Energies of $\sigma^*$ Orbitals from Extended Hückel Calculations in Combination with HAM Theory

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The extended Hückel theory has been given an approximate deduction from first principles. The use of experimental ionization energies for the atoms in the molecule implies that the correlation energy is taken care of. Koopmans' theorem therefore cannot be used. Instead, a $\Delta E_{SCF}$ calculation is performed by using ionization energies, which imply the use of a transition state in the secular determinant. The eigenvalues therefore denote ionization energies, for both occupied and unoccupied orbitals. To find the electron affinities from the ionization energies two procedures are used. From experimental data the relation can be obtained directly for two molecules, but to find a general rule theory is necessary. The result is that the electron affinities can be obtained from the eigenvalues for the unoccupied orbitals simply by adding about 7.0 eV (for hydrocarbons).

The extended Hückel method is in these respects analogous to the HAM method. Electron affinities for $\sigma^*$ orbitals are calculated for a number of molecules and compared with experiment. It appears that the extended Hückel method is useful for such studies. The increased knowledge may be of importance for the understanding of certain chemical reactions.

1. Introduction

In contrast to the occupied orbitals, whose energies are completely known for all small molecules from photoelectron spectroscopy and also from quantum-chemical calculations, most of the corresponding unoccupied valence orbitals are completely unknown.

The reason is that they have high energies, and if an electron enters one of these orbitals, the state will have an extremely short lifetime. The experimental studies are therefore difficult. Only a very small number of molecules have been studied and these only recently. Theoretical calculations seem to be still more problematic. Due to difficulties of calculating correlation energies, ab initio SCF computations can be expected to encounter difficulties in studies of electron affinities, and density functional methods, which appear to be universally useful, do not seem to have been tested yet on these problems.

We decided to test how the extended Hückel method performed for electron affinities. This is the simplest and most primitive of all all-valence-electron methodologies, and yet it describes reasonably well, with some limitations, the energies of occupied orbitals. Would it also be useful for the unoccupied orbitals? Our tests indicate that it is useful for these as well.

A difficulty is that the EH method gives only ionization energies (also for unoccupied orbitals). It is therefore necessary to transform them into electron affinities. We proceed by observing that the EH method can be understood as a special case of the general HAM theory (of which HAM/3 is an approximation). The relation between electron affinity and ionization energy in HAM could therefore be applied to the EHT eigenvalues.

The final procedure is simple: to the EH eigenvalues for the unoccupied orbitals one adds about $+7$ eV (for hydrocarbons). This gives the electron affinities.

In our opinion this has given excellent results. The uncertainty seems to be only a few electronvolts, which in many cases is good enough for a preliminary interpretation of experimental results.

We will first review the experimental methods and results and then describe the theory. Finally, we tabulate our results.

2. Review of Experimental Methods and Results

2.1. Excitation Studies. Although excitation of valence orbitals to $\sigma^*$ orbitals is probably common, we are not aware of any results of use for the present study. It is possible that the difficulties are due to the presence of Rydberg orbitals.

2.2. Temporary Negative Ions Produce Vibrational Excitation. The main method, due to Schulz and co-workers for the study of orbitals by formation of negative ions, is by a study of the vibrational excitation. Energy-analyzed electrons hit the molecule, and the ejected electrons are also energy analyzed. If the two energies differ by one vibrational quantum and if the cross section for this excitation exhibits a maximum, one knows that a temporary negative ion has been formed. The resonances are broad. Our discussion concerns always the vertical transitions (maxima).

Tronc and co-workers found in CO one EA at $-20$ eV and in CO$_2$ two EA's at $-10$ and $-30$ eV. These results prove that the electron enters $\sigma^*$ orbitals. Further results, $-15.5$ eV for NO, and $-9.5$ eV for O$_2$.

An important result concerns acetylene. Tronc and Malegat have found $\sigma^*$ at $-2.6$ eV, $4\sigma$ at $-6.4$ eV and $4\sigma$ at $-21.4$ eV. The symmetries ($g$ or $u$) were determined from the angular dependence. This means that the lower orbital $3\sigma_u$ was not observed.

Tronc and co-workers have further studied HCN with $\sigma^*$ at EA $= -2.3$ eV and $\sigma^*_{CH}$ at $-6.7$ eV, allene with $\sigma^*_{CH}$ at $-2$ eV and $\sigma^*$ (no type given) at $-8$ eV, and NH$_2$ with $\sigma^*_{NH}$ at $-7.3$ eV.

