Theoret. Chim. Acta (Berl.) 46, 157-164 (1977)

THEORETICA CHIMICA ACTA

Multipole Expansion of Diatomic Overlap

II. Application to Some Diatomic and Polyatomic Molecules

Othmar Steinhauser and Peter Schuster

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

The systematic extension of Ruedenberg's expansion formula proposed in Part I [1] is applied to a series of diatomic and polyatomic molecules (BH, NH, HF, Be_2, C_2, F_2, CO, BH_3, CH_4, NH_3, H_2O, HCN and H_2CO). In general, good agreement with the results of full SCF calculations with the same minimum STO basis set is achieved. Thus, the errors due to this integral approximation scheme called MEDO (Multipole Expansion of Diatomic Overlap) are almost negligible compared to those introduced by basis set truncation.

Key words: Diatomic overlap, multipole expansion of ~

1. Introduction

In the first paper of this series (Part I [1]) we presented an approximative method for the evaluation of many-center integrals involving Slater type orbitals (STO's). The main strategy of this approximation scheme is to achieve an economic balance between numerical accuracy of integral evaluation and errors due to basis set truncation.

Mathematically, the method consists in a multipole expansion of diatomic overlap (MEDO) and may be regarded as an extension of Ruedenberg's formula [2]. In Part I we have chosen LiH, Li_2 and N_2 as illustrative numerical examples. In order to demonstrate the applicability of our procedure to a wider range of molecules, we performed calculations on a number of closed-shell diatomics BH, NH, HF, Be_2, C_2, F_2 and CO, as well as some polyatomic molecules BH_3, CH_4, NH_3, H_2O, HCN and H_2CO, which are presented here.

Table 1. Comparison of SCF results for BH, NH, HF

		BH				NH				HF		
		SCF[a] MEDO	SCF[b]	SCF[c] EB		SCF[a] MEDO	SCF[b]	SCF[c] EB		SCF[a] MEDO	SCF[b]	SCF[c] EB
Total energies (a.u.)		−25.061	−25.062	−25.131		−54.22	−54.26	−54.98		−99.48	−99.48	−100.07
Orbital energies (a.u.)	1σ	−7.6985	−7.6997	−7.6863	1σ	−15.28	−15.32	−15.61	1σ	−26.16	−26.14	−26.29
	2σ	−0.6471	−0.6475	−0.6482	2σ	−0.85	−0.87	−1.04	2σ	−1.48	−1.48	−1.60
	3σ	−0.3460	−0.3459	−0.3484	$1\pi, 1\bar{\pi}$	−0.22	−0.24	−0.54	3σ	−0.58	−0.57	−0.77
									$1\pi, 1\bar{\pi}$	−0.48	−0.48	−0.65
Mulliken overlap populations	$2S$	1.81	1.81		$2S$	1.44	1.38		$2S$	2.00	1.95	
	PZ	1.07	1.07		PZ	0.08	0.08		PZ	1.14	1.21	
	$1S$	1.12	1.12		PX, PY	2.00	2.00		PX, PY	2.00	2.00	
					$1S$	0.48	0.54		$1S$	0.86	0.85	
Atomic charges (e_0)	B	0.12	0.12		N	−0.52	−0.46		F	−0.14	−0.16	
	H	−0.12	−0.12		H	0.52	0.46		H	0.14	0.16	
Dipole moment (D)		0.99	0.99	1.73[d]		1.75	1.54	1.63[d]		0.67	0.88	1.94[d]

[a] This work. [b] Values taken from Ref. [3]. [c] Values taken from Ref. [4]. [d] Values taken from Ref. [5].

