

The Woodward–Hoffmann Approach, the Extended Hückel Method, and the Barrier to Rigid Internal Rotation in Ethane

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Abstract: The extended Hückel MO (EHMO) method is subject to quantitative analysis in terms of Mulliken populations. Such an analysis shows that the EHMO “source” of the rigid internal rotation barrier in ethane comes from population changes all over the molecule, especially in the C–C bond. On the other hand, a frontier orbital (FO) or Woodward–Hoffmann (W–H) type of approach suggests the “source” to be repulsions between vicinal hydrogens. The EHMO energy change can be decomposed into two steps, the first being a “frozen-orbital” rotation and the second being a coefficient relaxation. The first step is the process actually treated in a W–H approach, and this step alone accounts almost exactly for the total EHMO barrier, allowing an alternative “source” description. Examination of the formula for this frozen-orbital step allows quantitative discussion of the W–H approach. The W–H approach is seen to be a shortcut for qualitatively predicting the outcome of an EHMO calculation. Knowing how the latter relates Mulliken populations to total energy enables us to list conditions where the EHMO method, and hence the W–H approach, should fail to agree with experiment.

There is a certain two-step method for qualitatively predicting energy changes in systems undergoing relative nuclear displacements. The steps are (1) select one of the highest energy occupied MO's (usually the highest) and (2) see if this MO shows a net increase or decrease of overlap among constituent AO's upon the nuclear displacement in question. The total (electronic plus internuclear repulsion) energy of the system is postulated to decrease or increase, respectively. This method has a long history and many names^{1,2} such as the frontier orbital (FO) approach or the Woodward–Hoffmann (W–H) approach. Variations involving empty MO's and also those employing symmetry correlation diagrams are very closely related.³

The success of the W–H approach in treating reaction pathways has intensified interest in finding a firm theoretical basis for this method. Here we describe two quantitative techniques for analyzing the results of extended Hückel MO (EHMO) calculations. One of these techniques is equivalent in spirit to the W–H approach and offers simple explanations for the rules cited above.

The analysis allows us to conclude that the W–H approach is a shortcut for predicting qualitatively the results of an EHMO calculation. Hence, the W–H approach should fail to agree with experiment when the EHMO method fails. Conditions where such failure occurs will be discussed.

The quantitative techniques also allow us to produce verbal “explanations” for EHMO results. The EHMO energy barrier to rigid internal rotation in ethane is used throughout this paper as an example.

(1) See, for example, H. Fujimoto and K. Fukui, *Advan. Quantum Chem.*, **6**, 177 (1972), and references cited therein.

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 814 (1969).

(3) Symmetry correlation diagrams offer a convenient, but not essential, way to determine which MO's “become” which other MO's. But it is still the nodal properties (i.e., overlap properties) that determine whether the new MO is relatively high or low in energy.

EHMO Energies and Mulliken Populations

It is a well-known fact that, in simple Hückel theory, the energy of an MO is a function of the charge densities and bond orders associated with the MO.⁴ It seems to be much less generally recognized that an *extended* Hückel⁵ energy level is a simple function of the orbital's contributions to Mulliken⁶ AO and overlap populations.^{7–10}

In a Hückel method, the total electronic wave function ψ is taken to be a single product of one-electron MO's ϕ .

$$\psi(1, 2, \dots, n) = \phi_1(1)\phi_2(2) \dots \phi_m(n) \quad (1)$$

Each MO ϕ is a linear combination of normalized AO's χ .

$$\phi_i = \sum_j^{\text{AO's}} c_{ji} \chi_j \quad (2)$$

The hamiltonian operator is assumed to be a sum of one-electron effective operators.

$$\hat{\mathcal{H}}(1, 2, \dots, n) = \hat{H}(1) + \hat{H}(2) + \dots + \hat{H}(n) \quad (3)$$

As a result, the total energy¹¹ is the sum of the one-electron energies

$$\bar{E} = \int \psi^* \hat{\mathcal{H}} \psi d\tau / \int \psi^* \psi d\tau = \epsilon_i + \epsilon_j + \dots + \epsilon_m \quad (4)$$

(4) See, for example, L. Salem, “Molecular Orbital Theory of Conjugated Systems,” W. A. Benjamin, New York, N. Y., 1966, pp 33 and 34.

