Theoret. chim. Acta (Berl.) 23, 285—290 (1971)

Relationes

Doubly Excited Configurations in Modified CNDO and INDO Methods

CARL BRABANT and D. R. SALAHUB*

Département de Chimie, Université de Montréal, Montréal, Québec, Canada

Received December 1, 1970

The effect of different CI basis sets, including doubly excited configurations, on transition energies calculated by modified CNDO and INDO methods is examined for H_2O, NH_3, CH_4, and H_2CO.

Introduction

Recently, there has been considerable interest shown in the calculation of excited state properties of molecules by semi-empirical methods of the CNDO type [1–15]. The most succesful of these involve semi-empirically determined integrals and are completed by limited configuration interaction among singly-excited virtual orbital states [8–15]. The CI expansion is usually severely truncated in order to fit available computer storage. Little account has been taken of the effects of this truncation or of the changes which would come about on including doubly and higher excited configurations.

In a series of articles, Giessner-Prettre and Pullman [12–14] have examined some of these effects using the CNDO/2 [3], INDO [4], and the modified CNDO method of Del Bene and Jaffé [9]. They were concerned with unsaturated molecules and of these, only formaldehyde was small enough to include all of the singly and doubly excited configurations.

In the present work we have chosen to study the molecules H_2O, NH_3, and H_2CO for which such a complete treatment is feasible. In addition calculations were carried out on CH_4, including all singly excited configurations and those doubly excited configurations not involving the deepest occupied MO. The more extensive CI calculation was not carried out for methane since this would have required a large amount of computer time and the results for the other three molecules (see below) indicate that little is to be gained from these configurations as far as excitation energies are concerned. We examine the effect on the calculated transition energies of various truncations of the CI expansion.

The methods used were the variations of the CNDO and INDO methods described in [15]. The expressions for the CI matrix elements were programmed directly from the formulas given by Čížek [16].

---

* To whom correspondence should be sent.

Present address: School of Molecular Sciences, The University of Sussex, Brighton BN 1 9QJ, England.

Results and Discussion

In Table 1, and in graphic form in Fig. 1, we present CNDO and INDO results for four different CI basis sets.

i) VO – the single configuration, virtual orbital approximation.
ii) SCI – CI among all singly excited configurations.
iii) TDCI – Truncated DCI – all doubly excited configurations involving the deepest occupied MO are removed from the CI basis of iv).
iv) DCI – CI among all singly and doubly excited configurations.

The truncation iii) was chosen on the basis of orbital energies. In all the cases studied the deepest MO has an orbital energy less than −28 eV and is at least 13 eV lower than the next deepest MO.

Where no results are given for the VO approximation (for NH_3 and CH_4) it is because the configurations result from transitions between two degenerate MO's and are not symmetry functions. This defect is removed by configurational mixing. Before we discuss the molecules individually it is perhaps worthwhile to point out several general features.

The transition energies often differ substantially between the CNDO and INDO methods at all levels of truncation of the CI basis. Differences as high as about 1.5 eV occur (the $A_1(\sigma^* \leftarrow n)$ state of NH_3) and, for formaldehyde the order of states changes in several cases. The inclusion of the one-center integrals removes several of the qualitative failures of the CNDO method (no separation of atomic states arising from the same configuration; no spin density in σ orbitals of planar aromatic radicals; no singlet-triplet split for $\pi \leftrightarrow \sigma$ transitions) and so the INDO method should perhaps be preferred on this basis although there is no absolute means of determining which method (if either) will give the correct prediction in a given case.

The lowering of the ground state energy upon inclusion of the doubly excited configurations varies greatly for the molecules studied. It increases with the size of the molecule (hence the number of configurations) and is in all cases greater in the INDO method than in CNDO. In every case the doubly excited configurations involving the deepest occupied MO account for an appreciable fraction of this lowering so that *for ground state properties* even relatively high-lying doubly excited configurations can be important.

As far as excitation energies are concerned, however, the results of the DCI and TDCI calculations are seen to be very similar. In most cases the excited states are lowered slightly less than the ground state on going from TDCI to DCI so that an overall small increase in transition energies results. In no case was the order of states changed between TDCI and DCI so that for the relatively low-lying states we are considering the truncation appears to be a reasonable one.

The effect of adding the doubly excited configurations (the differences between SCI and TDCI or DCI) is in most cases to lower the ground state and the lower excited states by similar amounts, leaving the transition energies nearly unchanged and only rarely causing changes in the order of states except for the addition of states which are predominantly doubly excited. These would be expected to give rise to extremely weak transitions and should not influence any interpretations of spectra.

