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Study of the Semiempirical HAM/3 MO Method

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The semiempirical HAM/3 molecular orbital method, recently proposed by Åsbrink and coworkers, is studied. The speed and accuracy are confirmed by computations of vertical ionization potentials of some small molecules, sixteen 22-electron molecules, and the carbazole molecule. The negative comments of de Bruijn are examined and found to be partly valid but generally overcritical. Other aspects of HAM/3 are also discussed.

Key words: HAM/3 method

1. Introduction

The rapid advances of electron spectroscopy have stimulated developments and applications of *ab initio* quantum chemical methods of computing vertical ionization potentials (VIP), such as Green's functions [1] equation-of-motion [2], electron propagator [3], Rayleigh-Schrödinger perturbation theory (RSPT) [4], and extensions of the conventional configuration-interaction method [5][1]. These various *ab initio* approaches share two common characteristics: a) they are capable of yielding reliable VIP, ranging from an average absolute deviation (from experiment) of ca. 0.5 eV for $1\frac{1}{2}$-zeta basis set of Slater-type orbitals to ca. 0.1 eV for much more extensive basis sets[2]; b) the computing times required are such that large molecules such as carbazole, 2,4,7-trinitro-9-fluorenone and their charge-transfer complex have not been treated by methods beyond Hartree–Fock or Hartree–Fock–Slater-$X\alpha$ accuracy.

On the other hand, the semiempirical CNDO and INDO molecular orbital (MO) methods [8] have often been used to calculate various physical properties for very large systems. However, the use of MO energies to interpret photoelectron spectra

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[1] See Ref. [6, 7] for a brief review.

[2] See Ref. [7].

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often requires a linear regression analysis[3]. Otherwise, the deviations of calculated VIP from experimental ones are usually about 2 eV.

Recently, Åsbrink, Fridh and Lindholm [10–12] described a new semiempirical MO scheme called HAM/3 (hydrogenic-atoms-in-molecules version 3) for the calculation of VIP and vertical excitation energies. The computing times are about the same as those of CNDO [10] and the accuracy [10–16] appears to be comparable to *ab initio* methods using double-zeta basis sets. However, some of the arguments behind the formulation of HAM/3 have since been critically examined by de Bruijn [17], who found fault with almost everything about HAM/3 (except its apparent success). Some of de Bruijn's criticisms are valid; but some of the negative comments are probably based on his misunderstanding of HAM/3.

In this work, we wish to undertake a study of the semiempirical HAM/3 method. In Sect. 2, we present the positive aspects of HAM/3, namely its speed and accuracy. In Sect. 3, other qualitative characteristics of the method will be discussed, especially in reference to de Bruijn's comments [17].

2. Computational Study of HAM/3

In order to assess the speed of HAM/3 computations and the reliability of the results, we decided to calculate the vertical ionization potentials (VIP) for a number of relatively small molecules, for a collection of molecules containing twenty-two electrons, and for a large molecule: carbazole. The results are presented in separate subsections below.

2.1. Twelve Small Molecules

The purpose of studying this set of molecules is to compare the accuracy of HAM/3 with *ab initio* RSPT corrections to Koopmans' theorem using various basis sets. Consequently, the geometry of each molecule is identical to that used in the *ab initio* computations [4, 18–24]. The results are summarized in Table 1. It can be seen that the accuracy of the semiempirical HAM/3 method is about the same as *ab initio* RSPT calculations with double zeta (DZ) and double-zeta plus polarization (DZP) basis sets. On the other hand, the total CPU time for all twelve molecules is only seven seconds on an IBM 370/168 computer.

2.2. Sixteen 22-Electron Molecules

To confirm the speed and accuracy of HAM/3 obtained in the computational study of small molecules presented above, a collection of 22-electron molecules is examined next. The geometry of all of these molecules has been conveniently compiled [35]. The speed of HAM/3 is again very impressive: all sixteen molecules required a total of 11.5 seconds of CPU time on an IBM 370/168 computer. The results are summarized in Tables 2 to 4. Although there may be exceptions (for example, HCNO), the VIP calculated by HAM/3 are on the whole quite reliable.

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[3] See Ref. [9] for example.