(5) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(6) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).

(7) Qualitative recognition of this relation is fairly widespread. See, for example, ref 8, p 228. Also such *energy partitioning* has been shown to apply to certain types of self-consistent field calculations. See ref 9 and 10 and references therein.

(8) L. C. Allen in “Sigma Molecular Orbital Theory,” O. Sinanoglu and K. B. Wiberg, Ed., Yale University Press, New Haven, Conn., 1970, pp 227–248.

(9) H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **16**, 163 (1970).

(10) M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, **93**, 7201 (1971).

(11) The total EHMO energy is assumed to include electronic and nuclear repulsion energies. The validity of this assumption will be discussed later.

where

$$\epsilon_i = \int \phi_i^*(1) \hat{H}(1) \phi_i(1) d\tau(1) / \int \phi_i^*(1) \phi_i(1) d\tau(1) \quad (5)$$

Henceforth we will assume all functions and coefficients to be real. If we now expand (5) in terms of AO's, we obtain

$$\epsilon_i = \frac{\sum_j^{\text{AO's}} c_{ji}^2 H_{jj} + 2 \sum_{j < k} c_{ji} c_{ki} H_{jk}}{\sum_j c_{ji}^2 + 2 \sum_{j < k} c_{ji} c_{ki} S_{jk}} \quad (6)$$

where

$$H_{jk} \equiv \int \chi_j(1) H(1) \chi_k(1) d\tau(1) \quad (7)$$

$$S_{jk} \equiv \int \chi_j(1) \chi_k(1) d\tau(1) \quad (8)$$

For the remainder of this section, we assume the MO's ϕ to be normalized, so the denominator of (6) is unity.

In simple Hückel MO theory, expression 6 leads immediately to an energy in terms of charge densities and bond orders.⁴

In the most commonly used variant⁵ of the EHMO method, H_{jj} is taken to be equal to the valence state ionization potential of the AO χ_j and H_{jk} is evaluated from the formula

$$H_{jk} = KS_{jk}(H_{jj} + H_{kk})/2 \quad (9)$$

K is a free parameter. Hoffmann⁵ suggested a value for K of 1.75. Substituting (9) into (6), we obtain

$$\epsilon_i = \sum_j c_{ji}^2 H_{jj} + \frac{K}{2} \sum_{j < k} 2c_{ji} c_{ki} S_{jk} (H_{jj} + H_{kk}) \quad (10)$$

which can be rewritten as

$$\epsilon_i = \sum_j q_j^i H_{jj} + \frac{K}{2} \sum_{j < k} p_{jk}^i (H_{jj} + H_{kk}) \quad (11)$$

where q_j^i is the contribution to the Mulliken net AO population⁶ of χ_j due to an electron in ϕ_i , and p_{jk}^i is the electron's contribution to the Mulliken overlap population⁶ between AO's j and k . Thus we have a quantitative relationship between an EHMO energy level and the orbital's AO and overlap populations.¹² Summing (11) over all electrons produces an equation for total EHMO energy in terms of total net atom and bond populations

$$E = \sum_j^{\text{AO's}} q_j H_{jj} + \frac{K}{2} \sum_{j < k} p_{jk} (H_{jj} + H_{kk}) \quad (12)$$

where q_j , the total Mulliken net AO population for χ_j , is given by

$$q_j = \sum_i^{\text{MO's}} n_i q_j^i = \sum_i^{\text{MO's}} n_i c_{ji}^2 \quad (13)$$

and P_{jk} , the total Mulliken overlap population between χ_j and χ_k , is given by

$$P_{jk} = \sum_i^{\text{MO's}} n_i p_{jk}^i = \sum_i^{\text{MO's}} 2c_{ji} c_{ki} S_{jk} \quad (14)$$

The occupation number of each MO is n_i . It is important to bear in mind that the sum of Mulliken AO

(12) Any expression for the H_{jk} elements which depends linearly on S_{jk} will lead to a similar kind of relation in which orbital energy is a sum of weighted populations.

and overlap populations is equal to the total number of electrons in the system. For EHMO calculations, only valence electrons are included in this "total."

