

Symmetry-Adapted HAM/3 Method and Its Application to Some Symmetric Molecules

Susumu Narita^a, Tai-ichi Shibuya^a, Fred Y. Fujiwara^b and Yuji Takahata^{*b}

^a Department of Chemistry, Faculty of Textile Science and Technology, Shinshu University, Tokida 3-15-1, Ueda, Nagano-ken 386-8567, Japan

^b Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13084-971 Campinas- SP, Brazil

O método semi-empírico HAM/3, desenvolvido por Lindholm e colaboradores há mais de duas décadas, tem uma deficiência. As energias de excitação calculadas por HAM/3 para estados degenerados são desdobradas. Recentemente foi proposto um método para corrigir esta deficiência. Apresentamos aqui resultados de aplicações deste novo método para algumas moléculas com simetria T_d , C_{3v} e D_{3h} . O esquema proposto apresenta a degenerescência correta para as moléculas estudadas.

The semiempirical HAM/3 method developed by Lindholm and coworkers about two decades ago has been known to have a deficiency that splits energies for the degenerate energy states. We have recently proposed a group-theoretical approach to remedy the internally broken symmetry of the HAM/3 Hamiltonians. In this paper, we present some results of its application to various small molecules with symmetry T_d , C_{3v} , and D_{3h} . The proposed scheme gives correct degeneracy for these molecules.

Keywords: symmetry, degeneracy, HAM/3, semiempirical method, excited states

Introduction

The semiempirical MO method “HAM/3” was developed by Lindholm and coworkers¹ about two decades ago. This is a semiempirical version of density functional theory (DFT), that treats atoms in molecules according to Slater’s idea of the shielding constants for the effective nuclear charges. A comparative study between HAM/3 and non-empirical DFT methods has been submitted elsewhere.² The HAM/3 method has been successfully applied to calculate ionization energies, electron affinities, and excitation energies of a wide variety of molecules. HAM/3 is a rare semiempirical SCF method that can calculate core electron binding energies (CEBEs). CEBEs calculated by HAM/3 have been recently correlated with biological activity of certain compounds.^{3,4} The principal limitation of HAM/3 is that it can treat molecules that contain only five types of atoms, namely, H, C, N, O and F.⁵⁻¹⁰

The HAM/3 method is therefore an alternative to more frequently used spectroscopic semiempirical methods such as CNDO/S and INDO/S. The original version of HAM/3, however, is known to have a deficiency that splits energies

for the degenerate energy states of symmetric molecules.^{7,9,10} Apparently, this has been a major obstacle to extensive examinations of HAM/3 in comparison with other methods. Chong⁷ analyzed the origin of the deficiency for linear molecules and pointed out that INDO-like approximation formula for the repulsion integrals were needed to remedy the deficiency.

In analyzing our results⁹ on fullerene C_{60} , which were obtained using the HAM/3 program purchased from QCPE,¹¹ we noticed that the energy splittings in each set of degenerate energy states were rather small and are an outcome of the fact that the original symmetry is lost in the HAM/3 Hamiltonians. To remedy the deficiency, we have proposed¹² a group-theoretical approach instead of adjusting the repulsion integrals. The basic idea of our proposal was to recover the lost nature of symmetry for the HAM/3 Hamiltonian by taking the average of its similarity transformations over the molecular symmetry group. The procedure was described in detail in a previous publication.¹³ The procedure is called symmetry-adapted HAM/3, abbreviated as SA-HAM/3. The object of the present work is to compare excitation energies of some symmetric molecules calculated by both the SA-HAM/3 and the original HAM/3 methods, and to discuss the effect of the symmetry adaptation in HAM/3.

