On the Relation between Hartree-Fock- and Maximum Overlap Molecular Orbitals

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It is pointed out that at the level of a minimum basis set ab initio HF-SCF-MO results and those from the maximum overlap method coincide. Calculated dipole moments for a variety of large molecules of the steroid type are presented.

The many procedures for the calculation of molecular orbitals (MO) are nearly all based upon the Hartree-Fock (HF) equation

$$\boldsymbol{F}\boldsymbol{D} = \boldsymbol{S}\boldsymbol{D}\boldsymbol{E}\,, \tag{1}$$

($\boldsymbol{D}$: matrix of HF-MO coefficients; $\boldsymbol{S}$: overlap matrix; $\boldsymbol{E}$: diagonal matrix of the MO energies) where the MO are obtained by the variation of total energy. There seems to be one exception to these methods, at least in a historical and methodological sense: Pauling's heuristic concept of maximum overlap[1]. This concept is based on the experience that in covalent bonds the bond energy is essentially controlled by the resonance energy which is proportional to the overlap of the two atomic orbitals. Hence, the maximum overlap theory is in fact also derived from the principle of energy variation.

Starting from these qualitative considerations Lykos and Schmeising have created a procedure for the calculation of MO[2]. For the MO

$$\Phi = \sum_i c_i \chi_i \tag{2}$$

in the representation of the basis $\{\chi_i\}$ the square sum of the projections of Φ onto the basis should be a maximum.

$$\sum_i |\langle \chi_i | \Phi \rangle|^2 = \max\,. \tag{3}$$

This implies that the coefficients c_i can be calculated by the secular equations

$$\boldsymbol{S}\boldsymbol{C} = \boldsymbol{C}\Lambda\,. \tag{4}$$

Summarizing, we have achieved a simple non-empirical all-electron method for the approximation of MO without explicit use of the total energy.

Some years later it was pointed out that with a minimal basis set (one basis function per electron pair)[3] the molecular properties calculated by (4) and those from (1) are identical[4]. This can easily be proved by the fact that the orbitals in $\boldsymbol{D}$ can be obtained from those in $\boldsymbol{C}$ by a unitary transformation. Thus we arrive at an interesting result:

With a minimal basis set the Hartree-Fock – and the maximum overlap results are identical.

It should be remarked that in the case of a minimal basis set the total energy is no longer a function of the coefficients in $\boldsymbol{D}$, and therefore the HF procedure degenerates to a single iteration step. Moreover, all other molecular properties are independent of $\boldsymbol{D}$ because the density matrix $\boldsymbol{P}$ now has the form

$$\boldsymbol{P} = 2\,\mathbf{S}^{-1}\,. \tag{5}$$

In other words, the maximum overlap method has lost its approximate character and has advanced to being an exact method within the framework of the one particle approximation. This may throw some light on the reasons for the success of the maximum overlap method. Another possibility in the search for a relationship between HF-MO and maximum overlap MO is the discussion of the commutator $[\mathbf{S}, \boldsymbol{F}]$[5].

The great number of successful applications of the maximum overlap method should not be presented in this short communication. However, in Table 1 the calculated dipole moments for a variety of molecules are listed prior to a more detailed discussion[6]. These results should give some insight into the accuracy, the range of application and the efficiency of computer work for the maximum overlap method.

Spherical Gaussians have been used for the basis set. Saturated molecules, such as methanol and androstane are described by a minimal basis set so that the dipole moments for both methods coincide. For molecules in which π electrons are present the basis set is near minimal (one basis function per

Tab. 1. Calculated[7] and observed[8] dipole moments (D).

Molecule	HF-SCF	Maximum Overl.	Exp.
Methanol	2.27	2.27	1.71
Formaldehyde	1.92	2.97	2.34
Butanol	2.09	2.09	1.81
Propylaldehyde	3.41	3.05	3.04
Acrolein	2.87	2.11	2.80
Cyclohexanone	4.17	4.06	3.00
Cyclohexenone	4.34	3.79	4.17
Bicyclononane	0.31	0.31	—
Androstane	0.41	0.41	—
17α-Hydroxyandrostane	1.68	1.68	1.67
17β-Hydroxyandrostane	1.60	1.60	1.64
Androstan-3-one	4.18	4.10	2.96
4-Androsten-3-one	4.50	4.34	4.10
α-Testosterone	6.22	3.97	5.15
β-Testosterone	4.57	2.74	4.15

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π electron), so that calculated results may be different for both methods. The ratio of computer time between these two methods is about 150:1.

The aim of the investigations was the calculation of the dipole moment for large molecules of biochemical interest. Important polar groups such as $-OH$, $>CO$, $>C=\underset{|}{C}-\underset{|}{C}=O$ have been checked by small molecules in order to analyze the composition of dipole moment in complex systems.

When comparing the calculated and the observed dipole moments it is important to notice that for extremely large molecules unknown geometric parameters may also be the reason for disagreements, as might be the case for testosterone. Another question concerns the basis set. The acroleinic fragment in testosterone was described by ethylene and formaldehyde fragments. Better results would probably be obtained by the use of an acroleinic fragment in testosterone.

For the forthcoming calculation of large molecule properties the limitations also seem to be unknown input data rather than computer and computational methods.

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