Table 1. Comparison of initial[a] vertical ionization potentials (in eV) calculated by HAM/3 and by RSPT corrections to Koopmans' theorem[b]

			Deviation = I(calc) − I(obs)			
				RSPT		
Molecule		Obs.	HAM/3	$1\frac{1}{2}\zeta$	DZ	DZP
H_2O	$1b_1$	12.62 [25]	0.30	−0.06 [18]	−0.43 [18]	−0.20 [18]
	$3a_1$	14.74	0.64	−0.36	−0.52	−0.01
	$1b_2$	18.51	−0.24	0.62	0.56	0.46
H_2CO	$2b_2$	10.88 [26]	−0.17	0.40 [18]	0.27 [4]	
	$1b_1$	14.5	0.30	0.37	0.23	
	$5a_1$	16.0	0.44	0.25	0.19	
F_2O	$2b_1$	13.26 [27]	0.19	0.36 [18]	0.03 [4]	
	$6a_1$	16.17	−0.30	0.47	0.16	
	$4b_2$	(16.32) [4]	−0.30	0.55	0.22	
	$1a_2$	16.47	−0.18	0.54	0.22	
CO	5σ	14.01 [28]	0.10	0.07 [18]		
	1π	16.91	−0.15	1.11		
HOF	$2a''$	13.0 [29]	0.18	0.07 [19]		
	$7a'$	14.8	0.04	0.29		
N_2	$3\sigma_g$	15.60 [28]	−0.17	0.47 [23]	−0.70 [20]	−0.17 [23]
	$1\pi_u$	16.98	−0.77	0.77	−0.31	−0.51
	$2\sigma_u$	18.78	−0.38	0.63	−0.39	0.26
F_2	$1\pi_g$	15.83 [30]	0.55		−0.17 [20]	
	$1\pi_u$	18.80	0.59		−0.11	
	$3\sigma_g$	21	−0.28		−0.20	
HF	1π	16.03 [31]	0.71	0.13 [21]		
	3σ	19.41	0.36	0.32		
CF_2	$6a_1$	12.27 [32]	0.09	0.10 [22]		
	$4b_2$	16.40	−0.03	1.14		
	$1b_1$	19.2	−0.12	0.91		
HCN	1π	13.80[c]	0.22		−0.32 [23]	−0.39 [23]
	5σ	14.15	0.53		−0.66	0.00
C_2H_2	$1\pi_u$	11.40 [28]	0.19		−0.35 [23]	−0.35 [23]
	$3\sigma_g$	16.72	0.46		0.28	0.35
	$2\sigma_u$	18.75	0.92		0.21	0.45
Ketene	$2b_1$	9.8 [34]	−0.10		−0.66 [24]	
	$2b_2$	14.2	0.17		0.26	
	$7a_1$	16.8	−0.05		0.24	
Ave. abs. dev.		(0)	0.31	0.46	0.32	0.29

[a] That is, the first VIP of each symmetry.

[b] Using $\Delta(E^{GA})$. See Ref. [4].

[c] Evaluated in Ref. [23] from the data of Ref. [33].

Table 2. Vertical ionization potentials (in eV) of ketene

	Obs. [34]	HAM/3	CEPA [34]	RSPT [24]	Koopmans [34]
$2b_1$	9.8	9.70	9.50	9.14	9.95
$2b_2$	14.2	14.38	14.46	14.23	15.33
$1b_1$	15.0	15.28	15.08	15.56	17.55
$1b_2$	16.3	16.45	16.79	16.61	17.91
$7a_1$	16.8	16.75	17.04	16.70	18.51
$6a_1$	18.2	18.26	18.57	18.44	20.68
$5a_1$		24.32			28.70
$4a_1$		35.96			40.22

Table 3. Vertical ionization potentials (in eV) of CO_2. See also Ref. [14]

	Centroid[a]	HAM/3	Green's fn [7]	MCSCF-CI[36]	Koopmans [37]
$1\pi_u$	13.82	13.79	13.66	12.64	14.81
$1\pi_g$	17.60	17.73	17.87	17.18	19.45
$3\sigma_u$	18.11	18.01	18.30	18.38	20.23
$4\sigma_g$	19.43	19.50	19.65	19.84	21.77
$2\sigma_u$		36.81			40.19
$3\sigma_g$		37.64			41.63

[a] Obtained from the data in Ref. [28].