Table 2. Comparison of SCF results for CO, Be_2, C_2, F_2

		CO				Be_2			C_2			F_2		
		SCF[a] MEDO	SCF[b]	SCF[c] EB		SCF[a] MEDO	SCF[b]		SCF[a] MEDO	SCF[b]		SCF[a] MEDO	SCF[b]	SCF[d] EB
Total energies (a.u.)		−112.33	−112.34	−112.79		−29.054	−29.056		−75.18	−75.21		−197.80	−197.86	−198.77
Orbital energies (a.u.)	1σ	−20.67	−20.71	−20.66	$1\sigma_g$	−4.7048	−4.7056	$1\sigma_g$	−11.357	−11.366	$1\sigma_g$	−26.2119	−26.2172	−26.4227
	2σ	−11.34	−11.35	−11.36	$1\sigma_u$	−4.7042	−4.7053	$1\sigma_u$	−11.356	−11.364	$1\sigma_u$	−26.2117	−26.2176	−26.4224
	3σ	−1.45	−1.50	−1.52	$2\sigma_g$	−0.43	−0.43	$2\sigma_g$	−1.03	−1.03	$2\sigma_g$	−1.56	−1.58	−1.76
	4σ	−0.76	−0.73	−0.80	$2\sigma_u$	−0.22	−0.22	$2\sigma_u$	−0.48	−0.50	$2\sigma_u$	−1.33	−1.32	−1.49
	$1\pi, 1\bar{\pi}$	−0.57	−0.58	−0.64				$1\pi_g, 1\bar{\pi}_g$	−0.41	−0.44	$1\pi_g, 1\bar{\pi}_g$	−0.55	−0.56	−0.81
	5σ	−0.48	−0.48	−0.55							$3\sigma_g$	−0.48	−0.50	−0.75
											$1\pi_u, 1\bar{\pi}_u$	−0.42	−0.43	−0.66
Mulliken overlap populations	C 2*S*	1.72	1.68		Be 2*S*	1.66	1.66	C 2*S*	1.49	1.58	F 2*S*	1.98	1.97	
	PX, *PY*	0.60	0.62		*PZ*	0.34	0.34	*PX*, *PY*	1.00	1.00	*PX*, *PY*	2.00	2.00	
	PZ	0.93	0.96					*PZ*	0.51	0.43	*PZ*	1.02	1.03	
	O 2*S*	1.98	1.85											
	PX, *PY*	1.40	1.38											
	PZ	1.38	1.52											
Dipole moment (D)		0.73	0.73	0.27										

[a] This work. [b] Values taken from Ref. [3]. [c] Values taken from Ref. [6]. [d] Values taken from Ref. [7].

For all MEDO-SCF calculations reported here we used minimal STO basis sets and exactly the same sets of one-center charge distributions (OC's) as described in Part I. Our calculations are compared with full SCF calculations without any integral approximation, which were performed with the same minimal STO basis sets.

2. MEDO Calculations on Diatomic Molecules

SCF results obtained for several diatomics are listed in Tables 1 and 2. The first two columns refer to SCF calculations with and without integral approximations but using the same minimal STO basis set. The expansion formulae [1] were applied to hybrid $\langle \chi_i^A \chi_j^B \mid \chi_k^A \chi_l^A \rangle$ and exchange integrals $\langle \chi_i^A \chi_j^B \mid \chi_k^A \chi_l^B \rangle$. Coulomb two-electron integrals and nuclear attraction integrals were evaluated exactly. The differences in the final results between MEDO and full SCF calculations thus give a direct estimate on the errors introduced by the approximation of hybrid- and exchange integrals.

On the other hand, the truncation of the molecular basis set causes errors in the SCF results, too. In order to have an idea of their magnitude results of SCF calculations using larger basis sets are listed in column 3. Some of these basis sets may be regarded as extended basis sets only, whereas some of them are of near Hartree–Fock quality. In every concrete example the errors introduced by the MEDO integral approximation are small compared to those due to the truncation of the basis to a minimal STO set.

In all MEDO-SCF calculations on diatomic molecules the matrix elements of the core-Hamiltonian $\hat{h}$ have been treated exactly. The approximation of hybrid and exchange integrals only effects the two-electron part $\hat{G}$ of the Fock operator $\hat{F} = \hat{h} + \hat{G}$. Thus errors in the final SCF results are due to errors in the G matrix only. Furthermore, a detailed analysis of integral values has shown that the MEDO approximation generally overestimates basic integrals. Usually, approximated integrals turn out to be somewhat too large. Combining both facts, we can draw an important conclusion: Within the framework of the MEDO method kinetic energy and nucleus–electron attraction are treated exactly, whereas electron–electron repulsion is overestimated by our approximation scheme. Clearly, this fact has a direct consequence on the final SCF results: Total energies obtained from MEDO-SCF calculations in practically all cases are upper bounds to corresponding energy values calculated without any integral approximation but using the same minimal STO basis set. On the average, the same holds for orbital energies. Finally, we want to stress that the previously mentioned arguments refer to diatomics only.

3. MEDO Calculations on Polyatomic Molecules

The values presented in Tables 3 and 4 have been arranged in the same way as before. Again, the values given in these tables show clearly that the truncation of the basis set causes larger errors than our integral approximation scheme.

