

Optimized Extended Hückel Theory for Calculating the Ionization Potentials and Dissociation Energies of Hydrocarbons

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The EH method is modified by introducing new parameters so as to obtain better agreement between theoretical calculations and experimental values concerning ionization potentials and dissociation energies.

Die EH Methode wurde durch Einführung neuer Parameter so geändert, daß bessere Übereinstimmung von theoretischen Berechnungen und experimentellen Werten für Ionisationspotentiale und Dissoziationsenergien erreicht wird.

La méthode EH est modifiée par l'introduction de nouveaux paramètres destinés à obtenir un meilleur accord entre les calculs théoriques et les valeurs expérimentales des potentiels d'ionisation et des énergies de dissociation.

Introduction

Among the theoretical methods available in quantum chemistry for describing molecular electronic structure, it is surprising to see that the oldest one is continuing to attract many authors. This success can mainly be attributed to its great simplicity. Despite the rapid development of electronic digital computers, theoretical *ab-initio* or even semi-empirical SCF methods are very long and costly for analyzing fairly large molecules.

Since the original research by Hückel [1] his method has undergone a great many changes. The main stages in this evolution are as follows: introduction of overlaps and addition of σ bonds [2] (EH), exact calculation of kinetic energy [3] (KEH), using formal charges to calculate diagonal elements in the Hamiltonian [4 5] (IEH). Unfortunately, this last method requires several iterations, and trouble with the convergence often greatly increases calculation time. So in this respect this method is not very different from semi-empirical ones such as CNDO or MINDO. On the other hand, kinetic energy can be taken into consideration more or less satisfactorily without being exactly calculated [7]. At the same time, EH calculations provide quite good correlations with experimental values, even when the absolute values are way off. This is what led us to modify the somewhat arbitrary parameters introduced in EH calculations. In this article we describe how a set of parameters is determined from experimental values relating to small molecules.

Parameters of the Optimized Extended Hückel Theory

The formulation and standard approximations of EH have already been described in detail elsewhere [6], and so we are concerned solely with the notations. Molecular orbitals are LCAOs

$$\Psi_j = \sum_{p=1}^{\tilde{n}} C_{jp} \Phi_p \quad j=1, \dots, n.$$

The matrix equation to be solved may be written

$$(H - \varepsilon S) C = 0$$

in which H is the Hamiltonian matrix

S is the overlap matrix,

ε is the diagonal matrix of the molecular-orbital energy with coefficients in the C matrix.

This equation may be solved by the standard Lowdin method, but we preferred Cholesky's decomposition of S [8]. The S matrix was calculated exactly by using QCPE's OVLAP subroutine for Slater type atomic orbitals.

For standard EH calculations the diagonal elements of the H matrix are taken minus the VOIP

$$H_{ii} = -\text{VOIP}(\Phi_i). \quad (1)$$

As in Ref. [6] this approximation may be justified by comparison with SCF calculations. We assume that H_{ii} is in some way a mean value of the corresponding F_{ij} . But with what is now known we cannot ascertain whether- $\text{VOIP}(\Phi_i)$ is a good mean value. So we are led to write

$$H_{ii}^A = \alpha(A, s \text{ or } p)$$

in which α is a parameter to be determined for each atom and each type of atomic orbital by model calculation.

For the off-diagonal terms of the H matrix, several formulas have been proposed:

$$H_{ij} = \frac{1}{2} K S_{ij} (H_{ii} + H_{jj}) \quad [2],$$

$$H_{ij} = -K S_{ij} \sqrt{H_{ii} \times H_{jj}} \quad [4],$$

$$H_{ij} = S_{ij} (1 - 0.5 |S_{ij}|) (H_{ii} + H_{jj}) \quad [5],$$

$$H_{ij} = S_{ij} (a + b S_{ij}) (H_{ii} + H_{jj}) \quad [9].$$

So we tried out the following formulas:

$$H_{ij}^{AB} = a(A, B, |) S_{ij} (H_{ii}^A + H_{jj}^B), \quad (I)$$

$$H_{ij}^{AB} = S_{ij} (1 + b(A, B, |) S_{ij}) (H_{ii}^A + H_{jj}^B), \quad (II)$$

$$H_{ij}^{AB} = S_{ij} (a(A, B, |) + b(A, B, |) S_{ij}) (H_{ii}^A + H_{jj}^B). \quad (III)$$

Parameters a and b were calculated for each pair of atoms and for $|\sigma$ or π bonds. The above three types of calculations are hereunder referred to as Methods I, II, and III. Formulas I, II and III must be written according to the

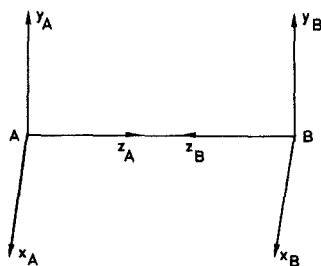


Fig. 1

coordinate system drawn in Fig. 1 in order to preserve their non-variance with respect to the molecular coordinate system.