Table 4. Vertical ionization potentials (in eV) of fourteen 22-electron molecules

Molecule		HAM/3	Observed
FCN	2π	14.07	13.65 [38]
	7σ	15.41	14.56
	1π	18.64	19.3
	6σ	22.77	22.6
	5σ	27.77	
	4σ	42.59	
FCCH	2π	11.70	11.26 [39]
	1π	17.57	17.8
	7σ	18.34	(18)
	6σ	21.28	(>20)
	5σ	25.15	
	4σ	41.26	
NNO	2π	12.48	12.89 [40]
	7σ	16.50	16.39
	1π	18.67	18.24
	6σ	20.68	20.11
	5σ	36.06	
	4σ	39.57	

Table 4 *contd.*

Molecule		HAM/3	*Observed*				
HCNO	2π	10.99	10.83[41]				
	1π	17.14	15.92				
	7σ	18.84	17.79				
	6σ	21.03	19.1				
	5σ	27.96					
	4σ	36.45					
HNCO	$2a''$	11.84	11.60[42]	11.62[43]			
	$9a'$	12.61	12.39	12.30			
	$8a'$	16.17	15.54	15.8			
	$1a''$	16.19	15.54	15.8			
	$7a'$	17.59	17.39	17.50			
	$6a'$	20.37		19.24			
	$5a'$	28.80					
	$4a'$	36.16					
HN_3	$2a''$	10.48	10.74[42]	10.72[43]	10.70[44]	10.74[41]	10.72[45]
	$9a'$	11.95	12.2	12.24	12.2	12.25	12.24
	$8a'$	15.48	15.47	15.37	15.47	15.45	15.47
	$7a'$	17.29		16.8	16.7	16.80	16.8
	$1a''$	17.41	16.8	16.8	17.4	20.34	20.6
	$6a'$	20.94			20.1	21.6	21.9
	$5a'$	31.02					
	$4a'$	38.46					
H_2NCN	$9a'$	10.76	10.65[46]				
	$2a''$	12.37	12.50				
	$8a'$	13.40	12.98				
	$7a'$	14.13	14.23				
	$1a''$	18.36	18.8				
	$6a'$	19.28	19.6				
	$5a'$	25.32					
	$4a'$	29.78					
CH_3CN	$2e$	12.16	12.18[47]				
	$7a_1$	13.10	13.11				
	$1e$	15.29	15.5				
	$6a_1$	16.87	(17.4)				
	$5a_1$	23.14					
	$4a_1$	25.97					
CH_3NC	$7a_1$	11.80	11.24[48, 49]				
	$2e$	12.24	12.46				
	$1e$	15.79	16.14				
	$6a_1$	17.68					
	$5a_1$	22.90					
	$4a_1$	28.43					
CH_3CCH	$2e$	10.27	10.37[47]				
	$1e$	14.58	14.4[a]				
	$7a_1$	15.01	15.5[a]				
	$6a_1$	17.64	17.2				
	$5a_1$	21.67					
	$4a_1$	24.40					

Table 4 *contd.*

Molecule		HAM/3	*Observed*
CH_2N_2	$2b_1$	8.97	9.00[41]
	$2b_2$	13.88	14.13
	$7a_1$	15.05	15.13
	$1b_1$	15.94	16.93
	$1b_2$	17.37	18.5
	$6a_1$	18.70	19.6
	$5a_1$	25.90	(22.7)
	$4a_1$	36.35	
diazirine	$3b_1$	10.76	10.75[50]
	$2b_2$	13.05	13.25
	$6a_1$	14.30	14.15
	$5a_1$	16.36	16.5
	$1b_2$	17.01	17.5
	$2b_1$	19.19	21.5
	$4a_1$	22.37	22.5
	$3a_1$	34.97	
cyclopropene	$2b_2$	10.01	9.86[50]
	$3b_1$	11.08	10.89
	$6a_1$	12.82	12.7
	$1b_2$	15.28	15.09
	$5a_1$	16.65	16.68
	$2b_1$	19.32	18.3
	$4a_1$	20.30	19.6
	$3a_1$	26.71	
allene	$2e$	10.06	10.02[51]
	$1e$	15.11	14.75
	$3b_2$	15.20	17.3
	$4a_1$	17.57	
	$2b_2$	21.82	
	$3a_1$	24.93	

[a] Incorrectly assigned on the basis of CNDO/2 and INDO calculations.

