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MÖBIUS AND HÜCKEL SYSTEMS IN THE SCF AND CI APPROXIMATIONS

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Abstract—Over the last 15 years since the introduction of Möbius–Hückel theory, a number of varied questions has accumulated. The most interesting of these deals with the question of whether or not the Möbius–Hückel theory is valid in the SCF and SCF–CI approximation. This paper presents a treatment which shows that the repulsion and exchange contributions are independent of the Möbius vs Hückel nature of the orbital array. Also it is shown that the one-electron terms are symmetry determined and derive from SCF coefficients. An analytical SCF–CI treatment is given. Several further unanswered questions are also considered.

Many years ago the present author noted that photochemical reactions fall into two categories, those leading directly to the ground state of photoproduct and those in which a radiationless decay process to the ground state surface occurs after some molecular change in bonding of the initial excited state.[1] Of the former, several examples were given including the Norrish Type I fission leading directly to a pair of acyl and alkyl radicals, and also hydrogen abstraction leading directly to an alkyl radical and a hydroxyalkyl radical.[1a,b] Of the latter variety, the Type A dienone rearrangement [1b] was considered, and later it was noted that pericyclic rearrangements should also be included.[1c]

Although both types of photochemical reactions involve diradicals, it is the latter type which is the subject of the present paper which focusses on pericyclic systems. That diradical-like species are indeed involved in pericyclic photo reactions is clear when one considers that for allowed examples, the one-electron treatment predicts a HOMO–LUMO crossing. It is at this point that one has a system which would be antiaromatic in the ground state but which in the excited state has an ideal arrangement of molecular orbitals for facile decay to the ground state.[1c] The relevance of the nonbonding degeneracy to facile decay was first noted by the author in 1966.[1c]

Thus the subject of diradicals and diradicaloids is intimately entwined with the matter of aromaticity, antiaromaticity, and the Möbius–Hückel concept.

The concept of aromaticity is germane to ground state molecules, to transition states, and to photochemistry. The beginning of our understanding of the subject was the Hückel $4N+2$ rule[2a] which put the idea of aromaticity [2b] on a firm basis.[3] The recognition that six electron transition states have low energies was first made by Evans.[4]

At the time, it was not recognized that the Hückel $4N+2$ rule applied to only half of the possible cyclic molecules and transition states. In 1966 the present author reported[6] the categorization of cyclic systems into two general types—Möbius and Hückel. With zero or an even number of sign inversions between adjacent orbitals of a cyclic system, one has a Hückel array, and the $4N+2$ rule is indeed followed. However, for orbital arrays with an odd number of inversions, one has a Möbius system, and the Hückel rule no longer holds. Here the requirements for aromaticity are inverted. A closed shell, stable transition state or molecule is now obtained instead with 4N electrons and an antiaromatic system with $4N+2$ electrons.

Indeed, prior to 1966 there were some molecules possessing Möbius orbital arrays. What was still lacking was the realization that all cyclic systems, whether in ground or transition states, fell into these two categories with the number of electrons and number of sign inversions controlling the aromaticity or anti-aromaticity of the system.[7,9–11]

The Möbius–Hückel generalization[6] was cited in two subsequent publications by Dewar,[12] publications which accepted Zimmerman's theoretical conclusions and which provided a second derivation of the Möbius–Hückel results. This derivation was based on the brilliant, but still approximate, NBMO perturbation method.[13]

However, subsequently a series of less enthusiastic publications by Dewar appeared, each one providing some new criticism of the concept as derived by Zimmerman. The first criticism appeared in 1969.[14a] Dewar argued that Hückel theory was unreliable as a guide to aromaticity and Hückel theory had been employed in the original Möbius–Hückel derivation.[6,14b,15,18]

Most recently, a 1978 paper by Dewar[21] introduced some further criticisms while acknowledging that "The idea that pericyclic transition states might be of the anti-Hückel" (i.e. Möbius) "type was first proposed in print by Zimmerman who restated Evans' theory of pericyclic reactions without acknowledgement".