Solving system (1) gives n eigenvalues, ε_i . For a $2p$ electron system, Koopman's theorem enables us to determine the molecular ionization potentials

$$-\varepsilon_p, -\varepsilon_{p-1}, \dots, \varepsilon_1.$$

Hoffman (2) has shown that

$$E_e = -2 \sum_{i=1}^p \varepsilon_i$$

is a satisfactory approximation of dissociation energy D , except for one constant. For a better scaling we can create the formula

$$D = E_e - \sum_A \left(\sum_{i \in A} \text{VOIP}_i(A) \right).$$

The VOIP is used for occupied atomic orbitals in the ground state. This formula can be rewritten in a more condensed form:

$$D = E_e - \sum_A e(A). \quad (2)$$

For more precise calculating (SCF formulation)

$$D = E_e + \frac{1}{2} \sum_{i,j} P_{ij} G_{ij} - \sum_{A < B} \frac{Q_A Q_B}{r_{AB}} - \sum_A e'(A) \quad (3)$$

with $e'(A)$ being the energy required to take all valence electrons away from atom A. In order to use Eq. (2) we must assume

$$\frac{1}{2} \sum_{i,j} P_{ij} G_{ij} + \sum_A (e(A) - e'(A)) - \sum_{A < B} \frac{Q_A Q_B}{r_{AB}} \neq 0. \quad (4)$$

In order to find the best $e(A)$ parameters for Eq. (4), calculations were made with reference to the experimental dissociation energies of small molecules.

Determining Parameters

The different parameters (α , a , b , e) were determined by the direct minimization of the function

$$F = \frac{1}{m} \sum_{i=1}^m Q_i^2 \left(\frac{Y_i^{\text{ex}} - Y_i^{\text{calc}}}{Y_i^{\text{ex}}} \right)^2$$

Table 1

	Y ^a	Exp. val.	Method I		Method II		Method III	
			q _i	Calc. val.	q _i	Calc. val.	q _i	Calc. val.
CH ₄	IP	12.98	100	13.41	100	13.24	100	12.80
	D	394	100	405.4	100	407	100	394.2
C ₂ H ₆	IP	11.51	100	11.76	100	11.59	100	11.52
	IP'	19.18	20	16.71	20	16.8	20	19.10
	D	674.6	100	659.9	100	657.7	100	680.9
C ₂ H ₄	IP	10.48	100	10.63	100	10.77	100	10.63
	IP'	12.50	20	12.93	20	12.46	20	12.14
	IP''	14.39	20	14.11	20	14.22	20	14.30
	IP'''	19.13	20	16.12	20	16.11	20	18.12
	D	537.7	100	520.3	100	528.5	100	533.6
C ₂ H ₂	IP	11.41	100	10.85	100	10.91	100	11.31
	IP'	16.41	20	16.17	20	15.79	20	17.00
	D	391.8	100	398.5	100	393.1	100	391.4
H ₂	$\frac{1}{re} \frac{\partial D}{\partial r}(re)$	0.0	0	—	0	—	100	0.001
	IP	15.427	100	15.22	100	15.38	100	15.54
	D	103.3	100	103.6	100	103.3	100	103.1
C ₂	$\frac{1}{re} \frac{\partial D}{\partial r}(re)$	0.0	0	—	0	—	100	0.009
	D	143.2	100	143.5	100	153.8	100	143.3
CH	$\frac{1}{re} \frac{\partial D}{\partial r}(re)$	0.0	0	—	0	—	100	0.022
	D	80.0	100	80.0	100	79.8	100	80.0
Mean diff.			# 2.3		# 2.0		# 0.7	

^a IP = ionization potential.

