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Extended Hückel Calculations of the Ionization Potentials of Some Conjugated Hydrocarbons

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The prediction of ionization potentials of conjugated hydrocarbons using extended Hückel theory is reevaluated. Consequently, two major modifications to the theory are proposed and then tested on five sample molecules. Allowance for distinct sigma and pi orbital parameters as well as for diagonal and off-diagonal parameters constitute the changes examined and are shown to arise naturally from the theory. Subsequent testing of the reproduction of photoelectron spectra indicates significant improvements over previous usage of extended Hückel theory.

Key words: Ionization potentials – Extended Hückel theory – Conjugated hydrocarbons.

1. Introduction

The interpretation of the photoelectron spectrum of a molecule can be greatly facilitated by the use of calculated ionization potentials (IPs) [1]. Unfortunately to compute IPs of the required accuracy by *ab initio* methods is difficult and time-consuming. Therefore it is natural that, over the last ten years, attempts have been made to find semi-empirical schemes which, for a modest effort, can be used to calculate satisfactory IP values. Of course, from their very nature, such schemes can never be regarded as more than methods of systematizing and correlating a large body of experimental information but they can be extremely useful and helpful for all that.

When semi-empirical methods were first applied in this area, considerable attention was devoted to the extended Hückel theory (EHT) [2]. This is perhaps the simplest of the semi-empirical procedures and it is disappointing that, on

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the whole, it does not produce IP values of sufficient reliability, even on a qualitative level, to be useful. It is the purpose of this paper to reexamine EHT and to consider whether, with suitable modifications, its performance in this respect, can be improved. Our conclusions are that this can be done but only at the cost of introducing more parameters into the theory. Moreover it does not appear possible to find a universal set of parameters which apply to all molecules; instead, one must be satisfied with parameters which apply only to a series of related molecules. The effect of these modifications is illustrated by applying them in EHT calculations of the ionization potentials of conjugated hydrocarbons.

2. Extended Hückel Theory

EHT requires the solution of the eigenvalues problem

$$H\psi_i = E_i\psi_i \tag{1}$$

where H is some effective one-electron Hamiltonian, and the ψ_i and E_i are orbitals and orbital energies. By expanding the ψ_i in terms of the valence orbitals $\{\omega_r\}$ of the atoms in the molecule under consideration, i.e.

$$\psi_i = \sum a_{ir}\omega_r$$

one obtains the matrix eigenvalue equation

$$\boldsymbol{H}\boldsymbol{a}_i = E_i\boldsymbol{S}\boldsymbol{a}_i \tag{2}$$

where $H_{rs} = \langle\omega_r|H\omega_s\rangle$, $S_{rs} = \langle\omega_r|\omega_s\rangle$ and $\boldsymbol{a}_i$ is the column vector with elements a_{ir}.

The diagonal elements of $\boldsymbol{H}$ are treated as parameters and, in the initial formulation of the method, were set equal to minus the atomic valence state ionization potentials (VSIP). The off-diagonal elements have taken on various forms in the literature; here, we make use of that due to Anderson [3] (based on a minor modification of the Wolfsberg–Helmholz approximation) viz,

$$H_{rs} = \tfrac{1}{2}M(H_{rr} + H_{ss})S_{rs}\exp(-0.13\boldsymbol{R}) \tag{3}$$

where $\boldsymbol{R}$ is the internuclear distance between atoms associated with the orbitals ω_r and ω_s respectively. The constant M has a value of about 2; Anderson takes $M = 2.25$.

For the purpose of calculating IPs the choice of $-H_{rr}$ equal to the VSIP of orbital ω_r has not proved to be very successful and a similar comment applies to other molecular properties. Therefore, the diagonal elements of $\boldsymbol{H}$ have often been selected on a purely empirical basis to give agreement between the computed and experimental values of the particular property of interest (see, for example, [4]). Unfortunately, as can be seen from the literature, the resulting parameters are far from unique and this leads one to question whether it is possible to find one single set of parameters which can give good theoretical values for a variety of properties of a single molecule or, alternatively, good values for a particular property for a wide variety of molecules.

