

Tempered Orbital Energies in SCF MO Calculations and Their Relation to the Ordinate in Mulliken–Walsh Correlation Diagrams and Extended Hückel Orbital Energies

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An “average state” of a molecule is defined by distributing the electrons equally among the valence orbitals of a minimal basis set Hartree–Fock calculation. The resulting eigenvalues, called tempered orbital energies, behave much more like the Mulliken–Walsh diagram energies or extended Hückel eigenvalues than do the Hartree–Fock canonical orbital energies.

Key words: Walsh orbitals

1. Introduction

The present paper is concerned with the following three interrelated questions:

- 1) What is to be identified as the ordinate in construction of Mulliken–Walsh [1, 2] (MW) diagrams from Hartree–Fock LCAO–MO SCF theory [3]?
- 2) What are the Hückel or extended¹ Hückel (EH) [4, 5] orbital energies, which generally parallel the ordinate of MW diagrams? And
- 3) In precisely what circumstances can the approximation be made that the total energy E in the Hartree–Fock theory is the simple sum of its canonical orbital energies ϵ_k ? Such an approximation has occasionally been used to justify the methodology of MW rules within the context of Hartree–Fock theory.

In a series of papers of supreme importance for chemistry Mulliken [1] and Walsh [2] formulated a set of rules for predicting the geometry and spectra of

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¹ The term “extended (or three-dimensional) Hückel” has been used in the literature for a number of different schemes, all of which share an assumption of some sort of proportionality of the off-diagonal elements of an effective Hamiltonian to the overlap. We include the special case of iterative EH calculations, considering the iteration a device to produce a suitable parameter set for such calculations. Some of the different forms of the EH method may be found in the following list, which is not comprehensive: Refs. [4a–4j].

triatomic and other polyatomic molecules. In a typical MW diagram one seeks the variations of certain loosely defined but heuristically useful orbital energies with respect to some internuclear coordinate, usually an angular variable. These orbital energies, which form the ordinate of the MW diagrams, were termed “ionization energies” and “binding energies” by their inventors. The changes in these orbital energies with respect to angular variations were deduced on the basis of simple hybridization and overlap arguments. From these changes inferences are drawn concerning the geometries of a family of molecules in their ground and excited states. Rules are derived relating the qualitative features of molecular geometry (whether a molecule is linear or bent) to the number of valence electrons in the molecule. The MW diagrams have had a tremendous impact on spectroscopy and on our feeling of understanding molecular structure in ground and excited states. It is no wonder then that since the original publications there have appeared in the literature numerous articles attempting to formulate or derive these diagrams in a rigorous manner from Hartree–Fock LCAO–MO SCF theory. These contributions have been reviewed by Buenker and Peyerimhoff [6].

As one tries to give a rigorous formulation of the MW diagrams, or the rules governing molecular geometry derived therefrom, the major problem that is confronted is that in the Hartree–Fock SCF theory the total energy E is not equal to a simple sum of orbital energies. Instead

$$E = \sum_k n_k \varepsilon_k - V_{ee} + V_{nn} \quad (1)$$

where the ε_k 's are the canonical orbital energies, n_k the orbital occupation numbers, V_{ee} the electron–electron, and V_{nn} the nuclear–nuclear repulsion energies respectively. Implicit in the MW formulation is a set of “orbital energies” having the property that the changes in the total energy are given at least approximately by the changes in the sum of these orbital energies. The Hartree–Fock energy expression does not present us with a unique or obvious energy partitioning into energy components associated with each molecular orbital such that their sum is the true total energy. Several ingenious energy partitioning schemes have been proposed [7], which have been reviewed by Buenker and Peyerimhoff [6]. In our opinion they have not met with much success. Perhaps most interesting is the recently proposed formalism of Davidson [8]. A set of Internally Consistent SCF (ICSCF) energies is constructed, whose sum is exactly equal to the total energy E , and which have many properties in common with Walsh's binding energies. We shall return to the subject of ICSCF energies later in the paper.

The semiempirical extended Hückel model determines orbital energies ε'_k from a one-electron effective Hamiltonian, whose matrix elements are assigned according to some definite prescription. The relation

$$E = \sum_k n_k \varepsilon'_k \quad (2)$$

is used for calculating the total energy. The orbital energies of EH calculations generally parallel the MW orbital energies, even when they are wrong! Like the

implicit assumption of the MW formalism, in the EH model the changes in the total energy are given by the changes in the sum of orbital energies.

Clearly the energy relations of Eqs. (1) and (2) are at variance. The use of formula (2) has occasionally been rationalized by suggesting that either V_{nm} and V_{ee} largely cancel each other, or $V_{nm} - V_{ee}$ is a slowly varying function of the internuclear separations. Allen, Buenker, Peyerimhoff and their coworkers [9]² have published a series of articles over a span of several years, their thesis being that the ordinate of MW diagrams in SCF theory should be identified with the SCF canonical orbital energy. They have reasoned that the equilibrium geometry is determined by the gradient of the total energy and not the total energy itself, and that the success of the MW rules is to be traced to the fact that for most molecules changes in $V_{nm} - V_{ee}$ are indeed slowly varying functions of geometrical variables. The initial studies in this area were very encouraging, but a number of failures was soon encountered.³ This has prompted Buenker and Peyerimhoff to suggest an alternative procedure [6] for constructing MW diagrams in *ab initio* calculations, and Davidson [8] to define a new set of orbital energies, as described earlier.

There have been suggestions in the literature [5a] to identify the ordinate in the MW diagrams as the orbital energy in the EH method, but the connection between the two remains unclear. It is of interest in this context to point out that in a recent paper Ruedenberg [10]⁴ reported a relationship between the total energy E in HF-SCF theory and the canonical orbital energies ε_k , i.e.

$$E = k \sum_i n_i \varepsilon_i \quad (3)$$

where $k = 1.5$ or 1.55 . This equation is based on previous studies by Politzer [11] and Fraga [12], and holds only at the equilibrium geometry of the molecule. While it is supportive of the general methodology of the EH scheme, it does not guarantee that changes in orbital energies ε_k should dominate the changes in the total energy E .

