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Some Analysis of the ω-Technique

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The ω-Technique is one of a number of ways of improving on the Hückel model by introducing a dependence on atomic orbital populations into the matrix-elements of the effective Hamiltonian. It requires iterative solution of secular equations until the populations calculated from the solutions are consistent with the populations used in setting up the Hamiltonian matrix. We derive simple equations showing how the *deviations* of the populations from their final self-consistent values change with successive iterations. The results of consideration of these equations in several special cases, imply that the populations oscillate about their final values on successive iterations, as has actually been found experimentally. This suggests a simple means of speeding up convergence.

Key word: ω-Technique

1. Introduction

The ω-Technique, discussed by Streitwieser [1], is an iterative approximate molecular orbital theory which is an improvement on the simple Hückel theory because it makes the diagonal matrix elements of the effective Hamiltonian (generally denoted by H_{ii} or α_i) depend on the populations of the atomic orbitals. Given a set of atomic orbital populations q_i, one puts

$$H_{ii} = \alpha_i = \alpha_0 + \omega\beta(1 - q_i) \tag{1}$$

for the diagonal matrix element corresponding to atomic orbital i. Here, α_0 is a constant, which may be taken as the value of this diagonal matrix element in the simplest Hückel theory, ω is a positive parameter of size unity whose value is chosen empirically, and β is an energy parameter whose value may be chosen as the matrix element of the Hamiltonian between nearest neighbors in the Hückel theory. Since α_0 and β are negative, an increase in q_i makes α_i less negative, so that orbital i becomes less attractive to electrons. Having recalculated α_i according to Eq. (1), one solves the secular equations to determine new molecular orbital energies and coefficients. Then the values of q_i and α_i may be recalculated and the procedure repeated. The recycling is continued until energies, molecular orbital coefficients, and α_i-values no longer change with each iteration (convergence).

The simplest Hückel theory, in this context, corresponds to assuming $q_i = 1$ for all i and making no effort to modify the α_i values according to populations or to achieve self-consistency between the molecular orbital coefficients calculated and the Hamiltonian integrals used. The choice, $q_i = 1$ for all i, is justified in calculations which in fact lead to equal populations. It is clear on physical grounds, however, that α_i should depend on the population of orbital i, and the ω-technique improves results for many electronic properties as compared with the Hückel model. In particular, charge buildups on atoms are reduced from unreasonably large values obtained when the Hückel model is used [2]. The dependence of the Hamiltonian on the wavefunction (through orbital populations, for instance) is an important ingredient of *ab initio* Hartree-Fock and related calculations [3], and the ω-Technique may be considered as a first step from the simplest molecular orbital calculations toward the more sophisticated and more realistic methods. In the present paper, we attempt to analyze the equations of the ω-Technique algebraically in order to make some statements about its convergence properties. Perhaps the results will be of interest in subsequent analysis of other molecular orbital theories, which incorporate a dependence of Hamiltonian matrix elements on molecular orbital coefficients and require iterated solutions of the secular equation until self-consistency is reached.

After introducing some notation, we derive the equations which relate the populations calculated from the solutions of the secular equation (i.e., the populations after the n'th iteration) to the populations used in setting up the secular equation (i.e., the populations after the $(n-1)$'th iteration). By assuming that deviations from the final self-consistent results are not too large, we are able to linearize the equations and evaluate some of the unknowns. The equations are rearranged in a form which simplifies some analysis, and enables us to derive rigorous results in certain special cases. These results imply that the deviations of the populations from their final self-consistent values alternate in sign on successive iterations. Such an alternation has in fact been found in actual calculations [4].

2. Basic Equations

In all our analysis, we assume that overlap integrals may be neglected. Their inclusion would probably not alter our results but would complicate the form of the equations. Ignoring overlaps means that the secular equation takes the form

$$\sum_j H_{ij} C_{jk} = E_k C_{ik} \tag{2}$$

and that the population of atomic orbital i is calculated according to

$$q_i = 2 \sum_k^{(\mathrm{occ})} C_{ik} C_{ik} \,. \tag{3}$$

We are assuming real coefficients here to simplify notation.