To answer this question, it is necessary to consider just what the effective Hamiltonian H in (1) is intended to represent. Mehrotra and Hoffmann [5] have suggested that it be interpreted as a transition-state Hamiltonian (for transitions between states with a fixed number of electrons). With this interpretation, the orbital energies E_i have the property that the differences between those associated with unoccupied and occupied orbitals should equal excitation energies. It will not then be the case that $-E_i$ will equal an ionization potential. On the other hand, if one wishes to equate $-E_i$ to IPs via the use of Koopman's theorem then, obviously, H ought to be equivalent to the Hartree–Fock Hamiltonian. However, it is known that Koopman's theorem does not always give accurate values so it may even be better to assume that H is a transition-state Hamiltonian between states with differing numbers of electrons so that it can apply to transitions between unionized and ionized states. For example, it would be similar to the transition-state "half-electron" Hamiltonian used in pseudopotential and X_α calculations.

If all this is correct then it is easy to understand why it has been found necessary to use different EHT parameters for different properties. Since H is defined only through its matrix elements, H_{rr}, different values of these correspond to different effective one electron Hamiltonians. In particular, it follows that the parameters – and hence the Hamiltonian H – which give good IPs are unlikely to be satisfactory for other properties and vice versa. As to the choice of parameters suitable for the calculation of IPs, we now discuss this point in the case of a related series of molecules, conjugated hydrocarbons.

3. EHT and Conjugated Hydrocarbons

Attempts to use EHT to calculate IPs of conjugated hydrocarbons such as ethylene and benzene have met with moderate success at best. It was quickly recognized that the original method of equating $-H_{rr}$ to VSIPs was far from satisfactory and, usually, therefore, the H_{rr} were chosen empirically so as to give the best fit to photoelectron spectra [4]. In view of the remarks in the previous section this is the procedure with the best prospects of success. But, in fact, the results obtained in this way are still disappointing, the major difficulty being the inability to reproduce both sigma and pi orbital IPs. As far as the pi IPs are concerned this is surprising since simple Hückel theory does give quite good values.

Because of this, it seems worth-while to begin a reevaluation of EHT by considering the pi orbitals of benzene, the most typical conjugated hydrocarbon. Due to symmetry, the E_i values for the two occupied pi orbitals can be expressed simply in terms of the H_{rr} parameter for the $2p$ valence orbital, i.e. in terms of a single parameter. The experimental IPs are available [6, 7] so that it would seem a simple matter to choose this parameter to give the best agreement with experiment. In fact the best fit is of rather poor quality. This is to be contrasted with simple Hückel theory which gives a quite satisfactory fit for all polyacenes [6] and other hydrocarbons [8], and the reason is instructive: in Hückel theory there are two parameters, one for the diagonal and one for the nearest-neighbour off-diagonal matrix elements of H whereas in EHT there is only one if we adopt Anderson's value for M in (3). This comparison with simple Hückel theory suggests that a second parameter must be introduced into EHT via the off-diagonal elements which, therefore, we could take initially to have the modified form

$$H_{rs} = \beta_{rs} S_{rs} \exp(-0.13R) \tag{4}$$

with β_{rs} being the new parameter.

Values of H_{rr} and β_{rs} for $2p$ Carbon orbitals could be found from the two experimental pi IPs for benzene but, to avoid using only two experimental values to fit two parameters and in order to make use of a wider sample of experimental information, it is better to use the results from at least one other molecule as well. If all of the available experimental pi IPs of benzene and naphthalene [9] are used the best fit is given by $H_{rr} = -6.44$ eV $\beta_{rs} = -26.73$ eV and with these values the EHT pi IPs of naphthalene and benzene agree quite well with experiment (cf. Table 1) as expected.

Unfortunately any attempt to use the same parameters to determine sigma IPs meets with a surprising lack of success and it quickly becomes clear that different values of H_{rr} and β_{rs} are required for $2p$ sigma orbitals. Thus we conclude that a second modification of EHT is needed whereby the two different types of $2p$ orbitals in conjugated molecules are treated in different ways, with different parameters being used for each. It almost goes without saying that the very different properties of these orbitals justify such an approach. Nevertheless, by adopting it, we have almost completely jettisoned the possibility of universal transferability of parameters which some have considered the most advantageous property of EHT: it is clear that our new assumptions will be applicable only to conjugated hydrocarbons and similar pi electron systems.