* e-mail: taka@iqm.unicamp.br

Dedicated to the late Dr. Einar Lindholm

Application to Symmetric Molecules

We present numerical results of methane CH_4 (T_d), ammonia NH_3 (C_{3v}), eclipsed ethane C_2H_6 (D_{3h}), and $\text{CH}(\text{CH}_3)(\text{CHO})\text{OH}$ (C_1). Geometrical structures of these molecules were obtained with MacSpartan at the AM-1 level and used for the present calculations. SCF-MO energies, excitation energies and oscillator strengths f for the singlet transitions, and triplet excitation energies were calculated. Excitation energies and oscillator strengths obtained from the HAM/3-CI calculations are of truncated active spaces. MO energies are shown only for those in the HOMO-LUMO vicinity of the molecules.

Tables 1 and 2 show the results for methane CH_4 (T_d). In Table 1, both the original HAM/3 and SA-HAM/3 show clear degeneracy for MO energies in t_2 levels. MO energies obtained from the SA-HAM/3 are identical to those obtained from the original HAM/3, that is, the symmetry-adapted procedure did not affect the values of MO energies for this molecule. In Table 2, the SA-HAM/3 shows clear degeneracy in T_2 , T_1 , E for the singlet excitation energies and oscillator strengths f , as well as for the triplet excitation energies. SA-HAM/3 shows that six singlet energy states

between 41.142 eV and 41.574 eV are grouped into three energy levels, T_1 , E and A_1 , whereas the original HAM/3 does not show how the corresponding six states between 41.086 eV and 41.581 eV are to be grouped. Also notice the difference in the f -values between the original HAM/3 and the SA-HAM/3. For the triplet states, a similar situation as for the singlet states prevails. According to SA-HAM/3, the lowest triplet state is a strictly degenerate T_2 level with 30.427 eV. The original HAM/3, however, gives split energies for the triplet states. The splitting of another T_2 states corresponding to 40.189 eV in SA-HAM/3 is more significant. The 10th excited state of SA-HAM/3 is a component of T_1 with 41.113 eV, while the 11th and 12th states are not shown in the Table.

Tables 3 and 4 show the results for ammonia NH_3 (C_{3v}). Table 3 shows no significant discrepancy in MO energies between the original HAM/3 and the SA-HAM/3. In Table 4, clear degeneracy corresponding to the E states are seen in the singlet excitation energies and oscillator strengths f , as well as in the triplet excitation energies in the case of SA-HAM/3 calculations. The Table shows three different energy values of E states: 12.313 eV, 14.297 eV, and 15.672 eV. They are all strictly doubly degenerate. Oscillator

Table 1. Methane CH_4 (T_d): MO Energies (eV) in the HOMO-LUMO Vicinity Obtained from the Symmetry-Adapted HAM/3 Scheme and the Original HAM/3

MO	Original	SA-HAM/3	
1	-19.48182	a_1	-19.48182
2 ^a	-10.79664	t_2	-10.79664
3 ^a	-10.79664	t_2	-10.79664
4 ^a	-10.79664	t_2	-10.79664
5 ^b	+20.80836	a_1	+20.80836
6	+30.27602	t_2	+30.27602
7	+30.27602	t_2	+30.27602
8	+30.27602	t_2	+30.27602

^a HOMO; ^b LUMO.

Table 2. Methane CH_4 (T_d): Excitation Energies (eV) and Oscillator Strengths f for Low-Lying Excited States Obtained from the Symmetry-Adapted HAM/3 and the Original HAM/3

Excited States	Original HAM/3			SA-HAM/3				
	singlet		triplet	singlet		triplet		
	f			f				
1	32.648	0.0174	30.427	T_2	32.648	0.0173	T_2	30.427
2	32.648	0.0173	30.432	T_2	32.648	0.0173	T_2	30.427
3	32.648	0.0172	30.433	T_2	32.648	0.0173	T_2	30.427
4	39.896	0.0002	38.574	A_1	39.902	0.0000	A_1	38.154
5	41.086	0.0010	40.119	T_1	41.142	0.0000	T_2	40.189
6	41.116	0.0002	40.284	T_1	41.142	0.0000	T_2	40.189
7	41.231	0.0015	40.492	T_1	41.142	0.0000	T_2	40.189
8	41.371	0.0040	40.649	E	41.449	0.0000	E	40.911
9	41.526	0.0014	40.752	E	41.449	0.0000	E	40.911
10	41.581	0.0100	40.879	A_1	41.574	0.0000	T_1	41.113
Active Space	4(occ.)x4(unocc.)			4(occ.)x4(unocc.)				