Walker, Stamatovic, and Wong had earlier studied ethylene in a similar machine. They found $\sigma^*$ with EA $= -2.0$ eV and $\sigma^*_{CH}$ as a broad band between about $-5$ eV and beyond $-12$ eV. The explanation is probably that ethylene has four such orbitals with different energies. An X$\alpha$ calculation could not clarify the problem.

Allan has used a similar apparatus, although linear, and has studied diazethene and p-benzoquinone. He finds that in these and other molecules the $\sigma^*_{CH}$ is found as a broad resonance in the range 2–10 eV.

CH$_3$ has been studied in a similar apparatus by Tanaka et al. They found $\sigma^*_{CH}$ at about $-7.5$ eV, but Rohr with a similar apparatus found $-5$ eV.

References

H$_2$O has a broad shape resonance around $-7$ eV.$^{16}$

2.3. The Transmission Method. In the transmission method (Schulz and co-workers$^1$) the scattering, due to formation of temporary negative ions, is studied. The $\sigma^*$ orbitals are easily observable and a large number of organic molecules have been studied.$^{18,19}$ For the interpretation HAM/3 calculations have been successful,$^{2,20}$ but also the Xa method has been used.$^{2,26}$

In earlier work there was usually little structure beyond $-5$ eV, but in recent work broad features are seen, which could be due to $\sigma^*$ orbitals. In neopentane a feature is seen at $-6.1$ eV, which has been interpreted as due to $\sigma^*$ in $C_2$. In methyl fluoride$^2$ a very broad band has been observed between $-5$ and $-8$ eV. In methane features were observed at $-7.8$ and $-12$ eV$^{30}$ and in ammonia at $-5.6$ eV.$^{30}$

2.4. Dissociative Attachment. Dissociative attachment means that first a negative ion is formed, which afterwards dissociates, giving one radical fragment and one anion fragment (for a review, see ref 31).

$$AB + e^- \rightarrow AB^- \rightarrow A + B^-$$

If this process is observed at a certain electron energy, this gives the electron affinity of the $\pi^*$ or $\sigma^*$ orbital, which is involved in the process. There are, however, complications. The dissociation process, which is observed in connection with the attachment, may require a geometry change of the anion. It is possible that in such a case the energy observed for the dissociation does not coincide with the energy in an anion before its geometry changes (see the discussion of fluorinated ethylenes below). The reason for such complications is that only those fragment anions which have a long lifetime can be observed. Much possible information is therefore unobservable.

The experimental arrangement consists of an electron monochromator, a collision chamber, and a mass spectrometer for measurement of the fragment anion.

In acetylene Dressler$^{31}$ observed formation of C$_2$H$^-$ at $E_A = -3$ eV, due to $\pi^*$. Between $-6.5$ and $-7.0$ eV C$_2$H$^-$ and also H$^-$ were formed, and at about $-8$ eV C$_2$H$^-$ and H$^-$.

In acetaldehyde Dressler$^{31,32}$ observed formation of C$_2$H$_2$- ions at $-6.5$ eV without any scrambling of the hydrogen atoms.

Ethylene and many fluorinated ethylenes were studied by Illenberger and co-workers.$^{33,34}$ In ethylene they found fragments (e.g., C$_2$H$^-$ and CH$_2^-$) around $-10.5$ eV but also at $-8$ eV. In tetrafluoroethylene$^{34}$ fragments were found at $-3$ eV ($\pi^*$), at $-11.5$ eV, and also at $-6.5$ eV. They studied also benzene and fluorinated benzenes.$^{35}$

In H$_2$O H$^-$ is formed around $-6.5$ eV.$^{36,37}$

3. Theory

3.1. The Extended Hückel Theory (EHT). The extended Hückel method$^{1,38}$ is a very simple, lightly parametrized one-electron theory. In it one solves the secular equations

$$\sum (H_{\mu \nu} - \varepsilon S_{\mu \nu}) c_{\mu \nu} = 0$$

with overlap included. The basis orbitals, denoted $\mu$ in this paper, are a set of valence orbitals, usually taken as Slater functions. The overlaps $S_{\mu \nu}$ are then calculated directly and the matrix elements of the Hamiltonian are approximated as follows:

$$H_{\mu \nu} = \varepsilon_{\mu} - \varepsilon_{\nu}$$

The constant $K$ is the same for all interactions and is traditionally set to 1.75.