The superscript in parentheses labels the molecular orbitals, each of which is written as a linear combination of atomic orbitals:

$$\psi^{(k)} = \sum_i C_{ik} \phi_i \,. \tag{4}$$

The number of atomic orbitals is n, and all sums run from 1 to n except where otherwise specified. In Eq. (3), the sum over molecular orbitals runs only over those occupied. For simplification, we assume all molecular orbitals are either doubly occupied or empty. The molecular orbitals are orthogonal and assumed normalized, which, with the neglect of atomic orbital overlaps, means:

$$\sum_i C_{ik} C_{il} = \delta_{kl} \,. \tag{5}$$

The coefficients also obey the "closure" relation,

$$\sum_k C_{ik} C_{jk} = \delta_{ij} \tag{6}$$

(the sum runs from 1 to n).

We label the exact, final, or self-consistent values of the Hamiltonian matrix elements, energies, populations, etc. by over-bars. They obey the Eq. (2) i.e.,

$$\sum_i \bar{H}_{ij} \bar{C}_{jk} = \bar{E}_k \bar{C}_{ik} \,, \tag{7}$$

where $i = 1, 2, \ldots, n$; $k = 1, 2, \ldots, n$. At some stage of the iterative process, suppose we have

$$C_{ik} = \bar{C}_{ik} + \delta C_{ik} \tag{8}$$

and we use these coefficients to calculate values of H_{ij} according to Eqs. (3) and (1). The solution of the secular equations with this Hamiltonian matrix leads to new coefficients $\tilde{C}_i^{(k)}$, where

$$\tilde{C}_i^{(k)} = \bar{C}_i^{(k)} + \delta' C_i^{(k)} \,. \tag{9}$$

We use δ to indicate deviations of various quantities from their final values *before*, and δ' to indicate deviations *after*, solution of the secular equations. Thus,

$$\sum_j (\bar{H}_{ij} + \delta H_{ij}) (\bar{C}_{jk} + \delta' C_{jk}) = (\bar{E}_k + \delta' E_k) (\bar{C}_{ik} + \delta' C_{ik}) \tag{10}$$

for $i = 1, \ldots, n$; $k = 1, \ldots, n$. If the deviations are not too large, products like $\delta \bar{H}_{ij} \delta' C_j^{(k)}$ may be neglected. Then we may use (7) to obtain linearized equations for the deviations after this stage of the iterative process in terms of the deviations before:

$$\sum_j (\bar{H}_{ij} \delta' C_{jk} + \delta H_{ij} \bar{C}_{jk}) = \bar{E}_k \delta' C_{ik} + \delta' E_k \bar{C}_{ik} \,. \tag{11}$$

Since only diagonal elements of the Hamiltonian matrix are changed in the ω-Technique, δH_{ij} is a diagonal matrix.

As in most problems of this kind (the linearization corresponds to first-order perturbation theory), one can find the change in the energy ($\delta' E_k$ here) in terms of the unchanged coefficients. Multiply (11) by $\bar{C}_{ik}$ and sum over i. Using Eqs. (7), (5), and (1),

$$\delta' E_k = \sum_i \bar{C}_{ik}^2 (-\omega \beta \delta q_i) \,. \tag{12}$$

The deviation of the orbital energy from its final value, *after* the iteration, is thus a weighted mean of the deviations of the populations from their final values *before* the iteration. The weighting factors are squares of the exact or final molecular orbital coefficients, but, consistent with our neglect of products of deviations in linearizing the equations, one could use C_{ik} (coefficient before iteration) or $\tilde{C}_{ik}$ (coefficient after iteration) for C_{ik} – see Eqs. (8)–(10).

We now substitute the result (12) into our Eq. (11) and rearrange to obtain:

$$\sum_j \bar{H}_{ij}\delta' C_{jk} - \bar{E}_k \delta' C_{ik} = \omega\beta \left(\delta q_i - \sum_j \bar{C}^2_{jk}\delta q_j\right) \bar{C}_{ik}\,. \tag{13}$$

Now we proceed to express populations after iteration ($\delta' q_i$) in terms of populations before iteration (δq_i). The quantities $\delta' q_i$ are given by

$$\begin{aligned}\frac{1}{2}\delta' q_i &= \sum_k^{(\mathrm{occ})} (\bar{C}_{ik} + \delta' C_{ik})^2 - \sum_k^{(\mathrm{occ})} \bar{C}^2_{ik} \\ &= \sum_k^{(\mathrm{occ})} 2(\bar{C}_{ik}\delta' C_{ik})\end{aligned} \tag{14}$$

since products like $\delta' C_{ik}\delta' C_{ik}$ are neglected. A useful expression is obtained from (14) when $\delta' C_i^{(k)}$ is expressed in terms of the $\bar{C}_j^{(l)}$. Without loss of generality, we can write

