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Some Remarks on the Extended Hückel Approximation in the Independent-Electron MO Theory

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The sum of one-electron energies in the extended Hückel MO theory has been related to the total energy in the LCAO SCF MO theory including electron repulsion and nuclear repulsion terms. The sum of one-electron energies in the extended Hückel MO theory can be divided into the two parts; one almost independent of nuclear configuration and one highly sensitive to the configurational change. Of these the latter is found to be responsible for the stabilization energy due to the bond formation. The role of the highest occupied MO and the lowest unoccupied MO toward chemical reaction has been also discussed in the framework of the extended Hückel calculations. The partial AO population in these particular MO's is shown to be almost valence-inactive one, being ready to be mobilized in case of chemical interaction with other systems.

In view of the difficulty in nonempirical calculations for complicated, three-dimensional organic molecules, independent-electron molecular orbital (MO) methods are employed for the purpose of an approximate understanding of molecular properties. The extended Hückel MO theory is one of such methods.[1] The conclusion obtained in previous papers with respect to the applicability of this method is summarized as follows: (1) The one-electron energy levels approximate to those

1) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2047, 2474, 2480, 2745 (1964), and many other subsequent papers.

obtained by nonempirical LCAO SCF MO calculations:[2] (2) The sum of one-electron energies becomes a measure of the total molecular energy (the total electronic energy plus the nuclear repulsion) in discussing the stable molecular shape.[2] What a theoretical feature the extended Hückel method should possess in order that such results may be expected?

This problem seems to be related to the question as to what the one-electron energy is. Peters connected the one-electron energy with the change in the ionization energy of the MO on molecule formation.[3] We consider in a similar manner the total molecular energy, E_{total}, in LCAO SCF MO method.[4] As is well known, this quantity is expressed in terms of the eigenvalue of the Hartree-Fock equation, ε_i, the electron interaction, and the nuclear repulsion, as

$$E_{\text{total}} = 2\sum_{i}^{\text{occ}} \varepsilon_i - \sum_{i,j}^{\text{occ}} \sum_{r,s,t,u} C_{ir}C_{is}C_{jt}C_{ju} \times \{2(rs|tu) - (rt|su)\} + \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \quad (1)$$

where C_{ir} is the coefficient of rth atomic orbital (AO), χ_r, in ith eigenvector of the form $\sum_r C_{ir}\chi_r$, Z_α is the nuclear charge of atom α, $r_{\alpha\beta}$ is the distance between atoms α and β, and $(rs|tu)$ represents the usual electron repulsion integral of the type

$$\iint \chi_r^*(1)\chi_t^*(2)\frac{e^2}{r_{12}}\chi_s(1)\chi_u(2)\mathrm{d}v(1)\mathrm{d}v(2)$$

Using the Mulliken approximation[5] we get

$$E_{\text{total}} = 2\sum_{i}^{\text{occ}} \varepsilon_i - \sum_r \sum_{s(\neq r)} \frac{M_{rs}}{1-\frac{1}{4}S_{rs}^2}\{2(rr|ss) - (rs|sr)\} - \sum_r \left\{\frac{4}{3}M_{rr} + \sum_s \frac{\frac{1}{2}S_{rs}^2 M_{rs}}{1-\frac{1}{4}S_{rs}^2}\right\} \times (rr|rr) + \sum_{\alpha<\beta}\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \quad (2)$$

where

$$M_{rs} = \frac{1}{4}\sum_t\sum_u (P_{rt}P_{su} - \frac{1}{4}P_{rs}P_{tu} - \frac{1}{4}P_{ru}P_{ts})S_{rt}S_{su}$$

$$P_{rs} = 2\sum_{i}^{\text{occ}} C_{ir}C_{is}$$

$$S_{rs} = \int \chi_r^*(1)\chi_s(1)\mathrm{d}v(1)$$

If we neglect the square terms of overlap integral S_{rs}, this reduces to

$$2\sum_{i}^{\text{occ}} \varepsilon_i - \sum_r \sum_{s(\neq r)} M_{rs}\{2(rr|ss) - (rs|sr)\} - 2\sum_r M_{rr}(rr|rr) + \sum_{\alpha<\beta}\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \quad (3)$$