Are the extended Hückel energies, ε'_k , just approximations to the correct HF canonical energies ε_k ? The previously mentioned work on the relationship of MW diagrams and HF canonical energies and other studies by L. C. Allen and coworkers [13] carry that implication. Several attempts at deriving, justifying, or understanding the EH model from the correct HF SCF theory have been made over the years [14, 15].⁵ Most of these consider the EH way of choosing Fock matrix elements as an approximation to the corresponding *ab initio* SCF Fock matrix elements of the ground state of the molecule. However, for neutral molecules

² The relationship between SCF canonical orbital energies and Walsh's rules was first discussed by means of actual *ab initio* calculations in a series of four papers: Ref. [9a] AH_2 , AH_3 systems; Ref. [9b] B_2H_6 and C_2H_6 ; Ref. [9c] F_2O , Li_2O , FOH , LiOH ; Ref. [9d] O_3 , N_3 . Subsequent calculations on this subject carried out by these workers include Refs. [9e-9p]. For some more references on this subject see footnote 10 of Ref. [6].

³ See pages 132-134 in the review article by Buenker and Peyerimhoff, Ref. [6].

⁴ The approximation of Eq. (3) is less well satisfied when second-row atoms are involved: Ref. [10b].

⁵ For a rather different approach, not based on the HF model, see Ref. [15].

SCF calculations generally put the virtual ε_k at positive energy, but the EH calculations usually have several vacant orbitals below ionization. This distinction has been noted on several occasions, but has not been pursued [16].⁶

In an *ab initio* SCF calculation the canonical orbital energies are functions of the specific state, ground or excited, on which the calculation is being performed. In many of the cases where the SCF ε_k 's do not parallel the MW results the discrepancy is due to the unsatisfactory character of the virtual orbitals in an HF SCF procedure. This difficulty has been described by Stenkamp and Davidson [8b] as follows:

“Because the RHF self-consistent-field procedure treats virtual orbitals in an unsatisfactory manner, the energy assigned to an orbital changes drastically depending on whether it is occupied or empty. Thus in contrast to Hückel theory and Walsh’s reasoning, the canonical orbital energy plots change appearance not only between the molecules, but also from state to state of the same molecule.”

Thus in variance with the MW binding energies, the SCF orbital energies are sensitive functions of the electronic configuration. The extended Hückel energies, though sensitive to parameter choice, are in this respect closer to the MW binding energies. The realization of the configuration dependence of the SCF ε_k 's leads naturally to the formulation of the following question, which we will endeavor to answer: “Can one define a set of canonical orbital energies within an SCF-MO procedure which is independent of the electronic configuration of the molecule? If yes, then how do these orbital energies compare to the EH energies and the MW binding energies?”

2. The Concept of the “Average State” and Tempered Orbital Energies

In a conventional HF SCF-MO calculation an antisymmetric determinant of the molecular orbitals is built for a given electronic state of the molecule (whether the molecule is in ground state, first excited state, etc.). These molecular orbitals are varied subject to the constraints of orthonormality and certain symmetry requirements, so as to make the total energy stationary. The result of such variation is a set of molecular orbitals which describe that electronic state of the molecule in a best way. Associated with these molecular orbitals are the canonical orbital energies which in Koopmans’ approximation are equal to the ionization energies. The tendency in the past has been to carry out a SCF calculation on the ground state of the molecule and identify the ground state canonical orbital energies as the ordinate of MW diagrams.

Our proposal is that the emphasis should be shifted from a variationally best ground state function to a compromise wavefunction which, while it cannot provide the total energy of any one state, tries to describe all the electronic states of the molecule in a democratic fashion. This can be done in one SCF calculation, if

⁶ See for instance footnote 20 of Ref. [13b].

instead of minimizing the energy of any specific state, we minimize some kind of average of the total energy of all the electronic states of the molecule, starting from a common set of orthonormal spin orbitals and imposing the constraints of the symmetry and orthonormality. The SCF canonical energies of this “average state” of the molecule will not provide the ionization energies of the molecule as well as the SCF canonical orbital energies do, but they will be some kind of average of SCF canonical orbital energies of various electronic states of the molecule. The hope is that the gradients of these configuration-averaged energies will control the total energy changes better than the canonical orbital energies.

In the following we describe the details of how the energy averaging is accomplished. The transition state concept developed in the Hartree–Fock theory by Pickup, Goscinski and coworkers [17] provides some of the necessary guidelines for our task. A similar energy averaging has been discussed at the multi-configuration SCF level by Hinze *et al.* [18]. The use of fractional occupancies as in our calculations is not novel, but has been used as well at several places in the past [19]. Our concept of the “average state” has some resemblance to the “standard excited state” of G. G. Hall [20], and the hyper-Hartree–Fock [21] method of Slater in conjunction with atomic calculations. Some recent work by I. Absar [22] is very similar to our approach.

We assume that the calculations are to be performed in the basis of m linearly independent real atomic orbitals (AO's). Let there be n electrons in the molecule, where the number $n < m$. In a conventional HF LCAO-MO calculation [3] we compose the $p = 2m$ orthonormal molecular spin-orbitals (MSO's) as linear combinations of m AO's. For simplicity and illustrative purposes we consider here the unrestricted Hartree–Fock approach and assume that p MSO's are associated with the p non-degenerate eigenvalues. The constraints of symmetry and degeneracy can, however, be easily introduced. In order to perform a SCF MO calculation the first thing to be specified is the electronic configuration of the molecule, i.e. how the n electrons are distributed in p MSO's (which MSO is occupied, which is empty, etc.). From the n occupied MSO we constitute an antisymmetric Slater determinantal wavefunction ψ , and the optimal MSO's are obtained by the usual variational procedure, making the energy

$$E = \langle \psi | H | \psi \rangle \quad (4)$$

stationary imposing the constraints of the orthonormality,

$$\langle \psi | \psi \rangle = 1. \quad (5)$$

This leads to a set of eigenvalue equations:

$$F_i = \varepsilon_i i, \quad i = 1, 2, \dots, p \quad (6)$$

where the Fock operator

$$F = h_0 + \sum_{j=1}^n \langle j || j \rangle, \quad (7)$$

h_0 is the one-electron operator containing the kinetic energy and the nuclear-

attraction operators. The notation $\langle j \| j \rangle$ is used to indicate

$$\langle j(2) \| j(2) \rangle r(1) = \int d\tau_2 j^*(2) \frac{1}{r_{12}} \{j(2)r(1) - r(2)j(1)\} \quad (8)$$

where j is j 'th MSO.