For the three sigma orbitals i.e. $2p_\sigma$, $2s$ on Carbon and $1s$ on Hydrogen there are three diagonal H_{rr} parameters and six off-diagonal ones β_{rs}. The number of effective off-diagonal elements can be reduced by making further assumptions about the form of β_{rs}. The number can be reduced to one, only, by taking

$$\beta_{rs} = \tfrac{1}{2} M (H_{rr} + H_{ss}) \tag{5}$$

Table 1. π orbital energies, experimental [6, 7, 8, 9] and calculated respectively for carbon $2p_\pi$ parameters $H_{pp} = -6.44$ and $H'_{pp} = -11.88$

Benzene		Naphthalene	
−9.25	−9.18	−8.15	−8.11
−12.40	−12.11	−8.88	−8.93
		−10.08	−10.06
		−10.85	−11.19
		−12.60	−12.64

with the constant M treated as the single parameter and this being equivalent to a rescaling of the off-diagonal elements. However, this seems to be too restrictive and gives rather poor results. Alternatively three parameters are required if we take

$$\beta_{rs} = 1.125(H'_{rr} + H'_{ss}) \tag{6}$$

where the H'_{rr} are the new parameters which differ from the diagonal elements H_{rr}. This choice does appear to be sufficiently flexible without departing too far from the original assumptions of EHT and without introducing an over-abundance of parameters. Furthermore, the original form of H_{rs} is regenerated. Therefore it is this final form which we have adopted. Together with the already determined two pi values this leads to eight parameters as opposed to the three used in the simplest form of EHT.

The sigma parameters were obtained in a similar manner to the pi ones by a fit of the experimental photoelectron spectra of benzene and butadiene [10], the butadiene sigma orbital energies being better known than those of naphthalene. The parameters thus obtained are given in Table 2. It was found that while the diagonal and off-diagonal parameters for hydrogen were much closer than those of carbon, they were quite distinct, differing by almost 2 eV. This along with the carbon off-diagonal parameters being 4–5 eV different from the diagonal ones makes it clear that a spectral fit as good as that obtained here could not be accomplished simply by adjusting the M, via the use of Eq. (3). The resulting photoelectron spectra of benzene and butadiene are given in Table 3. The largest discrepancy being the predicted $a_g(\sigma)$ energy level of butadiene at −13.21 eV which is about 0.7 eV too high[1]. In fact we believe that this discrepancy in itself is quite instructive. Firstly it may arise because the environment of the carbon valence orbitals in butadiene is sufficiently different from that of benzene so as to necessitate slightly different matrix elements H_{rr}, H'_{rr} for butadiene. However, in view of the closeness of fit and for all the other states it appears unlikely that this is the main error involved. Another source of error probably more important is the geometry used. The energy levels can be very sensitive to the geometry. Indeed the use of fixed experimental ground state geometries based on crystal measurements when modelling an ionization process can introduce unmeasured

Table 2. Diagonal (off-diagonal) parameters for carbon and hydrogen in electron volts. Slater exponents of 1.658, 1.618 and 1.3 were taken for carbon $2s$, $2p$ and hydrogen $1s$ orbitals throughout

Carbon		Hydrogen	
$2s$	−14.91 (−19.70)	$1s$	−9.89 (−11.69)
$2p_\sigma$	−9.37 (−13.25)		
$2p_\pi$	−6.44 (−11.88)		

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[1] Even so these EHT results are now superior to that given by ordinary Hückel theory.

