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Article

Is HAM/3 (Hydrogenic Atoms in Molecules, Version 3) a Semiempirical Version of DFT (Density Functional Theory) for Ionization Processes?

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Nós calculamos os potenciais de ionização verticais (VIPs) de nove moléculas pequenas, bem como, os potenciais de uracil e do C_2F_2 usando diferentes métodos: i) semi-empírico HAM/3; ii) semi-empírico AM1; iii) não empírico Teoria do Funcional de Densidade (TFD) com os modelos uDI(B88-P86)/cc-pVTZ e -ε(SAOP)/TZP; iv) *ab initio* HF/cc-pVTZ. Os resultados numéricos obtidos com HAM/3 são mais próximos dos resultados obtidos com o TFD do que o Hartree-Fock (HF). Nós também calculamos as energias de ligação de elétrons do caroço (CEBE) da anilina, nitrobenzeno, e p-nitroanilina com o HAM/3 e a TFD empregando o método ΔE. O modelo de DFT designado como ΔE_{KS} (PW86-PW91)/TZP produziu resultados precisos de CEBE, com desvio médio absolutos de 0,14 eV. Enquanto que a magnitude absoluta dos CEBEs calculados pelo método HAM/3 tem um erro de menos de 3 eV, os deslocamentos químicos (ΔCEBE) têm erros menores que 0,55 eV. Mesmo que os resultados de CEBE não apresentem uma resposta definitiva à pergunta do título, as tendências nos VIPs indicam que o HAM/3 não se aproxima do TFD com potenciais de troca-correlação precisos, mas indicam uma proximidade com funcionais semelhantes ao B88-P86.

We calculated valence-electron vertical ionization potentials (VIPs) of nine small molecules, plus uracil and C_2F_4, by several different methods: semiempirical HAM/3 and AM1 methods, different nonempirical DFT models such as uDI(B88-P86)/cc-pVTZ and –ε(SAOP)/TZP, and *ab initio* Hartree-Fock (HF) /cc-pVTZ. HAM/3 reproduced numerical values more closely to those calculated by the nonempirical DFTs than to those obtained by HF method. Core-electron binding energies (CEBEs) of aniline, nitrobenzene and p-nitro aniline, were also calculated by HAM/3 and nonempirical ΔFT using DE method. A nonempirical DFT model, designated as ΔE_{KS} (PW86-PW91)/TZP model, resulted accurate CEBEs (average absolute deviation of 0.14 eV) with high efficiency. Although absolute magnitude of HAM/3 CEBEs has error as much as 3 eV, the error in the chemical shifts ΔCEBE is much smaller at 0.55 eV. While the CEBE results do not lead to any definite answer to the question in the title, the trends in valence-electron VIPs indicate that HAM/3 does not approximate DFT with accurate exchange-correlation potentials, but seems to simulate approximate functionals such as B88-P86.

Keywords: HAM/3, DFT, vertical ionization potential, CEBE, ESCA

Introduction

The semiempirical molecular orbital (MO) method known as Hydrogenic Atoms in Molecules, Version 3 (HAM/3) was developed by group of Lindholm and coworkers in 1977.[1] The method has been successfully applied to the calculation of mainly vertical ionization potentials (VIPs), excitation energies, and electron affinities of wide variety of molecules. Some selected works are listed in references 2-7. However, extensions of HAM/3 to the calculation of X-ray emission spectra,[8] Auger electron spectra,[9] valence-electron shake-up satellites,[10] core-electron shake-up satellites,[11] and relative intensities for valence region of X-ray photoelectron spectra will not be discussed in this paper. The theoretical foundation of HAM/3 has been described in detail in the book of Lindholm and Åsbrink.[12] According to the authors, theoretical foundation of HAM/3 method is based on

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density functional theory (DFT).[13,14] In other words, HAM/3 was considered to be a semiempirical version of DFT. In their book, Parr and Yang[15] called attention to the HAM model being a semiempirical version of the Kohn-Sham method.

The increasing popularity of DFT in the last decade is quite remarkable. DFT is one of the most promising theoretical methods to study electronic structure of medium and relatively large molecular system as well as solid state in high accuracy. Although there are empirical parameters in most choices of the exchange-correlation functional E_{xc}, the parameters are assumed to be universal for all systems (and hence not empirical for each element), and consequently DFT calculations are often considered to be *a priori*, first-principle, or nonempirical. The advancement of DFT is due to development of more and more reliable exchange-correlation functionals E_{xc}, together with availability of powerful computers with relatively low cost. However, there still remains an area in which a semiempirical method such as HAM/3 can play. Computer times of calculation for a large molecular system by HAM/3 are orders of magnitude smaller than nonempirical DFT calculation. There are occasions when calculation of approximate molecular properties of a large number of molecules is desired in short time. In such cases, a semiempirical method is the natural method of choice. The object of the present paper is to investigate numerically to determine whether or not HAM/3 is really a semiempirical version of DFT for ionization processes. We therefore calculate vertical ionization potentials (VIPs) of outer valence electrons as well as core-electron binding energies (CEBEs) of some molecules for comparable studies.