Table 1. *Calculated energies in various truncations of the* CI *basis set (see text) by modified* CNDO *and* INDO *methods* (eV). *The zero of energy is the* SCF *ground state*

Molecule	State	VO		SCI		TDCI		DCI	
		CNDO	INDO	CNDO	INDO	CNDO	INDO	CNDO	INDO
H_2O	$A_1(gnd)$	0	0	0	0	−0.12	−0.18	−0.18	−0.37
	$B_1(\sigma^*\leftarrow n)$	8.17	7.87	8.17	7.87	7.96	7.72	7.92	7.65
	$A_2(\sigma^*\leftarrow n)$	9.44	9.15	9.44	9.15	9.19	8.98	9.15	8.88
	$A_1(\sigma^*\leftarrow \sigma)$	11.57	10.43	11.31	10.33	11.13	10.14	11.09	10.04
	$B_2(\sigma^*\leftarrow \sigma)$	12.44	11.92	12.32	11.88	12.12	11.65	12.07	11.57
	$B_2(\sigma^*\leftarrow \sigma)$	14.29	14.59	14.37	14.58	14.25	14.38	14.24	14.34
NH_3	$A_1(gnd_1)$	0	0	0	0	−0.21	−0.32	−0.31	−0.60
	$A_1(\sigma^*\leftarrow n)$	7.47	6.00	7.35	5.94	7.17	5.74	7.14	5.67
	$E(\sigma^*\leftarrow n)$	9.25	8.42	9.20	8.41	8.98	8.19	8.94	8.11
	$E(\sigma^*\leftarrow \sigma)$	12.01	12.05	11.92	11.92	11.76	11.66	11.72	11.61
	$A_2(\sigma^*\leftarrow \sigma)$	—	—	13.51	13.77	13.29	13.55	13.24	13.49
	$E(\sigma^*\leftarrow \sigma)$	—	—	14.07	14.66	13.93	14.49	13.90	14.43
CH_4	$A_1(gnd)$	0	0	0	0	−0.32	−0.48		
	T_2	10.05	10.56	9.95	10.41	9.72	10.18		
	T_1	—	—	12.17	12.42	11.90	12.15		
	E	—	—	12.17	12.70	11.86	12.51		
	T_2	—	—	13.00	13.53	12.88	13.44		
	A_1	—	—	14.51	14.27	14.33	14.23		
H_2CO	$A_1(gnd)$	0	0	0	0	−0.65	−0.87	−0.82	−1.16
	$A_2(\pi^*\leftarrow n)$	4.32	4.56	4.27	4.54	3.84	4.00	3.78	3.93
	$B_2(\sigma^*\leftarrow n)$	6.65	6.11	6.57	6.03	5.47	5.11	5.37	5.03
	$B_1(\pi^*\leftarrow \sigma)$	9.60	9.58	9.57	9.56	9.20	8.99	9.14	8.96
	$A_1(\sigma^*\leftarrow n)$	9.97	9.87	9.41	9.38	8.33	8.44	8.25	8.35
	$A_1(\pi^*\pi^*\leftarrow nn)$	9.52	10.90	—	—	9.32	10.40	9.32	10.36
	$A_1(\sigma^*\leftarrow \sigma)$	11.87	10.99	12.59	10.69	10.34	9.67	10.25	9.76
	$B_1(\sigma^*\leftarrow \pi)$	10.71	11.25	10.68	11.22	9.95	10.28	9.88	10.22
	$B_1(\sigma^*\pi^*\leftarrow nn)$	10.91	11.72	—	—	10.45	10.98	10.44	10.94
	$B_2(\sigma^*\leftarrow n)$	12.05	11.87	12.00	11.87	11.45	11.29	11.41	11.21
	$A_1(\pi^*\leftarrow \pi)$	12.40	12.93	11.06	12.85	11.87	12.34	11.83	12.26
	$A_1(\sigma^*\sigma^*\leftarrow nn)$	14.10	13.50	—	—	12.89	11.99	12.87	11.97
	$A_2(\pi^*\leftarrow \sigma)$	13.15	13.57	13.20	13.54	12.06	12.35	12.05	12.32
	$B_2(\sigma^*\leftarrow \sigma)$	14.57	13.93	14.44	13.89	13.30	12.96	13.22	12.94
	$A_2(\sigma^*\leftarrow \pi)$	13.63	14.26	13.63	14.31	12.96	13.52	12.90	13.45
	$A_2(\pi^*\sigma^*\leftarrow nn)$	14.33	14.94	—	—	13.79	14.26	13.79	14.20
	$B_2(\sigma^*\leftarrow \sigma)$	14.84	14.98	14.96	14.95	13.94	13.99	13.88	13.96

The interpretation of the electronic spectra of these molecules as given by the SCI truncation has been discussed previously [15, 17, 18]. Below we discussed only the effects due to the doubly excited configurations.

For water and ammonia the effects of CI are minimal at all levels of truncation, the results for the VO approximation being in complete qualitative agreement with those of DCI.

