a number of methodological features of our integral approximation scheme:

- 1) The set of OC's applied for the expansion of diatomic overlap has been defined once for all calculations reported. No adjustment has been made for special molecules or types of interactions as in previous papers, e.g. [13].
- 2) Our choice of OC's is by no means unique and we feel that further research might lead to even more accurate reproduction of integral values, which was not necessary for our purpose here. Additionally, the number of OC's may be increased to yield higher accuracy, if desired.
- 3) It seems to be justified to bring again one of our initial arguments. No matter how large the OC basis may be, two-electron integrals are always summed up from *quadratic* manifolds, expansion coefficients and Coulomb integrals. This fact should be contrasted with the well known N^4 -problem of direct integration procedures.

Acknowledgements. The authors are indebted to the Interfakultäres Rechenzentrum der Universität Wien for generous supply with computer time. The idea to try a systematic approach of integral approximations dates back to discussions with Doz. Dr. M. Jungen and Dr. H. Kollmar, which are gratefully acknowledged here.

References

1. Rosenberg, B. J., Shavitt, I.: J. Chem. Phys. **63**, 2162 (1975)
2. Goepfert-Mayer, M., Sklar, A. L.: J. Chem. Phys. **6**, 645 (1938)
3. Parr, R. G., Mulliken, R. S.: J. Chem. Phys. **18**, 1338 (1950)
4. Pariser, R., Parr, R. G.: J. Chem. Phys. **21**, 466 (1953)
5. Pariser, R., Parr, R. G.: J. Chem. Phys. **21**, 767 (1953)
6. Pople, J. A.: Trans. Faraday Soc. **49**, 1375 (1953)
7. Pople, J. A., Segal, D. P., Santry, G. A.: J. Chem. Phys. **43**, S129 (1965)
8. Pople, J. A., Segal, D. P., Santry, G. A.: J. Chem. Phys. **43**, S136 (1965)
9. Mulliken, R. S.: J. Chim. Phys. **46**, 497 (1949)
10. Harris, F. E., Rein, R.: Theoret. Chim. Acta (Berl.) **6**, 73 (1966)
11. Cizek, J.: Mol. Phys. **6**, 19 (1963)
12. Cizek, J.: Mol. Phys. **10**, 83 (1965)

13. Body, R. G.: *Theoret. Chim. Acta (Berl.)* **18**, 107 (1970)
14. Ruedenberg, K.: *J. Chem. Phys.* **19**, 1433 (1951)
15. Steinhauser, O., Schuster, P.: to be published
16. Wahl, A. C., Cade, P. E., Roothaan, C. C. J.: *J. Chem. Phys.* **41**, 2578 (1964)
17. Harris, F. E., Michels, H. H.: *J. Chem. Phys.* **42**, 3325 (1965)
18. Harris, F. E., Michels, H. H.: *J. Chem. Phys.* **43**, S165 (1965)
19. Harris, F. E., Michels, H. H.: *J. Chem. Phys.* **45**, 116 (1966)
20. Wahl, A. C., Land, R. H.: *Intern. J. Quantum Chem.* **1**, 375 (1967)
21. Wahl, A. C., Land, R. H.: *J. Chem. Phys.* **50**, 4725 (1967)
22. Silverstone, H. J.: *J. Chem. Phys.* **48**, 4098 (1968)
23. Silverstone, H. J.: *J. Chem. Phys.* **48**, 4106 (1968)
24. Silverstone, H. J., Kay, K. G.: *J. Chem. Phys.* **48**, 4108 (1968)
25. Kay, K. G., Silverstone, H. J.: *J. Chem. Phys.* **51**, 956 (1969)
26. Kay, K. G., Silverstone, H. J.: *J. Chem. Phys.* **51**, 4287 (1969)
27. Billingsley, F. P., Bloor, J. E.: *Chem. Phys. Letters* **4**, 48 (1969)
28. Billingsley, F. P., Bloor, J. E.: *J. Chem. Phys.* **55**, 5178 (1971)
29. Newton, M. D., Ostlund, N. S., Pople, J. A.: *J. Chem. Phys.* **49**, 5192 (1968)
30. Newton, M. D.: *J. Chem. Phys.* **51**, 3917 (1969)
31. Newton, M. D., Lathan, W. A., Hehre, W. J., Pople, J. A.: *J. Chem. Phys.* **51**, 3927 (1969)
32. Roothaan, C. C. J.: *J. Chem. Phys.* **19**, 1445 (1951)
33. Ruedenberg, K.: *J. Chem. Phys.* **19**, 1459 (1951)
34. Ruedenberg, K., Roothaan, C. C. J., Jaunzemis, W.: *J. Chem. Phys.* **24**, 201 (1956)
35. Roothaan, C. C. J.: *J. Chem. Phys.* **24**, 947 (1956)
36. Ransil, B. J.: *Rev. Mod. Phys.* **32**, 245 (1960)
37. Fraga, S., Ransil, B. J.: *J. Chem. Phys.* **35**, 669 (1961)
38. Cade, P. E., Huo, W. M.: *J. Chem. Phys.* **47**, 614 (1967)
39. Das, G., Wahl, A. C.: *J. Chem. Phys.* **44**, 87 (1966)
40. Cade, P. E., Sales, K. D., Wahl, A. C.: *J. Chem. Phys.* **44**, 1973 (1966)
41. Cade, P. E., Huo, W. M.: *J. Chem. Phys.* **45**, 1063 (1966)

Received January 31, 1977