The present paper deals with the main criticisms of substance, namely that the Möbius–Hückel concept[6,8] suffers a weakness due to the original derivation using Hückel theory.[22]

The question has been addressed by Borden and Salem[23] in the special case of 4-ring pericyclic transition states. Here it was shown that an explicit SCF calculation of the two alternative species, Möbius and Hückel, still led to the Zimmerman prediction deriving from Hückel theory.

In proceeding more generally, we provide an analytical solution to the general SCF problem of cyclic Möbius and Hückel systems.

The starting point is the double group table (Table 1) which encompasses both Möbius and Hückel symmetries.

Table 1.

C_n		C_o	C_1	C_2	C_3	C_4	C_5	C_6	....	C_{N-1}
A		ν^{0}	ν^{0}	ν^{0}	ν^{0}	ν^{0}	ν^{0}	ν^{0}	....	
E_1^M	E_1'	ν^{0}	ν^{1}	ν^{2}	ν^{3}	ν^{4} -	ν^{5}	ν^{6}	....	
	E_1''	ν^{0}	ν^{-1}	ν^{-2}	ν^{-3}	ν^{-4}	ν^{-5}	ν^{-6}	....	
E_2^H	E_2'	ν^{0}	ν^{2}	ν^{4}	ν^{6}	ν^{8}	ν^{10}	ν^{12}	....	
	E_2''	ν^{0}	ν^{-2}	ν^{-4}	ν^{-6}	ν^{-8}	ν^{-10}	ν^{-12}	....	
E_3^M	E_3'	ν^{0}	ν^{3}	ν^{6}	ν^{9}	ν^{12}	ν^{15}	ν^{18}	....	
	E_3''	ν^{0}	ν^{-3}	ν^{-6}	ν^{-9}	ν^{-12}	ν^{-15}	ν^{-18}	....	
E_4^H	E_4'	ν^{0}	ν^{4}	ν^{8}	ν^{12}	ν^{16}	ν^{20}	ν^{24}		
	E_4''	ν^{0}	ν^{-4}	ν^{-8}	ν^{-12}	ν^{-15}	ν^{-20}	ν^{-24}	....	
⋮		⋮			⋮			⋮		
B		ν^{0}	ν^{N}	ν^{2N}	ν^{3N}	ν^{4N}	ν^{5N}	ν^{6N}	....	

Here ν is defined as in eqn (1) and N is the number of basis orbitals.

$$\nu = e^{i\pi/N} \tag{1a}$$

$$\nu^{N} = -1 \quad \text{and} \quad \nu^{2N} = +1. \tag{1b, c}$$

Thus Möbius systems can contain the representations E_1, E_3, E_5, etc...... and B while Hückel systems can contain the A, E_2, E_4, E_6,..... etc. representations.[24] The significance of eqns (1b) and (1c) is that a 360° rotation in a Möbius system converts each basis orbital into its negative while in a Hückel system the basis orbital is regenerated with the original sign. This can be seen in eqn (2) where R is the 360° rotation operator $R = \nu^{kN}$, N is the number of basis orbitals and k is the MO number which will be odd for Möbius systems and zero or even for Hückel ones.

$$R\chi_r = \nu^{kN}\chi_r = (e^{i\pi kN})\chi_r = \pm\chi_r \tag{2}$$

(with the + sign for k being 0 or even and − sign for k odd). Here the subscript r is used to represent any arbitrary orbital in the basis set.

In constructing a Möbius or Hückel MO we use as LCAO MO coefficients the characters selected from the appropriate representation. For example, we use the A characters for the lowest energy Hückel MO, followed by the E_2^H characters for the next degenerate pair of MO's. For Möbius systems, we begin with the E_1^M characters for the first degenerate pair of MO's followed by E_3^M for the next pair, etc. This is justified in the basic derivation of the eigenvectors.[25] The system's energy is given by:

$$E = \sum_k n_k I_k + \sum_{k \le m} n_{km} G^{MO}_{kmkm} - \sum_{k \le m} m_{km} G^{MO}_{kmmk} \tag{3}$$

where n_k is the occupation number of MO k, n_{km} gives the number of pairs of electrons with one from MO k and the other from MO m, and m_{km} gives the number of pairs of electrons from MO's k and m, but with the same spin.