where $\sum_r$ implies the summation over all AO's. Here we divide these terms into two, the one being the intraatomic and the other the interatomic, obtaining

$$E_{\text{total}} \sim 2\sum_{i}^{\text{occ}} \varepsilon_i - \sum_\alpha \left[\sum_{r}^{\alpha}\sum_{s(\neq r)}^{\alpha} M_{rs}\{2(rr|ss) - (rs|sr)\} + 2\sum_{r}^{\alpha} M_{rr}(rr|rr)\right] - \Delta \quad (4)$$

where

$$\Delta = \sum_{\alpha<\beta}\left[2\sum_{r}^{\alpha}\sum_{s}^{\beta} M_{rs}\{2(rr|ss) - (rs|sr)\} - \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}\right]$$

in which $\sum_r^\alpha$ *etc.* means the summation over all AO's belonging to atom α, *etc.*

The electron interaction and the nuclear repulsion in Δ with regard to an atom pair will never cancel each other in general, except to pairs of neutral atoms locating distant from each other. Also the value of M_{rs} with respect to the AO pair, r and s, both belonging to an atom α is not always independent of the nuclear configuration. However, if we assume, in a roughest approximation, that

(1) The electron interaction and the nuclear repulsion with respect to the same pair of atoms compensate each other.

(2) The value of M_{rs} with respect to the AO's r and s belonging to the same atom is fixed,

then it follows that

$$E_{\text{total}} \sim 2\sum_{i}^{\text{occ}} \varepsilon_i - \sum_\alpha (\text{the intraatomic electron interaction of atom } \alpha) \quad (5)$$

Thus, we get to an equation which is appropriate to understand the reason why the sum of the one-electron energies in the independent-electron theory, which are in any sense an approximation to ε_i's, can be a measure of E_{total}. Namely, it is expected that in the extended Hückel method a relation like

$$2\sum_{i}^{\text{occ}} \varepsilon_i^{(\text{ext. Hückel})} \sim E_{\text{total}} + C \quad (6)$$

must hold at least in an approximate sense, where C is a term which is independent of the nuclear configuration.

2) L. C. Allen and J. D. Russell, *J. Chem. Phys.*, **46**, 1029 (1967), and many other papers in which the extended Hückel calculation is employed. One of the present authors (K. F.) is grateful to Professor Allen for sending the manuscript before publication.
3) D. Peters, *Trans. Faraday Soc.*, **62**, 1353 (1966).
4) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
5) R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1944).

If the opinion disclosed above is right, the pertinency of the concept of "one-electron Hamiltonian operator" in relation to the total Hamiltonian operator widely held in independent-electron theories becomes doubtful. In most of existing literatures,[6] the sum of one-electron Hamiltonian operators is regarded as an approximation to the "exact" electronic Hamiltonian operator. But, if so, the sum of ε_i's must necessarily cope with $(E_{\text{total}} - \sum_{\alpha<\beta}(Z_\alpha Z_\beta/r_{\alpha\beta}))$, which will never be a measure of configurational stability. The concept of "effective Hamiltonian operator," h_{eff}, in independent-electron theories is relevant in this view, if it implies an approximate "averaged" form of the Hartree-Fock one-electron operator.

