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Simplified *Ab-Initio* Calculations on Hydrogen-Containing Molecules

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The simplified *ab-initio* method described in an earlier paper is tested on some hydrogen-containing molecules. The performance is slightly below that found previously for molecules composed entirely of first-row atoms but should be suitable for applications where limited numerical accuracy is sufficient. The hope of improved performance through limited expansion of the basis, especially on hydrogen, is not realised and so alternative treatments of the two-electron many-centre integrals should be sought if greater numerical accuracy is required.

Introduction

We recently described a simplified *ab-initio* method for performing SCF MO calculations on molecules and illustrated this performance for some small molecules that did not contain hydrogen [1]. The deviations from corresponding results obtained without arithmetic simplification were a few tenths of one per cent in total energy and comparable performance for some one-electron operator expectation values. The NDDO approximation based on Löwdin functions was found to be very accurate, the main source of the discrepancy just mentioned appearing to arise from the use of a truncated Ruedenberg approximation for the Slater-based 3- and 4-centre integrals. Here we report the result of applying the same procedure to some small system containing one or more hydrogen atoms.

In a previous paper it was speculated that even better agreement with exact *ab initio* calculations would be obtained by using extended basis sets. In the present study we have explored this, to the extent possible with out computing facilities, by extending the basis on each hydrogen atom, since the use of a single function on a centre seemed likely to render the truncated Ruedenberg expansion particularly unreliable.

Method

The procedure described previously [1] consisted of starting with a Slater basis, directly computing all one-electron integrals for the core hamiltonian $\boldsymbol{H}^{\lambda}$. This matrix was then transformed to a Löwdin basis. The two-electron integrals were also considered in a Löwdin basis. The NDDO approximation was invoked on this basis and the requisite integrals remaining for evaluation were expressed in terms of Slater-based integrals. The Slater-based two-electron integrals were separated into two categories – those that would be retained on an NDDO approximation were exactly evaluated, those that would be neglected on such an approximation (we shall term them "non-NDDO" integrals) were estimated by a Ruedenberg expansion, truncated to the Slater basis that was selected at the outset. Finally $\boldsymbol{G}^{\lambda}$ and $\boldsymbol{H}^{\lambda}$ were combined to form $\boldsymbol{F}^{\lambda}$ for the SCF procedure.

The results previously reported [1] had been obtained using a minimal basis set of Slater functions. In the present study we examined the effect of extending the Slater basis for the hydrogen atom. This extension generates new problems that stem primarily from the combination of the Ruedenberg expansion and the Löwdin transformation.

Orbital Exponents

The exponents used in our simplified *ab initio* [SAI] calculations using a minimal basis set were the same as those used in the previously reported exact calculations. They are summarized in Table 1. For the extended basis set calculations the exponents for the heavy atom orbitals were Ransil's best atom exponents [5].

The choice of exponents for the hydrogen 2*s* orbital or 1*s*′ orbital used to extend the basis was guided by some preliminary calculations on H_2 and HF and by the more elaborate calculations on H_2O by Aung, Pitzer, and Chan [2]. The various sets that were tried are listed in Table 2.

Table 1. *Orbital exponents in* MBS *calculations*

		H_2O [2]	NH_3 [3]	HCN [4]	HF [5]
H	1*s*	1.27	1.2	1.0	1.0
O	1*s*	7.66			
	2*s*	2.25			
	2*p*	2.21			
N	1*s*		6.70	6.6652	
	2*s*		1.95	1.9236	
	2*p*		1.95	1.9170	
C	1*s*			5.6726	
	2*s*			1.6082	
	2*p*			1.56805	
F	1*s*				8.6501
	2*s*				2.5639
	2*p*				2.54985

Table 2. H *bases sets and exponents*

Set	(1*s*)	(2*s*)	(1*s*′)
(1)	[a]		
(2)	1.20	0.15	
(3)	1.20	0.65	
(4)	1.33		2.47
(5)	1.40	2.33	

[a] See Table 1.

Discussion of Results

The calculated total electronic energies and expectation values of one-electron operators for the four molecules studied here are collected in Table 3. The minimal basis set (MBS) SAI method yields total energies within about 0.3–0.4 a.u. of the exact calculation, which is comparable to the errors found in our previously reported studies [1] but, since the total energies are smaller for the present molecules, the percentage error is rather greater – up to 0.8%. For the various one-

Table 3. *Total electronic energies and expectation values of one-electron operators*