It is possible to use (12) to demonstrate that there is a tendency for the EHMO method to maximize overlap populations at the expense of AO populations as the energy is minimized. Consider a very simple system consisting of two identical AO's χ_a and χ_b on identical nuclei. Initially an EHMO calculation leads to AO populations $q_a = q_b$ and an overlap population p_{ab} . Suppose we now move the nuclei closer together and find that new EHMO results show a decrease in each AO population of δ and a commensurate increase of p_{ab} by 2δ . It follows from (12) that the energy change is equal to $2\delta H_{aa}(K - 1)$. If $K > 1$, the energy change will be negative (since H_{aa} is negative). Hence, the choice of 1.75 for K leads to weighting factors which usually make overlap population energetically more important than an equal amount of AO population.¹³ When this is true, we can cite two useful guidelines. (1) For a given nuclear configuration, the EHMO method minimizes the total energy by maximizing the weighted Mulliken overlap populations at the expense of the weighted net AO populations. (2) The EHMO total energy of a system will decrease whenever nuclei move in such a way that the weighted overlap populations can increase.¹⁴ Thus, the EHMO method is a kind of computational equivalent to the qualitative notion that MO energy is lowered when orbital overlap is maximized between AO's making up that MO. Expression 12 will enable us to study such qualitative notions in detail.

EHMO Energy Changes in Ethane

We will now use (12) to obtain a detailed analysis of an EHMO energy change in terms of population changes. The process we consider is the rigid internal rotation of ethane from the staggered to the eclipsed conformation. This is not a reaction in the usual sense, but it is a process where a nuclear displacement is accompanied by an energy change, so it is a legitimate candidate for treatment by the simple two-step method. Some data produced by EHMO calculations on staggered and eclipsed ethane¹⁵ are given in Table I. Let us first see how these EHMO energy changes accord with the two-step W-H approach and with the general idea that energy change correlates with orbital overlap change as described above. Step 1 of the W-H approach is selection of a high-energy occupied MO. The highest-energy MO has a_g symmetry. But this is not the MO we should use. For reasons which will become apparent later, the second highest energy degenerate pair of MO's (e_g symmetry) is the appropriate choice.^{9,16,17} The second step is to see whether this MO undergoes an increase or decrease of overlap when we go from the staggered to the eclipsed conformation.

(13) It is possible to imagine situations (e.g., highly heteropolar bonds) where this generalization could fail.

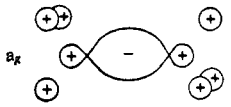
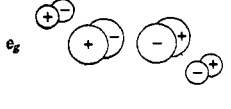
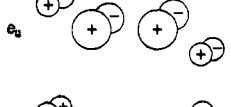
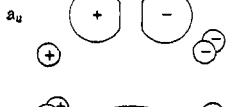

(14) For recent applications of this principle as applied to molecular shape problems in the spirit of Walsh's rules, see B. M. Gimarc, *J. Amer. Chem. Soc.*, **92**, 266 (1970); **93**, 593, 815 (1971).

(15) All angles were assumed tetrahedral. A C-C bond length of 1.54 Å, C-H bond lengths of 1.1 Å, and a 1s hydrogen AO exponent of 1.2 were used.

(16) J. P. Lowe, *J. Amer. Chem. Soc.*, **92**, 3799 (1970).

(17) In other methods of computation, the energy-level order may be different so that e_g becomes the highest occupied MO. See J. P. Lowe, *J. Amer. Chem. Soc.*, **94**, 3718 (1972).

Table I. EHMO Energy Changes in Ethane

MO (staggered)	Energy, au	Energy change (ecl - stag), au
	-0.479669	-0.000216
	-0.513802	+0.003349
	-0.563733	-0.002122
	-0.756036	+0.000161
	-0.903140	+0.000011
Net ^a	-8.587826	+0.004816 (3.02 kcal/mol)

^a One must double contributions from e-type MO's and then double all energies because of double orbital occupancy.