Table 3. Ammonia NH_3 (C_{3v}): MO Energies (eV) in the HOMO-LUMO Vicinity Obtained from the Symmetry-Adapted HAM/3 Scheme and the Original HAM/3

MO	Original	SA-HAM/3	
1	-20.3905	a_1	-20.3905
2	-8.27184	e	-8.27184
3	-8.27183	e	-8.27183
4 ^a	-7.13297	a_1	-7.13297
5 ^b	3.21508	a_1	3.21508
6	6.57787	e	6.57789
7	6.57792	e	6.57790

^a HOMO; ^b LUMO.**Table 4.** Ammonia NH_3 (C_{3v}): Excitation Energies (eV) and Oscillator Strengths f for Low-Lying Excited States Obtained from the Symmetry-Adapted HAM/3 and the Original HAM/3

Excited States	Original HAM/3			SA-HAM/3				
	singlet		triplet	singlet		triplet		
	f			f				
1	11.390	0.0150	9.071	A_1	11.390	0.0150	A_1	9.145
2	12.313	0.0209	10.469	E	12.313	0.0211	E	10.462
3	12.314	0.0214	10.470	E	12.313	0.0211	E	10.462
4	14.294	0.1371	12.909	E	14.297	0.1417	A_1	12.922
5	14.300	0.1461	12.984	E	14.297	0.1417	E	12.979
6	14.850	0.0000	12.991	A_2	14.850	0.0000	E	12.979
7	15.617	0.4796	14.156	E	15.672	0.4757	E	14.084
8	15.727	0.4722	14.227	E	15.672	0.4757	E	14.084
9	16.868	0.9965	14.824	A_1	16.868	0.9965	A_2	14.850
10	24.997	0.2855	22.387	A_1	24.997	0.2855	A_1	22.519
Active Space	4(occ.) \times 3(unocc.)			4(occ.) \times 3(unocc.)				

Table 5. Eclipsed Ethane C_2H_6 (D_{3h}): MO Energies (eV) in the HOMO-LUMO Vicinity Obtained from the Symmetry-Adapted HAM/3 Scheme and the Original HAM/3

MO	Original	SA-HAM/3	
3	-12.2636	e'	-12.2636
4	-12.2636	e'	-12.2636
5	-9.6482	a_1'	-9.6482
6 ^a	-9.4037	e''	-9.4037
7 ^a	-9.4037	e''	-9.4037
8 ^b	13.1477	a_2''	13.1477
9	14.2577	a_1'	14.2577
10	23.9962	e'	23.9962
11	23.9962	e'	23.9962
12	25.6366	a_2''	25.6366

^a HOMO; ^b LUMO.**Table 6.** Eclipsed Ethane C_2H_6 (D_{3h}): Excitation Energies (eV) and Oscillator Strengths f for Low-Lying Excited States Obtained from the Symmetry-Adapted HAM/3 and the Original HAM/3

Excited States	Original HAM/3			SA-HAM/3				
	singlet		triplet	singlet		triplet		
	f			f				
1	22.802	0.1466	20.853	E'	22.802	0.1467	A_2''	20.920
2	22.802	0.1466	22.253	E'	22.802	0.1467	E'	22.258
3	24.035	0.0000	22.253	E''	24.035	0.0000	E'	22.258
4	24.035	0.0000	23.126	E''	24.035	0.0000	E''	22.961
5	24.275	0.5493	23.126	A_2''	24.275	0.5493	E''	22.961
6	24.466	0.0000	23.300	A_1'	24.466	0.0000	A_1'	23.246
7	25.766	0.0000	25.105	E''	25.766	0.0000	E''	25.111
8	25.766	0.0000	25.105	E''	25.766	0.0000	E''	25.111
9	27.021	0.0005	25.895	E'	27.021	0.0006	E'	25.641
10	27.021	0.0006	25.895	E'	27.021	0.0006	E'	25.641
Active Space	7(occ.) \times 7(unocc.)			7(occ.) \times 7(unocc.)				