2.3. *The Carbazole Molecule*

Åsbrink *et al.* reported that HAM/3 required 76 seconds on an IBM 370/165 computer for naphthalene (including a 46-term single-excitation configuration-interaction), and the naphthalene anion radical together [15], and 64 seconds for tetracyanoquinodimethane [16]. In this work, carbazole was selected as an example of a large molecule to be studied by HAM/3. Although no advantage was taken of its C_{2v} symmetry, the carbazole molecule required 30.4 seconds of CPU time on our new Amdahl 470 V/6-II computer, which is about 1.75 times the speed of the old IBM 370/168. The results are summarized in Table 5 and compared with experiment [52], semiempirical CNDO/S calculations [52, 53], SCF-scattered wave procedure [54], and *ab initio* molecular orbitals [55, 56]. While the other calculations require an empirical adjustment (see Ref. [9]) such as *A–Bε* before the calculated orbital energies can provide an adequate representation of the observed photoelectron spectrum [52], the results from HAM/3 can be used directly as in Fig. 1.

Table 5. Vertical ionization potentials (in eV) of carbazole

			CNDO/S			*ab initio* MO	
	HAM/3	Obs[a] [52]	[52][b]	[9][c]	X_α[d] [53]	[54][e]	[55][f]
$4b_1(\pi)$	8.42	7.68	9.30	9.66	14.7	9.36	9.38
$3a_2(\pi)$	8.78	8.08	9.36	9.56	15.2	9.68	9.54
$2a_2(\pi)$	9.53	9.09	10.50	10.76	15.8	11.24	11.16
$3b_1(\pi)$	10.14	9.78	11.40	11.81	16.1	12.28	12.00
$2b_1(\pi)$	11.02	10.82	13.25	13.90	17.1	14.12	13.82
$1a_2(\pi)$	11.71	11.4		15.08	17.7	15.29	14.78
$20a_1$	12.16		12.29	12.68	16.3	14.63	14.76
$17b_2$	12.18	12.4	12.24	12.63	16.3	14.77	15.14
$19a_1$	12.73			13.63	17.4	15.45	15.86
$16b_2$	12.81			13.82	17.4	15.62	16.08
$1b_1(\pi)$	13.32			17.72	19.0	17.68	17.10
$15b_2$	13.73	13.8		15.94	18.2	17.64	17.26
$18a_1$	13.84			16.20	18.2	17.41	17.38
$17a_1$	14.08	14.2		16.60	19.3	18.11	18.00
$14b_2$	14.48			16.60	19.9	17.84	17.79
$16a_1$	15.00	14.8		18.23		19.11	
$13b_2$	15.14			18.26		18.93	
$15a_1$	16.14	16.1		20.24		20.26	
$12b_2$	16.45					20.75	
$14a_1$	17.30	17				21.68	
$11b_2$	17.97					23.30	
$13a_1$	18.51	18.5				23.66	
$10b_2$	19.43					24.03	
$12a_1$	20.40					25.66	
$9b_2$	22.38					28.50	
$11a_1$	22.98					28.57	
$8b_2$	24.04					29.52	
$10a_1$	24.52					30.40	
$9a_1$	26.53					32.40	
$7b_2$	26.75					32.85	
$8a_1$	30.26					36.32	

[a] Haink *et al.* [52] assigned the first five VIP only. Values of other observed VIP have been estimated from their spectrum and have been associated with the nearest VIP calculated by HAM/3.

[b] With modified γ-integrals.

[c] With Pariser γ-integrals.

[d] These are the absolute values of the ground-state molecular orbital energies, as estimated by Nitzsche *et al.* [55] from the graphical data of Liberman and Batra [53].

[e] Minimal basis set of contracted Gaussian-type orbitals.

[f] Using the recommended formula: $0.8783[-\varepsilon(\text{molecular fragment procedure})]+0.2297$, for VIP in hartree.