The first term in eqn (3) is the total of one-electron energies for the Möbius and Hückel systems under consideration. We note that the LCAO MO coefficients taken from our double group table are symmetry determined and thus are SCF coefficients. That this term is lower in energy for Möbius systems with 4N electrons or for Hückel systems with 4N+2 electrons has already been established in our earlier work.[6]

Hence it is the last two terms which need to be compared for Hückel and Möbius systems. The positive term is the sum of molecular orbital repulsion integrals, and the negative term is the sum of MO exchange integrals.

These MO repulsion and exchange integrals are readily expressed in terms of atomic orbital or other (e.g. hybrid) localized orbitals. Thus, in the ZDO approximation,

$$G^{MO}_{kmkm} = \sum_{r,s} C_{rk}C_{sm}C^*_{rk}C^*_{sm}\gamma_{rs} \tag{4}$$

and

$$G^{MO}_{kmmk} = \sum_{r,s} C_{rk}C_{sm}C^*_{rm}C^*_{sk}\gamma_{rs} \tag{5}$$

where γ_{rs} is a two-center integral representing repulsion between two electrons, one in basis orbital r and one in s. The asterisk signifies the complex conjugate. In this connection we note that the pairs of vectors given by any representation in the double group table are indeed composed of complex conjugates

Furthermore, the group table provides the SCF LCAO MO coefficients needed to evaluate the MO repulsion and exchange integrals. Thus substitution into eqns (4) and (5) from the character table leads to eqns (6) and (7a) respectively.

$$G^{MO}_{kmkm} = (1/N^2)\sum_{r,s} \nu^{rk}\nu^{sm}\nu^{-rk}\nu^{-sm}\gamma_{rs}$$

$$= (1/N^2)\sum_{r,s} \gamma_{rs} = (1/N)\sum_{r} \gamma_{0r} \tag{6}$$

Here k and m are MO numbers: 0 for Hückel representation A, 1 and −1 for Möbius representation E_1^M, 2 and −2 for Hückel representation E_2^H, etc.

It is seen that the MO repulsion integral G_{kmkm} has a value which is independent of k and m and therefore not dependent on the Möbius or Hückel nature of the orbital array. In fact, the repulsion energy is seen to be just the sum of all of the one-center and two-center electron–electron repulsions.

For the exchange integral, insertion of the LCAO-coefficients gives

$$G^{MO}_{kmmk} = (1/N^2)\sum_{r,s} \nu^{rk}\nu^{sm}\nu^{-rm}\nu^{-sk}\gamma_{rs}$$

$$= (1/N^2)\sum_{r,s} \nu^{(r-s)(k-m)}\gamma_{rs} \qquad (7a)$$

For any given Möbius or Hückel molecule, there will be a group of occupied MO's. Each pair of occupied MO's corresponds to a k value and an m value and thus a (k − m). It is readily seen that two corresponding Möbius and Hückel molecules with the same number of orbitals have the same set of (k − m) values.

This means that the Möbius and Hückel systems will consist of the same summation (note eqn 7a) of exchange integrals.

That the (k − m) values do come in matching pairs can be seen by reference to Fig. 1. This might be pictured as part of a generalized circle mnemonic[6,8,26] giving the energies of both some Möbius system and its Hückel isomer. This is then a juxtaposition of the Zimmerman circle mnemonic[6,8] for Möbius systems with that of Frost and Musulin[27] for Hückel ones.

It can be seen that for any pair of isomers, there will be the same distributions of differences in occupied MO's (i.e. in their k and m values) as a consequence of these MO's being in a regular sequence.... −3, −2, −1, 0, +1, +2, +3,... with the differences being 0 or some multiple of 2 for both Möbius and Hückel arrays.