In order to carry out a SCF calculation on the "average" state of the molecule, we start from a common set of p orthonormal MSO's and build $q = p!/n!(p-n)!$ antisymmetric Slater determinants corresponding to the q different electronic configurations. Instead of applying the usual variational procedure to make the energy E of a particular state stationary, in the "average state" calculation, the energy E_{av}

$$E_{av} = \frac{x_1 E^1 + x_2 E^2 + \dots + x_n E^n}{x_1 + x_2 + \dots + x_n} \quad (9)$$

is made stationary subject to the constraints of the orthonormality of p MSO's. In Eq. (9) E^1, E^2, \dots , etc. denote the energy of the electronic configuration 1, 2, ... etc. calculated from the common set of p -orthonormal MSO's by the relation of Eq. (4). In practice, variation of E^{av} reduces to the usual HF eigenvalue equations,

$$F^{av}k = \varepsilon_k k, \quad k = 1, 2, \dots, p. \quad (10)$$

The Fock operator F^{av} is given by the following relation

$$F^{av} = h_0 + \sum_{j=1}^p n_j \langle j \| j \rangle \quad (11)$$

where n_j is the occupancy of the j 'th MSO.

Thus far our discussion has been vague concerning the actual values of the weighting factors x_1, x_2, \dots, x_n in Eq. (9) and the occupancies n_j in Eq. (11). We now consider some specific cases. First let us put x_1, x_2, \dots, x_n all equal to 1. This is tantamount to weighting all the states equally during energy variation in Eq. (9). In such a case it is easy to see that all the occupancies n_j in Eq. (11) are equal to p/n . Alternatively the n electrons are distributed equally among the p MSO's.

In any LCAO MO SCF calculation the orbital occupancies determine the density matrix, which in turn is required to construct the Fock matrix. Let us take a closer look at the density matrix of the present "average state". In matrix notation the density matrix P is written in terms of the MO coefficient matrix C and the occupation matrix n as follows

$$P = C^\dagger n C. \quad (12)$$

Here n is the diagonal matrix whose diagonal elements are the occupation numbers of each molecular orbital. In the present special case where all the MO's are equally populated the matrix n commutes with C

$$P = C^\dagger n C = C^\dagger C n \quad (13)$$

Without any loss of generality the coefficient matrix C can be considered in the basis of orthonormal atomic orbitals. Then

$$C^\dagger C = CC^\dagger = 1 \quad (14)$$

and Eq. (13) reduces to

$$P = n. \quad (15)$$

Eq. (15) has the important implication that the density matrix P is independent of the choice of the coefficient matrix C . In a typical SCF calculation an iterative procedure is followed to obtain a self-consistent density matrix. The density matrix of Eq. (15) is internally self-consistent in the sense that, if the Fock matrix elements are set up in terms of this matrix, the self-consistent eigenvectors and the associated canonical orbital energies are obtained in just one cycle. The property is strikingly similar to extended Hückel-type calculations.

The problem arises of what one should call the orbital energies of the "average state" Fock matrix. They could be designated as "configuration independent average" orbital energies, since in some sense they are independent of the electronic configuration of the molecule. We prefer to call them "tempered" orbital energies, ϵ_k^{temp} . Here the descriptor "tempered" is used in the sense of admixture of orbital energies in various electronic states in due proportion to soothe or moderate the gradient of these energies, such that these variations are the foremost factor in determining the changes in the total energy, as is true of MW binding energies. The meaning of this term will become more explicit when the actual numerical results are provided.

We first explored the "average state" concept within the framework of an all valence-electron calculation of the CNDO/2 type. In Fig. 1 the angular variation of the CNDO/2 canonical orbital energies is plotted for the H_2O molecule. This graph shows the problems with the assumption that the ordinate in MW diagrams is to be identified with the canonical energies. For example Walsh's rules imply

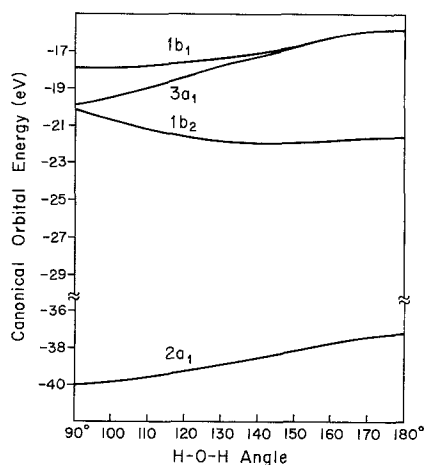


Fig. 1. CNDO/2 canonical orbital energies for H_2O as a function of HOH angle

that a four valence electron molecule should be linear, but that would not follow from Fig. 1. If one simply were to sum orbital energies, one would get a bent H_2O molecule (eight valence electrons) but bent too much, with the HOH angle less than 45° .

The extended Hückel orbital diagram, Fig. 2, would indicate a linear four-electron system and, while it also does not predict the structure of water correctly, it does have an appearance closer to that of the MW diagram. Another distinct difference

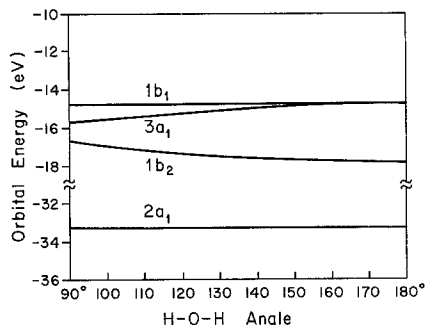


Fig. 2. Extended Hückel energies for H_2O as a function of HOH angle

between it and the CNDO/2 diagram is in the slope of the highest occupied MO, the π_u . In the SCF calculation it is stabilized with bending, in the original Walsh diagram as well as the EH calculation it is constant in energy.