The sum of one-electron energies in the extended Hückel calculation is represented in terms of Coulomb and resonance integrals, h_{rr} and $h_{rs}(r \neq s)$, respectively, as

$$E' = 2\sum_i^{\text{occ}} \varepsilon_i^{(\text{ext. Hückel})}$$

$$= 2\sum_i^{\text{occ}}\sum_r C_{ir}^2 h_{rr} + 2\sum_i^{\text{occ}}\sum_r\sum_{s(\neq r)} C_{ir}C_{is}h_{rs} \quad (7)$$

in which

$$h_{rs} = \int \chi_r^*(1) h_{\text{eff.}}(1)\chi_s(1)\mathrm{d}v(1)$$

Following Hoffmann,[1] we adopt the Wolfsberg-Helmholtz scheme for the approximate evaluation of the resonance integral

$$h_{rs} = \frac{1}{2}K(h_{rr} + h_{ss})S_{rs} \qquad (K\text{: constant})$$

and introduce this relation into Eq. (7), obtaining

$$E' = \sum_r \{N_r + (K-1)(N_r - P_{rr})\}h_{rr} \quad (8)$$

in which P_{rr} represents $2\sum_i^{\text{occ}} C_{ir}^2$ and N_r stands for

Table 1. The values of $\sum_r N_r h_{rr}$, $(K-1)\sum_r (N_r - P_{rr})h_{rr}$ and $\sum_r \nu_r h_{rr}$ for some saturated and unsaturated compounds

Compound	$\sum_r N_r h_{rr}$, eV	$(K-1)\sum_r (N_r - P_{rr})h_{rr}$, eV	$\sum_r \nu_r h_{rr}$ eV
Ethane *staggered*	−194.9964	−48.9605	−192.9800
skew	−194.9857	−48.8863	
eclipsed	−194.9749	−48.7991	
Cyclohexane *chair*	−505.4983	−120.7564	−497.3400
boat	−505.4730	−120.0245	
Butene-1	−337.2518	−82.3226	−331.5600
Butene-2	−337.0252	−82.6478	
Butadiene *s-trans*	π −45.6800	π −7.1500	
	σ −264.9286	σ −68.9009	π −45.6800
s-cis	π −45.6800	π −7.0714	σ −258.6800
	σ −264.8333	σ −68.6872	
Ethylchloride *staggered*	−296.9811	−47.3166	−296.5400
skew	−296.9694	−47.2263	
eclipsed	−296.9574	−47.1167	
Methyl sp^2	−97.9970	−23.5608	−96.4900
sp^3	−97.9922	−22.8225	

1) The value of K was taken as 1.75.

2) The values of h_{rr}'s were taken as:

H	1s	−13.60 eV
C	2s	−21.43 eV
	2p	−11.42 eV
Cl	3s	−25.23 eV
	3p	−13.34 eV

3) The geometry of the molecules employed here was taken as follows:

Ethane, Cyclohexane: C-C 1.54Å
C-H 1.09Å
all angles are tetrahedral

Butene: C-C 1.54Å
C=C 1.38Å
angles in sp^3 carbon are all tetrahedral and in sp^2 carbon are 120°.

Butadiene: C=C 1.37Å
C-C 1.47Å
C-H 1.06Å
all angles are 120°

Ethylchloride: C-Cl 1.77Å
∠ C-C-Cl 110°

Methyl: C-H 1.09Å

6) For instance, J. Lennard-Jones, *Proc. Roy. Soc. (London)*, **A198**, 1 (1949), and many other papers and books.

the population of AO r, *viz.* $2\sum_{i}^{occ}\sum_{s}C_{ir}C_{is}S_{rs}$. This equation will be helpful in understanding the nature of this approximate method.

In a strict sense, N_r depends on the nuclear configuration of a molecule. But in most of the extended Hückel cases we are able to assure that

$$\sum_{r} N_r h_{rr} \sim \text{const.} \quad (\sim\sum_{r} \nu_r h_{rr})$$

where ν_r is the occupation number (2, 1, or 0) of rth AO in a valence state atom. Namely, this term represents the sum of the ionization potential of all valence electrons. The energy of stabilization due to the molecule formation originates exclusively in the term which is proportional to (N_r-P_{rr}) in the right side of Eq. (8). This quantity serves as a measure of "effusion" of valence electrons from a particular atomic orbital into the others, as is easily understood from the definition of N_r and P_{rr}. The results of calculation for some compounds are given in Table 1. It may be clear that the differences in energies among stereochemical or structural isomers dominantly come from the term owing to the effusion of valence electrons.