Before we begin, let us briefly review the theoretical studies of VIPs and CEBEs. Early studies of VIPs, using semiempirical (such as CNDO, MINDO, AM1, *etc.*) or *ab initio* Hartree-Fock (HF) methods, rely on Koopmans' theorem (KT). HAM/3 is an exception, using a simplified version of Slater's transition-state model[16] called diffuse ionization (DI) for VIPs.[1] On the other hand, a number of DFT calculations of VIPs have been performed previously. Initial studies[17] showed that the VIPs for the lowest cationic states of each symmetry can be computed quite well, with average absolute deviations (AADs) of 0.3 eV from experiment, regardless of whether one uses local density approximation or generalized gradient approximations such as B88[18]-P86[19] or PW86[20]-PW91,[21] and regardless of whether one uses Slater's transition-state method or total energy difference ΔE. However, the list of molecules has not been extensive enough. Shapley and Chong used the PW86-PW91 functional and calculated 181 VIPs of 41 molecules by ΔE method.[22] The overall AAD from experiment was 0.55 eV. The most important impact of that study is that many VIPs, even for the lowest cationic state of each symmetry, for perfluoro molecules were in error by over 2 eV (even with several other functionals). More recently, Chong and his collaborators[23] showed that the energies ε_k of the outer-valence occupied Kohn-Sham orbitals gave approximate relaxed VIPs better than KT. Excellent agreement between $-\varepsilon_k$ of outer-valence Kohn-Sham MOs for N_2, CO, HF and H_2O and experimental VIPs of the molecules were obtained, especially when accurate V_{xc} was used, the average absolute deviation from experiment being less than 0.1 eV. In addition, calculations of 64 molecules were performed with the approximate V_{xc} known as the statistical averaging of orbital potentials (SAOP). Reasonable agreement between $-\varepsilon_k$(SAOP) and the outer valence VIPs (including many perhalo molecules) was found, with AAD of 0.4 eV, much better than KT with HF MOs. In this study, we shall designate the use of $-\varepsilon_k$ of Kohn-Sham orbital k (instead of Hartree-Fock orbital) to approximate VIP_k as meta-Koopmans' theorem (mKT).

Let us now turn to CEBEs. Since the early days of development of experimental technique of X-ray photoelectron spectroscopy, the electrostatic potential models or the thermochemical equivalent-core approximation,[24] were used to interpret chemical shifts of CEBEs. Since then, several reviews have been published.[25] In a potential model, for instance, the chemical shift is related to the atomic charge of the atom concerned and to those of surrounding atoms. There are empirical parameters that have to be determined by a least-squares fit to the experimental data in the model. Hence, the potential model can be called as an empirical model. There is fairly good correlation between observed and calculated chemical shift for many cases. However, there are cases where correlation is poor, depending on type of molecules treated. The semiempirical HAM/3 gives the CEBE directly as the difference between the ground-state molecule and the core-hole cation. Chong[26] compared CEBEs of a variety of molecules calculated by HAM/3 with observed ones. A persistent error associated with C-H bonds was also reported.[26] Recently, Chong[27] proposed a method that enabled one to calculate accurate CEBEs by the density-functional theory. The method employs an unrestricted generalized transition-state (uGTS) model.[28] Pulfer *et al.* have confirmed the reliability of the method with a total of seventy-six cases.[29] More recently, a more reliable method, called ΔE_{KS}(PW86-PW91)/cc-pCVTZ, was found by Cavigliasso and Chong.[30] In the shorthand notation, ΔE_{KS} is the difference in the total energies E's of core-ionized cation and neutral parent molecule calculated by DFT using correlation consistent polarized core-valence triple zeta (cc-pCVTZ) basis set; PW86 is Perdew-Wang 1986 exchange functional,[20] and PW91 is Perdew-Wang 1991 correlation functional.[21] They used a modified version of DeMon computational package[31] for the calculations. The initial high accuracy of molecular CEBEs, with AAD of only 0.15 eV for 32 cases, was confirmed later with a total of 78 cases.[32] An extensive review of DFT calculation of CEBE has been given in a chapter contributed by Chong.[33] In this chapter, he also proposed the use of Amsterdam Density Functional (ADF) package[34] for calculation of accurate CEBEs, because localizing a core hole is much easier with ADF than with other program such as DeMon.