The output from this method gives the eigenvalues of the molecular orbitals. For the occupied orbitals the eigenvalues $\varepsilon_1$ agree reasonably well with experimentally determined ionization potentials from photoelectron spectroscopy (PES). They are typically 2–3 eV too low in energy.

For the unoccupied orbitals of $\pi^*$ type (which are the only ones for which we have full information) the eigenvalues $\varepsilon_1$ are such that excitation energies are calculated as $\varepsilon_1 - \varepsilon_0$. The unoccupied orbitals in EHT could therefore be denoted as "excited orbitals". In this respect EHT differs from Hartree–Fock SCF theories in which the excitation energy is obtained as $\varepsilon_1 - \varepsilon_0$. They studied also benzene and fluorinated benzenes.$^{35}$

The explanation for this complicated result is that the compensation of self-repulsion is performed by use of the exchange integral in such a way that it is effective for occupied orbitals but not for unoccupied orbitals. In HF SCF theory they are therefore denoted as "virtual".

There are only two methods which are similar to EHT in their treatment of the excitation, namely density functional methods, of which the Xa procedure$^{40}$ is best known in the molecular field, and the HAM method. In the Xa method the compensation of self-repulsion is performed by replacement of the exchange integral by the $V_{Xa}$ term, which is the same for occupied and unoccupied orbitals. In HAM it is replaced by a term $-1$, which removes all self-repulsion and is the same for occupied and unoccupied orbitals.

Finally, in EHT there are no repulsions at all and hence no need for compensation of self-repulsion. This explains the similarities. Since the Xa method is complicated to use, we will treat only HAM in the following.

3.2. Deduction of EHT from HAM. Although the HAM/3 method was proposed on purely intuitive grounds, it could be expected from the very good agreement for many types of experiments that the method could be deduced from first principles. The deduction of a more general model, HAM, has now been published.$^{34,45}$ Since the HAM/3 procedure was based on a