It may be interesting to cite here Ruedenberg's opinion[7] on the nature of chemical binding that the delocalization of the valence electrons lowers the kinetic-energy pressure, causing a firmer attachment of these electrons to the nuclei, resulting in a potential energy lowering.

The rate of such a lowering in one-electron energy may be proportional to the effused fraction of AO population, represented by the following equation or the like:

$$\frac{\Delta h_{rr}}{h_{rr}} \sim k_r(N_r-P_{rr}) \tag{9}$$

where k_r is a positive proportionality constant so that we obtain

$$E' = \sum_{r}\{N_r + k_r(N_r - P_{rr})\}h_{rr} \tag{8'}$$

Thus, we see, from the comparison of Eqs. (8) and (8'), that the constant $(K-1)$ in Eq. (8) is in reality equal to the proportionality constant in Eq. (8'), which is chosen in common with respect to all AO's.

The effused fraction of population of the rth AO, N_r-P_{rr}, is highly sensitive to the change in the overlap integrals with other AO's, as can be easily understood from the definition of N_r and P_{rr}. This is also dependent on the way of taking the Coulomb integrals, namely the effused population of an AO pair (say, r and s) decreases as the difference between h_{rr} and h_{ss} increases. The results of the calculation on the systems containing nitrogen, oxygen, fluorine, *etc.*, can make sure of these circumstances.

To discuss the chemical reactivity in terms of the extended Hückel calculation is an attracting problem. Already we have several papers published,[8-13] in which this problem is discussed in the frame of the frontier electron theory.[14,15] Namely, the reactivity toward an electrophilic reagent is discussed by the partial AO population of the highest occupied (HO) MO, and that toward a nucleophilic reagent by the partial AO population of the lowest unoccupied (LU) MO of the reactant molecule.

The partial population at rth AO of ith MO, $n_r^{(i)}$, is represented by

$$n_r^{(i)} = p_r^{(i)} + v_r^{(i)} \tag{10}$$

where $p_r^{(i)}=2C_{ir}^2$, and $v_r^{(i)}=2\sum_{s(\neq r)} C_{ir}C_{is}S_{rs}$ are the "valence-inactive" and "valence-active" partial AO populations of ith MO, respectively, after Ruedenberg.[7] With regard to a number of compounds and with regard to most of AO's, it can be shown that, in HO MO, v_r is positive while it is negative in LU MO, and $p_r^{(HO)}$ as well as $n_r^{(HO)}$ parallels with $v_r^{(HO)}$, $p_r^{(LU)}$ and $n_r^{(LU)}$ being parallel to $|v_r^{(LU)}|$. A general illustrative example is given from the π electronic part of planar conjugated molecules. In this case the circumstances are very simple because we can put $h_{rr}=\text{constant}=\alpha$, so that the relations hold for all i's and r's.

$$\frac{v_r^{(i)}}{n_r^{(i)}} = \frac{\dfrac{\varepsilon_i}{\alpha} - 1}{K-1}, \quad \frac{p_r^{(i)}}{n_r^{(i)}} = \frac{K - \dfrac{\varepsilon_i}{\alpha}}{K-1} \tag{11}$$

It is easily seen from this equation that, when $\varepsilon_i<\alpha<0$, $v_r^{(i)}$ is positive and, when $\varepsilon_i>\alpha$, it is negative. Since HO and LU are those MO's whose energy is in most cases nearest to α, the partial AO population in these MO's is almost valence inactive one, being ready to be mobilized in case of reaction with other system. This fact is important in regard to the role of these particular MO's in the theory of chemical reactivity. Several examples are given in Table 2.