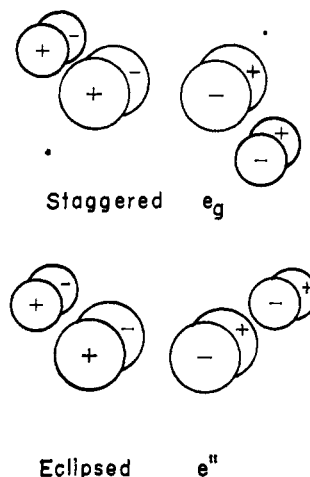
Inspection of Figure 1 leads to the conclusion that the overlap between vicinal hydrogens in this MO decreases (*i.e.*, becomes more negative). Therefore, this MO should rise in energy upon rotation to the eclipsed form¹⁸ and should dominate all the other orbital energy changes, causing the *total* energy to be higher for the eclipsed conformation. The data in Table I show that the EHMO energy changes are in accord with this W-H approach. If we further examine the directions of all the other EHMO energy changes, we see that they all accord with our qualitative orbital overlap argument except for the lowest energy MO. This one, of a_g symmetry, prefers to keep the hydrogen AO's staggered even though they are in phase. We will explain this exception later.

The foregoing observations suggest that the EHMO energy barrier is "due to" vicinal hydrogen interactions.^{19,20} We might anticipate, then, that our population analysis of the EHMO barrier *via* (12) will show that the changes in Mulliken overlap populations between vicinal hydrogens dominate all other changes. However, the data (Table II) do not show this at all. The largest individual contribution to the total EHMO energy change comes from the C-C bond, which suffers a population decrease upon rotation from the staggered to the eclipsed form. (This arises almost entirely from the p_π type overlap populations which become more negative.) This contribution alone is more than twice

(18) Notice that rotation by 180° of a CH₃ group of staggered ethane would cause $e_g \rightarrow e'$ if the p AO rotates. A rotation of only the hydrogens does not lead to any of the eclipsed MO's. In order to go from e_g to e' , we could flip two hydrogens up and one hydrogen down. In other words, the usual techniques of following AO's through a nuclear translation or setting up a symmetry correlation diagram just produce trouble here. We are better off simply comparing similar MO's in the two forms without worrying about interconnecting routes.

(19) For a recent review of theories of the source of the barrier, see J. P. Lowe, *Science*, **179**, 527 (1973).

(20) M. S. Gordon, *J. Amer. Chem. Soc.*, **91**, 3122 (1969).

**Figure 1.** One of the degenerate MO's of ethane shown in the staggered and in the eclipsed conformations.**Table II.** Population Changes and Related EHMO Energy Changes for Ethane^{a-d}

AO's	Δ pop (total)	ΔE (total)	$\Delta\epsilon_{e''-e_g}$
h_a-h_b	-0.0072	+0.0063	+0.0078
h_a-h_a'	+0.0012	-0.0010	-0.0014
h_a-h_a	-0.0048	+0.0024	+0.0040
$2s_a-2s_b$	-0.0008	+0.0005	0.0
$2s_a-2p_b$	+0.0016	-0.0015	0.0
$2p_a-2p_b$	-0.0169	+0.0112	+0.0016
Net C_a-C_b	-0.0161	+0.0102	+0.0016
$2s_a-2s_a$	+0.0018	-0.0013	0.0
$2p_a-2p_a$	+0.0176	-0.0067	-0.0051
Net C_a-C_a	+0.0194	-0.0080	-0.0051
h_a-2s_a	-0.0012	+0.0013	0.0
h_a-2p_a	+0.0138	-0.0106	-0.0046
Net h_aC_a	+0.0126	-0.0094	-0.0046
h_a-2s_b	-0.0006	+0.0006	0.0
h_a-2p_b	-0.0048	+0.0037	+0.0006
Net h_aC_b	-0.0054	+0.0043	+0.0006

^a Energies are in au. ^b Δ means eclipsed minus staggered. ^c The population and energy changes are summed over all contributors of a given type. Thus h_a-h_b refers to all nine interactions between vicinal hydrogens. C_aC_a refers to AO populations on *both* carbons. ^d a and b label the two ends of ethane.

the EHMO barrier. The overlap populations between vicinal hydrogens do change in the anticipated direction and contribute a large term, but many other large contributions exist also, and it is evident that *this* total EHMO energy difference cannot be attributed to a single population change in the molecule.