Table 3. Comparison of SCF results for BH_3, CH_4, NH_3, H_2O

		BH_3			CH_4			NH_3			H_2O		
		SCF[a] MEDO	SCF[b]		SCF[a] MEDO	SCF[b]		SCF[a] MEDO	SCF[b]		SCF[a] MEDO	SCF[c]	SCF[d] EB
Total energies (a.u.)		−26.35	−26.34		−40.15	−40.11		−56.03	−56.01		−75.74	−75.70	−76.06
Orbital energies (a.u.)	$1a_1$	−7.68	−7.68	$1a_1$	−11.26	−11.27	$1a_1$	−15.52	−15.52	$1a_1$	−20.550	−20.555	−20.558
	$2a_1$	−0.71	−0.71	$2a_1$	−0.93	−0.93	$2a_1$	−1.10	−1.10	$2a_1$	−1.281	−1.285	−1.352
	$1e_x$	−0.52	−0.51	$1t_{2x}$	−0.55	−0.54	$1e_x$	−0.59	−0.58	$1b_2$	−0.65	−0.63	−0.72
	$1e_y$	−0.52	−0.51	$1t_{2y}$	−0.55	−0.54	$1e_y$	−0.59	−0.58	$3a_1$	−0.48	−0.47	−0.58
				$1t_{2z}$	−0.55	−0.54	$3a_1$	−0.37	−0.37	$1b_1$	−0.40	−0.40	−0.51
Mulliken overlap populations	B 2*S*	1.17	1.12	C 2*S*	1.33	1.27	N 2*S*	1.64	1.60	O 2*S*	1.92	1.84	
	PX	1.01	1.03	*PX*	1.07	1.09	*PX*	1.03	1.06	*PX*	1.11	1.12	
	PY	1.01	1.03	*PY*	1.07	1.09	*PY*	1.03	1.06	*PY*	2.00	2.00	
	PZ	0.00	0.00	*PZ*	1.07	1.09	*PZ*	1.77	1.76	*PZ*	1.43	1.50	
	H 1*S*	0.94	0.94	H 1*S*	0.86	0.87	H 1*S*	0.84	0.84	H 1*S*	0.77	0.77	
Atomic charges (e_0)	B	−0.18	−0.17	C	−0.54	−0.53	N	−0.46	−0.47	O	−0.46	−0.46	
	H	0.06	0.057	H	0.135	0.133	H	0.153	0.154	H	0.23	0.225	
Dipole moment (D)								1.69	1.76		1.72	1.92	1.995

[a] This work. [b] Values taken from Ref. [8]. [c] Values taken from Ref. [9]. [d] Values taken from Ref. [10].

Table 4. Comparison of SCF results for HCN, H_2CO

		HCN				H_2CO		
		SCF[a] MEDO	SCF[b]	SCF[c] EB		SCF[a] MEDO	SCF[b]	SCF[c] EB
Total energy (a.u.)		−92.60	−92.59	−92.91		−113.47	−113.45	−113.89
Orbital energies (a.u.)	1σ	−15.64	−15.65	−15.60	$1a_1$	−20.57	−20.59	−20.57
	2σ	−11.31	−11.34	−11.29	$2a_1$	−11.33	−11.36	−11.34
	3σ	−1.17	−1.22	−1.24	$3a_1$	−1.34	−1.37	−1.40
	4σ	−0.79	−0.78	−0.81	$4a_1$	−0.85	−0.84	−0.86
	5σ	−0.56	−0.53	−0.58	$1b_1$	−0.66	−0.68	−0.69
	$1\pi, 1\bar{\pi}$	−0.48	−0.48	−0.50	$5a_1$	−0.58	−0.57	−0.65
					$1b_2$	−0.46	−0.47	−0.53
					$2b_1$	−0.40	−0.38	−0.44
Mulliken overlap populations	C 2*S*	1.21	1.09		C 2*S*	1.23	1.15	
	PX	0.98	1.02		*PX*	1.10	1.09	
	PY	0.98	1.02		*PY*	0.95	1.03	
	PZ	0.93	1.01		*PZ*	0.87	0.88	
	N 2*S*	1.90	1.76		O 2*S*	1.96	1.86	
	PX	1.02	0.98		*PX*	1.91	1.92	
	PY	1.02	0.98		*PY*	1.05	0.97	
	PZ	1.17	1.35		*PZ*	1.18	1.35	
	H 1*S*	0.79	0.78		H 1*S*	0.88	0.88	
Atomic charges (e_0)	C	−0.11	−0.14		C	−0.15	−0.15	
	N	−0.10	−0.08		O	−0.10	−0.09	
	H	0.21	0.22		H	0.12	0.12	
Dipole moment (D)		1.86	2.11	3.29[d]		0.86	1.02	1.11

[a] This work.

[b] Values taken from Ref. [8], [13] respectively.

[c] Values taken from Ref. [11], [14] respectively.

[d] Value taken from Ref. [12].