H_2O

	Exact	SAI (1)	H(1s)(2s) (2)	H(1s)(2s′) (3)	H(1s)(1s′) (4)	H(1s′)(2s″) (5)
E (a.u.)	−75.703	−75.387	−75.637	−76.089	−75.429	−75.377
$\langle r^{-1}\rangle_{H}$	5.833	5.766	5.574	5.767	5.750	5.798
$\langle z\rangle_{O}$	1.463	1.149	1.599	1.675	0.953	1.182
$\langle r^2\rangle_{O}$	17.85	16.84	158.11	29.44	16.02	16.42
$\langle x^2\rangle_{O}$	7.19	6.63	84.93	13.26	6.20	6.47
$\langle y^2\rangle_{O}$	4.56	4.48	35.69	7.23	4.37	4.32
$\langle z^2\rangle_{O}$	6.10	5.74	37.48	8.95	5.45	5.63
$\mu(D)$	1.92	2.72	1.58	1.38	3.22	2.64
σ_d	103.5	102.3	98.9	102.4	102.1	102.9

HF

	Exact	(1)	(2)	(3)	(5)
E (a.u.)	−99.479	−99.346	−99.349	−99.502	−99.329
$\langle r^{-1}\rangle_{H}$	6.054	5.909	6.015	5.972	6.084
$\langle z\rangle_{H}$	16.036	16.717	16.597	16.419	16.573
$\langle r^2\rangle_{H}$	38.59	39.31	43.54	43.19	38.54
$\langle x^2\rangle_{H}$	3.66	3.43	4.92	4.95	3.27
$\langle y^2\rangle_{H}$	3.66	3.43	4.92	4.95	3.27
$\langle z^2\rangle_{H}$	31.28	32.46	33.71	33.28	32.00
$\mu(D)$	1.12	2.85	2.55	2.09	2.49
σ_d	107.5	104.9	106.8	106.0	108.0

NH_3

	Exact	(1)	(2)	(5)
E (a.u.)	−56.006	−55.590	−56.093	−55.620
$\langle r^{-1}\rangle_{H}$	5.385	5.372	5.117	5.420
$\langle z\rangle_{N}$	1.454	1.386	1.724	1.334
$\langle r^2\rangle_{N}$	24.41	24.59	246.45	23.31
$\langle x^2\rangle_{N}$	9.20	8.86	96.55	8.36
$\langle y^2\rangle_{N}$	9.20	8.86	96.55	8.36
$\langle z^2\rangle_{N}$	7.02	6.87	53.34	6.60
$\mu(D)$	1.78	1.95	1.09	2.08
σ_d	95.6	95.4	90.8	96.2

HCN

	Exact	(1)	(2)	(5)
E (a.u.)	−92.547	−92.922	−92.924	−92.946
$\langle r^{-1}\rangle_{H}$	5.466	5.281	5.280	5.427
$\langle z\rangle_{C}$	14.133	14.294	14.290	14.197
$\langle r^2\rangle_{C}$	64.19	60.23	62.20	59.57
$\langle x^2\rangle_{C}$	8.71	8.74	9.38	8.49
$\langle y^2\rangle_{C}$	8.71	8.74	9.38	8.49
$\langle z^2\rangle_{C}$	46.77	42.75	43.44	42.62
$\mu(D)$	2.09	2.50	2.49	2.26
σ_d	97.0	93.7	93.7	96.3

electron operators the differences in the values obtained by use of the MBS SAI method and the corresponding values derived from the exact MBS calculation are similar to those found previously.

Comparison of columns (1) and (2) of Table 1 for each of the molecules listed shows that for all systems the NDDO approximation based on Löwdin functions is very accurate, as already indicated by our previous less extensive tests [1].

When the basis set is increased at the hydrogen nucleus by addition of a $2s$ function the calculated energy comes closer to the exact MBS value, perhaps because the Ruedenberg integral approximation is improved. However this expansion of the basis set can have an adverse effect on the calculated values of some one-electron operators, as shown especially by the values obtained for $\langle r^2 \rangle$. This poor performance arises when bonding molecular orbitals, containing an appreciable contribution from the very diffuse $2s$ functions, make an abnormal contribution to $\langle r^2 \rangle$ because of the very large value of $\langle 2s | r^2 | 2s \rangle$. The small but appreciable $2s$ contribution to the final bonding molecular orbitals is clearly overestimated by our procedure, principally because of the very large value of $\langle 2s_A | 2s_B \rangle$ for the diffuse functions on different centres. Thus the values of $\langle r^2 \rangle$ are not unreasonable for HF and HCN where only one diffuse $2s_H$ function is included in the basis.

When a less diffuse $2s_H$ function was used [$\zeta = 0.65$, columns (4) for H_2O and HF, Table 3] the effect on $\langle r^2 \rangle$ was less dramatic, as would be expected. Total energies are perceptibly lowered – below the value obtained in the best extended basis set calculations for H_2O, illustrating that the variation theorem is not strictly valid when integral approximations are employed. The one-electron operator expectation values are not noticeably in better agreement with the exact MBS calculation, or nearer to values obtained by more elaborate exact extended-basis-set calculations. With the most contracted $2s_H$ function however [columns (6) of Table 3] there are signs of slightly improved agreement, although not sufficient to make it clear that the use of this extended basis is worthwhile.