Table 7. CH(CH₃)(CHO)OH (C₁): MO Energies (eV) in the HOMO-LUMO Vicinity Obtained from the Symmetry-Adapted HAM/3 Scheme and the Original HAM/3

MO	Original		SA-HAM/3
11	-10.7921	a	-10.7921
12	-10.452	a	-10.452
13	-9.35167	a	-9.35167
14	-8.78427	a	-8.78427
15 ^a	-6.76901	a	-6.76901
16 ^b	-2.46868	a	-2.46868
17	4.81370	a	4.81370
18	7.71148	a	7.71148
19	12.40075	a	12.40075
20	13.9429	a	13.9429

^a HOMO; ^b LUMO.

Table 8. CH(CH₃)(CHO)OH (C₁): Excitation Energies (eV) and Oscillator Strengths *f* for Low-Lying Excited States Obtained from the Symmetry-Adapted HAM/3 and the Original HAM/3

Excited States	Original HAM/3		SA-HAM/3					
	singlet	triplet	singlet		triplet			
	<i>f</i>		<i>f</i>					
1	3.950	0.0002	3.351	A	3.950	0.0002	A	3.351
2	6.620	0.0090	4.228	A	6.620	0.0090	A	4.343
3	6.930	0.2879	6.355	A	6.930	0.2879	A	6.357
4	8.123	0.0668	7.374	A	8.123	0.0668	A	7.384
5	8.436	0.0205	8.032	A	8.436	0.0205	A	8.039
6	8.557	0.0506	8.237	A	8.557	0.0506	A	8.236
7	9.078	0.0340	8.879	A	9.078	0.0340	A	8.878
8	10.162	0.0167	9.928	A	10.162	0.0167	A	9.928
9	11.272	0.0185	10.877	A	11.272	0.0185	A	10.869
10	11.424	0.0356	10.932	A	11.424	0.0356	A	10.920
Active Space	15(occ.)×11(unocc.)		15(occ.)×11(unocc.)					

strengths are also doubly degenerate. The original HAM/3 results do not show strict degeneracy both in the excitation energies and the oscillator strengths *f*. A similar situation prevails for triplet excitation energies. Tables 5 and 6 show the results of *eclipsed* ethane C₂H₆ (D_{3h}). In Table 5, MO energies obtained from SA-HAM/3 are identical to those obtained from original HAM/3 and the symmetry-adapted procedure did not affect the values of MO energies. In Table 6, clear degeneracies are seen in the singlet excitation energies and oscillator strengths *f* of the E' as well as E'' states both in the SA-HAM/3 and original HAM/3. The values of triplet excitation energies calculated with SA-HAM/3, however, differ from those calculated with original HAM/3. The discrepancy is due to the error involved in the original subroutine CICAL of the HAM/3 program¹¹ for triplet states, which has been properly corrected in the SA-HAM/3 program.¹³ Tables 7 and 8 show the results for CH(CH₃)(CHO)OH (C₁). Since this molecule has no symmetry, one expects no effect of the symmetry-adapted procedure. In Table 7, MO energies obtained from original HAM/3 and SA-HAM/3 are listed. Both sets are identical as expected. The same is observed in Table 8 for the singlet excitation energies and the oscillator strengths

f. However, some values of triplet excitation energies calculated with SA-HAM/3 differ from those calculated with original HAM/3, which is due to the error involved in the original subroutine¹¹ "CICAL" for triplet states.