The MW diagram of Fig. 3 is constructed with the tempered orbital energies of the CNDO/2 calculation. This diagram looks much more like the original H_2O Walsh diagram, with the mistake of Walsh regarding the slope of the lowest occupied orbital, as later pointed out by Mulliken, corrected. The highest occupied orbital is constant in energy, a feature in common with the original Walsh diagram as well as the EH results. There are now no dangers involved in making predictions about the

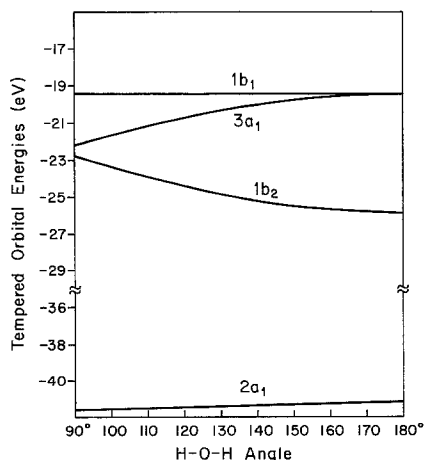


Fig. 3. CNDO/2 tempered orbital energies for H_2O

geometry of a four valence-electron system in the ground state – these are suggested to be linear. The sum of the occupied tempered orbital energies is lowest at an HOH angle of 135° , in reasonable agreement with the 107.5° obtained from the CNDO/2 calculation when the correct total energy expression, including V_{ee} and V_{nn} , is employed. Similar results are obtained for methylene and ethane.

Encouraged by these results, we proceeded to an evaluation of the tempered orbital energies in all-electron *ab initio* calculations. Some exploratory studies told us that the “average state” concept works much better if we keep frozen to 2 the occupancies of the core orbitals, and distribute the remaining electrons equally among the remaining MO’s of a minimal basis set calculation. This is equivalent to saying that in Eq. (9) we are only looking for a common set of orthonormal MSO’s for the different electronic configurations in the manifold of MSO’s constructed only from the valence orbitals. Moreover, the density matrix P in Eq. (13) for the all-electron calculation is not any longer internally self-consistent, as we shall point out later in the paper. However, despite the non-commutation of n with C in Eq. (13), the *ab initio* calculations in the “average state” converge in just 2 to 3 SCF cycles, much quicker than normal SCF calculations.

The MW diagram for H_2O has been constructed once more in Fig. 4, now employing the canonical orbital energies of the STO-3G *ab initio* calculation [23]. It has the same features as the CNDO diagram of Fig. 1. Two total energies are plotted in Fig. 4 – one calculated in a rigorous manner, the other a simple sum of valence orbital energies. Notice the large difference between the shapes of the two curves.

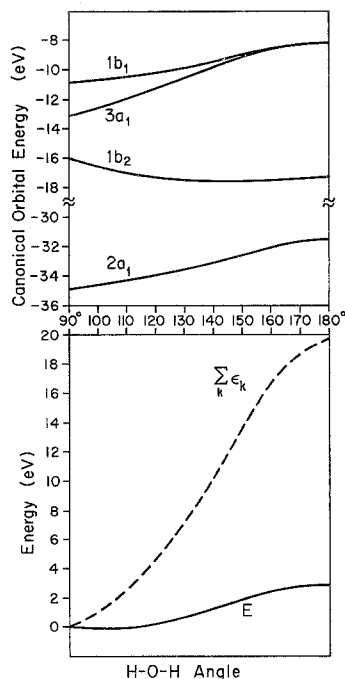


Fig. 4. Hartree-Fock canonical energies (top) for H_2O as a function of HOH angle. Plotted at bottom is the correct total energy E and the sum of the canonical orbital energies $\sum_k \epsilon_k$ for the valence orbitals, both referred to a common arbitrary zero at 90°

While $\sum \epsilon_k$ correctly gives the molecule bent, it yields a much too large difference between the 180° and 90° geometries (19 eV compared to 3 eV).

The angular variation of *ab initio* tempered energies is presented in Fig. 5. Once again, as in the case of the CNDO/2 tempered orbital energies, the four valence-electron AH_2 systems are correctly predicted to be linear. The sum of the tempered orbital energies for H_2O nicely parallels the correct total energy curve.

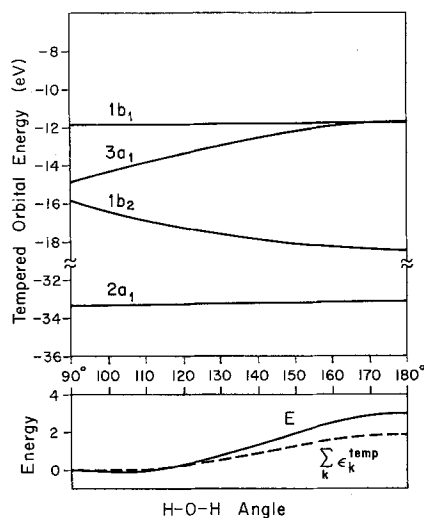


Fig. 5. Tempered orbital energies (top) from a HF calculation for H_2O . At bottom is plotted the correct total energy E and the sum of tempered orbital energies for the valence orbitals, both referred to a common arbitrary zero at 90° .

The sum of the valence tempered orbital energies not only parallels better the total energy than does the sum of canonical energies, but also any changes as a function of angle are concentrated into the valence orbitals. For instance, on going from 180° to 90° , the H_2O core orbital, $1s$ on O, changes its ϵ_k by 0.184 a.u., but ϵ_k^{temp} changes by only 0.014 a.u.