It is possible to use (11) to analyze the energy change of an individual orbital. An orbital of special interest is the e_g MO, sketched in Figure 1, which we used for the W-H approach. The energy-population analysis for this MO is in the right-hand column of Table II. For this MO energy change, the end-to-end hydrogen population changes do indeed dominate. But, again, other large terms are present.

This analysis forces us to conclude that EHMO energy changes are arising from population changes all over the molecule. This would suggest that "explanations" based solely on end-to-end hydrogen interactions are unrealistic. However, we will now show that this conclusion is dependent on our point of view.

Frozen-Orbital EHMO Energy Change

The population and energy changes calculated above were obtained by comparing the results of two independent variational calculations. Let us refer to these as "variational" population and energy changes. Upon consideration, it seems that these variational changes are not the same quantities that are dealt with in the W-H approach. In the W-H approach, we pick an MO and guess whether the AO overlaps will increase or decrease upon distortion of the framework, *assuming no changes in the MO coefficients*. This suggests that we should treat the total process as the sum of two steps. In step 1, the nuclei move but the MO coefficients remain unchanged except for a renormalization to keep the total MO population fixed at an integral number of electrons. We will call the EHMO energy change associated with this step the "frozen-orbital" energy change. In step 2, the coefficients in all the MO's are allowed to vary to reach their final values as determined by the variational procedure. We refer to this step as a "frozen-orbital relaxation." Because the MO's are not all necessarily orthogonal after step 1, one of the tasks of step 2 is to reorthogonalize the MO's.^{21,22}

A simple and exact computational equivalent for step 1 can be constructed from our existing equations. Suppose we had a normalized MO ϕ_i with energy ϵ_i as given by (10) and that we then caused two AO's, χ_a and χ_b , to move with respect to each other so that $S_{ab}' = S_{ab} + \delta_{ab}$. Assuming no other overlap changes and no changes in the coefficients, the new energy for this MO is (by inspection of (10) and (6))

$$\epsilon_i' = \frac{\epsilon_i + [2c_{ai}c_{bi}\delta_{ab}K(H_{aa} + H_{bb})/2]}{1 + 2c_{ai}c_{bi}\delta_{ab}} \quad (15)$$

Let

$$\Delta_{ab}^i \equiv 2c_{ai}c_{bi}\delta_{ab} = p_{ab}^i\delta_{ab}/S_{ab} \quad (16)$$

The quantity Δ_{ab}^i is the i th MO's contribution to the Mulliken overlap population change resulting from the overlap change. In terms of this quantity, the new orbital energy is

$$\epsilon_i' = \frac{\epsilon_i + \Delta_{ab}^i K(H_{aa} + H_{bb})/2}{1 + \Delta_{ab}^i} \quad (17)$$

and the orbital energy change is

$$\epsilon_i' - \epsilon_i = \frac{\Delta_{ab}^i}{1 + \Delta_{ab}^i} [(K(H_{aa} + H_{bb})/2) - \epsilon_i] \quad (18)$$

(When several overlaps change upon nuclear motion, the individual terms in (17) depending on a and b must be replaced by sums. To keep the discussion as simple as possible, we will continue to suppose that only one overlap change has occurred, although data from our ethane example have required us to use sums.)

Before discussing these equations further, let us see how well the frozen-orbital EHMO energy changes (step 1) agree with the variational changes (steps 1 + 2) in ethane. The changes are compared in Table III,

(21) In a molecule with high symmetry in the "before" and "after" conformation, like ethane, symmetry differences will continue to guarantee orthogonality between many MO's after step 1.

(22) The orthogonality problem will create difficulties if one tries to do a frozen-orbital calculation in the Hartree-Fock framework. For a somewhat different frozen-orbital calculation on ethane, see O. J. Sovers, C. W. Kern, R. M. Pitzer, and M. Karplus, *J. Chem. Phys.*, **49**, 2592 (1968).

