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The Iterative Extended Hückel Method (IEHM)

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The iterative extended Hückel method for σ-electrons, analogous to the ω-technique for π-electrons, is used to calculate wave functions for BH_4^-, NH_4^+, CH_4, C_2H_6, B_2H_6, C_2H_4 and C_6H_6. Results are compared with the simple extended Hückel method and with published self-consistent field molecular orbital wave functions. It is found that iterating the extended Hückel method does not always lead to improvements in the wave function but that some improvements are found particular for ionic molecules. It is suggested that the reason for the failure of the iterated method is the neglect of terms due to charges on adjacent atoms.

Die Wellenfunktionen von BH_4^-, NH_4^+, CH_4, C_2H_6, B_2H_6, C_2H_4 und C_6H_6 werden mittels des erweiterten Hückelverfahrens mit Iteration, analog der ω-Methode für π-Elektronen, berechnet und die Resultate mit denen des analogen Verfahrens ohne Iteration verglichen. Dabei zeigt sich, daß die iterative Methode nur im Fall von Ionen zu wesentlichen Verbesserungen führt. Dies dürfte daran liegen, daß bei ihr die Terme, die von Ladungen an Nachbaratomen herrühren, vernachlässigt werden.

La méthode de Hückel étendue itérative pour les électrons σ, analogue à la technique ω utilisée pour les électrons π, est utilisée pour calculer les fonctions d'onde de BH_4^-, NH_4^+, CH_4, C_2H_6, B_2H_6, C_2H_4 et C_6H_6. Les résultats sont comparés avec ceux de la méthode de Hückel étendue simple et ceux de la méthode des orbitales moléculaires S.C.F. L'itération en méthode de Hückel étendue n'améliore pas toujours les fonctions d'onde mais certaines améliorations sont particulières pour les molécules ioniques. La raison de cet échec de la méthode avec itérations semble dûe à la négligence des termes correspondant aux charges sur les atomes adjacents.

Introduction and Method

The extended Hückel method (EHM) has in recent years proved remarkably successful for the study of molecules which are too large to be treated by more precise methods [1, 2]. It gives approximate molecular orbitals and orbital energies, and can thus be used to predict ionization potentials, spectra, geometries and other properties. The main justification for the method is that it works. Boer, Newton and Lipscomb [3] have compared the EHM matrix elements with Hartree Fock matrix elements and given some theoretical justification for its success and its failure in certain respects. They suggest that its success lies in the closeness with which the Hartree-Fock matrix elements are estimated and thus the molecular orbitals and orbital energies should be approximations to the self-consistant field molecular orbital (SCF) method. There have been few actual comparisons of EHM orbitals and energies with the SCF results. This comparison is reported here for a few molecules.

The original method has been improved in two ways. The off-diagonal matrix elements have received much attention and the approximation due to Cusachs

[4] is now widely used. The diagonal matrix elements have received less attention but are probably more important. Work was therefore initiated to introduce the ω-technique [5], where the diagonal matrix elements are considered as a function of net atomic charge and the method iterated on charges to consistency. Since that time other workers have independently published results obtained by this method. CARROLL, ARMSTRONG and MCGLYNN [6] have used a linear dependence of the diagonal matrix elements α_i on charge q_i and orbital population p_i

$$\alpha_i = A_i\, p_i + B_i\, q_i + C_i$$

q_i is the same for all orbitals centred on a given atom. p_i is a property only of orbital i. For the hydrogen $1s$ orbital α_i is taken as a quartic in q_i. Charges and orbital populations are calculated using the Mulliken population density matrix [7]. REIN, FUKUDA, WIN, CLARKE and HARRIS [8] have proposed a slightly different scheme in which α_i is related only to q_i in a linear manner

$$\alpha_i = \alpha_i^0 + \Delta\alpha_i\, q_i\,.$$

A similar method has been proposed by AZMAN, BOHTE and OCVIRK [9].

Our method differs only in detail from the method proposed by REIN et al. Values for α_i were selected for charges of 0, -1 and $+1$ using valence state ionization energies, valence state electron affinities and second valence state ionization potentials respectively given by HINZE and JAFFE [10]. These values are not exactly linear in charge so to avoid an arbitary smoothing process a quadratic was fitted through the three points. The resulting function differs only slightly from the function used by REIN et al. For the H-$1s$ orbital α, a linear function through the points for $q = 0$ and $q = -1$ was used and this is virtually identical to the function used by REIN et al.

A further modification is the dependence on charge of the orbitals used. Slater orbitals with exponents varying with charge according to

$$\delta_i = \delta_i^0 + D_i\, q_i$$

were used. δ_i^0 is the exponent for a neutral atom given by Slater's rules. D_i is a constant, also taken from Slater's rules, with the value 0.3 for H-$1s$ orbitals and 0.175 for orbitals on first row atoms. These parameters are shown in Tab. 1.