One field in which both extended Hückel calculations and minimum basis set *ab initio* and semiempirical SCF calculations have had moderate success is in the calculation of conformational barriers. A CNDO/2 calculation on the ethane torsional barrier gives the staggered form preferred by 0.093 eV, while a simple sum of SCF ϵ_k 's is not very different, 0.091 eV. Similar results are obtained from *ab initio* calculations. A sum of tempered orbital energies also yields the staggered form more stable, by 0.135 eV. Ethane is not a very stringent test of the theory, because almost any calculation gives a barrier that is approximately correct. A more interesting comparison is provided by H_2O_2 in Table 1.

The correct total energy decreases with increasing dihedral angle. In contrast, the sum of canonical orbital energies increases. However, when the total energy is expressed as the sum of tempered orbital energies, once again these energy changes approximately parallel the real total energy changes. Thus the tempered orbital energies appear to be promising for making qualitative predictions of molecular conformational preferences.

Table 1. *Ab initio* (STO-3GTO) total energy (a.u.) as a function of HOOH dihedral angle^a for H₂O₂ molecule

Dihedral angle in deg.	E_T	$\sum_{\text{valence}} \varepsilon^{\text{SCF}}$	$\sum_{\text{valence}} \varepsilon^{\text{tempered}}$
10	-148.7312	-10.0402	-9.2000
55	-148.7405	-10.0117	-9.2211
100	-148.7473	-9.9549	-9.2350
140	-148.7498	-9.9213	-9.2408
165	-148.7503	-9.9172	-9.2421
180	-148.7504	-9.9165	-9.2424

^aA dihedral angle of 180° corresponds to a *trans* geometry. Other geometrical parameters used are $r_{\text{O-H}}=0.95$ Å, $r_{\text{O-O}}=1.475$ Å, angle OOH=95°.

Before we present some further numerical results based on STO-3G *ab initio* calculations, we would like to introduce a further approximation that improves the performance of the tempered orbital energies. So far in the “average state” the distinction between core and valence orbitals has been recognized by keeping the occupancies of the former at two, and distributing the remaining electrons equally among the remaining molecular orbitals. In matrix notation this corresponds to a partitioning of the occupancy matrix n in Eq. (12) into two blocks

$$n' = \begin{pmatrix} n_c & 0 \\ 0 & n_v \end{pmatrix} \quad (16)$$

where the n_c are all equal to two and the n_v are all equal to each other but not equal to two. n' is no longer a multiple of the unit matrix and so does not commute with the coefficient matrix C . The density matrix

$$P = C^\dagger n' C \quad (17)$$

of Eq. (17), unlike the one in Eq. (13), is not internally self-consistent.

The n' could still commute with C , provided that the latter can also be partitioned into core and valence regions, respectively, i.e.

$$C = \begin{pmatrix} C_c & 0 \\ 0 & C_v \end{pmatrix}. \quad (18)$$

This would be true only if there were no interaction between core and valence orbitals. In practice in *ab initio* calculations such interactions are unavoidable. Nevertheless, there are means to separate core and valence orbitals. One way, which however leads to many computational difficulties, is to orthogonalize the valence orbitals to the core. Another way is to follow through the consequences of simply assuming that n' does commute with C even in all-electron calculations. Then Eq. (17) will reduce to (19)

$$P = n' \quad (19)$$

and once again, as in the “valence only” calculation, the computations for the

average state will require only one SCF cycle. The implementation of this concept encounters some computational difficulties for reasons that are tied to the way in which Roothaan's iterative procedure is typically implemented, for instance in the Gaussian-70 package. This we describe now.

For closed-shell molecules the secular equation to be solved is

$$FC = SCE \quad (20)$$

where F is the Fock matrix, C the MO coefficient matrix, S the overlap matrix, and E is the diagonal eigenvalue matrix. Eq. (20) is generally reduced to a matrix eigenvalue problem (21)

$$F'C' = C'E \quad (21)$$

by transforming F , C , and S to an orthogonal AO basis. A typical cycle of the iterative procedure is executed by setting up the Fock matrix in the basis of non-orthogonal AO's, transforming F to F' , then diagonalizing F' to yield C' and E . The matrix C' is then transformed back to C in the basis of nonorthogonal AO's. C is used to form the density matrix P , in turn utilized in the construction of F and so the process iterates.

The point of repeating this well-known protocol is to point out that the employment of Eq. (19) in place of (17) will be justifiable only in conjunction with Eq. (21) and not with (20). However, as stated earlier, computationally it is much easier to obtain F' from F rather than calculating F' directly in the basis of orthogonal atomic orbitals. The evaluation of F requires knowledge of Eq. (18) and not (19). Eq. (18) requires knowledge of the coefficient matrix C , which can be achieved only through self-consistency. It can, however, be easily shown that the employment of Eq. (19) in conjunction with Eq. (20) is correct if the Mulliken approximation is involved to partition the Fock operator of the molecule into atomic Fock operators.

The use of Eq. (19) does lead to an improved performance of the tempered orbital energies for all-electron calculations. Now these require only one SCF cycle for an "average state", like the valence-only computations. A major consequence of the

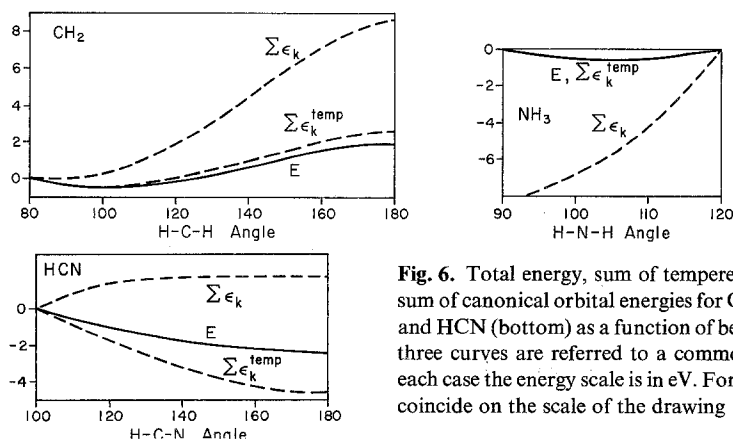


Fig. 6. Total energy, sum of tempered orbital energies, and sum of canonical orbital energies for CH₂ (left), NH₃ (right), and HCN (bottom) as a function of bending. In each case the three curves are referred to a common energy zero, and in each case the energy scale is in eV. For NH₃ two of the curves coincide on the scale of the drawing