Method

In this work, we calculate the VIPs of nine small molecules, as well as uracil and C_2F_4, by several different methods: HAM/3, two models within nonempirical DFT, *ab initio* HF,[35] and the semiempirical MO method called Austin Model, Version 1 (AM1).[36] In the first DFT method studied here, ionization energies of a system (neutral molecule M) can be calculated employing an approximate version of Slater's transition state (TS) method, in which one half electron is removed from the system. Absolute values of occupied MO energies of the species $M^{+0.5}$ give the ionization energies. The HAM/3 calculations were performed with the computer program purchased from QCPE.[37] In calculations of VIPs of the molecules by HAM/3 using the keyword PES, the restricted diffuse ionization (rDI) model was automatically employed. This model is the first model and it is designated as HAM/3 (rDI). The rDI model is a simplification of Slater's transition state method, by distributing the +0.5 charge over all the valence MOs, with electrons with α and β spins occupying the same spatial orbitals. We also calculated negative of k-th molecular orbital energy ($-\varepsilon_k$) of a neutral form of the nine small molecules by HAM/3 for the sake of comparison. This is the second model and it is designated as HAM/3 ($-\varepsilon_k$). The negative of k-th molecular orbital energy ($-\varepsilon_k$) of a neutral molecule would represent KT-like ionization potential. One nonempirical DFT model for calculation of valence electron VIPs is unrestricted diffuse ionization (uDI) model, uDI(B88-P86)/cc-pVTZ, which is the third model and it is designated simply by uDI. The calculations were done with DeMon computational package. In uDI model, +0.5 charge is distributed only α-spin valence MOs. We used the exchange-correlation potential labeled as B88-P86, made from Becke's 1988 exchange functional[18] and Perdew's 1986 correlation functional[19] in the uDI calculations. We also calculated negative of k-th molecular orbital energy ($-\varepsilon_k$) of a neutral form of the nine small molecules by nonempirical DFT(B88-P86)/cc-pVTZ, which is our fourth model. It is designated as DFT(B88-P86)/cc-pVTZ(mKT). The other DFT model tested is $-\varepsilon$(SAOP)/TZP(mKT), which is the fifth model and it is designated simply by SAOP, using the ADF program with a triple-zeta polarized (TZP) basis set of Slater-type orbitals. In SAOP, electron density is calculated with the exchange-correlation potential V_{xc}^{SAOP} in SCF process, while energy is calculated with PW91x-PW91c functionals.[21] In HF/cc-pVTZ (6th model) and AM1 (7th model) calculations with Gaussian 94 program,[38] KT was assumed. The use of the notation KT is restricted for HF and approximate HF methods (such as AM1 method) in this work, while mKT is reserved for the case of DFT, in which $-\varepsilon$ of Kohn-Sham orbitals is used to approximate VIPs. The calculated results are compared to each other. Total energy (E) in DFT is exact in the sense that it includes "correlation energy", while total energy in HF theory does not contain the correlation energy. Because of this, ΔE method works well in DFT for calculation such as ionization energy of a system, in which ΔE is the difference of total energies between ionized and neutral molecules.

CEBEs of aniline, nitrobenzene, *p*-nitroaniline, and uracil were calculated by HAM/3 and DFT with the ΔE method. The ADF package was used for the DFT calculations. In all DFT calculations with ADF, we used the exchange-correlation potential labeled as PW86-PW91, made from Perdew-Wang 1986 exchange functional[20] and Perdew-Wang 1991 correlation functional.[21] Basis set of triple zeta plus one polarization, TZP, was used. This model can be expressed as ΔE_{KS}(PW86-W91)/TZP. Experimental CEBEs of uracil were observed in solid-state. CEBE (solid) and CEBE(gas) can be related by equation 1,

$$\text{CEBE(gas)} = \text{CEBE(solid)} + \text{WD} \tag{1}$$

where WD (W for work function and D for delta, other energies) is energy shift due to solid-state effects. We adopt molecular solids model. We estimate WD to be average absolute deviation between calculated CEBE (gas) and observed CEBE (solid). The results were compared with those observed and those calculated with nonempirical DFT and HAM/3. Experimental geometry was used for H_2O and uracil. Molecular geometries were calculated for the remaining molecules with HF/6-31G*.

Results and Discussion

Table 1 summarizes VIPs of a total of 30 cases originating from the nine small molecules, calculated by the seven different models; (1) HAM/3(rDI), (2) HAM/3($-\varepsilon_k$), (3) uDI(B88-P86)/cc-pVTZ, (4) DFT (B88-P86)/cc-pVTZ($-\varepsilon_k$), (5) $-\varepsilon$(SAOP)/TZP, (6) HF/cc-pVTZ, and (7) AM1. In case of H_2O, for example, all models, except the models (2) and (4), reproduce experimentally obtained vertical ionization energies fairly satisfactorily for the lowest three energies corresponding to $1b_1$, $3a_1$ and $1b_2$. However, the error of the calculated VIP for the low-lying $2a_1$ orbital by both HF and AM1 is more than 4 eV (see Figure 1). Errors of (1) HAM/3 (rDI) and the two DFT models, (3) uDI and (4) SAOP, for the same event are much smaller than 4 eV. In DFT, the error due to correlation effect is expected to be small. The fact that the large errors registered in VIP($2a_1$) by HF and AM1 may be due to mainly electron correlation effect, since no correlation effect is taken into account in HF methods. In case of the two models, (2) HAM/3($-\varepsilon_k$) and (4) DFT (B88-P86)/cc-pVTZ($-\varepsilon_k$), the discrepancy between experimental ionization potentials and corresponding negative values of k-th molecular orbital energy ($-\varepsilon_k$) of the neutral form of H_2O is very large. The $-\varepsilon_k$ values in the two models are uniformly smaller than the experimental ionization potentials by approximately 5 eV. The numerical $-\varepsilon_k$ values in the models (2) are fairly close to those in the model (4). Situations similar to those seen in H_2O can be observed in

Table 1. Ionization potentials (in eV) of nine small molecules calculated by seven different models; (1) HAM/3(rDI), (2) HAM/3($-\varepsilon_k$), (3) uDI(B88-P86)/cc-pVTZ, (4) DFT (B88-P86)/cc-pVTZ($-\varepsilon_k$) (5) $-\varepsilon$(SAOP)/TZP, (6) HF/cc-pVTZ, and (7) AM1. Average absolute deviations (AAD's) are listed in the last row of the table. rDI and uDI are the two transition state methods. $-\varepsilon_k$ signifies negative of orbital energy of a neutral molecule. KT signifies Koopmans's theorem