Table III. EHMO Variational and Frozen-Orbital Energy Changes in Ethane

MO	$-\Delta\epsilon$, au	
	Frozen orbital	Variational
$a'-a_g$	-0.000374	-0.000216
$e'-e_g$	+0.003398	+0.003349
$e'-e_u$	-0.002084	-0.002122
$a'-a_u$	+0.000181	+0.000161
$a'-a_g$	+0.000004	+0.000011
Net	+0.00487 (3.06 kcal/mol)	+0.00482 (3.02 kcal/mol)

and the degree of agreement can be seen to be very good. The total frozen-orbital EHMO barrier is only 1% higher than the variational barrier. We do not expect that EHMO frozen-orbital energy changes will always agree so well with EHMO variational energies. But for processes like rigid conformational change, where the perturbation on populations is small,²³ the agreement should be good. In such cases, any qualitative argument which correctly predicts the frozen-orbital EHMO energy change will also be correct for the variational EHMO energy change. We will argue that this is the case for the W-H approach.

Notice that the frozen-orbital energy change for the lowest energy MO shows the same "reversed" behavior as the variational energy change described earlier. For some reason, an overlap increase between AO's in this MO leads to an energy increase instead of the expected decrease. A mathematical explanation for this is provided by (18). The sign of the energy change is determined by two factors: the sign of Δ_{ab}^i and the sign of the term in square brackets. If ϵ_i is higher in energy than $K(H_{aa} + H_{bb})/2$, then a positive Δ_{ab}^i will produce the expected energy decrease. Reversed behavior occurs when ϵ_i falls below this value. In the case of hydrogen-hydrogen interactions, $K(H_{aa} + H_{bb})/2$ equals -0.875 au. From Table I, we see that all MO's but the lowest are above this energy, so only the lowest energy MO displays this reversed behavior.

The connections between (18) and the two-step W-H approach are very direct. The W-H approach seeks to focus on the MO having the largest energy change. By choosing a high-energy occupied MO, we maximize the magnitude of the term in square brackets. By guessing the sign of the orbital overlap change, we guess the sign of Δ_{ab}^i and therefore the sign of $\epsilon_i' - \epsilon_i$. It is evident that the remaining important factor is the *magnitude of Δ_{ab}^i* and that this factor is not explicitly included in our two-step formulation of the W-H approach. It is this factor that made us choose the e_g MO of ethane for our W-H argument, rather than the slightly higher energy a_g MO. The a_g MO has such high symmetry that the rotation from staggered to eclipsed form results in a rather small Δ . An e type MO is more lopsided and produces a much larger Δ . This need sometimes to appeal to other than the highest occupied MO has also been recognized in other applications of the W-H approach.²⁴ Because

(23) One must be careful, in using these population-change formulas, to avoid situations where a reversal of phase relations between AO's occurs upon rotation. The formulas assume no coefficient change in relative magnitude or sign. The sign-reversal difficulty comes up, for instance, in treating the mate of the e_g MO shown in Figure 1.

(24) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972); S. David, O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffmann, *J. Amer. Chem. Soc.*, **95**, 3806 (1973).

of the close connections between the W-H approach and (18), we maintain that *the W-H approach is a shortcut procedure for qualitatively predicting the results of a frozen-orbital EHMO energy change*. When the frozen-orbital energy change is in qualitative agreement with the variational energy change (and this should normally be the case), then *the W-H procedure is a shortcut for qualitatively predicting the results of EHMO energy calculations*.

There is a simple physical picture associated with the frozen-orbital energy changes. Consider (17). The numerator gives the new energy as the old energy plus a contribution from the population change times $K(H_{aa} + H_{bb})/2$. (It is the sign of this contribution that step 2 of the W-H procedure provides.) But, when we change (say, increase) the Mulliken overlap population in the a-b region while keeping it fixed elsewhere, we end up with a total MO population corresponding to more electronic change than we began with. To compensate, we renormalize, which means that we remove bits of population from all AO's and overlaps in the system. But these bits were contributing to the energy, so we pay an energy price for their removal. This is accounted for by the denominator of (17). The net result is that an EHMO frozen-orbital energy change is the change resulting from shifting bits of Mulliken population from everywhere in the molecule to the region of increasing overlap (or from the region of decreasing overlap to everywhere in the molecule). The lower the energy of the orbital, the more the energy change reflects the energy involved in taking bits from, or giving bits to, the entire molecule and the less it reflects the energy involved in increasing or decreasing the a-b population. Picking a high-energy MO, then, may be viewed as picking an MO where the electronic charge is very polarizable so that charge is available at low-energy cost for shifting in or out of some overlap region. This is in complete qualitative accord with the standard arguments based on perturbation theory.²⁵