Equation (7a) can be recast in real form by recognizing that r and s are arbitrary indices. Rewriting (7a) as (7b)

$$G^{MO}_{kmmk} = (1/N^2)\sum_{r,s} \nu^{(s-r)(k-m)}\gamma_{rs} \qquad (7b)$$

and then adding eqns (7a) and (7b) and dividing by two, we obtain

$$G^{MO}_{kmmk} = (1/N^2)\sum_{r,s} [\mathrm{Cos}\,(s-r)(k-m)\pi/N]\gamma_{rs} \qquad (8)$$

If we begin numbering our atoms at s = 0 and realize due to symmetry that the double summation just provides N duplicates of each term, we have

$$G^{MO}_{kmmk} = (1/N)\sum_{\substack{r=0\\N-1}} [\mathrm{Cos}\, r(k-m)\pi/N]\gamma_{r0}. \qquad (9)$$

Independent of the Möbius and Hückel character of the array, (k − m) is some multiple of 2; and, as noted above, the G^{MO}_{kmmk} values come in matching pairs for the Möbius and Hückel systems.

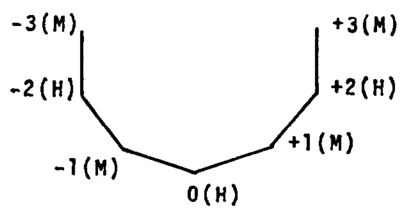


Fig. 1. Distribution of k and m values in Möbius and Hückel systems.

Hence the total SCF energy is readily shown to be

$$E_{SCF} = 2\sum_{k}^{occ} I_k + (Z(2Z-1)/N)\sum_{\substack{r=0\\N-1}} \gamma_{ro}$$

$$-(2/N)\sum_{r,k<m}^{occ} [\mathrm{Cos}\,(r(k-m)\pi/N)]\gamma_{r0} \qquad (10)$$

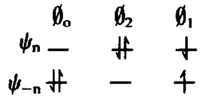
(Z is the number of occupied MO's)

and the two-electron contribution to this energy is independent of the Möbius or Hückel nature of each N orbital array. The two-electron contributions to the SCF energies as well as some typical integrals are listed in Table 2.

Thus, in the SCF ZDO approximation both the repulsion and the exchange modifications of the one-electron Hückel energies are the same for the Möbius as for the Hückel cycle. Also, the one-electron contributions derive from SCF coefficients as a result of symmetry.

It is to be noted that the above comparison of a Möbius and Hückel rings of the same size uses simple SCF wave functions. In this, one of the two systems has a closed shell configuration and the other an open shell. The use of a single configuration in this approximation could be justified since it is the one approached adiabatically in a pericyclic reaction as the degeneracy is reached.

However, at the degeneracy the approximation is not ideal. The actual states of the open shell systems are really linear combinations of the three configurations $\emptyset_o$, $\emptyset_2$ and $\emptyset_1$:



where ψ_n and ψ_{-n} are the highest doubly occupied degenerate pair of MO's for a given open shell molecule.

In each case $\emptyset_o$ and $\emptyset_2$ are degenerate and $\emptyset_1$ is of higher energy by $2G_{kmmk}$ (i.e. $2G_{k^*m^*mk}$) where k and m must be taken as the degenerate pair of MO's (i.e. +n and −n) containing the two electrons. This integral can be evaluated by use of eqns (7), (8) or (9) (note below).

Admixture of the three configurations $\emptyset_o$, $\emptyset_2$ and $\emptyset_1$ requires knowledge of the off-diagonal matrix elements. Those between $\emptyset_1$ and $\emptyset_o$ or $\emptyset_2$ can be shown to be zero, signifying that $\emptyset_1$ does not mix further. The matrix element between $\emptyset_o$ and $\emptyset_2$ is G_{kkmm} (i.e. $G_{k^*k^*mm}$) where, again, k and m are the doubly occupied degenerate pair.