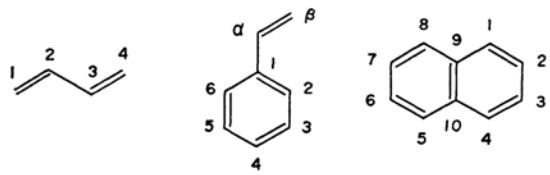
In the cases in which $p_r^{(i)}$ parallels $n_r^{(i)}$ in each

7) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).
8) H. Kato, T. Yonezawa, K. Morokuma and K. Fukui, This Bulletin, **37**, 1710 (1964).
9) H. Kato, K. Morokuma, T. Yonezawa and K. Fukui, *ibid.*, **38**, 1749 (1965).
10) H. Kato, K. Yamaguchi, T. Yonezawa and K. Fukui, *ibid.*, **38**, 2144 (1965).
11) K. Fukui and H. Fujimoto, *Tetrahedron Letters*, **1965**, 4303.
12) T. Yonezawa, O. Yamamoto, H. Kato and K. Fukui, *Nippon Kagaku Zasshi*, (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 26 (1966).
13) H. Fujimoto and K. Fukui, *Tetrahedron Letters*, **1966**, 5551.
14) K. Fukui, "Molecular Orbitals in Chemistry, Physics, and Biology," ed. by P.-O. Löwdin and B. Pullman, Academic Press, New York (1964), p. 513.
15) K. Fukui, "Modern Quantum Chemistry," Vol. 1, ed. by O. Sinanoglu, Academic Press, New York (1965), p. 49.

TABLE 2. THE VALENCE-ACTIVE AND THE VALENCE-INACTIVE ELECTRONS IN PI MOLECULAR ORBITALS OF PLANAR CONJUGATED SYSTEMS

Atomic orbital r	p_r	v_r	ε	Atomic orbital r	p_r	v_r	ε
s-trans-Butadiene*				2	0.0063	−0.0021	
1	0.2296	0.0958	−13.9410	4	0.7121	−0.2403	−7.0581
2	0.4761	0.1986		β	0.3790	−0.1279	
1	0.6272	0.0880	−12.4740	2	0.5998	−0.2752	
2	0.2496	0.0350		4	0.3978	−0.1825	−4.1589
1	0.8416	−0.1670	−9.3003	β	0.0545	−0.0250	
2	0.4059	−0.0805		Naphthalene*			
1	0.4443	−0.1595	−6.6219	1	0.1091	0.0758	−14.9334
2	1.1158	−0.4007		2	0.0708	0.0493	
Styrene*				1	0.0995	0.0423	−13.9749
2	0.1971	0.1218		2	0.2513	0.1068	
4	0.1457	0.0901	−14.6921	1	0.2541	0.0729	−13.3283
β	0.0259	0.0160		2	0.0472	0.0136	
2	0.0007	0.0002		1	0.0008	0.0001	−12.7277
4	0.2905	0.0980	−13.5803	2	0.2755	0.0497	
β	0.3023	0.1020		1	0.3284	0.0281	−12.0943
2	0.3964	0.0783		2	0.1322	0.0113	
4	0.0010	0.0002	−12.8334	1	0.4468	−0.0886	−9.3009
β	0.0007	0.0001		2	0.1769	−0.0351	
2	0.1894	0.0227		1	0.0005	−0.0001	−8.1836
4	0.3383	0.0405	−12.3352	2	0.4709	−0.1292	
β	0.5476	0.0655		1	0.4659	−0.1518	−7.2819
2	0.2497	−0.0521		2	0.0811	−0.0264	
4	0.3871	−0.0807	−9.1637	1	0.2325	−0.0890	−6.1061
β	0.8310	−0.1733		2	0.5777	−0.2212	
2	0.6378	−0.1710		1	0.3397	−0.1670	−3.1324
4	0.0028	−0.0007	−8.2831	2	0.1916	−0.0942	
β	0.0020	−0.0005					