While the same comments apply to most of the states of methane, the E and T_1 states as calculated by the CNDO method are rather interesting. These are accidentally degenerate in the SCI truncation because of the CNDO approxima-

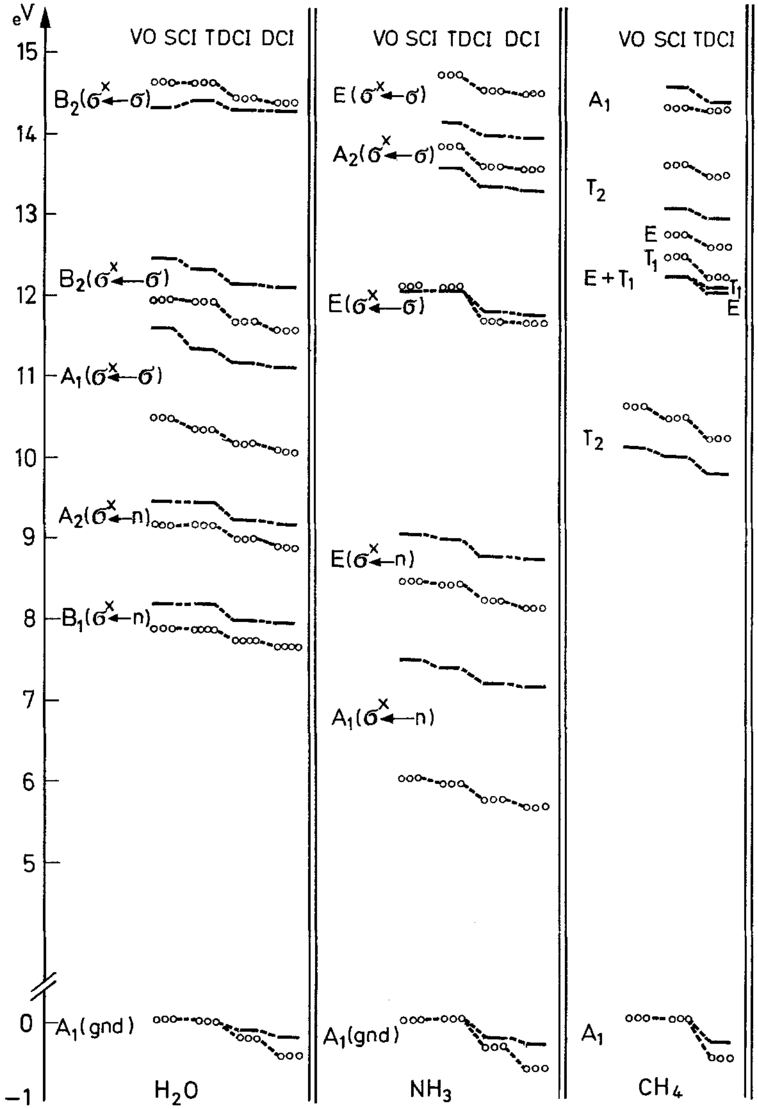
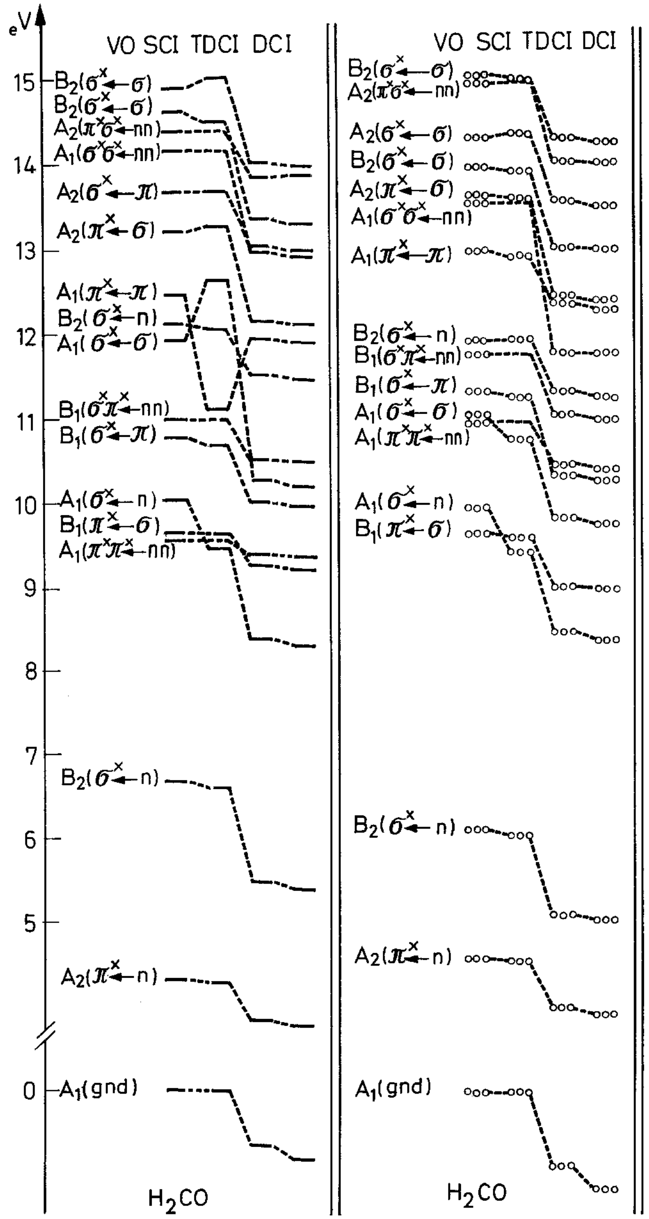


