# On the Parameterization in the Semi-Empirical LCAO MO Method

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Although in the last decade Pariser and Parr's semi-empirical LCAO MO method[1] has been extensively and successfully used for the prediction of the electronic spectra of unsaturated molecules,[2] its applicability to the description of the ground-state electronic properties has not yet been clearly established. In fact, as will be shown in this paper, Pariser and Parr's approximation, with its original parameterization, if applied to benzene, gives the unexpected result that a skew structure ($D_{3h}$) is energetically favored as compared with the symmetric one ($D_{6h}$). In this paper we will, then, point out the origin of such an absurd result and propose a new parameterization applicable to the calculation of ground-state electronic properties as well as to the spectral calculation.

## The SCF-MO's of Benzene

The Pariser and Parr approximation, with its original parameterization, is applied to benzene in conjunction with the self-consistent field technique of Roothaan.[3] In computing interaction terms for adjacent atoms, the internuclear distances were predicted at each step of the iterative process from the $\pi$-bond orders, $p$, using the formula:[4]

$$r\,(\text{in Å}) = 1.520 - ap \tag{1}$$

with

$$a = 0.186 \tag{2}$$

However, nonneighbor internuclear distances were calculated by assuming the ring to be regular, with all bonds of an equal length (1.397Å). The Coulomb repulsion integrals ($pp/qq$) were evaluated using the procedure of Pariser and Parr, and the core resonance integrals, $\beta$, for various distances were obtained from the Pariser and Parr curve;

$$\beta(r) = \beta_0 \exp[b(1.39 - r)] \tag{3}$$

with

$$\beta_0 = -2.39\ \text{eV. and}\ b = 5.6864\ \text{Å}^{-1} \tag{4}$$

The starting molecular orbitals used were of the Hückel type.

For the symmetric benzene ($D_{6h}$), the SCF-MO's are given directly by the Hückel type orbitals and are independent of parameterization. It is particularly noteworthy that the use of the above parameterization results also in the achievement of a self-consistency of molecular orbitals for an asymmetric benzene with the $D_{3h}$ molecular symmetry. The obtained self-consistent bond orders for the skew benzene indicate that the bond lengths vary considerably, the length of the shorter bonds being 1.347Å and that of the longer bonds 1.465Å. The refinement of the values of the Coulomb repulsion integrals (vide infra) leads to a further increase in skewness.

Now let us enquire which of the symmetric and asymmetric structures is more favorable in energy. It has been recognized[5,6] that a conclusion regarding the stability or the equilibrium configuration of a conjugated molecule cannot be based on $\pi$-electron calculations only; allowance for the effects of the $\sigma$-bond compression must also be made. Unfortunately, there is at present no theoretical method of estimating the $\sigma$-bond compression energy in the same degree of approximation as Pariser-Parr's. Longuet-Higgins and Salem's modification[5] of the Hückel MO theory is adopted here to obtain an estimate of the desired difference in energy between the two structures. According to Longuet-Higgins and Salem, the total binding energy of a conjugated molecule,

1) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 446, 767 (1953).
2) R. G. Parr, "The Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York (1963).
3) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
4) T. Nakajima and S. Katagiri, *Mol. Phys.*, **7**, 149 (1963).
5) H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.*, **A251**, 172 (1959).
6) C. A. Coulson, *Tetrahedron*, **12**, 193 (1961); C. A. Coulson and A. Golebiewski, *Mol. Phys.*, **5**, 71 (1962).

taken to be the sum of the $\pi$-bond energy and the $\sigma$-bond energy, is given by:

$$V=E_\pi+E_\sigma=\sum_{p<q}2\int(\mathrm{d}p_{pq}/\mathrm{d}r)\bar{\beta}_{pq}(r)\mathrm{d}r \qquad (5)$$

where $\bar{\beta}(r)$, the resonance integral parameter in the Hückel MO theory, is interpreted as an "effective resonance integral" which includes an electron interaction term; it is assumed to be given as:*

$$\bar{\beta}_{pq}(r)=[2\beta_{pq}(r)-(p_{pq}/2)(pp/qq)]/2 \qquad (6)$$

Then, using Eqs. 1—4 and the Pariser and Parr quadratic formula:

$$(pp/qq)=0.2157r^2-2.625r+10.53 \qquad (7)$$

and integrating Eq. 5, we obtain:

$$V=\sum_{p<q}[1.8909\beta_{pq}(r)-0.7794r^4+14.2252r^3-104.9285r^2+231.3215r]+\text{const.} \qquad (8)$$

where the last term is the constant of integration, which is canceled in estimating the desired difference in $V$.