* Numbering is as follows:



s-trans-Butadiene Styrene Naphthalene

MO, like that of Eq. (11), we can take $n_r^{(f)}$ as well as $p_r^{(f)}$ as the reactivity indices where (f) signifies (HO) or (LU). However, in view of the physical meaning of valence-inactive population we should employ $p_r^{(f)}$ as the reactivity index of rth AO. If it is permitted to take into account only one AO with respect to an atom at which a given reaction is to take place, *e. g.* the $2p\pi$ AO in the substitution at a carbon atom of a planar conjugated molecule, the hydrogen 1s AO in the hydrogen abstraction of a hydrocarbon, and so forth, $p_r^{(f)}$ *per se* is qualified as a reactivity index of that atom. Such is the cases of Refs. 11, 13, and 14. In Fig. 1, the ratio of p_r to n_r of hydrogen 1s AO in methane, ethane and propane with respect to the doubly occupied MO's is presented. We can see that, in HO MO of these hydrocarbons, more than 75% of partial population serves as the valence inactive one.

In many other kinds of chemical reactions,

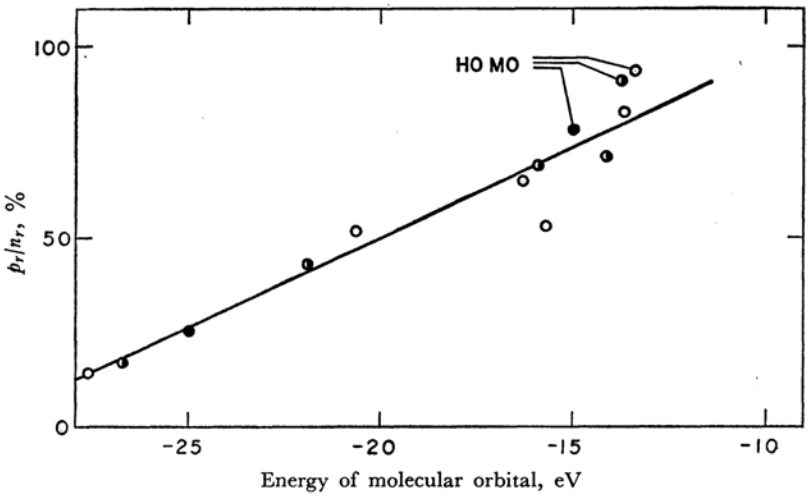


Fig. 1. The portion of valence-inactive electron in partial population of hydrogen 1s atomic orbitals.
● methane ◑ ethane ○ propane (secondary hydrogen)

however, we have to consider more than one AO[16] of an atom simultaneously participating. In such cases it is convenient to transform the basis of AO's to that of the valence atomic orbitals (VAO).[7] In this manner we can discuss the orientation and the spatial direction of approach of the reagent by the partial population of HO or LU MO at each VAO. Although only approximately, the cases of Refs. 8, 9, 10, 12, and 15 belong to such VAO treatment.

In the light of many evidences[8-15] obtained for the availability of $p_r^{(f)}$, including the case using VAO population, calculated by the Hückel, the semiempirical LCAO SCF MO and the extended Hückel methods, as the reactivity index for many kinds of reactions, we can imagine, in terms of the extended Hückel quantities, the possible pathway of chemical reactions in the following manner. The reagent approaches to the AO (including VAO) of the largest $p_r^{(f)}$ ((f) implies (HO) or (LU)) from the direction in which the overlapping of that AO and the reagent AO is maximum. At that AO the value of $v_r^{(f)}$ ($|v_r^{(f)}|$ when (f) is (LU)) is usually also largest so that the charge-transfer from (or to) the (f) MO loosens the "bonding" of that AO with all other AO's most intensely, making easy the bond formation between that reactant AO and the attacking reagent AO.

16) By the term "AO" is meant here the AO associated with the space-fixed Cartesian coordinates, like usual Slater AO's, and not any hybridized orbital.

The calculation was carried out on a HITAC 5020 E computer at the computation center of the University of Tokyo.

The authors are grateful to Professor Teijiro Yonezawa of Kyoto University for making the computer program for the extended Hückel calculation, available for them.