Table 3. Photoelectron spectra of benzene and butadiene for Table 2 parameters

Benzene (D_{6h})				Butadiene (trans.) (C_{2h})			
Expt[a]		EHT		Expt[a]		EHT	
−9.25	$e_{1g}(\pi)$	−9.18	$e_{1g}(\pi)$	−9.03	$b_g(\pi)$	−8.72	$b_g(\pi)$
−11.49	e_{2g}	−11.75	e_{2g}	−11.46	$a_u(\pi)$	−11.16	$a_u(\pi)$
−12.4	$a_{2u}(\pi)$	−12.11	$a_{2u}(\pi)$	−12.2	a_g	−11.98	a_g
−14.0	e_{1u}	−14.21	e_{1u}	−13.4	b_u	−13.21	a_g
−14.8	b_{2u}	−14.82	b_{2u}	−13.9	a_g	−13.49	b_u
−15.45	b_{1u}	−15.28	b_{1u}	−15.5	b_u	−15.43	b_u
−16.84	a_{1g}	−16.80	a_{1g}	−15.5	a_g	−15.78	a_g
−19.0	e_{2g}	−18.96	e_{2g}	−18.1	b_u	−17.89	b_u
−23.0	e_{1u}	−23.02	e_{1u}	−19.2	a_g	−19.33	a_g
−25.9	a_{1g}	−25.76	a_{1g}	−22.6	b_u	−22.8	b_u
				−24.8	a_g	−24.79	a_g

[a] See Ref. [8].

and unpredictable errors. This will almost certainly play an increasingly important role the smaller the molecules considered. EHT and the transferability of parameters inherent therein neglects these sources of error in the expectation that their effects will be small.

In order to further investigate the usefulness of our method the spectra of ethylene, styrene and naphthalene were determined using the parameters of Table 2. The spectrum presented for ethylene (cf. Table 4) was calculated using the experimental geometry and the orbitals were assigned according to the point group D_{2h}. As can be seen the orbital assignment agrees with the currently accepted ones [11] and all energy levels except that of the $b_{2u}(\pi)$ orbital are within 0.5 eV of the experimental values. Recalling that the $2p_\pi$ parameters were obtained from a fit of benzene and naphthalene energy levels it could again be argued that the environment of the carbon $2p_\pi$ valence orbital in ethylene is sufficiently different from that of both benzene and naphthalene that this ought really to be allowed for by using slightly different matrix elements H_{rr}, H'_{rr} for the two cases. More to the point, if the ionization process in ethylene pi orbitals is distinct from that of benzene and naphthalene different parameters would be necessary. This being the case, great care would need to be exercised in transferring parameters between even similar molecules. However, as all the orbital energies of ethylene are within 0.7 eV only relatively minor gains in accuracy to these could be expected by further adjustment of the existing parameters and these would be at the expense of the other spectra.

The photoelectron spectra of (planar) styrene (of Table 4) was obtained using a MINDO/3 geometry as an exact experimental geometry was unavailable. Furthermore the experimental orbital energy values have been estimated from graphs of Lindholm, Fridh and Asbrink [9] which indicate peak maxima. The π, σ orbital assignments correspond to their theoretical determination using SPINDO. While there is controversy regarding the lowest pi orbital assignment, it is generally accepted that the first three IPs belong to π orbitals. The EHT

Table 4. Photoelectron spectra of ethylene, styrene and naphthalene for Table 2 parameters

Ethylene (D_{2h})			
Expt[a]		EHT	
−10.51	$b_{2u}(\pi)$	−9.87	$b_{2u}(\pi)$
−12.85	b_{2g}	−12.40	b_{2g}
−14.66	a_g	−14.22	a_g
−15.87	b_{3u}	−15.97	b_{3u}
−19.23	b_{1u}	−18.95	b_{1u}
−23.70	a_g	−23.74	a_g

Styrene			
Expt[b]		EHT	
−8.5	π	−8.62	π
−9.4	π	−9.10	π
−10.6	π	−10.46	π
−11.5	σ	−11.37	σ
−12.0	σ	−11.75	σ
−12.3	σ	−12.22	π
−12.7	π	−12.66	σ
−13.8	σ	−14.08	σ
−14.0	σ	−14.09	σ
−14.6	σ	−14.67	σ
−15.2	σ	−15.02	σ
−15.5	σ	−15.61	σ
−16.6	σ	−16.53	σ
−17.8	σ	−17.85	σ
−18.9	σ	−18.89	σ
−19.3	σ	−19.37	σ
−22.0	σ	−22.55	σ
−22.6	σ	−22.89	σ
		−24.09	σ
		−25.84	σ