use of Eq. (19) in the construction of the Fock operator is the cutting down of the changes in core orbital energies to near zero. For instance, for the H_2O case mentioned earlier the difference between O $1s$ core orbital energies between 180° and 90° , both “tempered” is reduced from 0.014 a.u. to 0.00001 a.u. The results shown in Fig. 6 for CH_2 , NH_3 and HCN shows just how much better $\sum \epsilon_k^{\text{temp}}$ is than $\sum \epsilon_k$ in predicting molecular geometries. In each case only the valence orbital energies are summed. For the $\sum \epsilon_k^{\text{temp}}$ the curves are essentially unchanged by inclusion of the core, while for $\sum \epsilon_k$ the disagreement with the correct total energy curve is made worse.

This pleasing success of tempered orbital energies was, however, only short-lived. We soon discovered, to our disappointment, a case where the sum of SCF canonical energies tracked better the total energy than did the sum of tempered energies. This is OF_2 , as shown in Fig. 7. Was the previous good performance of the tempered

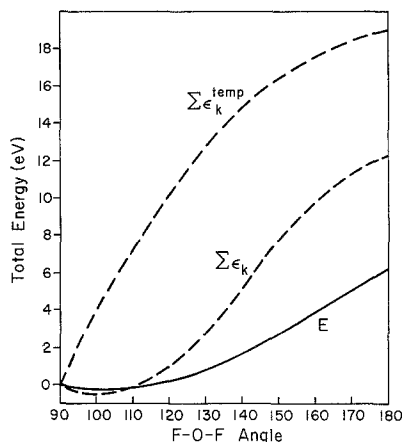


Fig. 7. Correct total energy E , sum of canonical orbital energies $\sum \epsilon_k$, and sum of tempered orbital energies $\sum \epsilon_k^{\text{temp}}$ for OF_2 , with respect to a common arbitrary zero at 90°

orbital energies merely fortuitous? A closer look at the density matrix of Eq. (19) will help us to understand the matter better. The Fock operator constructed from this density matrix, whose eigenvalues are the tempered orbital energies, can be simply viewed as a superposition of atomic Fock operators. For example, the H_2O average state density matrix that was used in the calculations that led to Fig. 5 was

$$P = \begin{array}{c} \begin{array}{l} \text{O}_{1s} \\ \text{O}_{2s} \\ \text{O}_{2p_x} \\ \text{O}_{2p_y} \\ \text{O}_{2p_z} \\ \text{H}_{1s} \\ \text{H}_{1s} \end{array} \end{array} \begin{array}{ccccccc} \text{O}_{1s} & \text{O}_{2s} & \text{O}_{2p_x} & \text{O}_{2p_y} & \text{O}_{2p_z} & \text{H}_{1s} & \text{H}_{1s} \\ \hline 2.0 & & & & & & \\ & 1.333 & & & & & \\ & & 1.333 & & & & \\ & & & 1.333 & & & \\ & & & & 1.333 & & \\ & & & & & 1.333 & \\ & & & & & & 1.333 \end{array} \begin{array}{l} \\ \\ \\ \\ \\ \\ \\ \end{array}$$

The Fock operator constructed from this density matrix is the sum of a Fock operator for an oxygen atom containing 7.333 electrons plus the Fock operators of two hydrogen atoms each containing 1.333 electrons in their respective $1s$ orbitals.

Thus a certain ionicity is imposed on the molecule as an inevitable result of the prescription of dividing up valence electrons democratically. This ionicity may not be far from the correct one for H_2O , NH_4 , CH_2 and HCN , but turns out to be incorrect for F_2O .

It has been recognized earlier in the literature that the extended Hückel Hamiltonian may be considered as the superposition of Fock operators associated with neutral atoms in the molecule. We will use this idea as a starting point by construction of an averaged Fock matrix

$$F^{av} = \sum F^{nao} \quad (22)$$

as the sum of F^{nao} which are neutral atom Fock matrices. The density matrix which will be used to construct the Fock operator of (22) can be described as follows. It is a diagonal matrix, divided into atomic blocks, further subdivided into subblocks associated with atomic orbitals of different principal quantum number. The various atomic orbitals in a given subblock are given equal occupancies. For instance, for H_2O the density matrix is:

$$P = \begin{array}{c} \begin{array}{l} O_{1s} \\ O_{2s} \\ O_{2p_x} \\ O_{2p_y} \\ O_{2p_z} \\ H_{1s} \\ H_{1s} \end{array} \end{array} \left| \begin{array}{cccccc} O_{1s} & O_{2s} & O_{2p_x} & O_{2p_y} & O_{2p_z} & H_{1s} & H_{1s} \\ 2.0 & & & & & & \\ & 1.5 & & & & & \\ & & 1.5 & & & & \\ & & & 1.5 & & & \\ & & & & 1.5 & & \\ & & & & & 1.0 & \\ & & & & & & 1.0 \end{array} \right|$$

The six valence electrons are distributed equally among the $2s$ and $2p$ orbitals of oxygen. The atoms are kept neutral. It is this kind of density matrix which is adopted in our final definition of tempered orbital energies and used throughout the rest of the paper.

In Figs. 8 to 11 the various energy sums are presented for H_2O , NH_3 , HCN , HOF , F_2O , $LiOH$, and Li_2O . The reason for this choice of molecules is that we wish to cover a range of molecules with different symmetry and degree of covalency, ones which obey Walsh's rules and ones which do not, so as to give a broad and fair comparison between SCF canonical energies and the tempered orbital energies.

As a general observation, the sum of tempered orbital energies in all cases clearly approximates the rigorous total energy changes much better than does the sum of SCF canonical orbital energies. The individual tempered orbital energies also behave much more like the MW diagram energies.