MO	Exp.	(1)HAM/3 (rDI)	(2)HAM/3 ($-\varepsilon_k$)	(3)uDI(B88-(P86)/cc-pVTZ	(4)DFT/(B88-P86)/cc-pVTZ ($-\varepsilon_k$)	(5)$-\varepsilon$(SAOP) /TZP ($-\varepsilon_k$)	(6)HF/ cc-pVTZ KT	(7)AM1 KT
H_2O[44]								
$1b_1$	12.62	12.95	7.62	12.99	6.94	12.37	13.73	12.46
$3a_1$	14.74	15.38	10.19	15.02	9.06	14.31	15.69	14.87
$1b_2$	18.51	18.33	13.24	19.21	13.09	17.95	19.37	18.33
$2a_1$	32.2	32.88	27.51	31.52	25.21	30.34	36.62	36.48
HF[45,46]								
1π	16.19	16.82	9.85	16.33	9.30	15.68	17.50	13.99
3σ	19.82	19.80	13.15	20.00	13.23	19.18	20.69	17.10
2σ	39.58	39.66	32.63	36.80	29.83	36.05	43.39	48.17
NH_3[47,48]								
$3a_1$	10.85	10.72	6.38	11.14	5.96	10.68	11.55	10.57
1e	15.8	16.58	12.35	16.59	11.23	15.64	16.97	15.74
$2a_1$	27.7	28.04	23.63	26.64	21.15	25.59	30.90	32.50
CH_4								
$1t_2$	14.4	14.49	10.82	14.26	9.60	13.85	14.84	13.44
$2a_1$	22.9	23.37	19.53	22.01	17.21	21.50	25.68	29.37
CO								
5σ	14.01	14.11	9.11	14.04	9.09	13.74	15.07	13.12
1π	16.91	16.76	11.35	17.41	11.86	16.53	17.39	16.90
4σ	19.72	19.73	14.22	19.70	14.19	18.97	21.87	22.10
CO_2								
$1\pi_g$	13.79	13.74	9.21	13.86	9.05	14.42	14.76	13.30
$1\pi_u$	17.60	17.69	13.08	17.51	12.69	17.83	19.37	18.50
$3\sigma_u$	18.08	17.95	13.33	17.53	12.71	17.89	20.15	18.74
$4\sigma_g$	19.40	19.47	14.85	18.59	13.84	19.09	21.74	22.68
N_2								
$3\sigma_g$	15.60	15.43	10.16	15.68	10.32	15.23	16.66	14.30
$1\pi_u$	16.98	16.21	10.90	17.19	11.60	16.44	17.21	16.31
$2\sigma_u$	18.78	18.40	13.14	18.82	13.51	18.54	21.16	21.40
F_2								
$1\pi_g$	15.87	16.43	10.30	15.49	9.36	15.80	18.09	14.23
$1\pi_u$	18.8	19.41	13.18	18.81	12.74	19.04	20.40	17.57
$3\sigma_g$	21.1	20.72	14.50	21.51	15.35	21.29	22.02	19.41
H_2CO								
$2b_2$	10.89	10.78	6.39	10.73	6.15	11.01	12.04	10.77
$1b_1$	14.5	14.85	10.32	16.25	9.99	14.51	14.46	14.74
$5a_1$	16.0	16.45	11.85	16.36	10.87	15.49	17.56	16.16
$1b_2$	16.6	17.59	13.50	17.69	12.32	16.81	18.98	17.46
$4a_1$	21.8	21.31	17.26	19.86	15.70	20.27	23.55	25.00
AAD	(0)	0.34	4.94	0.57	5.62	0.65	1.61	1.83

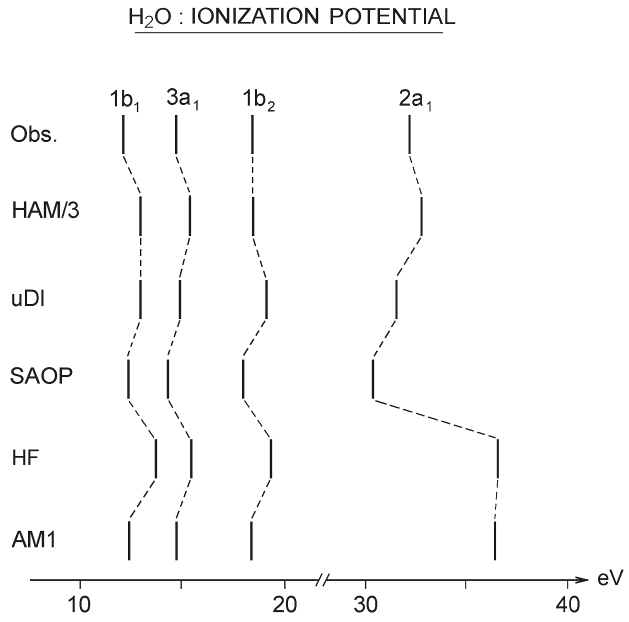

Figure 1. Comparison of vertical ionization potentials of H_2O calculated with five different methods; HAM/3 (rDI), uDI, SAOP, HF and AM1.