Table 1. *Diagonal matrix elements and orbital exponents*[a]

Orbital	$\alpha(q = +1)$	$\alpha(q = 0)$	$\alpha(q = -1)$	δ^0
H-$1s$		−13.60	− 0.75	1.0
B-$2s$	−25.40	−14.91	− 5.70	1.30
B-$2p$	−19.46	− 8.42	− 0.32	
C-$2s$	−33.03	−21.01	− 8.91	1.625
C-$2p$	−23.93	−11.27	− 0.34	
N-$2s$	−41.84	−26.92	−14.05	1.95
N-$2p$	−28.69	−14.42	− 2.54	

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[a] α's are reported in eV but all results are converted to a.u. for direct comparison with published S.C.F. energies.

Several approximations for the off-diagonal matrix elements β_{ij} were tried. The simple form used by HOFFMANN [1] was used for the results reported here

$$\beta_{ij} = K \frac{\alpha_i + \alpha_j}{2} S_{ij} .$$

S_{ij} is the overlap integral and K a constant fixed as 1.75. All overlap integrals were calculated exactly and included in the secular equations.

The objective of comparing results with SCF calculations is paralleled by the work of ALLEN and RUSSELL [11], who used the above approximation for β_{ij} but did not vary the α_i's. The molecules studied by them were all triatomic molecules while our results are for slightly larger molecules. This work thus compliments ALLEN and RUSSELL's and adds the extra feature of comparing an iterated result with the simple non-iterated result. The SCF wave functions used in the comparison are however probably less accurate than theirs as a result of the larger size of the molecules studied. A selection of molecules for which reasonable SCF functions are available was used. These are BH_4^-, NH_4^+, CH_4, C_2H_6, B_2H_6, C_2H_4 and C_6H_6.

Computationally the same difficulty on obtaining convergence, which has been reported by other workers, was found. It was overcome by similar methods. Our approach is a combination of the method used by EHRENSON [12], in which charges resulting from a group of three iterations are used to predict a new set of input charges for a following group of three iterations, and the method used by REIN et al. [8] and other workers [6]. In the latter case a fraction of the predicted change in charge only is used to predict input charges for the next iteration. This method combined with the former allows a large value of λ — the fraction of the predicted change in charge used — to be selected. A value of 0.5 proved adequate in most cases while other workers have used values near 0.1. In a few difficult it was necessary to use a value less than 0.5.

Borohydride and Ammonium Ions

Ionic species are clearly treated incorrectly by the simple EHM if the same parameters are used as for neutral species. Selfconsistency with respect to charges might be expected to improve the situation. The results for these two ions are compared in Tab. 2 with SCF results obtained for BH_4^- by HEGSTROM, PALKE and LIPSCOMB [13] using a limited basis set of slater orbitals with optimized exponents and for NH_4^+ by KRAUSS [14] using Gaussian orbitals. HEGSTROM et al. find the

Table 2. *Orbital energies and charges for* BH_4^- *and* NH_4^+

BH_4^-	EHM	IEHM	SCF (13)
a_2	−0.7556	−0.6303	−0.4200
t_2	−0.4989	−0.3861	−0.1697
q_B	−0.360	−0.260	+0.044 (−0.222)
q_H	−0.160	−0.186	−0.261 (−0.195)
NH_4^+			(14)
a_2	−1.0694	−1.1570	−1.5418
t_2	−0.6167	−0.6979	−0.9930
q_N	−0.500	+0.080	—
q_H	+0.375	+0.230	—

charge distribution to be very dependent on the choice of exponent. The IEHM charges are very similar to those obtained by them using Slater exponents (shown in brackets) but are different from the charges found using optimized exponents. No charges are available for NH_4^+ but the converged EHM results appear more reasonable. In both cases the charges are strongly dependent on the choice of α's. Orbital energies in both cases are incorrect compared with the SCF orbital energies but are somewhat better for IEHM than for EHM (s. Tab. 2).

Methane and Ethane

Both methane and ethane have received much attention in recent years. Of particular interest have been one-centre expansion wave functions for the former and the energy barrier for rotation in the latter. No population density results appear to have been published for methane. EHM and IEHM orbital energies are compared in Tab. 3 for methane with the SCF orbital energies obtained by Krauss [14] using a Gaussian orbital expansion and Woznick [15] using a Slater type orbital expansion. The EHM results are better than those obtained from the iterative method.