What does all this lead to in the way of a simple explanation for the source of the EHMO energy barrier to rigid internal rotation in ethane? We can say that eclipsed ethane is disfavored by the frozen-orbital energy change of the e_g - e'' MO because the change in energy due to changes in overlap populations between vicinal hydrogens dominates the population-change effects everywhere else in the molecule for this MO. Furthermore, we can say that this MO dominates the total frozen-orbital energy change because of its high energy and large overlap population change. Finally, we can say that subsequent population shifts occurring in the frozen-orbital relaxation step have almost no effect on the energies.²⁶ *Within the context of these remarks*, it is correct to state that the barrier in the total EHMO energy is due to a "repulsive" interaction between vicinal hydrogens due to a negative overlap

(25) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543 (1968).

(26) We can tell that significant population shifts occur in step 2 by examining Table II. The data for the e_g MO indicate that the carbon atom populations must have increased upon rotation from staggered to eclipsed, while the hydrogen populations decreased. These changes are the sum of changes from steps 1 and 2. The renormalization process involved in step 1 could not produce changes in opposite directions like this. Therefore, significant shifting of population occurs in step 2. It is well known that significant shifts of population may have very little effect on the energy when we are near the variational minimum, where ϵ is by definition stable with respect to variations of coefficients in ϕ .

population in the e_g MO.^{9,16,20} However, it is equally valid to refer to the data in Table II and say that the principal component of the EHMO energy barrier comes from a decreased C-C population in the eclipsed form. Different modes of analysis lead to different verbal descriptions.

The W-H Approach, the EHMO Method, and Experiment

In view of the above discussion, we expect the W-H approach to be in accord with experiment only when the EHMO method is in such accord. We put the question as follows. When does a change in EHMO energy (accompanying nuclear displacement) qualitatively agree with the actual change in electronic plus nuclear-repulsion energy for a system? There are two general conditions which must be met. First, the Mulliken population changes calculated by the EHMO method must be reasonably correct. Second, the actual system's total energy change must parallel the changes in Mulliken populations roughly in the way posited by the EHMO method.

The first requirement is not met in cases where a single-product wave function, or configuration, is not representative of the actual wave function. In such a case an EHMO treatment is analogous to a valence bond treatment with important structures omitted. It is necessary to do configuration interaction calculations to get around this difficulty. Epiotis²⁷ has considered the effects of configuration interaction on W-H rules for several types of reaction.

The second requirement is clearly not met in several important situations. These may be illustrated by considering a simple example. Suppose two 1s AO's are separated by a variable distance R . These AO's combine to form σ_g and σ_u type MO's. As R decreases, the σ_g MO develops larger overlap population while that for the σ_u MO becomes more and more negative. As a consequence, the EHMO energy for the σ_g MO decreases monotonically as R approaches zero while that for the σ_u MO increases. If we imagine that we are dealing with H_2 (σ_g^2), we have an EHMO energy which decreases all the way to $R = 0$ and an actual electronic plus nuclear repulsion energy which decreases with R down to R_e and then rises. For this system, our EHMO energy posit is not obeyed for relative nuclear motions at ranges less than a bond length. If we imagine that we are dealing with He_2^{2+} (σ_g^2), our EHMO energy again falls monotonically as R approaches zero. But the actual total energy for this system rises monotonically due to the dominance of coulomb repulsion (not included in ordinary EHMO calculations), so, for this ionic system, the EHMO energy posit is not obeyed at any range of R . If the system is taken to be He_2 ($\sigma_g^2\sigma_u^2$), the EHMO energy rises monotonically due to the dominance of σ_u .²⁸ Since the total energy also rises monotonically (excluding van der Waals forces), this system satisfies the posited relation at all distances. This example indicates that, when we are dealing with a neutral, non-polar, half-filled-valence-shell system, we cannot trust the EHMO posit for relative displacements of nuclei separated by distances on the order of a bond length

(27) N. D. Epiotis, *J. Amer. Chem. Soc.*, **95**, 1191, 1200, 1206, 1214 (1973).