the remaining eight small molecules in the Table 1. The AADs obtained for the 30 cases in Table 1 of the seven different models, (1)-(7), are (1) 0.34 eV, (2) 4.94 eV, (3) 0.57 eV, (4) 5.62 eV, (5) 0.65 eV, (6)1.61 eV, and (7) 1.83 eV. AADs of the models (1) HAM/3 (rDI) and the two nonempirical DFT models, (3) uDI and (5) SAOP, are less than half of those of (6) HF and (7) AM1 models. On the other hand, AAD of the model (2) HAM/3($-\varepsilon_k$) is 4.94 eV, while that of the model (4) DFT (B88-P86)/cc-pVTZ($-\varepsilon_k$) is 5.62 eV. The two models gives close AAD values to each other indicating the similarity of the model (2) to the model (4). Because the existence of the close parallelism in the numerical values in the pair of the two models (2) and (4), at the same time in the other pair of the two models, (1) and (3), HAM/3 can be considered as a semiempirical version of nonempirical DFT (B88-P86)/cc-pVTZ. On the other hand, AM1 semiempirical method reproduces VIPs of *ab initio* HF method well. This is because AM1 is a semiempirical version of HF method, and not that of DFT. The model (5) $-\varepsilon$(SAOP)/TZP resulted AAD of 0.65 eV, which is to be compared with AAD of 1.61 eV resulted from (6) *ab initio* HF/cc-pVTZ (KT). The model $-\varepsilon$(SAOP) with nonempirical DFT is superior to KT in *ab initio* HF.

Since the model (2) HAM/3($-\varepsilon_k$) and the model (4) DFT (B88-P86)/cc-pVTZ($-\varepsilon_k$) resulted large systematic errors for calculating VIP's of the small molecules in Table 1, we shall not consider them any further and work only with the remaining five models for the rest of discussions. Table 2 compares 13 lowest VIPs of uracil calculated by the five different models. The experimental VIPs were observed in gas-phase.[39] Only the five lowest ionization events (5a", 24a', 4a", 23a', and 3a") have been assigned. AAD, corresponding only to the five lowest ionization events, of HAM/3 (rDI) is ca. 0.2 eV, while AADs of the three models, uDI, SAOP, and AM1, are in the neighborhood of 1 eV. AAD of HF is ca. 1.5 eV. If the 13 ionization events are taken into account (based on the ordering of HAM/3 and SAOP), the AADs take the values of 0.19 eV (HAM/3), 0.80 eV (uDI), 0.94 eV (SAOP), 2.20 eV (HF) and 1.27 eV (AM1). AAD of HAM/3 (rDI) is the smallest; AADs of the

Table 2. Ionization energies (in eV) of uracil calculated by HAM/3 (rDI), uDI, SAOP, HF, and AM1. Average absolute deviations (AAD's) are listed in the last row of the table

MO	Exp.[a]	HAM/3(rDI)	uDI(B88-P86)/cc-pVTZ	$-\varepsilon$(SAOP)/TZP	HF/cc-pVTZ	AM1
5a"	9.59	9.83	8.92	10.95	10.11	10.09
24a'	10.12	10.22	9.14	11.00	12.15	11.41
4a"	10.56	10.52	9.77	11.73	11.79	11.17
23a'	11.00	10.70	9.82	11.81	13.08	12.16
3a"	12.63	12.44	11.93	13.63	14.11	13.32
AAD	(0)	(0.17)	(0.86)	(1.04)	(1.47)	(0.85)
2a"	(13.3)	13.62	12.94	14.62	15.47	15.18
22a'	(14.0)	14.07	13.03	14.81	16.41	14.74
21a'	(14.3)	14.43	13.24	14.95	16.77	15.03
20a'	(14.6)	14.97	13.91	15.70	17.74	16.45
19a'	(15.2)	15.21	14.62	16.23	18.42	17.25
1a"	(15.7)	15.28	14.77	16.36	17.95	17.08
18a'	(16.8)	17.09	15.99	17.45	19.42	18.45
17a'	(17.6)	17.30	16.94	18.31	20.63	19.56
AAD(all)	(0)	0.19	0.80	0.94	2.20	1.27

[a]The experimental VIPs were observed in gas-phase. The values in parentheses are those read from photoelectron spectrum of uracil in the literature (Reference 39).

two DFT models are close to each other; and AAD of HF is more than twice to those of DFT. In other words, VIPs calculated with rDI in HAM/3 and the two nonempirical DFT models are closer to observed values than those calculated with KT in *ab initio* HF. The spectral patterns for the five lowest ionization events obtained by HAM/3 (rDI), uDI and SAOP reproduce that observed fairly well (see Figure 2). AM1 results parallel closely to those of HF, but neither reproduces the observed spectral pattern well.

Shapley and Chong[40] calculated VIPs of C_2F_4 with ΔE approach using seven different DFT exchange–correlation functionals. Most AADs were in the neighborhood of 1.5 eV.

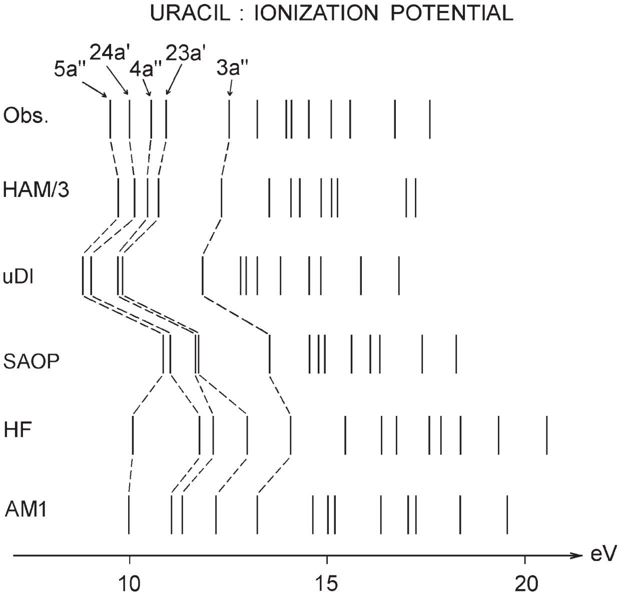

Figure 2. Comparison of vertical ionization potentials of uracil calculated with five different methods; HAM/3 (rDI), uDI, SAOP, HF and AM1.