Proceeding along lines similar to those for the earlier integrals we can obtain the expression in eqns (11) and (12).

$$G_{kkmm} = (1/N^2)\sum_{r,s} \nu^{(r+s)(k-m)}\gamma_{rs} \qquad (11)$$

$$G_{kkmm} = (1/N^2)\sum_{r,s} \cos\,[(r+s)(k-m)\pi/N]\gamma_{rs}. \qquad (12)$$

We note that in general this integral is not the same as G_{kmkm} due to the first two subscripts representing complex conjugates. However, for the special case of even

Table 2. Typical values of integrals and total 2-electron contributions to the SCF energies in analytic form

Species	Possible MO Repulsion Integrals G_{kmkm}	Possible Exchange Integrals G_{kmmk}	Summed 2-Electron Energies
Three-Ring Cations	$G^{MO}_{-1-1-1-1}$, G^{MO}_{1111} G^{MO}_{0000} Each = $(1/3)\gamma_{11} + (2/3)\gamma_{12}$	None	Repulsion Contribution: $(1/3)\gamma_{11} + (2/3)\gamma_{12}$ Exchange Contribution: None Total Electron-electron Interaction Energy: $(1/3)\gamma_{11} + (2/3)\gamma_{12}$
Three-Ring Anions	$G^{MO}_{-1-1-1-1}$, G^{MO}_{1111}, G^{MO}_{-11-11} G^{MO}_{0000}, G^{MO}_{2222}, $G^{MO}_{-2-2-2-2}$, G^{MO}_{0202} Each = $(1/3)\gamma_{11} + (2/3)\gamma_{12}$	G^{MO}_{1-1-11} G^{MO}_{0220}, G^{MO}_{0-2-20} Each = $(1/3)\gamma_{11} - (1/3)\gamma_{12}$	Repulsion Contribution: $2\gamma_{11} + 4\gamma_{12}$ Exchange Contribution: $-[(2/3)\gamma_{11} - (2/3)\gamma_{12}]$ Total Electron-electron Interaction Energy: $(4/3)\gamma_{11} + (14/3)\gamma_{12}$
Four-Ring	$G^{MO}_{-1-1-1-1}$, G^{MO}_{1111}, G^{MO}_{1-11-1}, G^{MO}_{0000}, $G^{MO}_{-2-2-2,-2}$ G^{MO}_{2222}, G^{MO}_{-20-20} Each = $1/4\gamma_{11} + 1/2\gamma_{12} + 1/4\gamma_{13}$	G^{MO}_{0220}, G^{MO}_{-111-1} Each = $(1/4)\gamma_{11} - (1/4)\gamma_{13}$	Repulsion Contribution: $(3/2)\gamma_{11} + 3\gamma_{12} + (3/2)\gamma_{13}$ Exchange Contribution: $-[(1/2)\gamma_{11} - (1/2)\gamma_{13}]$ Total Electron-electron Interaction Energy: $\gamma_{11} + 3\gamma_{12} + 2\gamma_{13}$
Benzene	G^{MO}_{0000}, $G^{MO}_{-2-2-2-2}$, G^{MO}_{2222}, G^{MO}_{-20-20}, G^{MO}_{0202}, G^{MO}_{-22-22} $G^{MO}_{-1-1-1-1}$, G^{MO}_{1111}, G^{MO}_{3333}, $G^{MO}_{-3-3-3-3}$, $G^{MO}_{-3-1-3-1}$, G^{MO}_{-31-31}, G^{MO}_{-11-11}, G^{MO}_{-13-13}, G^{MO}_{1313} Each = $(1/6)\gamma_{11} + (1/3)\gamma_{12} + (1/3)\gamma_{13} + (1/6)\gamma_{14}$	G^{MO}_{-200-2}, G^{MO}_{0220}, G^{MO}_{-222-2} $G^{MO}_{-3-1-1-3}$, G^{MO}_{-311-3}, G^{MO}_{-11-11}, G^{MO}_{-133-1}, G^{MO}_{1331} For k-m = ±2, G_{kmmk} = $(1/6)\gamma_{11} + (1/6)\gamma_{12} - (1/6)\gamma_{13} - (1/6)\gamma_{14}$ For k-m = ±4, G_{kmmk} = $(1/6)\gamma_{11} - (1/6)\gamma_{12} - (1/6)\gamma_{13} + (1/6)\gamma_{14}$	Repulsion Contribution: $(5/2)\gamma_{11} + 5\gamma_{12} + 5\gamma_{13} + (5/2)\gamma_{14}$ Exchange Contribution: $-[\gamma_{11} + (1/3)\gamma_{12} - \gamma_{13} - (1/3)\gamma_{14}]$ Total Electron-electron Interaction Energy: $(3/2)\gamma_{11} + (14/3)\gamma_{12} + 6\gamma_{13} + (17/6)\gamma_{14}$