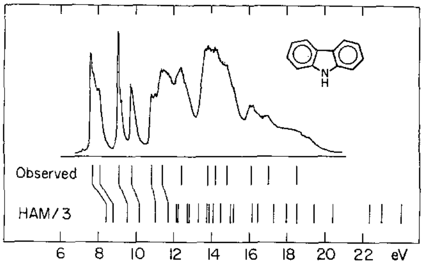

Fig. 1. Comparison of the experimental photoelectron spectrum of carbazole [52] with the vertical ionization potentials calculated using the semiempirical HAM/3 molecular orbital method

3. Discussion

Although most of the molecules studied in this work are among the 80 molecules used in the parametrization process[4], the speed and accuracy of the semiempirical HAM/3 MO method are still very impressive. The results in Sect. 2 show that the functional form of the energy expression in HAM/3 is capable of being parametrized to give fairly reliable VIP at the equilibrium geometry of the parent molecules and that, once parametrized (and HAM/3 does contain many parameters), HAM/3 requires very little computing time. Thus, HAM/3 appears to be quite successful in yielding reliable VIP despite the criticism of de Bruijn [17].

Let us now consider de Bruijn's comments [17]. 1) De Bruijn is correct in criticizing the claim of Åsbrink and coworkers [10] that the correlation energy in atoms is treated correctly in HAM/3 and the implication that the "correct" treatment comes from the supposed interdependence of the ζ's, which is non-existent for atoms. Instead, one should consider an analogous treatment of Hartree–Fock or Hartree–Fock–Slater atoms whereby the HF atomic levels form the target model, resulting in a different set of parameters. Changing parameters then is simply a means of getting closer to the experimental atomic energy levels. 2) The same consideration applies to molecules: one can regard the final set of parameters as that modified from a set of parameters which would give Hartree–Fock molecules. De Bruijn misunderstood the dependence of the ζ's on the P matrix. The choice of the ζ's is not fixed from the ground-state P matrix but depends on the state (or transition state) of interest. 3) The question of self-repulsions cannot be easily settled. Because a portion of the repulsions is buried in the atomic screening constants in HAM/3 and because γ_{AB} occurs only in the "electrostatic interaction" term and other relatively small "correction" terms, it is impossible to translate HAM/3 formulas into Hartree–Fock language. Åsbrink and coworkers [56] believed that de Bruijn's analysis of self-repulsions (that each electron feels the repulsion from $2n$ electrons) is incorrect, due to difficulties in transforming HAM/3 expressions into HF language. 4) Finally, de Bruijn criticized that HAM/3 allows an electron to be "anti-shielded" by itself when $P_{\mu\mu} < 2$. Although the criticism is valid, it can be removed by using $P^{\beta}_{\mu\mu}$ instead of $P_{\mu\mu} - 1$ in S^{α}_{μ} and $P^{\alpha}_{\mu\mu}$ in S^{β}_{μ}.[5] Such a change would improve the theoretical basis of HAM/3, but would require new parametrization.

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[4] E. Lindholm and L. Åsbrink (private communication). The exceptions are HNCO, propyne, allene, HCNO and carbazole.

[5] For molecules, the expression is actually: $P_{\mu\mu} - 1 + \sum_{B \neq A} \sum_{\lambda}^{B} P_{\mu\lambda} S_{\mu\lambda}$, instead of $P_{\mu\mu} - 1$.

The major weakness of HAM/3, more serious than the criticism of de Bruijn [17], is the large number of parameters. Some chemists may feel that, with such a large number of parameters, one can "fit an elephant". Some of the parameters can perhaps be eliminated in future development of HAM by using values from Hartree–Fock atomic and molecular orbital calculation, but HAM/3 is essentially an empirical method which takes advantage of the transition state concept.

So far, we have confined ourselves to VIP of parent molecules at the equilibrium geometry. The HAM/3 method has been formulated to give electron affinities, non-Rydberg excitation energies and intensities, and heats of formation [10–16]. The results so far have been encouraging. However, the energy expressions in HAM/3, such as $E_\mu = -\zeta_\mu^2$, lead one to regard the HAM/3 energy as the negative of the kinetic energy. Consequently, any HAM/3 result for molecules not at equilibrium geometry should be regarded with extreme caution.

In summary, although some of de Bruijn's comments [17] are valid, we believe that they are overcritical and that experimental photoelectron spectroscopists can use HAM/3 results to make better assignments of their spectra when no reliable *ab initio* calculations are available. On the other hand, it should be remembered that HAM/3 is a semiempirical method based on many parameters and intended to be used for large molecules.

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