$$\delta' C_{ik} = \sum_l a_l^k \bar{C}_{ik} \tag{15}$$

and solve for the coefficients a_l^k, which will be independent of i. Substituting (15) into (13), multiplying by $\bar{C}_{im}(m \neq k)$ and summing over i, and using (7) and (5), we can solve for a_m^k. Then substitution into (15) yields

$$\delta' C_{ik} = \omega\beta \sum_l^{(l \neq k)} (\bar{E}_l - \bar{E}_k)^{-1} \sum_j \bar{C}_{jl}\bar{C}_{jk}\delta q_j \bar{C}_{il}\,. \tag{16}$$

The value of a_k^k, which could not be determined from (16), has been set equal to zero, which is equivalent to demanding that the molecular orbitals be normalized at each stage of the iterative process $\left(\text{and hence } \sum_i \bar{C}_{ik}\delta' C_{ik} = 0\right)$. The result of (16) is substituted into (14).

Some further manipulations on the resulting equation put it in a more useful form. Note that k runs over occupied molecular orbitals, but l runs over all values not equal to k.

$$\delta' q_i = 4 \sum_k^{(\mathrm{occ})} \omega\beta \sum_l^{(l \neq k)} (\bar{E}_l - \bar{E}_k)^{-1} \sum_j \delta q_j \bar{C}_{ik}\bar{C}_{jl}\bar{C}_{jk}\bar{C}_{il}\,. \tag{17}$$

Consider the terms corresponding to $l =$ occupied. In the double sum over k and l, each pair of molecular orbitals (k, l) will appear twice. The sum of products of coefficients is the same each time (interchange of k and l leaves it unchanged) but the energy denominator changes sign. Thus, the sum of the two contributions vanishes and we are left with

$$\delta' q_i = 4\omega\beta \sum_j \delta q_j \sum_k^{(\mathrm{occ})} \sum_l^{(\mathrm{unocc})} (\bar{E}_l - \bar{E}_k)^{-1}\, \bar{C}_{ik}\bar{C}_{il}\bar{C}_{jl}\bar{C}_{jk}\,. \tag{18}$$

Equation (18) is the desired result. It gives the deviations of populations from their final values, after an iteration, in terms of their deviations before the iteration.

It should be noted that all the energy denominators in Eq. (18) are positive if the occupied orbitals are those of lowest energy, as is appropriate for the ground state. It may easily be shown that the sum of the deviations $\delta' q_i$ is zero, as it should be: the sum of the populations is equal to the number of electrons and hence the same at each iteration. We have

$$\begin{aligned} \sum_i \delta q_i' &= 4\omega\beta \sum_k \delta q_j \sum_k^{(\mathrm{occ})} \sum_l^{(\mathrm{unocc})} (\bar{E}_l - \bar{E}_k)^{-1} \sum_i \bar{C}_{ik}\bar{C}_{il}\bar{C}_{jl}\bar{C}_{jk} \\ &= 4\omega\beta \sum_j \delta q_j \sum_k^{(\mathrm{occ})} \sum_l^{(\mathrm{unocc})} (\bar{E}_l - \bar{E}_k)^{-1} \bar{C}_{jl}\bar{C}_{jk}\delta_{kl} \end{aligned} \tag{19}$$

on using (5). The factors δ_{kl} lead to vanishing contributions when the sums over k and l are carried out since the conditions on the summations mean that k and l can never be equal.

3. Special Cases

We are interested in the relation of $\delta' q_i$ to δq_i. Suppose first that the effect of δq_j for $j \neq i$ can be neglected in (18). This could be due to the smallness of $\delta q_j (j \neq i)$ or to cancellation between terms of different signs. Then we have

$$\delta' q_i = 4\omega\beta\, \delta q_i \sum_k^{(\mathrm{occ})} \sum_l^{(\mathrm{unocc})} (\bar{E}_l - \bar{E}_k)^{-1}\, \bar{C}_{ik}^2 \bar{C}_{il}^2 .$$

Every term in the double summation is positive. Since β is negative we can conclude that the $\delta' q_i$ is opposite in sign to δq_i. Thus, if the population of atomic orbital i is larger than its exact or final value before this iteration it will be smaller than its final value after the iteration and vice versa.