Naphthalene (D_{2h})			
Expt[c]		EHT	
−8.15	$a_u(\pi)$	−8.11	$a_u(\pi)$
−8.88	$b_{1u}(\pi)$	−8.93	$b_{1u}(\pi)$
−10.08	$b_{2g}(\pi)$	−10.06	$b_{2g}(\pi)$
−10.85	$b_{3g}(\pi)$	−11.19	$b_{3g}(\pi)$
−11.3	$\sigma(a_g)$	−11.21	a_g
−11.7	$\sigma(b_{1g})$	−11.34	b_{1g}
−12.3	$\sigma(b_{2u})$	−12.62	b_{2u}
−12.6	$b_{1u}(\pi)$	−12.64	$b_{1u}(\pi)$
−13.4	$\sigma(b_{3u})$	−13.32	b_{3u}
−13.6	$\sigma(b_{2u})$	−13.84	b_{2u}
−13.9	$\sigma(b_{1g})$	−14.19	b_{1g}
−14.3	$\sigma(a_g)$	−14.68	b_{3u}
−14.7	$\sigma(b_{3u})$	−14.72	a_g
−15.9	$\sigma(a_g)$	−15.87	a_g
−16.2	$\sigma(b_{2u})$	−16.36	b_{1g}
−16.8	$\sigma(b_{1g})$	−16.59	b_{2u}
−18.6	σ	−18.49	a_g
−18.8	σ	−18.93	b_{3u}
−19.1	σ	−19.36	b_{2u}
−22.1	σ	−22.19	b_{1g}
−22.4	σ	−22.69	a_g
		−23.67	b_{3u}
		−24.83	b_{2u}
		−26.32	a_g

[a] See Ref. [8, 11].
[b] See Ref. [9].
[c] See Ref. [9, 12].

results are seen to compare quite favourably with the experimental values, generally being within 0.5 eV even assuming that the lowest π orbital has been displaced upwards. While a comparison of these results under such circumstances is not conclusive, we hope that as more accurate experimental IPs become available for styrene, our results will compare favourably.

In the case of naphthalene, the experimental geometry used did not include accurate angular positioning of the hydrogens and so reasonable angles were assumed so as to maximise the distance from the next nearest carbons. The resulting spectra (cf. Table 4) again agrees very favourably with the experimental values. Once again the experimental sigma energy levels have been estimated from the peak maxima indicated on the graphs of Lindholm et al. [9]. The orbital assignments in brackets are those of H. J. Chiang and S. D. Worley [12] in a recent MNDO calculation. Once again there is still controversy over these orbital assignments, the comparability of our EHT energy values being within 0.5 eV is quite striking, being much closer than the MNDO calculated values.

4. Conclusion

By reparametrizing the EHT to include off-diagonal and distinct pi and sigma orbital parameters it has become possible to obtain IPs of conjugated hydrocarbons comparable to much more sophisticated semi-empirical SCF and *ab initio* SCF calculations. The error in the predicted energy levels is normally within 0.5 eV for a single set of parameters. Adopting the approach of fitting experimental photoelectron spectra in order to obtain these parameters essentially predefines how transferable and therefore how useful this method will be. One is essentially modelling the ionization process of the molecules fitted and using this, interprets the energy levels of the subsequent molecules examined. Clearly then, energy requirements of the ionization process itself which involve conformational or vibrational changes for example could influence the resulting IPs in an undetermined manner. Consequently the parameters obtained will only correctly model groups of molecules where these influences will be the same. Coupled with this is the geometry selected for use in the calculations. Where possible a consistent set (i.e. experimental geometries throughout) should be used if possible as the use of approximate ones can result in very misleading results. Clearly, methods as simple and empirical as that proposed here make it extremely hard to quantify the errors involved. However, from the results given here we feel that our reparametrization has corrected the long standing inability of EHT to come even close to reproducing photoelectron spectra of both pi and sigma orbitals.

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