The effect of extending the basis with an alternative function centred on hydrogen was studied by adding a second $1s_H$ function to the basis. Results for water [column (5) of Table 3] show that although the value for $\langle r^2 \rangle$ is now more in line with the exact MBS value, neither it nor other expectation values show a better agreement with the exact MBS values than were obtained from the approximate MBS calculation.

A final trial with a more extended H basis, including $2s$ and $2p$ functions of relatively low exponents, yielded wildly erroneous values for energy and all other properties. It does not seem worth reproducing such data here but this study showed the way in which the variational theorem can fail if the energy expectation value is not accurately evaluated. The transformation to the Löwdin basis in this case causes a very great mixing of basis functions on different centres. This greatly affects the core hamiltonian when transformed to the Löwdin basis and the matching transformation of the $\boldsymbol{G}$ matrix is rendered faulty owing to the approximation used for multicentre integrals so that the resultant $\boldsymbol{F}^\lambda$ matrix elements are far too negative. Thus we do *not* recommend the use of our technique of using the Löwdin transformation combined with the Ruedenberg approximation and a final NDDO approximation in the Löwdin basis whenever the Löwdin transformation produces considerable mixing of basis functions on different centres. This trouble has not been encountered in MBS calculations.

When orbital energies or expectation values of one electron operators are compared orbital by orbital for the simplified *ab initio* method and the exact *ab initio* calculation the differences are much the same as were found previously [1]. Data for H_2O are presented in Table 4. Values for the other molecules show comparable behaviour.

Table 4. H_2O *orbital by orbital values*

Property		Calculation	Molecular orbital					Total value
			$1a_1$	$2a_1$	$1b_2$	$3a_1$	$1b_1$	
ε_i		Exact	−20.556	−1.285	−0.624	−0.466	−0.403	−75.703
	(1)	SAI	−20.316	−1.276	−0.438	−0.338	−0.306	−75.387
	(2)	H(1*s*)(2*s*)	−20.732	−1.544	−0.674	−0.623	−0.602	−75.637
	(3)	H(1*s*)(2*s*′)	−20.753	−1.512	−0.856	−0.655	−0.600	−76.089
	(4)	H(1*s*)(1*s*′)	−20.220	−1.278	−0.390	−0.294	−0.258	−75.429
	(5)	H(1*s*′)(2*s*″)	−20.280	−1.235	−0.448	−0.317	−0.288	−75.377
$\langle r_H^{-1}\rangle$		Exact	1.104	1.229	1.418	1.080	1.002	5.833
	(1)	SAI	1.104	1.249	1.402	1.009	1.002	5.766
	(2)	H(1*s*)(2*s*)	1.104	1.220	1.261	0.985	1.004	5.574
	(3)	H(1*s*)(2*s*′)	1.104	1.203	1.456	1.001	1.004	5.767
	(4)	H(1*s*)(1*s*′)	1.104	1.245	1.379	1.018	1.004	5.750
	(5)	H(1*s*′)(2*s*″)	1.104	1.247	1.422	1.022	1.004	5.798
$\langle z_O\rangle$		Exact	0.006	0.710	0.942	−0.190	0	1.463
	(1)	SAI	0.000	0.807	0.880	−0.538	0	1.149
	(2)	H(1*s*)(2*s*)	0.000	0.767	1.318	−0.486	0	1.599
	(3)	H(1*s*)(2*s*′)	0.000	0.656	1.371	−0.352	0	1.675
	(4)	H(1*s*)(1*s*′)	0.001	0.882	0.659	−0.588	0	0.953
	(5)	H(1*s*′)(2*s*″)	0.000	0.758	0.924	−0.500	0	1.182
$\langle r_O^2\rangle$		Exact	0.104	4.071	6.249	4.357	3.071	17.853
	(1)	SAI	0.107	4.243	5.935	3.387	3.071	16.843
	(2)	H(1*s*)(2*s*)	0.108	11.202	123.603	20.166	3.027	158.016
	(3)	H(1*s*)(2*s*′)	0.107	4.139	15.729	6.437	3.027	29.440
	(4)	H(1*s*)(1*s*′)	0.111	4.656	5.047	3.179	3.027	16.019
	(5)	H(1*s*′)(2*s*″)	0.107	4.115	5.821	3.347	3.026	16.415

Conclusions

The performance of the MBS simplified *ab initio* calculations for the present molecules is similar to that found for other molecules in a previous publication. However the hope previously expressed of obtaining still more accurate results by extending the basis set have not materialized and it does not seem useful to pursue this line further. If the numerical accuracy achieved by the present technique is insufficient then it seems necessary to turn to alternative methods of handling the two-electron integral problem. This will be pursued in a subsequent publication.

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