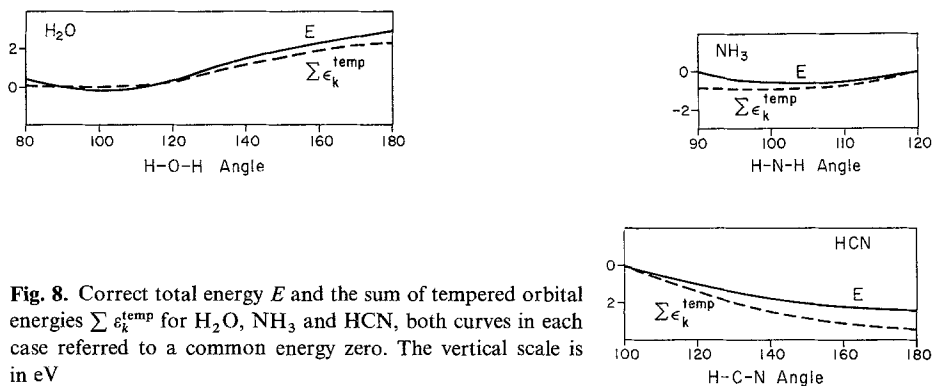


Fig. 8. Correct total energy E and the sum of tempered orbital energies $\sum \epsilon_k^{\text{temp}}$ for H_2O , NH_3 and HCN , both curves in each case referred to a common energy zero. The vertical scale is in eV

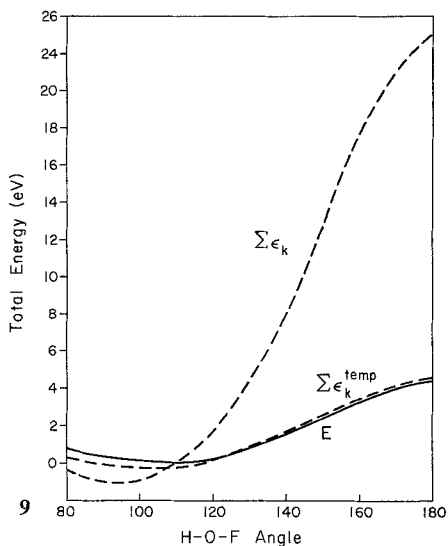


Fig. 9. E , $\sum \epsilon_k$, and $\sum \epsilon_k^{\text{temp}}$ for HOF as a function of bending. All curves are referred to a common energy zero at 120°

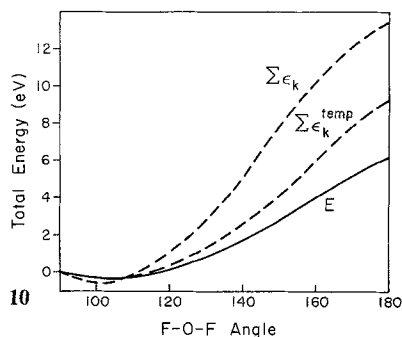


Fig. 10. E , $\sum \epsilon_k$, and $\sum \epsilon_k^{\text{temp}}$ for F_2O as a function of bending. All curves are referred to a common energy zero at 90°

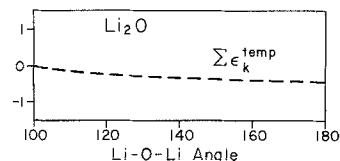
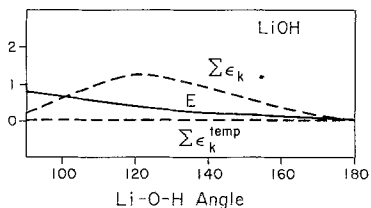


Fig. 11. (Left) E , $\sum \epsilon_k$, and $\sum \epsilon_k^{\text{temp}}$ for LiOH as a function of bending. (Right) $\sum \epsilon_k^{\text{temp}}$ for Li_2O . The vertical scale is in eV for both molecules

LiOH and Li₂O are interesting cases in that they are eight valence electron AH₂, yet linear. The sum of tempered orbital energies is essentially flat in going from 90° to 180°, with a small preference for the latter. Our STO-3G calculations for Li₂O did not converge; however, it is known from extended basis *ab initio* calculations that the sum of the canonical energies leads to a bent geometry.

We now discuss the energy changes due to inner shell orbitals. In *ab initio* calculations it is generally argued that since MW diagrams plot changes in valence orbitals, only a sum of the valence orbital canonical energies should be used in approximating the total energy. Yet in the very same *ab initio* calculations the core energies vary widely with geometrical change, i.e. the sum or core orbital energies are not constant. This may be seen in Table 2. The changes in SCF canonical

Table 2. Changes in core orbital energies (eV)

Molecule	Core orbital		Canonical	Tempered
CH ₂	C _{1s}	$\epsilon(180^\circ) - \epsilon(80^\circ)$	2.945	0.005
OH ₂	O _{1s}	$\epsilon(180^\circ) - \epsilon(90^\circ)$	4.992	0.001
NH ₃	N _{1s}	$\epsilon(120^\circ) - \epsilon(109.5^\circ)$	1.106	0.001
CH ₄	C _{1s}	$\epsilon(90^\circ) - \epsilon(109.5^\circ)$	7.030	0.000
HCN	N _{1s}	$\epsilon(100^\circ) - \epsilon(180^\circ)$	0.788	0.019
	C _{1s}	$\epsilon(100^\circ) - \epsilon(180^\circ)$	-0.540	-0.011
OF ₂	F _{1s}	$\epsilon(180^\circ) - \epsilon(90^\circ)$	-3.699	-0.003
	O _{1s}	$\epsilon(180^\circ) - \epsilon(90^\circ)$	+8.420	0.001
HOF	F _{1s}	$\epsilon(180^\circ) - \epsilon(110^\circ)$	-0.541	-0.008
	O _{1s}	$\epsilon(180^\circ) - \epsilon(110^\circ)$	+5.850	0.003

energies sometimes even exceed the valence orbital changes, as for F₂O. On the other hand the tempered orbital energy changes are practically negligible. Thus these satisfy much better the assumptions inherent in the MW picture.