Table 2^a

		I	II	III
H	α (1s)	-0.4463	-0.4307	-0.3853
	e	-0.4768	-0.4827	-0.4892
C	α (2s)	-0.5103	-0.4900	-0.6324
	α (2p)	-0.3456	-0.3402	-0.3126
	e	-1.7459	-1.7098	-1.9318
H-H	a (σ)	0.8146	1.0	1.4228
	b (σ)	0.0	-0.1670	-0.5080
C-C	a (σ)	0.8874	1.0	2.0287
	a (π)	0.8052	1.0	0.7854
	b (σ)	0.0	-0.2844	-2.4838
	b (π)	0.0	-0.4299	1.1070
C-H	a (σ)	0.8798	1.0	1.3101
	b (σ)	0.0	-0.1282	-0.4261

^a α and e are given in atomic units.

in which Y_i^{ex} and Y_i^{calc} are, respectively, the experimental and calculated values of the ionization potentials and the dissociation energies for Methods I and II together with the

$$q_i^2 2 \left(\frac{\partial D}{\partial r} (r_e) \right)^2$$

amounts for the diatomic molecules in Method III, with q_i being weighting factors. Optimization was done using the subroutine RSMOD [10] until a precision of 10^{-4} was reached for each variable. Table 1 gives the experimental values and the corresponding calculated values after optimization, together with the q_i factors. The mean deviation (MD) is the quantity \sqrt{F} . Ionization potentials (in eV) were found in Ref. [11] and [12], and bond lengths and angles in international tables [14]. Table 2 lists all the parameters required, along with their numerical values after optimization (α and e are in atomic units).

Findings and Discussion

The parameters determined in this way were first used to calculate the ionization energies (Table 3) and dissociation energies (Table 4) for 31 hydro-

Table 3

	Exp.	C	I	II	III
CH ₄	12.99	13.77	13.41	13.24	12.80
C ₂ H ₆	11.49	12.69	11.75	11.59	11.52
C ₃ H ₈	11.07	12.19	11.40	11.10	10.69
n-C ₄ H ₁₀	10.50	11.73	11.05	10.67	9.97
i-C ₄ H ₁₀	10.78	12.02	11.28	10.92	10.40
C ₂ H ₄	10.48	12.32	10.63	10.77	10.63
C ₃ H ₆	9.84	11.81	10.46	10.47	10.22
CH ₂ =C(CH ₃) ₂	9.35	11.66	10.37	10.53	10.05
C ₃ H ₄	10.16	11.84	10.47	10.48	10.16
cis 1.3 C ₄ H ₆	9.29	11.58	10.17	10.12	10.07
trans 1.3 C ₄ H ₆	9.27	11.64	10.21	10.17	10.09
C ₂ H ₂	11.41	12.44	10.85	10.91	11.31
HC≡CCH ₃	10.36	11.97	10.68	10.63	10.82
CH ₃ C≡CCH ₃	9.85	11.50	10.50	10.32	10.34
HC≡CCH=CH ₂	9.9	11.71	10.30	10.24	10.32
HC≡C-C≡CH	10.2	11.76	10.39	10.30	10.63
C ₆ H ₆	9.25	11.64	10.35	10.38	9.99
C ₆ H ₅ CH ₃	9.20	11.50	10.24	10.19	9.52
o-C ₆ H ₄ (CH ₃) ₂	8.96	11.35	10.18	10.09	9.14
m-C ₆ H ₄ (CH ₃) ₂	9.01	11.44	10.20	10.13	9.29
p-C ₆ H ₄ (CH ₃) ₂	8.86	11.29	10.13	10.00	9.25
C ₁₀ H ₈	8.26	11.07	9.86	9.73	8.67
cyclo C ₃ H ₆	10.53	12.04	10.87	10.74	10.76
cyclo C ₄ H ₈	10.53	11.53	10.88	10.38	10.02
cyclo C ₅ H ₁₀	10.92	11.75	11.28	10.78	10.26
cyclo C ₆ H ₁₂	9.79	11.39	10.99	10.48	9.76
CH ₃	9.84	11.09	9.66	9.50	8.84
C ₂ H ₅	8.80	10.47	9.40	9.09	8.24
n-C ₃ H ₇	8.69	10.34	9.29	8.96	7.92
sec-C ₃ H ₇	7.90	10.10	9.18	8.77	7.82
C ₂ H ₃	9.35	10.68	9.52	9.21	8.28