Footnotes: Where an option is available of which degenerate members to use, all possible integrals of interest are given in the second column. The basis set integrals are numbered in the more common fashion (e.g. γ_{11}, γ_{12}, etc.) rather than the γ_{01}, γ_{02}, etc. equivalents used in the text, for mathematical simplicity. Both integrals encountered in Möbius systems and those for Hückel systems are listed. The calculated energies are independent of which degenerate member is occupied for the antiaromatic system and are self-consistent as a consequence of the symmetry. The same energy is obtained for single occupation of each of the two degenerate members by opposite spin electrons but the operator will not be self-consistent in this case.

systems, k − m = N; and, it can be shown that then G_{kkmm} does become equal to G_{kmmk}.

Beyond this, it can be demonstrated that for the odd series G_{kkmm} vanishes. For the even series G_{kkmm} can be shown to have the form

$$G_{kkmm} = G_{kmmk} = (1/N)\gamma_{11} - (2/N)\gamma_{12} + (2/N)\gamma_{13} \ldots - (1/N)\gamma_{1N}. \quad (13)$$

Here the signs weighting the one-center and two-center basis set repulsion integrals alternate. A weighting of 1/N is found when each center has only one other at the appropriate distance, while 2/N results when there are two centers at the same distance.

Hence, prior to configuration interaction in the open shell cases we have a degenerate pair of configurations, ϕ_o and ϕ_2, and a higher energy configuration ϕ_1. For the odd sized rings, no further interactions occur and these correspond to final states; linear combinations such as $(1/\sqrt{2})(\phi_o \pm \phi_2)$ are equally acceptable. Thus, for the

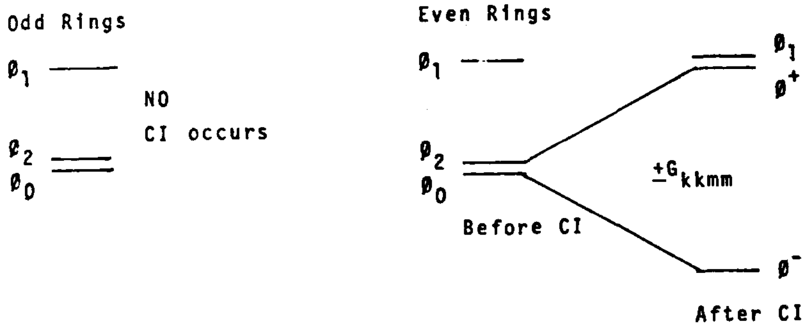


Fig. 2. Patterns of states of open shell systems.

odd ring cases the energy comparisons of the SCF level are unchanged by any configuration interaction of the type considered.

For the even rings, the result of configuration interaction is splitting of the $\emptyset_o$ and $\emptyset_2$ configurations to give a lower energy and a higher energy state. The higher state $(1/\sqrt{2})(\phi_o+\phi_2)=\phi^+$ becomes degenerate with ϕ_1. The ground state is $S_o=\phi^-=(1/\sqrt{2})(\phi_o-\phi_2)$ and is lower than the separate configurations by G_{kkmm}. This situation is depicted in Fig. 2 and some typical energies are given in Table 3. The 4-ring example is in agreement with the results of Borden and Salem for S_o.[21] Also, the

Table 3. Energies after CI

Möbius 3-Ring, 2 Electrons

$E_0 = E_2 = 2I_1 + (1/3)\gamma_{11} + (2/3)\gamma_{12}$

$E_1 = 2I_1 + (2/3)\gamma_{11} + (1/3)\gamma_{12}$

$G_{-111-1} = (1/3)\gamma_{11} - (1/3)\gamma_{12}$

$G_{-1-111} = 0$

Hückel 3-Ring, 4 Electrons

$E_0 = E_2 = 2I_0 + 2I_2 + (4/3)\gamma_{11} + (14/3)\gamma_{12}$

$E_1 = 2I_0 + 2I_2 + (5/3)\gamma_{11} + (13/3)\gamma_{12}$

$G_{-222-2} = (1/3)\gamma_{11} - (1/3)\gamma_{12}$

$G_{-2-222} = 0$

Hückel 4-Ring, 4 Electrons

$E_0 = 2I_0 + 2I_2 + (3/4)\gamma_{11} + (7/2)\gamma_{12} + (7/4)\gamma_{13}$

$E_2 = E_1 = 2I_0 + 2I_2 + (5/4)\gamma_{11} + (5/2)\gamma_{12} + (9/4)\gamma_{13}$