The total energy values thus calculated for the two structures indicate that the skew structure is more favorable in energy than the symmetric one, the deformation energy which favors the skew structure being 0.29 eV.—about 7 kcal./mol.—an appreciable amount.

## Stable Configurations in the $(4n+2)$ Cyclic Polyenes

In order to investigate the cause of the unreasonable results above, let us now examine the equilibrium configurations with respect to bond length distortion in cyclic polyenes generally having $(4n+2)$ carbon atoms. The Longuet-Higgins and Salems modification of the Hückel MO theory is again adopted to estimate the change in energy caused by the distortion.

At the outset, we define the bond alternation parameter, $k$, as

$$k=\bar{\beta}_s/\bar{\beta}_d \qquad (9)$$

where the subscripts s and d indicate the single and double bonds in an unexcited Kekulé structure respectively. As was taken in Longuet-Higgins and Salem's original theory, $\bar{\beta}(r)$ is now assumed to vary exponentially with $r$:

$$\bar{\beta}(r)=\bar{\beta}_0\exp[\bar{b}(1.39-r)] \qquad (10)$$

The total electronic energy, taken to be the sum of the $\pi$-bond energy and the $\sigma$-bond energy, is then given by:

$$V=(2/a\bar{b})\sum_{p<q}\bar{\beta}_{pq}(r)+\text{const.} \qquad (11)$$

For a given molecule, using Eqs. 1, 10 and 11, we can calculate the total electronic energies for various $k$ values (0—1), and the $V$-$k$ curve can be obtained.

The static equilibrium configurations of a given molecule are then given by the points of the $V$-$k$ curve where $\partial V/\partial k=0$; namely,

$$\exp[a\bar{b}(p_s-p_d)]=k \qquad (12)$$

where

$$p_s-p_d=\sum_{l=-n}^{n}(k-1)\left(1-\cos\frac{2\pi l}{2n+1}\right)\Big/(2n+1)\left(1+2k\cos\frac{2\pi l}{2n+1}+k^2\right)^{1/2} \qquad (13)$$

It should be noted that Eq. 12 is nothing but the condition for the self-consistency of MO's with respect to $k$.

From Eq. 13 it follows at once that Eq. 12 is always satisfied by the point $k=1$, regardless of the value of $n$. It may be shown further that the sign of $(\partial^2V/\partial k^2)_{k\to1}$ coincides with that of the quantity:

$$A=1-a\bar{b}[\partial(p_s-p_d)/\partial k]_{k\to1} \qquad (14)$$

where

$$[\partial(p_s-p_d)/\partial k]_{k\to1}=\left(\frac{1}{2n+1}\right)\sum_{l=-n}^{n}\left|\sin\frac{\pi l}{2n+1}\tan\frac{\pi l}{2n+1}\right| \qquad (15)$$

Thus, if $A\geqq0$, the configuration $k=1$ is one of stable equilibrium, but if $A>0$, though it is one of static equilibrium, the configuration $k=1$ is one of unstable equilibrium. In the latter case a stable equilibrium is given by a point $k<1$, one in which $\partial V/\partial k=0$ and $\partial^2V/\partial k^2>0$.

For benzene the symmetric configuration with $k=1$ should, of course, be one of stable equilibrium. This yields

$$a\bar{b}\leqq1 \qquad (16)$$

This condition severely restricts our choice of $\bar{b}$ value, the value of $a$ being fairly narrowly determined empirically.

As was pointed out in the preceding section, the Pariser and Parr approximation, if applied to benzene, brings about the conclusions that the SCF MO's are achieved for the two symmetry types and that a skew structure is energetically favored as compared with the symmetric one. It is now clear that this absurd result is due to too large a value of $b$

* The resonance integral parameter, $\bar{\beta}_{pq}$, in the simple Hückel MO theory should explicitly be considered to be the arithmetic mean of the core resonance integral, $\beta_{pq}$, and the corresponding Fock matrix element, $\beta^F_{pq}$ $(=\beta_{pq}-(p_{pq}/2)(pp/qq))$. If $\bar{\beta}_{pq}$ is interpreted merely as $\beta^F_{pq}$, electron interactions are included twice in the total $\pi$-electronic energy.[7]

7) R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry," Interscience, New York (1963), p. 303.

having being assigned by Pariser and Parr in their original parameterization. In fact, if we rewrite Eq. 6 in an approximately exponential form like Eq. 10, using the Pariser and Parr parameterization, the value of $\bar{b}$ turns out to be about $7\text{Å}^{-1}$,* which does not satisfy Eq. 16 when multiplied by $a=0.186$.