At this point we digress to discuss the calculation of conformational barriers, a field in which nearly all calculational procedures have met with moderate success. Consider the series CH₃CH₃, CH₃NH₂ and CH₃OH. Experimental results, *ab initio* calculations and EH calculations yield barriers for this series in the approximate ratio of 3:2:1. This is not the case for the sum of the SCF canonical valence orbital energies, which gives 8.3, 6.7, 6.7 kcal/mole respectively for the barrier. The sum of tempered orbital energies is 4.4., 2.7, and 1.2 kcal/mole respectively.

An interesting feature of the EH calculations is that certain orbitals are singled out as carrying most of the total energy change. This is not so for the SCF canonical orbitals, but does follow for the tempered orbital energies. The point is demonstrated in Table 3 for ethane, and obtains for CH₃NH₂ and CH₃OH as well. Thus again we see a resemblance between the tempered orbital energies and the extended Hückel orbital energies.

Thus far we have focussed only on the gradient characteristics of the two sets of orbital energies. Since the tempered orbital energies are associated with some sort

Table 3. $\epsilon_{\text{ccl}} - \epsilon_{\text{stag}}$ orbital by orbital for the ethane molecule

Orbital ^a	Canonical	Tempered	EH
<i>e</i>	0.080	0.140	0.101
<i>a</i> ₁	0.020	-0.005	-0.005
<i>e</i>	-0.022	-0.093	-0.056
<i>a</i> ₂	0.025	-0.018	0.002
<i>a</i> ₁	0.020	0.015	0.001
Core	0.050	0.000	0.000

^aFor degenerate *e* levels the energy difference is for one orbital of the pair.

of average state of the molecule, it is not to be expected that they will be equal to the experimental ionization potentials in the Koopmans' approximation. As Table 4 nevertheless demonstrates, the ordering of the tempered orbitals generally parallels the one derived from SCF canonical orbital energies. The CO, NO⁺, CN⁻ set also reproduces the trends of SCF energies in a series of molecules which is important in defining a constant scale of σ and π donor and acceptor properties of molecules. A separate detailed comparison of SCF and tempered gross atomic populations and overlap populations for all the molecules studied shows that all the trends are parallel in the two calculational procedures.

The occupied tempered orbital energies are generally observed to be pushed up relative to the canonical orbital energies, whereas the unoccupied or virtual orbitals come down in energy. These energy shifts are consistent with the averaged density matrix formalism. They also reduce the gap between filled and unfilled levels, much as the EH calculations do, but not to the extent that is observed in EH calculations. Quantitatively, however, there is little in common between the EH and the tempered orbital energies, except for the first few occupied MO's. The reasons for this difference will be discussed elsewhere.

We now approach the third question raised in the beginning of the paper – in what circumstances can the approximate relation of the total energy E as the sum of canonical orbital energies ϵ_k , Eq. (23), be used?

$$E = \sum n_k \epsilon_k \quad (23)$$

From the aforesaid studies it appears that the approximate relation of the total energy E as the sum of the tempered orbital energies

$$E = \sum n_k \epsilon_k^{\text{temp}} \quad (24)$$

is safer to use for the gradient properties of the rigorous total energy expression in place of Eq. (23).

In conclusion the important implications of this paper can be summarized as follows:

- 1) Within the HF-LCAO-MO theory there exists a set of orbital energies, called tempered orbital energies in this paper, which behave much more like the MW diagram energies than do the SCF canonical orbital energies.
- 2) The sum of these tempered orbital energies in many circumstances can provide a shortcut to the rigorous energy changes.

Table 4. Molecular orbital energies

Molecule	Orbital, symmetry	Energies		
		Canonical	Tempered	EH
CH ₂ (D _{∞h} , 1A ₁)	1b ₁	7.56	0.81	-11.40
	3a ₁	-5.81	0.81	-11.40
	1b ₂	-14.93	-12.76	-16.22
	2a ₁	-20.64	-17.76	-23.67
OH ₂ (C _{2v} , 120°)	2b ₂	21.47	17.76	9.80
	4a ₁	15.43	13.57	0.87
	2b ₁	-10.24	-7.49	-14.80
	3a ₁	-11.26	-9.84	-15.25
	1b ₂	-17.31	-17.85	-17.41
	2a ₁	-33.91	-33.85	-33.27
NH ₃ (C _{3v} , 100°)	2e	18.62	15.70	0.74
	4a ₁	17.31	16.08	17.88
	3a ₁	-10.12	-6.41	-13.98
	1e	-15.17	-13.31	-16.27
	2a ₁	-29.89	-29.45	-27.90
OF ₂ (C _{2v} , 130°)	5b ₂	15.16	10.58	-5.43
	7a ₁	8.40	4.34	-7.93
	2b ₁	-10.48	-2.83	-14.00
	6a ₁	-11.65	-7.15	-15.71
	4b ₂	-14.41	-10.10	-18.01
	1a ₂	-15.28	-10.23	-18.07
	5a ₁	-17.06	-12.93	-18.55
	3b ₂	-17.88	-17.42	-18.57
	1b ₁	-17.98	-23.27	-19.24
	4a ₁	-30.67	-24.09	-27.97
	2b ₂	-41.93	-37.36	-40.00
	3a ₁	-44.67	-40.48	-42.90
	CO	π*	8.50	6.09
σ		-12.15	-4.23	-13.49
π		-14.96	-11.06	-15.62
NO ⁺	π*	-8.57	2.91	-11.07
	σ	-29.89	-9.18	-14.61
	π	-30.66	-12.00	-16.08
CN ⁻	π*	22.71	7.35	-8.003
	σ	1.15	-3.57	-12.267
	π	-1.78	-8.84	-14.782

- 3) The gradient properties of EH orbital energies are more like those of the tempered orbital energies than the SCF canonical orbital energies.
- 4) These tempered orbital energies appear to provide a long sought missing link among SCF canonical energies, extended Hückel orbital energies, and Mulliken-Walsh binding energies.

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