In polyatomic molecules there are several types of difficult to evaluate molecular integrals which have to be approximated: two-center hybrid and exchange integrals as well as three- and four-center integrals. In the framework of the MEDO method all these integrals are approximated as linear combinations of Coulomb type integrals involving OC's. With respect to the MEDO approximation there is a fundamental difference between diatomic and polyatomic molecules. In diatomics nuclear attraction integrals are of two-center type only. Thus the core-Hamiltonian is treated exactly as stated above. When dealing with polyatomics three-center nuclear attraction integrals occur. As mentioned above electron repulsion integrals are overestimated by the MEDO method. It turns out that the same is true for three-center nuclear attraction integrals $\langle \chi_i^A | 1/r_C | \chi_j^B \rangle$. In order to get the contribution of these integrals to the core-Hamiltonian $\hat{h}$, they have to be multiplied by the negative nuclear charge $-Z_C$. Thus matrix elements of $\hat{h}$ are actually underestimated and one can expect a partial cancellation of errors between the matrix elements of $\hat{h}$ and $\hat{G}$. Consequently, this partial cancellation of errors enables a better description of polyatomic molecules. Indeed, a detailed comparison of SCF results for diatomics and polyatomics shows that on the average errors introduced by the MEDO method are smaller for polyatomic than for diatomic molecules. Usually, nuclear attraction integrals are of larger absolute value than electron repulsion integrals. Thus errors in $\hat{h}$ are of greater weight than those in $\hat{G}$. Consequently, the too high energy values obtained for diatomics are converted into too low values in case of polyatomic molecules.

4. Population Analysis and Dipole Moments

In general, population analysis performed by Mulliken's formalism in approximated (MEDO) and full SCF calculations leads to roughly the same values thus demonstrating that the wave functions obtained in the MEDO-SCF procedure are good approximations to those obtained by full SCF calculations with the same basis sets. Looking more carefully, however, some small systematic deviations can be detected: generally the $2s$ atomic orbitals are higher populated in MEDO-SCF than in full SCF calculations. Gross population numbers of the $2p_z$ orbitals on the contrary are obtained somewhat too low by the MEDO method.

Dipole moments obtained by MEDO calculations show some deviations from the results of full SCF calculations: In the polyatomic molecules investigated here and in the HF molecule the dipole moment derived from MEDO-SCF wavefunctions is somewhat too small in absolute value. In NH molecule the opposite result is found. The dipole moments of all other polar diatomics reported here show no significant difference to the values obtained by full SCF calculations using the same basis sets.

5. Conclusion and Future Aspects

So far we have shown that the proposed procedure of integral approximation (MEDO) can be applied successfully to diatomic and polyatomic molecules. The degree of accuracy chosen is in accord with the size of the basis set applied. In our opinion it does not appear to be meaningful or economic to combine high accuracy of integral evaluation with the use of highly truncated basis sets, like e.g. minimum STO sets.

By the MEDO formalism we were able to save a substantial amount of computer time, although we have not invested extreme efforts to optimize our computer program. The computer time required increases with N^2 (N being the number of basis functions) and hence, the computational efforts saved by our approximation can be estimated to increase substantially with growing N. Additional computer time can be saved when the N^2 formalism is incorporated directly into the algorithm for evaluation of the elements of the Hartree–Fock matrix, which we have not tried yet.

Furthermore, the MEDO procedure has another important advantage: the accuracy of integral evaluation is controlled by the size of the OC basis set. In case higher precision is desired the number of OC's has to be increased only in an appropriate and efficient way. An increase of the molecular basis set, of course, implies an increase of the OC basis too.

Acknowledgement. Generous supply with computer time by the Interfakultäres Rechenzentrum (Univ. Wien) is gratefully acknowledged.

References

1. Steinhauser, O., Schuster, P.: Theoret. Chim. Acta (Berl.), **45**, 147–156 (1977)
2. Ruedenberg, K.: J. Chem. Phys. **19**, 1433 (1951)
3. Ransil, B. J.: Rev. Mod. Phys. **32**, 245 (1960)
4. Cade, P. E., Huo, W. M.: J. Chem. Phys. **47**, 614 (1967)
5. Cade, P. E., Huo, W. M.: J. Chem. Phys. **45**, 1063 (1966)
6. Huo, W. M.: J. Chem. Phys. **43**, 624 (1965)
7. Wahl, A. C.: J. Chem. Phys. **41**, 2600 (1964)
8. Palke, W. E., Lipscomb, W. N.: J. Am. Chem. Soc. **88**, 2384 (1966)
9. Switkes, E., Stevens, R. M., Lipscomb, W. N.: J. Chem. Phys. **51**, 5229 (1969)
10. Neumann, D., Moskowitz, J. W.: J. Chem. Phys. **49**, 2056 (1968)
11. McLean, A. D., Yoshimine, M.: Suppl. IBM J. Res. Dev. (1967)
12. McLean, A. D., Yoshimine, M.: Intern. J. Quantum Chem. **1S**, 313 (1967)
13. Foster, J. M., Boys, S. F.: Rev. Mod. Phys. **32**, 303 (1960)
14. Neumann, D., Moskowitz, J. W.: J. Chem. Phys. **50**, 2216 (1969)

Received May 6, 1977