### A Refined Parameterization

Pariser and Parr's $b$ value was determined from $\beta$ values so adjusted as to reproduce the observed excitation energies of ethylene and benzene. Actually, at the time of the original development of the Pariser and Parr method the bond lengths of these molecules were not accurately known. In order to improve the $b$ value, we follow Pariser and Parr's procedure but use the recently observed bond lengths, 1.333 Å for ethylene[8] and 1.397 Å for benzene.[9] Moreover, the one-center electronic repulsion integral, given in the Pariser and Parr theory as $I_c-A_c$ is taken to be $11.54-0.46=11.08$ eV.[10] The two-center repulsion integrals were determined by the normal extrapolation procedure of Pariser and Parr.

Thus, adjusting the $\beta$ values of ethylene and benzene to fit the observed spectra, we obtain:

$$\beta(1.333\text{Å})=-2.80\text{ eV}. \quad (17)$$

and

$$\beta(1.397\text{Å})=-2.38\text{ eV}. \quad (18)$$

From these, we obtain $b=2.5801\text{Å}^{-1}$.* This value of $b$ is considerably smaller than Pariser and Parr's original value, and for benzene for use of this $b$ value results in the achievement of self-consistency only for the symmetric configuration. Furthermore, for butadiene the SCF MO's obtained by using the new parameterization lead to a good reproduction of experimental bond lengths and spectral data; the bond lengths for the double and single bonds are predicted to be 1.34 and 1.47 Å respectively, and the lowest singlet excitation energy is calculated to be 6.0 eV. If we rewrite Eq. 6 in an exponential form like Eq. 10, using the $b$ value obtained above, the value of $\bar{b}$ turns out to be about $4.5\text{Å}^{-1}$, which satisfies Eq. 16, and which is in good agreement with the value $4.5988\text{Å}^{-1}$,[4] which was determined by reference to the observed bond length alternation in butadiene. The latter $\bar{b}$ value has been successfully used in accounting for the ground-state electronic properties and electronic spectra of fundamental nonbenzenoid aromatic hydrocarbons.[12-14],**

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* The SCF MO's obtained above for the skew benzene correspond to the MO's calculated by the simple Hückel method with $k=0.45$. To the degree of approximation, self-consistency is achieved for configurations with a static equilibrium, and for the skew benzene the $V$-$k$ curve should have a minimum at the point $k=0.45$. We obtain such a curve if we set $\bar{b}=6.7712\text{Å}^{-1}$, using $a=0.186$.

8) L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **31**, 400 (1959).

9) A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956); A. Almenningen, O. Bastiansen and L. Fernholt, *Kgl. Norske Vid. Selsk. Skr.*, No. 3 (1958).

10) H. D. Pritchard, *Chem. Revs.*, **52**, 529 (1955).

* Very recently Allinger[11] has proposed a value of $3.0323\text{Å}^{-1}$ for $b$. Allinger, however, predicted that the skew benzene would be more, though only slightly, stable than the symmetric one.

11) N. L. Allinger, *J. Org. Chem.*, **27**, 443 (1962).

12) T. Nakajima, Y. Yaguchi, R. Kaeriyama and Y. Nemoto, This Bulletin, **37**, 272 (1964).

13) T. Nakajima, "Molecular Orbitals in Chemistry, Physics, and Biology," Ed. by P. O. Löwdin and B. Pullman, Academic Press, New York (1964), p. 457.

14) T. Nakajima, T. Saijo and H. Yamaguchi, *Tetrahedron*, **20**, 2119 (1964).

** Recently Julg[15] has proposed a value of $5.26\text{Å}^{-1}$ for $\bar{b}$. This value was derived from the relation $a\bar{b}=1$ with $a=0.19$.

15) A. Julg, *Tetradron*, **19**, Suppl. 2, 25 (1963).