More complete results are available for ethane. Tab. 4 shows the orbital energies, charges and barrier to rotation obtained by EHM and IEHM compared with the Gaussian orbital expansion of Clementi and Davis [16] and the Slater orbital expansion of Pitzer and Lipscomb [17]. Of particular interest is the fact that the EHM does not over-estimate the charge difference between the carbon and hydrogen atoms. As expected the IEHM reduces the charges and thus gives a

Table 3. *Orbital energies and charges for* CH_4

	EHM	IEHM	SCF (Krauss [14])	SCF (Woznick [15])
a_1	−0.9042	−0.8806	−0.9421	−0.9497
t_2	−0.5472	−0.5262	−0.5411	−0.5437
q_C	−0.494	−0.100	—	—
q_H	+0.124	+0.025	—	—

Table 4. *Orbital energies, charges and barrier to rotation for ethane*

	EHM	IEHM	SCF (Clementi and Davis [16])	SCF (Pitzer and Lipscomb [17])
a_{1g}	−0.9665	−0.9404	−1.0427	−1.0400
a_{2g}	−0.7945	−0.7823	−0.8544	−0.8588
e_u	−0.5793	−0.5632	−0.6191	−0.6273
a_{1g}	−0.5136	−0.4800	−0.5094	−0.5361
e_g	−0.5029	−0.4913	−0.5066	−0.5150
q_C	−0.322	−0.076	—	−0.339
q_H	+0.107	+0.025	—	+0.113
Barrier (EXP. 0.0048)	0.0064	0.0124	0.0058	0.0052

poorer agreement with the SCF results than does the EHM. The orbital energies from the EHM agree closer with the SCF orbital energies than the IEHM. These results are for the staggered form of ethane. The results for the eclipsed form are very similar. The barrier to rotation as estimated by the EHM or IEHM total energy (sum of orbital energies) is predicted to be closer to the experimental result by the EHM than by the IEHM.

Thus for both methane and ethane there seems to be no advantage in using the iterative scheme, at least in the form of it presented here.

Diborane

Diborane is a particularly interesting molecule for study using this method. The simple EHM gives the following charges

$$q_B = +0.337$$
$$q_H - \text{terminal} = -0.174$$
$$q_H - \text{bridge} = +0.011\ .$$

These are similar to those originally obtained by HOFFMANN and LIPSCOMB [18] and are contrary to the results obtained, using a limited basis set SCF treatment, by YAMASAKI [19]. Better agreement was obtained by HOFFMANN and LIPSCOMB when different α's were taken for the bridge and terminal hydrogen orbitals but this choice was somewhat arbitary. Their method has however been used for a large number of calculations on boranes [18]. Recently several good wavefunctions for diborane have been published. These make use of a more complete basis set than YAMASAKI's and all integrals have been calculated exactly. The charges obtained differ slightly from one calculation to another but all agree that all charges are very small. These results are shown in Tab. 5 along with the IEHM results. The agreement is quite close with the possible exception of the bridge hydrogen charge which N.M.R. evidence suggests is more negative than the terminal hydrogen charge [20]. Palke and Lipscomb's [21] wave function, which uses

Table 5. *Charges for diborane*

	IEHM	SCF	SCF
		(PALKE and LIPSCOMB [21])	(BURNELLE and KAUFMANN [22])
q_B	+0.083	+0.064	−0.088
q_{H-t}	−0.061	−0.032	+0.045
q_{H-b}	+0.039	−0.001	−0.002

Table 6. *Orbital energies for diborane*

	EHM	IEHM	SCF (P. and L. [21])	SCF (B. and K. [22])
a_g	−0.7870	−0.8067	−0.8700	−0.8979
b_{1u}	−0.6566	−0.6519	−0.6278	−0.6457
b_{2u}	−0.5188	−0.5501	−0.5521	−0.5558
b_{3u}	−0.5283	−0.5267	−0.5322	−0.5446
a_g	−0.4804	−0.4968	−0.5098	−0.5174
b_{2g}	−0.4877	−0.4807	−0.4612	−0.4737

Slater orbitals with optimized exponents, gives an energy slightly higher than that given by the Gaussian orbital function of BURNELLE and KAUFMANN [22] but is based on a different geometry for the molecule. The orbital energies are shown in Tab. 6. The simple EHM has the ordering of levels incorrect in two instances although this is strongly influenced by small changes in the α's. The converged result shows a much better agrument with the SCF results.