(28) C. A. Coulson, *Mol. Phys.*, **15**, 317 (1968).

or less.²⁹ When we are dealing with an ionic or highly polar system,⁸ we cannot trust the posit for any nuclear displacement.

Listing situations where the EHMO posit fails does not prove that it will always succeed in the remaining "acceptable" situations. At present, probably the best evidence we have that the posit is usually roughly correct for such acceptable situations is the qualitative agreement between EHMO energy changes (or W-H predictions) and experiment.³⁰

The process of rigid internal rotation about single bonds in most simple molecules avoids the above-listed difficulties, and the EHMO method is rather successful in predicting stable conformations and some approximate barrier values. Because the value of K was selected to guarantee a reasonable ethane barrier,⁵ we might expect the method to be most successful for cases where changes in overlap are occurring between hydrogens separated by distances similar to those between vicinal hydrogens in ethane. Situations where the separation distance is very different (e.g., dimethylacetylene) might be expected to show substantial numerical error in EHMO results since it is unlikely that the K value appropriate for relating total energy change to overlap change is invariant to distance.³¹

For the more varied kinds of nuclear motions involved in reaction paths,² we expect less quantitative accuracy from the EHMO method. However, if the reactions involve uncharged nonpolar molecules, if

(29) The EHMO prediction that H₂ collapses has been recognized from the outset (ref 5). This collapse is not predicted for C-H bonds because the overlap between a hydrogen 1s AO and one of the carbon 2p AO's can first increase and then decrease as R_{C-H} decreases. As a result, the EHMO total energy is lowest at around $R_{C-H} = 1 \text{ \AA}$, and then it rises toward a finite energy limit as R_{C-H} approaches zero. This finite limit (which is infinite in the actual system) is characteristic of the weighted populations assigned by the EHMO method as the molecule approaches collapse to a united atom. For an example of EHMO energies as a function of R_{C-H} , see ref 5, Figures 1 and 2.

(30) Another approach, perhaps more satisfying for some, would be systematically to compare changes in Mulliken populations and total energies as given by *ab initio* calculations. An alternative method, the direct comparison of EHMO and *ab initio* MO energy changes, is not appropriate for purposes of examining the posited relation because the physical interpretations of these energies are so different. Such an approach is useful in other ways, however (ref 8).

(31) Note that K has been evaluated by reference to a half-filled valence-shell system. As a result, all the nuclear-nuclear repulsion changes must be included in the energy changes of the lowest energy half-set of ethane MO's. It seems likely, then, that this K value will be most appropriate for neutral systems having only half their valence MO's doubly occupied.

the activation energy maximum occurs while the pertinent atoms are well separated, and if the activated complex is reasonably well represented by one MO configuration,³² the qualitative results of EHMO calculations and of W-H approaches should be correct. The experience seems to be that W-H predictions for reactions within these limitations are generally successful.

Summary and Conclusions

(1) An EHMO energy change is quantitatively related to Mulliken population changes. Analysis of a total EHMO energy change in such terms provides one kind of explanation for the change.

(2) An EHMO energy change may be subdivided into (a) a frozen-orbital energy change (normality of individual MO's maintained) followed by (b) relaxation of coefficients to reach the variational minimum. The first of these steps provides a second kind of explanation, one which is similar in spirit to the Woodward-Hoffmann or frontier orbital approach. A formula for step 1 enables one to assess quantitatively the postulates underlying the Woodward-Hoffmann approach.

(3) The understanding of the dependence of EHMO total energy on the Mulliken populations enables one to identify the conditions where EHMO total energy changes should not follow observed total energy changes. These conditions involve ionic or polar systems, nuclear displacements at short range, and systems having partial open shell character requiring configuration interaction for reasonable accuracy. Such conditions have been recognized already to lead to failure of EHMO and W-H techniques.^{5,8,27}

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(32) Another possibility is that a single configuration is a poor description of the transition state but that the energy orderings established for a reactant only slightly distorted, and hence well described by a single configuration, persist in the transition state.