$G_{-222-2} = (1/4)\gamma_{11} - (1/2)\gamma_{12} + (1/4)\gamma_{13}$

$G_{-2-222} = G_{-222-2}$

Hückel 5-Ring, 4 Electrons

$G_{-2-222} = 0$

Mobius 6-Ring, 6 Electrons

$E_0 = E_2 = 2I_1 + 2I_3 + (4/3)\gamma_{11} + 5\gamma_{12} + (17/3)\gamma_{13} + 3\gamma_{14}$

$E_1 = 2I_1 + 2I_3 + (5/3)\gamma_{11} + (13/3)\gamma_{12} + (19/3)\gamma_{13} + (8/3)\gamma_{14}$

$G_{-3-333} = (1/6)\gamma_{11} - (1/3)\gamma_{12} + (1/3)\gamma_{13} - (1/6)\gamma_{14}$

$G_{-3-333} = G_{-333-3}$

results are the same as derived from use of real MO's and configuration interaction.

Then, we are left with the observation that the open shell systems with an even number of orbitals are stabilized by configuration interaction to the extent given in eqn (13) and Table 3 while the closed shell, aromatic systems do not have parallel stabilization. However, inspection of eqn (13) with insertion of typical values leads us to minuscule stabilization (0.26 eV for the 4-ring, 0.13 eV for the 6-ring, precise values depending on parameterization) compared to the several eV stabilization of the one-electron Möbius–Hückel effects we considered earlier.[28]

The conclusion then is that the Möbius–Hückel approach to dealing with pericyclic reactions and ground state species is unchanged when electron–electron interactions are included.

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[4a] The realization that transition states have delocalization energies and that 6-membered ring transition states would be benzene-like and aromatic was clearly stated. However, it was also stated that stabilization increased with increasing numbers of electrons (i.e. rather than following the 4N + 2 *vs* 4N Hückel rule). Also, 2 + 2 cycloaddition was presented without clear indication whether this was a contrasting or similar example, although it is possible to read this into the text; [b] M. G. Evans, *Trans. Faraday Soc.* **35**, 824 (1939); [c] Note especially unpublished lectures by M. G. Evans as quoted by M. J. S. Dewar.[5]

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[8] H. E. Zimmerman, *Accounts of Chem. Research* **4**, 272 (1971).

[9a] Craig[9b] had considered a series of cyclic phosphorous-nitrogen heterocycles with assumed d-orbital inclusion in a manner such that in retrospect one can detect sign inversions in proceeding around the rings. Both Hückel and Möbius type rings are to be found in this p_π–d_π series which contrasted with a simple cyclic polyene series in showing a smooth energy change on increase of ring size. [b] D. P. Craig, *J. Chem. Soc.* 997 (1959).

[10] Still another isolated example in the literature was an intriguing and elegant treatment by Heilbronner[10b] of twisted cyclic polyenes. As a consequence of the cosine dependence of the resonance integrals between vicinal p-orbitals, an energy expression for the Möbius polyenes was obtained which did not permit a Möbius polyene to be more stable with 4N electrons than the corresponding Hückel one with 4N + 2 electrons. Still, it was this publication which triggered the present author's recognization that Möbius systems already existed generally and could be more stable than Hückel ones; [b] E. Heilbronner, *Tetrahedron Letters* 1923 (1964).