Fig. 1. Calculated energies in various truncations of the CI basis set (see text) by modified CNDO (——) and INDO (∘∘∘) methods (eV). The zero of energy is the SCF ground state

tions and because there are no other states of these symmetries to split them. Mixture with doubly excited states does split them so that in this case the doubly excited configurations do make a qualitative difference.

The case of formaldehyde is somewhat more complicated by the existence of relatively low-lying doubly-excited states resulting from the promotion of both lone-pair electrons. As stated above, these would not be expected to appear in the spectrum. If these are ignored then once again there are no qualitative



changes in the results for low-lying states on going from SCI to TDCI, although the energy differences between states are somewhat affected.

The $\pi^* \leftarrow \pi$ state of formaldehyde deserves comment. As was found by Giessner-Prettre and Pullman [13], no state in this molecule can really be called $\pi^* \leftarrow \pi$ after CI, the $\pi^* \leftarrow \pi$ configuration always mixing very heavily with a close-lying $A_1(\sigma^* \leftarrow \sigma)$ configuration. The level marked $\pi^* \leftarrow \pi$ in Fig. 1 is that with the largest contribution from the $\pi^* \leftarrow \pi$ configuration. In the CNDO method, the addition of doubly excited configurations results in the $\sigma^* \leftarrow \sigma$ state becoming lower than the $\pi^* \leftarrow \pi$ in agreement with the INDO results, although as we have just stated this is somewhat semantical.

Conclusions

We have examined the effect of doubly-excited configurations in modified CNDO and INDO methods. The ground state energy is found to be lowered considerably and these configurations may be quite important for the calculation of ground state properties (see [14]).

For excitation energies, however, their effect is minimal, for these molecules, and especially in light of the approximate nature of the methods it is questionable whether the added computational effort is worthwhile.

Acknowledgements. We wish to express our thanks to Professor C. Sandorfy who sponsored this research and read the manuscript. The calculations were carried out at the Centre de Calcul de l'Université de Montréal, the staff of which, we thank for their co-operation.

D.R.S. thanks the National Research Council of Canada for the award of a 1967 Science Scholarship.

References

1. Pople, J. A., Santry, D. P., Segal, G. A.: J. chem. Physics **43**, S 129 (1965).
2. — Segal, G. A.: J. chem. Physics **43**, S 136 (1965).
3. — — J. chem. Physics **44**, 3289 (1966).
4. — Beveridge, D. L., Dobosh, P. A.: J. chem. Physics **47**, 2026 (1967).
5. Dixon, R. N.: Molecular Physics **12**, 83 (1967).
6. Kroto, H. W., Santry, D. P.: J. chem. Physics **47**, 792 (1967).
7. — — J. chem. Physics **47**, 2736 (1967).
8. Clark, P. A., Ragle, J. L.: J. chem. Physics **46**, 4235 (1967).
9. Del Bene, J., Jaffé, H. H.: J. chem. Physics **48**, 1807 (1968).
10. — — J. chem. Physics **48**, 4050 (1968).
11. — — J. chem. Physics **49**, 1221 (1968).
12. Giessner-Prettre, C., Pullman, A.: Theoret. chim. Acta (Berl.) **13**, 265 (1969).
13. — — Theoret. chim. Acta (Berl.) **17**, 120 (1970).
14. — — Theoret. chim. Acta (Berl.) **18**, 14 (1970).
15. Salahub, D. R., Sandorfy, C.: Theoret. chim. Acta (Berl.) **20**, 227 (1971).
16. Čížek, J.: Theoret. chim. Acta (Berl.) **6**, 292 (1966).
17. Salahub, D. R., Sandorfy, C.: Theoret. chim. Acta (Berl.) **22**, 325, 330 (1971).
18. Salahub, D. R.: Thesis, Université de Montréal (1970).

Dr. D. R. Salahub
School of Molecular Sciences
The University of Sussex
Brighton BN1 9QJ, England