The smallest AAD attained was 0.79 eV. We wanted to know if any one of our five methods can give better result than this. Table 3 lists VIPs of C_2F_4 calculated with the five different methods. The value of AAD increases in the order HAM/3 (rDI) < SAOP < AM1 < uDI < HF. The smallest AAD, 0.27 eV, is registered by the semiempirical HAM/3 (rDI) method. This may be because C_2F_4 is one of the molecules that were used for parametrization of the method. Next, the SAOP model gave AAD of 0.36 eV, which is much smaller than 1.5 eV. In fact, Chong *et al.*[23] obtained AAD of 0.35 eV with SAOP model for calculated VIPs of ten perhalo molecules. Our result is just a confirmation of the success of the SAOP model. The semiempirical AM1 showed AAD of 0.77 eV. The AAD of nonempirical uDI and *ab initio* HF showed larger AAD values, more than 1.5 eV's. B88-P86 functional used in the uDI calculation was not appropriate for the type of molecule. Sharpley and Chong[40] obtained similar results as our uDI result using various other types of functionals. The $-\varepsilon$(SAOP)/TZP model proved to be a good choice for this type of molecules, as found earlier.[23] Error due to correlation effect, together with the approximate nature of KT, is large in HF method for C_2F_4.

Table 4 lists CEBEs of substituted benzenes (X-C_6H_4-Y) such as benzene, aniline, nitrobenzene and *p*-nitroaniline calculated with HAM/3 and with ΔE_{KS} (PW86-PW91)/TZP-ADF models. AAD obtained with HAM/3 is 3.25 eV, which is much larger than 0.14 eV, the AAD obtained with the nonempirical DFT calculations. The ΔE_{KS} (PW86-PW91)/TZP method works very well.[41] AAD of 0.15 eV had also been obtained previously for exactly the same set of molecules using the uGTS model.[42] The DeMon DFT program was employed in the uGTS calculations. We designate this as uGTS(DeMon) model. Both ΔE_{KS} (PW86-PW91)/TZP(ADF) method and the uGTS(DeMon) model

Table 3. Ionization potentials (in eV) of C_2F_4 calculated by HAM/3 (rDI), uDI, SAOP, HF, and AM1. Average absolute deviations (AAD's) are listed in the last row of the table

MO	Exp [a]	HAM/3(rDI)	uDI(B88-P86)/cc-pVTZ	$-\varepsilon$(SAOP) /TZP	HF/ cc-pVTZ	AM1
$2b_{3u}$	10.69	10.94	9.96	11.10	10.81	10.19
$4b_{3g}$	15.9	16.14	14.32	15.75	18.42	15.42
$6a_{1g}$	16.6	16.47	14.85	16.12	18.91	14.41
$4b_{2u}$	16.6	16.29	14.89	16.27	19.26	15.43
$1a_u$	16.6	16.45	14.94	16.41	19.48	15.83
1b1g	16.6	16.52	15.10	16.56	20.18	15.93
$5b_{1u}$	17.6	17.48	15.74	17.10	20.91	16.52
$1b_{2g}$	18.2	17.76	16.50	17.84	21.72	17.82
$1b_{3u}$	19.4	19.45	17.73	18.93	22.10	19.92
$3b_{3g}$	19.4	19.82	18.24	19.24	23.18	18.39
$3b_{2u}$	21.0	20.37	19.39	20.33	23.854	20.61
$5a_g$	21.0	20.61	19.54	20.43	25.18	20.88
AAD	(0)	0.27	1.53	0.36	2.87	0.77

[a] Reference 49.

Table 4. Calculated core-electron binding energies (in eV) for benzene(C_6H_6), aniline(C_6H_5-NH_2), nitrobenzene(C_6H_5-NO_2), and *p*-nitroaniline (*p*-NH_2-C_6H_4-NO_2), using HAM/3, and density functional theory with TZP basis sets and PW86x-PW91c functional. The ΔE method was employed. Absolute deviations (AD) from experiment are given in parenthesis immediately after calculated CEBEs