Ethylene and Benzene

The best SCF wave functions for ethylene and benzene are by MOSKOWITZ et al. [23, 24] using Gaussian orbitals. No charges from the population density analysis are reported for benzene. Orbital energies and charges are compared in Tab. 7. The

Table 7. *Orbital energies and charges forethylene and benzene*

	EHM	IEHM	SCF		EHM	IEHM	SCF
C_2H_4			(23)	C_6H_6			(24)
a_g	−0.9766	−0.9518	−1.0584	a_{1g}	−1.0687	−1.0503	−0.9895
b_{3u}	−0.7545	−0.7457	−0.8067	e_{1u}	−0.9336	−0.9207	−0.8909
b_{2u}	−0.5920	−0.5808	−0.6604	e_{2g}	−0.7248	−0.7181	−0.7139
a_g	−0.5257	−0.5004	−0.5829	a_{1g}	−0.6052	−0.5981	−0.5709
b_{1g}	−0.5035	−0.4988	−0.5174	b_{1u}	−0.6056	−0.6079	−0.5625
b_{1u}	−0.4796	−0.4475	−0.3814	e_{1u}	−0.5331	−0.5258	−0.4792
				$a_{2u}(\pi)$	−0.5281	−0.5095	−0.4519
q_C	−0.219	−0.066	−0.330	b_{2u}	−0.5195	−0.5004	−0.4482
q_H	+0.110	+0.033	+0.165	e_{2g}	−0.4665	−0.4567	−0.3742
				$e_{1g}(\pi)$	−0.4654	−0.4486	−0.2877
				q_C	−0.092	−0.035	—
				q_H	+0.092	+0.035	—

EHM does not over-estimate the charge differences for ethylene and is thus again better than the IEHM. The orbital energies from the EHM agree closer with the SCF orbital energies than do those from the IEHM for ethylene. For benzene however the orbital energies from the IEHM are slightly better than those from EHM, although the agreement is rather poor in some cases. It would be interesting to have the charge distribution from the SCF method for comparison with the EHM and IEHM charges.

Discussion

The most remarkable result is the very close agreement that is found between SCF orbital energies and the EHM and IEHM orbital energies. Both methods are clearly reasonable approximations to the SCF result. However it does not appear that iterating the EHM to consistancy on charges necessarily improves the method. The ω-technique in π electron theory is sometimes justified on the grounds that simple Hückel theory over estimates the charge differences between different atoms. It is clear that the EHM for σ-systems does not always follow the analogous π-electron method in this respect. The charge difference between carbon and hydrogen atoms in ethane, ethylene and probably methane is under-estimated and iterating on charges makes the situation worse.

For ionic species the iterated method appears more satisfactory but the agreement with SCF orbital energies is poor. For BH_4^- the orbital energies for both the EHM and IEHM are much lower than the SCF energies and for NH_4^+ much higher. In both cases iterating on charges improves the agreement with SCF energies but only slightly. The predicted charges for these species are very dependent on the choice of α in the EHM and on the choice of orbital exponent in the SCF method. For BH_4^- the IEHM charges agree better with the SCF charges and for NH_4^+ where no SCF charges are available, the IEHM charges appear more reasonable than the EHM charges.

Diborane is probably a special case but the IEHM results are most satisfactory when compared with the EHM results which have never been very reliable.

Several calculations have been repeated using the geometrical mean approximation or the Cusach approximation for the off-diagonal matrix elements. There is nothing significantly different about the results. The most important factor is always the choice of diagonal matrix elements.

It is important to attempt to understand why the IEHM is less successful than the ω-technique in π-electron theory. The form of the diagonal matrix elements in SCF theory using neglect of differential overlap suggests that a good approximation would be

$$\alpha_i = \alpha_0 - A q_i - \sum_{j \neq i} B_{ij} q_j \, .$$

The last term is a sum over the charges on other atoms. B_{ij} is an average Coulomb integral between the orbital i and all orbitals on atom j. The EHM uses only the first term. The IEHM adds the second term. For π-electron systems the last term will be small and excluding it will lead to reasonable results. This gives the ω-technique. For σ-systems however the last term will not be small. For ions it will probably be of the same sign as the second term and for both NH_4^+ and BH_4^- the discrepency between SCF and extended Hückel orbital energies is in the direction expected by the exclusion of such a term. The IEHM for ions will however still be an improvement over the EHM. For some neutral molecules, the third term will be of opposite sign to the second. Its inclusion would increase the charge differences between atoms. For CH_4 where each atom is surrounded by near atoms of opposite charge, the third term might cancel the second term and the EHM would then be better than the IEHM. Of the hydrocarbons studied the size of the last term is likely to be least for C_6H_6 and thus in this case the IEHM will be an improvement over the EHM. For diborane the effect of the last term is also likely to be small.

It is thus possible to obtain a qualitative understanding of why the IEHM is less successful than ω-technique and why it leads to improvements over the EHM in some cases but not in others. It seems that it is always worthwhile to iterate on charges using the second term for ions but that for some neutral molecules it is better to exclude the second term containing the charge unless all terms including charge can be used. The IEHM is being further investigated in this laboratory.

This work was completed while the author was at the University of Newcastle upon Tyne Computing Laboratory using a KDF9 computer. Many fruitful discussions on computing techniques with colleagues there are gratefully acknowledged.

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