Of course, it is impossible to have δq_i non-zero and $\delta q_j (j \neq i)$ zero because the deviations δq_j must sum to zero. One possible situation is to have all δq_j equal for j not equal to i. This means

$$\delta q_j = -(n-1)^{-1}\, \delta q_i (j \neq i) \tag{21}$$

where n is the number of atomic orbitals. In this case we can also show that the sign of $\delta' q_i$ is opposite to that of δq_i. Equation (18) becomes:

$$\begin{aligned} \delta' q_i = 4\omega\beta\, \delta q_i \sum_k^{(\mathrm{occ})} \sum_l^{(\mathrm{unocc})} \frac{\bar{C}_{ik}^2 \bar{C}_{il}^2}{\bar{E}_l - \bar{E}_k} &+ \frac{4\omega\beta\, \delta q_i}{n-1} \sum_k^{(\mathrm{occ})} \sum_l^{(\mathrm{unocc})} \frac{\bar{C}_{ik}^2 \bar{C}_{il}^2}{\bar{E}_l - \bar{E}_k} \\ &- \frac{4\omega\beta\, \delta q_i}{n-1} \sum_j \sum_k^{(\mathrm{occ})} \sum_l^{(\mathrm{unocc})} \frac{\bar{C}_{ik}\bar{C}_{jl}\bar{C}_{jk}\bar{C}_{il}}{\bar{E}_l - \bar{E}_k} \end{aligned}$$

We have written the sum over $j\,(j \neq i)$ as the sum over j (all j) minus the term for $j = i$. Carrying out the sum over all j, we obtain in the numerator factors of δ_{kl}, as in Eq. (19). Again, the conditions on k and l mean the sum of terms vanishes.

The remaining terms then give

$$\delta' q_i = 4\omega\beta\, \delta q_i \left(\frac{n}{n-1}\right) \sum_k^{(\text{occ})} \sum_l^{(\text{unocc})} \frac{\bar{C}_{ik}^2 \bar{C}_{il}^2}{\bar{E}^{(l)} - \bar{E}^{(k)}} \tag{23}$$

which shows that δq_i and δq_i have opposite signs.

Since we have shown that $\Sigma\, \delta' q_i$ vanishes, the sum of the other deviations after this iteration is opposite in sign to what it was before. If they are all about equal (they were assumed equal before the iteration), each has changed sign. Actually, it can be shown that $\delta' q_h$ is opposite in sign to δq_h if

$$\sum_k^{(\text{occ})} \sum_l^{(\text{unocc})} (\bar{E}_l - \bar{E}_k)^{-1}\, \bar{C}_{hk} \bar{C}_{ik} \bar{C}_{hl} \bar{C}_{il}$$

is negative. Since $\bar{C}_{hk}\bar{C}_{ik}$ summed over all k vanishes, $\bar{C}_{hk}\bar{C}_{ik}$ must take on different signs in different molecular orbitals, and it seems quite likely that the above double sum is indeed negative. The change in sign between $\delta' q_j$ and δq_j means that the populations q_i oscillate about their final values during the iterative process, being alternately too large and too small.

To discuss whether convergence to these final values actually takes place, one must know more about the problem being considered. Under the assumptions of Eq. (21), the ratio of the magnitudes of $\delta' q_i$ and δq_i (and also of the magnitudes of $\delta' q_j$ and δq_j) is

$$|\delta' q_i| / |\delta q_i| = (4n/n-1)\, |\omega\beta| \sum_k^{(\text{occ})} \sum_l^{(\text{unocc})} \bar{C}_{ik}^2 \bar{C}_{il}^2 / (\bar{E}_l - \bar{E}_k)\,.$$

In a calculation on a linear π-electron system using a Hückel method, $\bar{E}_l - \bar{E}_k$ will be some negative multiple of $\beta (\beta < 0)$, but does not increase with n: it never gets larger in size than $|4\beta|$ or smaller than $|2\beta|$. The quantities $\bar{C}_{ik}^2$ are each certainly less than unity because of normalization, but $\bar{C}_{ik}^2$ and $\bar{C}_{il}^2$ cannot simultaneously be close to unity because of (6). In the worst case, each factor could equal $\frac{1}{2}$ for one particular choice of k and l. The sum reducing to one term, we would have

$$|\delta' q_i| / |\delta q_i / = (4n/n-1)\, |\omega\beta| \tfrac{1}{4} (\Delta E)^{-1}$$

where ΔE is between -2β and -4β. This would lead to convergence for $\omega < n - 1/n$, which is about unity. In general, we might expect a distribution of $\bar{C}_{ik}^2$ over the filled and empty molecular orbitals, which would favor convergence with larger values of ω. A commonly used value is 1.4. However, it is known [2, 4] that the method leads to divergence for some molecules and smaller values of ω must be used than 1.4. In general, Eq. (18) implies improved convergence (smaller ratios of $|\delta' q_i|$ to $|\delta q_i|$) for larger molecular orbital energy differences, particularly between the highest occupied and the lowest unoccupied levels. Delocalization should also help convergence, since it would make individual molecular orbital coefficients smaller and lead to sign changes in the last factor.