Molecule	Core hole	HAM/3	ΔE_{KS}(PW86-PW91)/TZP	Observed[50-53]
C_6H_6	C	286.20(4.21)	290.44(0.03)	290.41
C_6H_5-NH_2	C1	288.32(2.97)	291.38(0.09)	291.29
	C2	286.11(3.84)	289.99(0.04)	289.95
	C3	285.94(4.31)	290.17(0.08)	290.25
	C4	285.84(4.01)	289.82(0.03)	289.85
	N	401.21(4.17)	405.49(0.11)	405.38
C_6H_5-NO_2	C1	289.88(2.21)	292.06(0.03)	292.09
	C2	287.26(4.04)	291.29(0.01)	291.3
	C3	287.01(3.99)	291.19(0.19)	291.0
	C4	286.98(4.12)	291.21(0.11)	291.1
	N	409.22(2.42)	411.35(0.29)	411.64
	O	537.85(0.60)	538.48(0.03)	538.45
p-NH_2-C_6H_4-NO_2	C1(-NH_2)	289.12	292.23	
	C2	286.75	290.64	
	C3	286.78	290.91	
	C4(-NO_2)	289.26	291.30	
	C(average)[a]	287.57(3.53)	291.11(0.01)	291.1
	N(in NO_2)	408.34(2.86)	410.39(0.81)	411.2
	N(in NH_2)	402.06(0.82)	406.23(0.23)	406.0
	O(in NO_2)	537.08(3.94)	537.68(0.22)	537.9
AAD		(3.25)	(0.14)	(0)

[a] CEBEs for carbons of *p*-NH_2-C_6H_4-NO_2 are averaged over four types of carbon.

resulted almost the same AAD. Although the quality of the two models is equivalent, one major difference is the presence/absence of a fortuitous partial cancellation between model error and functional error, making the ΔE_{KS} method more reliable conceptually. On the other hand, the main difference between the two programs DeMon and ADF resides on efficiency. ΔE_{KS} (PW86-PW91)/TZP using ADF is almost five- to ten-fold more efficient than the uGTS(DeMon) model, or ΔE_{KS} (PW86-PW91)/cc-pCVTZ(DeMon) method. It should be mentioned that ΔE_{KS} (PW86-PW91)/cc-pCVTZ(DeMon) gives almost identical CEBEs as ΔE_{KS} (PW86-PW91)/TZP(ADF), but much less efficiently. On the other hand, CEBEs calculated with HAM/3 are uniformly shifted toward smaller values with respect to the observed values by approximately 4 eV, in case of carbon atoms. Table 5 lists chemical shift ΔCEBE, defined by equation 2,

$$\Delta\text{CEBE} = \text{CEBE}(\text{X-C}_6\text{H}_4\text{-Y}) - \text{CEBE}(\text{H-C}_6\text{H}_4\text{-H}) \qquad (2)$$

ΔCEBE is the difference between CEBE of an atom in a substituted benzene and CEBE of the corresponding atom of unsubstituted benzene (the reference molecule). ΔCEBE at C1 atom is positive in the two molecules with the values of *ca*. +0.9 eV in case of aniline and *ca*. +1.7 eV in nitrobenzene. These large positive shifts are due to the substituent, either –NH_2 or -NO_2, at C1 position. The ΔCEBEs at C2, C3 and C4 atoms are negative in aniline because –NH_2 has strong electron donating nature. Electron density increases at C2, C3 and C4 in the phenyl ring that causes destabilization of the core electrons. Absolute value of shift increases in the order C3 < C2 < C4. This is due to the fact that the electron donating effect of –NH_2 in aniline increases in the order: C3 < C2 < C4. Nonempirical DFT results reproduce the observed results of ΔCEBEs and tendency very well (see Figure 3). HAM/3 resulted ΔCEBE for C1 position too large, by more than 1 eV, in comparison to the observed value. ΔCEBEs of HAM/3 at C2, C3 and C4 atoms are approximately equal to those of observed values. However, the order of shift is C2 < C3 < C4, disagreeing with the observed order of C3 < C2 <C4 (Figure 3). HAM/3 did not reproduce correctly the order. In the case of nitrobenzene, the signs of ΔCEBEs at C2, C3 and C4 atoms are all positive. This is because -NO_2 group has a strong electron withdrawing character. Electron density in the phenyl ring decrease because of -NO_2. This stabilizes core electrons of the atoms in the ring causing the substantial increase of CEBEs. The magnitude of the shift

Table 5. Observed and calculated chemical shifts ΔCEBEs (in eV), of carbon atoms in benzene ring of substituted benzenes (C_6H_5-X). ΔCEBEs in the table have been calculated as the difference between CEBE of carbon atom in the substituted benzene and CEBE of the carbon atom in benzene (equation 2)

Molecule	Hole, 1s	Observed	HAM/3	ΔE_{KS}(PW86-PW91)/TZP	Hammett σ
C_6H_5-H	C	0.00	0.00	0.00	0.000
C_6H_5-NH_2	C1	+0.88	+2.12	+0.94	
	C2	-0.46	-0.09	-0.45	
	C3	-0.16	-0.26	-0.27	-0.161
	C4	-0.56	-0.36	-0.62	-0.660
C_6H_5-NO_2	C1	+1.68	+3.68	+1.62	
	C2	+0.89	+1.06	+0.85	
	C3	+0.59	+0.81	+0.75	+0.710
	C4	+0.69	+0.78	+0.77	+0.778
NH_2-C_6H_4-NO_2	C1		+2.92	+1.79	
	C2		+0.54	+0.20	
	C3		+0.58	+0.47	
	C4		+3.06	+0.86	