[11a] In a 1965 publication of which the author was previously unaware, Mason[11b] set up four categories of cyclic systems comprising (i) ordinary Hückel cyclic polyenes, (ii) Heilbronner's[10] Möbius annulenes, (iii) Craig's[9] cyclic p_π–d_π systems, and (iv) a corresponding singly twisted p_π–d_π cycle. He quite correctly recognized which of these in present terms are aromatic and which have an open shell. He recognized that alternating members of the Craig p_π–d_π series fell into both of the types typified by Heilbronner's twisted and untwisted annulenes and similarly dissected series iv. In this he noted dependence on the number of resonance integrals of reverse sign. Mainly lacking was the recognition that such an analysis was general and could be applied to organic transition states and molecules and with just two categories. [b] S. F. Mason, *Nature* **205**, 495 (1965).

[12a] M. J. S. Dewar, *Tetrahedron* Suppl. 8, Part I, 75–92 (1966), published in 1967; [b] Note also *Aromaticity* The Chemical Society, London (1967) especially pp. 212–213, which concurred in philosophy and nomenclature (e.g. "Möbius") but noted only ref. 12*a*.

[13] M. J. S. Dewar, *J. Am. Chem. Soc.* **74**, 3350 (1952).

[14a] M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, p. 330. McGraw-Hill, New York (1969); [b] This publication erroneously reported that Craig[9b] discussed the role of phase dislocations (i.e. inversions). However, neither the words nor the concept is to be found in this paper.

[15] Two years later the criticism was posed[16] that the term Möbius was employed to signify systems which were antiaromatic. This, of course, would be an error, but this was not an error made in the Zimmerman publications.[17]

[16] M. J. S. Dewar, *Angew. Chem.* **10**, 761 (1971).

[17] Ref. 16 has several other errors. It is suggested that Dewar in ref. 13 suggested the term *Antiaromaticity* in 1952. This or its equivalent is not found in the 1952 Dewar publication. The introduction of this term and clear definition seems due to Breslow.[19a] Also, in the same 1971 article[15b] it is again stated erroneously that Craig[9b] was the first to point out the topological distinction between aromatic and antiaromatic systems; as noted the paper cited[9b] does not do this and placed Möbius and Hückel systems in one group.

[18] In 1974, in a remarkable publication,[5] Dewar repeated the previous points. Similarly, the Woodward–Hoffmann rules were termed *the Evans Principle*, although Evans' papers[4] did not include Möbius type systems and did not discuss allowed and forbidden reactions.

[19a] R. Breslow, J. Brown and J. J. Gajewski, *J. Am. Chem. Soc.* **89**, 4383 (1967); R. Breslow, *Chem. Eng. News* 2 June, 90 (1965); [b] Note also M. J. S. Dewar, *Adv. Chem. Phys.* **8**, 121 (1965).

[20] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.* **87**, 395 (1965); *Ibid.* 2511; *Ibid.* 2046; *Ibid.* 4389 (1965); [b] For a more contemporary version note *Accounts Chem. Res.* **1**, 17 (1968).

[21] M. J. S. Dewar, *J. Am. Chem. Soc.* **100**, 7499 (1978).

[22] It is to be noted that the alternative Dewar derivation of our concept makes use of first order perturbation theory and nonbonding MO coefficients which are not generally self-consistent.

[23a] T. Borden and L. Salem, *J. Am. Chem. Soc.* **95**, 932 (1973); [b] Note W. T. Borden and E. R. Davidson, *Accounts Chem. Res.* **14**, 69 (1981), for further relevant and more recent results.

[24] The characters of this table are related by a power to those LCAO MO coefficients used in a trial eigenvector in a different approach[25] to determining Möbius and Hückel energies and coefficients.

[25] H. E. Zimmerman, *Quantum Mechanics for Organic Chemists*, p. 113. Academic Press, New York (1975).

[26] H. E. Zimmerman, *Pericyclic Reactions* (Edited by A. P. Marchand and R. E. Lehr). Academic Press, New York (1977).

[27] A. Frost and B. Musulin, *J. Phys. Chem.* **21**, 572 (1953).

[28a] This is the point noted by Salem and Borden[23] in the special case of the 4-ring; [b] This result derives from the alternating sign of the two-center repulsion integrals as weighted in the exchange integral G_{-k-kmm}.