Perhaps one more special case deserves comment. Suppose all δq_j vanish except two, δq_i and δq_h. Necessarily, we must have $\delta q_h = -\delta q_i$, which leads to

$$\delta' q_i = 4\omega\beta\, \delta q_i \sum_k^{(\text{occ})} \sum_l^{(\text{unocc})} (\bar{E}_l - \bar{E}_k)^{-1} (\bar{C}_{ik}^2 \bar{C}_{il}^2 - \bar{C}_{ik} \bar{C}_{il} \bar{C}_{hl} \bar{C}_{hk})\,. \tag{24}$$

While $\bar{C}_{ik}^2\bar{C}_{il}^2$ is necessarily positive for all k and l, the following terms have different signs for different molecular orbitals. Some cancellation of their contributions is to be expected ($\bar{E}_l-\bar{E}_k$ is always positive), suggesting that the result of the sums over k and l will be positive. The coefficient term in (24) may be rearranged to

$$Q_{kl}=(\bar{C}_{ik}\bar{C}_{il})^2-(\bar{C}_{hk}\bar{C}_{hl})^2+(\bar{C}_{ik}\bar{C}_{il}-\bar{C}_{hk}\bar{C}_{hl})^2 .$$

The corresponding quantity for calculations of $\delta' q_h/\delta q_h$ is obtained by interchanging i and h, which interchanges the signs of the first two terms; call it Q'_{kl}. For each choice of k and l, at least one if not both of Q_{kl} and Q'_{kl} must be non-negative. Q_{kl} will be non-negative if

$$|\alpha|^2-1+|\alpha-1|^2\geqq 0$$

where $\alpha=(\bar{C}_{ik}\bar{C}_{il})/(\bar{C}_{hk}\bar{C}_{hl})$, which is satisfied whenever $\alpha<0$ or $\alpha>1$. Thus, we expect that $\delta' q_i/\delta q_i$ will be negative. Of course, complete reversal of signs of δq_j is impossible here since the $\delta q_j (j\neq i$ and $j\neq h)$ are zero and the corresponding $\delta' q_j$ will not necessarily vanish.

Let us summarize what has been shown. Assuming deviations of populations from their final values are not too large, we derived the linearized Eq. (18) expressing the deviations after an iteration in terms of the deviations before the iteration. These equations are of the form

$$\delta' q_i=\sum_j \delta q_j \sum_k^{(\mathrm{occ})} \sum_l^{(\mathrm{unocc})} C_{kl}^{ij} . \tag{25}$$

The quantities C_{kl}^{ij} had the following properties:

(a) $C_{kl}^{ii}<0$ or all k and l, (b) C_{kl}^{ij} $(i\neq j)$ can be of either sign, but $\sum_i C_{kl}^{ij}=0$ and $\sum_j C_{kl}^{ij}=0$. This made it possible to show $\delta' q_i/\delta q_i<0$ in several special cases. This means that the deviations of populations from their final values alternate in sign on successive iterations.

4. Conclusions

Therefore, the calculated population of a given atomic orbital will oscillate with successive iterations, as has actually been observed in numerical calculations [4]. Values of populations for *alternate* iterations follow relatively smooth curves. The correct final self-consistent populations are to be found between the extremes of the oscillations. This suggests more rapid convergence could be obtained by averaging each population with that resulting from the previous iteration, and using the average as the starting population for the next iteration. Such a scheme, implemented by Ettinger and by Davis and Potts [5], actually produced great improvements in the convergence rate of the iterative process, making possible large decreases in computation time because of the decreased number of iterations necessary. Furthermore, convergence could be obtained [5] for all molecules, even with ω equal to 1.4. The procedure, and the analysis given above, should be applicable to any theoretical model [3] which, like the ω-Technique, modifies matrix elements of the Hamiltonian as a function of calculated populations in order to make large population buildups unfavorable.

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