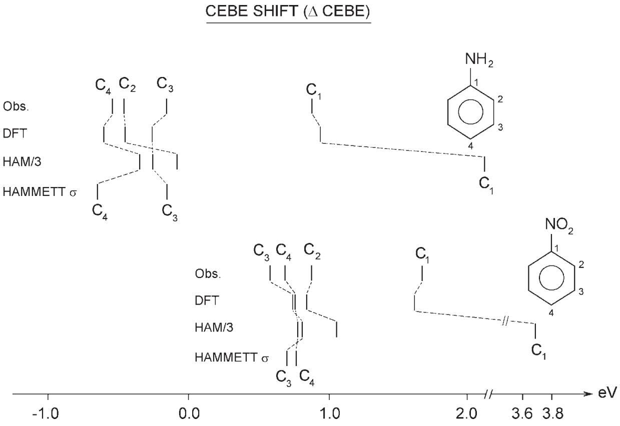

Figure 3. Comparison of CEBE shifts (ΔCEBEs) of aniline and nitrobenzene calculated with nonempirical DFT and semiempirical HAM/3. Hammett sigma constants at *meta* (C_3) and *para* (C_4) positions are also included.

increases in the order C3 < C4 < C2 < C1 (observed). The nonempirical DFT calculations reproduce the observed results fairly well. The HAM/3 ΔCEBE at C1 atom are more than 2 eV in error. However, ΔCEBE values of C3, C4 and C2 are close to the observed ones. The order of shifts of C3 and C4 is inverted in HAM/3. Lindberg *et al.*[43] had shown that ΔCEBE correlate linearly to the Hammett sigma constants (σ) in substituted benzenes. Good agreements between Hammett σ's and ΔCEBEs at C3 (*meta-*) and C4 (*para-*) positions in C_6H_5-NO_2 can be seen in those observed, and calculated with DFT by ΔE_{KS} (PW86-PW91)/TZP. Fairly good agreements are also obtained with HAM/3. This indicates a potential utility of HAM/3 in investigations of chemical reactivity and/or biological activity of series of molecules. When one works with a series of molecules studying *relative* chemical and/or biological activity, it is not necessary to have accurate CEBEs themselves, if reliable ΔCEBE values are available. As far as we know, HAM/3 is the only semiempirical SCF method that is capable of calculating molecular CEBEs by ΔE method. Consequently, calculations of ΔCEBEs of medium and large molecular systems can be done conveniently with HAM/3.

Table 6 lists CEBEs of solid-state uracil calculated by equation 1 using CEBEs of gas-phase uracil calculated with ΔE_{KS} (PW86-PW91)/TZP-ADF model and HAM/3. In principle, there is only one true value of WD for the system we study. However, we adopted two empirical values of WDs (WD1 and WD2) for the two different theoretical methods. This is a consequence of the method of approximation of WD that we adopted. Nonempirical DFT

Table 6. Comparison of experimental CEBEs (in eV) of uracil and those calculated with ΔE_{KS}(PW86-PW91)/TZP-ADF and HAM/3 (equation 1)

	Observed	Calcd.-WD1 DFT	Calcd.-WD2 HAM/3
C2	289.75	289.37	289.92
C4	288.95	288.43	288.33
C5	285.65	285.45	284.37
C6	286.85	287.14	285.67
N1	400.7	400.98	400.94
N3	400.8	401.45	400.97
O2	531.85	531.97	533.34
O4	531.85	531.64	532.86
AAD	0	0.33	0.77
WD		5.69	3.22

resulted AADs of 0.33 eV while HAM/3 of 0.77 eV, both of which are reasonable.

Although number of molecules and examples treated in this work is very limited, we can expect to obtain similar results for any other molecules and any number of examples. Within about a dozen examples studied, HAM/3 reproduced the VIP values obtained with nonempirical DFT more closely than those obtained with KT in *ab initio* HF. It should be noted that HAM/3 resulted the smallest AAD of calculation of VIPs among the five different approaches for the molecules treated (mainly because the semiempirical parameters in HAM/3 were chosen in such a way to reproduce observed VIPs).

The $-\varepsilon$(SAOP)/TZP model consistently gave results similar to (or better than) uDI(B88-P86)/cc-pVTZ model for calculation of VIPs. This indicates superiority of the exchange-correlation potential V_{xc} = SAOP in comparison to B88-P86. The $-\varepsilon$(SAOP)/TZP model is like KT, but for Kohn-Sham orbitals, and so we call it meta-Koopmans' theorem, or mKT. In other words, if one has accurate functionals, then there is no need for uDI or uTS model. It is because B88-P86 functional and most other functionals are poor, especially in the large-r region, that we need to use uDI (or uTS) model to get better results. It appears that HAM/3 is approximating such an approximate procedure. Therefore, strictly speaking, HAM/3 is not an approximation for DFT, but rather an approximation for the restricted diffuse ionization (rDI) model, which is an approximation used in some DFT calculations of VIPs. We demonstrated numerically that values and trend of VIPs calculated by HAM/3 reproduces those obtained by uDI(B88-P86)/cc-pVTZ and $-\varepsilon$(SAOP)/TZP models.

In calculation of accurate CEBEs of the molecules, we confirmed high efficiency of the ΔE_{KS} (PW86-PW91)/TZP method. HAM/3 also calculates CEBE by ΔE, with even greater efficiency, but with errors of more than 3 eV. Hence, the present study of CEBEs based on HAM/3 and accurate DFT procedure cannot answer the question in the title of this work. Fortunately, the results showed that ΔCEBEs (chemical shifts) obtained with HAM/3 are fairly close to the corresponding observed values. Hence, it may be useful for computational studies of relative chemical and/or biological activities of large systems.

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