Table 4

	Exp.	C	I	II	III
CH ₄	394	242.2	405.3	407	394.2
C ₂ H ₆	674.6	380.7	659.7	657.7	680.9
C ₃ H ₈	954.3	511.9	915.3	908.8	962.6
n-C ₄ H ₁₀	1234.7	623.1	1174.7	1160.7	1240.9
i-C ₄ H ₁₀	1236.7	635.5	1174.3	1162.2	1242.3
C ₂ H ₄	537.7	285.5	520.1	528.5	533.8
C ₃ H ₆	820.4	423.7	776.5	780.9	818.1
CH ₂ =C(CH ₃) ₂	1091.4	564.0	1034.4	1034.3	1092.4
C ₃ H ₄	675.2	344.9	636.0	647.2	651.4
cis 1.3 C ₄ H ₆	969.8	472.9	892.7	903.0	947.4
trans 1.3 C ₄ H ₆	967.5	478.9	897.0	908.9	959.8
C ₂ H ₂	391.8	135.4	398.3	393.1	391.4
HC≡CCH ₃	676.8	359.1	644.6	647.8	696.6
CH ₃ C≡CCH ₃	951.0	497.4	902.0	897.9	950.0
HC≡CCH=CH ₂		410.2	767.1	777.1	844.6
HC≡C-C≡CH		339.8	641.7	648	699.6
C ₆ H ₆	1318.1	574.2	1146.1	1151.0	1188.2
C ₆ H ₅ CH ₃	1582.7	709.0	1402.9	1402.6	1458.3
o-C ₆ H ₄ (CH ₃) ₂	1861.9	842.7	1658.9	1652.8	1721.9
m-C ₆ H ₄ (CH ₃) ₂	1862.1	843.9	1659.8	1654.2	1728.5
p-C ₆ H ₄ (CH ₃) ₂	1861.9	843.4	1659.7	1653.9	1728.0
C ₁₀ H ₈		828.7	1763.6	1756.7	1780.0
cyclo C ₃ H ₆	812.6	412.5	778.5	785.7	870.6
cyclo C ₄ H ₈		538.1	1029.3	1019.8	1171.3
cyclo C ₅ H ₁₀	1374.9	639.2	1286.4	1259.1	1392.6
cyclo C ₆ H ₁₂	1680.0	792.1	1543.0	1516.2	1691.4
CH ₃	293 (b)	164.7	291.7	295.3	284.6
C ₂ H ₅	584 (b)	311.1	547.9	549.5	577.7
n-C ₃ H ₇	≈ 859 (b)	444.4	805.5	803.2	861.2
sec-C ₃ H ₇	≈ 859 (b)	446.8	805.0	802.3	861.2
C ₂ H ₃	≈ 430 (b)	217.2	400.9	409.7	416.3

carbons and hydrocarbon radicals. This enabled us to compare our three methods with the standard EH theory using standard parameters [15] and Cusachs's approximation [5] (hereunder referred to as C). For the ionization potentials we found the following root mean squares:

- C 1.82 eV,
- I 0.76 eV,
- II 0.68 eV,
- III 0.53 eV.

Less agreement was found for conjugated diolefins and aromatics.

Dissociation energy calculations were not so satisfactory. However, Methods I, II and III give much better results than Method C which is about 50% off. With Method III we found a root mean square of 12.5 kcal, excepting cyclic hydrocarbons.

The method we have outlined in this article can be generalized and applied to series of compounds that are wider than hydrocarbons, as would seem to be

proved by preliminary research. However, less agreement can be predicted for more polar molecules (e.g. containing chlorine or fluorine) where the approximation of uniform electron density is unsatisfactory.

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References

1. Hückel, E.: Z. Physik **60**, 423 (1930).
2. Hoffmann, R.: J. chem. Physics **39**, 1397 (1963).
3. Newton, M. D., *et al.*: J.A.C.S. **88**, 2353 (1966).
4. Viste, A., Gray, H. B.: Inorg. Chemistry **3**, 1113 (1964).
5. Cusachs, L. C., Reynolds, J. W.: J. chem. Physics **43**, 5160 (1965).
6. Blyholder, G., Coulson, C. A.: Theoret. chim. Acta (Berl.) **10**, 316 (1968).
7. Cusachs, L. C.: J. chem. Physics **43**, 5157 (1965).
8. Wilkinson, J. H.: The algebraic eigenvalue problem 1964.
9. Ferreira, R.: Theoret. chim. Acta (Berl.) **3**, 147 (1965).
10. Vigne, J.: Etude et mise en oeuvre d'algorithmes de recherches d'un extremum d'une fonction de plusieurs variables, thesis (1969).
11. Al-Joboury, M. I., Turner, D. W.: J.C.S. 4434 (1964).
12. Vedeneyer, V. I., *et al.*: Bond energies, ionization potentials and electron affinities, ed. Coudon E. Arnold 1962.
13. Rossini: Selected values of properties of hydrocarbons 1947.
14. Interatomic Distances. London: The chemical society 1958.
15. Basch, H., *et al.*: Theoret. chim. Acta (Berl.) **3**, 458 (1965).

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