Conclusions

We have demonstrated the effect of a symmetry adaptation of HAM/3 (SA-HAM/3) on calculated excitation energies and oscillator strengths *f* of fairly simple molecules with various symmetries, by comparing them with those calculated by the original HAM/3. SA-HAM/3 showed clear degeneracy of excited states in symmetrical molecules that were treated, while original HAM/3 failed. Since the object of the present work is a comparison between SA-HAM/3 and original HAM/3, neither observed values nor other theoretical results were included in the discussions. The HAM/3 method is an alternative to a limited number of spectroscopic semiempirical methods like CNDO/S and INDO/S. The latter methods are widely applied to planar conjugated molecules as the parameter values are determined essentially for ππ* transitions. On the other hand, the application of the HAM/3 method to

planar conjugated molecules with high symmetries has been avoided because of its deficiency that it gives split energies for the degenerate energy states. However, SA-HAM/3 can now be employed for any large conjugated system with high symmetry including C_{60} without difficulty.

Acknowledgements

We are grateful to Professor Delano P. Chong for stimulating discussions on the symmetry deficiency of HAM/3. We thank Noriyuki Fujimoto and Yukiko Arimura for doing numerical calculations with the HAM/3 programs and preparing data for this paper. A fellowship awarded to T. S. from FAPESP, S. Paulo, Brazil, is greatly appreciated.

References

1. Åsbrink, L.; Fridh, C.; Lindholm, E.; *Chem. Phys. Lett.* **1977**, *52*, 63; *ibid.* **1977**, *52*, 69; *ibid.* **1977**, *52*, 72; Åsbrink, L.; Fridh, C.; Lindholm, E.; de Bruijn, S.; *ibid.* **1979**, *66*, 411.
2. Takahata, Y.; Chong, D.P.; *J. Braz. Chem. Soc.* **2004**, *15*, 282.
3. Costa, M.C.A.; Takahata, Y.; *J. Braz. Chem. Soc.* **2002**, *13*, 806.
4. Costa, M.C.A.; Gaudio, A.C.; Takahata, Y.; *J. Mol. Struct. (Theochem)* **2003**, *664*, 171.
5. Åsbrink, L.; Fridh, C.; Lindholm, E.; *Chem. Phys.* **1978**, *27*, 159; *ibid.* **1978**, *27*, 169.
6. Lindholm, E.; Bieri, G.; Åsbrink, L.; Fridh, C.; *Int. J. Quantum Chem.* **1978**, *14*, 737; Åsbrink, L.; Fridh, C.; Lindholm, E.; *J. Electron Spectr. Related Phenom.* **1979**, *16*, 65; Åsbrink, L.; Fridh, C.; Lindholm, E.; Chong, D.P.; *Chem. Phys.* **1979**, *43*, 189.
7. Chong, D.P.; *Theoret. Chim. Acta* **1979**, *51*, 55; *Can. J. Chem.* **1980**, *58*, 1687.
8. Takahata, Y.; *Int. J. Quantum Chem.* **1986**, *30*, 453; *ibid.*; *J. Mol. Struct. (Theochem)* **1993**, *283*, 289; *ibid.* **1995**, *335*, 229.
9. Takahata, Y.; Hara, T.; Narita, S.; Shibuya, T.; *J. Mol. Struct. (Theochem)* **1998**, *431*, 219.
10. Takaoka, K.; Maeda, S.; Miura, H.; Otsuka, T.; Endo, K.; Chong, D.P.; *Bull. Chem. Soc. Jpn.* **2000**, *73*, 43.
11. Åsbrink, L.; Fridh, C.; Lindholm, E.; *QCPE (Quantum Chemistry Program Exchange)* **1980**, *12*, 393.
12. Narita, N.; Shibuya, T.; Takahata, Y.; *JCPE J.* **1999**, *11*, 161.
13. Narita, N.; Takahata, Y.; Shibuya, T.; *J. Mol. Struct. (Theochem)* **2002**, *618* 147.

Received: September 2, 2003

Published on the web: May 10, 2004

FAPESP helped in meeting the publication costs of this article.