(20) HAM/3 calculations of electron affinities have recently been tested for aromatic molecules by Burrow, Michelda, and Jordan (ref 21). They find that for naphthalene, anthracene, and tetracene the HAM/3 results can be used but with some systematic errors. We wish to point out that at least part of the systematic errors may be due to a mistake during the parametrization of HAM/3 (see ref 2; p 125). It was not observed that the final parameters gave incorrect order of the $a_{2g}$ and $e_{2g}$ orbitals in the PES of benzene (at 12.2 and 11.8 eV, respectively, as shown in ref 22). The 2$p$–2$p$ interaction is therefore slightly incorrect, which influences not only aromatics but also butadiene, hexatriene, and other $\pi$ systems.
(38) Hoffmann, R. JCPCE 344.
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rather primitive model, it can best be considered as an effort to
obtain an approximation to the HAM method.
The total energy expression $E$ in HAM is the sum of the
well-known Hartree–Fock total energy expression and an ex-
pression (see ref 2, p 97)
\[ E = \sum_{\nu} \left( \sum_{\mu} P_{\mu} P_{\mu}^* \right) + \sum_{\mu=\nu} \sum_{\sigma=\nu} S_{\nu\sigma} S_{\nu\sigma} (\mu|\mu|) - \frac{1}{2} \sum_{\nu} \left[ P_{\mu} P_{\mu}^* S_{\nu\nu} (\mu|\mu|) \right] \]
which is identically zero, since it describes the orthonormality of
the molecular orbitals (idempotency of density matrix). After
this addition the total energy expression $E$ can be rearranged into
(see ref 2, p 94)
\[ E \approx -\sum_{A=1}^A \left( \sum_{\mu=1}^\mu N_{\nu\sigma}^\mu \right)^2 - \sum_{\mu} P_{\mu} P_{\mu}^* + \sum_{A=\nu} \sum_{\mu=\nu} Q_{\mu} Q_{\mu} R_{AB}^{-1} + \text{some small terms} (5) \]
Here, in the first sum the one-center term $p^\mu_\mu$ is the orbital exponent
as proposed by Slater46,47 (see also ref 2, p 43)
\[ p^\mu_\mu = \frac{1}{n^\mu} \left[ Z - (N^\mu - 1) \alpha^\mu_\mu + N^\mu \alpha^\mu_\mu + \sum_{r^\mu} (N^r \alpha^r_\mu + N^r \alpha^r_\mu) \right] \]
where $N^\mu$ is the total gross population belonging to $\phi_\mu$ on atom
A and $\alpha$ are the shielding efficiencies. The term $-1$ originates
from the exchange integral in the Hartree–Fock total energy
expression together with the idempotency relation eq 4. It takes
care of the self-repulsion completely. The third sum in eq 5 is
the electrostatic interaction.
The remaining terms are two-center terms.
From this total energy expression Roothaan's equations are
obtained by using variational calculus in the conventional way,
giving the Fock matrix element $F_{\mu \nu}$ (see ref 2, p 90)
\[ F_{\mu \nu} = \frac{\partial E}{\partial P_{\mu \nu}} \]
and
\[ F_{\mu \nu} = \frac{\partial E}{\partial P_{\mu \nu}} \]
Solving the SCF problem gives the HAM orbital energies, which
describe the neutral molecule in a mathematical way and which
have no physical interpretation. The corresponding total energy
gives, of course, the total energy of the neutral molecule.
To obtain the ionization energy of the molecule a lengthy
discussion is necessary in HAM (see ref 2, pp 103–108).
The ionization energy for the molecular orbital $\psi^\nu$ is
\[ \text{IP}^\nu = E(q^\nu - 1) - E(q^\nu) \]
where the first term denotes the energy of the ion in which one
electron has been removed from orbital $\psi^\nu$. It can be shown that
if we study a partially ionized molecule, in which half an electron
has been removed from the molecular orbital $\psi^\nu$, then
\[ \text{IP}^\nu = -q^\nu \]
where the superscript $t$ denotes the transition state and $q^\nu$ the
eigenvalue for the molecular orbital $\psi^\nu$ in the partially ionized
molecule.
This means that all SCF calculations have now to be performed
for the partially ionized molecule, and instead of the Fock matrix
element $F_{\mu \nu}(q^\nu - 1/2)$ in the secular determinant in our HAM calculation.
Solving the secular determinant then gives eigenvalues of which
that for orbital $i$ denotes $-\text{IP}$, and those for the other orbitals give
approximate values for their IP's (see ref 2, pp 105–107). These
results are valid for both occupied and unoccupied orbitals, at-
though in the last case the concept "ionization energy" has only
a formal meaning.
We will now show in a qualitative way how the HAM procedure
can be transformed into the EH procedure.
First we neglect the electrostatic interaction in eq 5, since it
is small in a molecule with covalent bonded atoms.
Then we observe that $F_{\mu \nu}(q^\nu)$ and $F_{\mu \nu}(q^\nu - 1/2)$ differ little
in a large molecule in which the charge $-1/2$ is partitioned among
many atoms.
Next we observe that the one-center terms in eq 5 are completely
separated, and atom A is for instance represented by only
one term:
\[ -\frac{1}{2} \sum_{\mu} N^\mu_\mu = (\text{AE}) \]
The Fock matrix element in HAM is thus
\[ F_{\mu \nu} = \frac{\partial E_A}{\partial P_{\mu \nu}} \]
for $\mu$ on atom A (neglecting the electrostatic interaction). Since
$\text{IP}^\nu = P_{\mu \nu} + \sum_{\nu} P_{\mu \nu} S_{\nu\nu}$
(see ref 2, p 9) it can be written
\[ F_{\mu \nu} = \frac{\partial E_A}{\partial q_\mu} \]
To discuss the corresponding matrix element in EHT we observe
that the total energy of atom A can be written (see ref 2, p 47)
\[ E_A = -\frac{1}{2} \sum_{\mu=\nu} N^\mu_\nu \]
(11)
The ionization energy of the atom is then
\[ \text{IP}_A = E_A(q^\nu - 1) - E_A(q^\nu) = -\frac{\partial E_A}{\partial q_\mu} \]
(12)
The use of the negative ionization potentials in EHT follows thus
in a qualitative way from the HAM procedure.
The general rules in HAM are therefore applicable also in EHT.
The first and simplest observation is that, if the parameters in
EHT have been chosen in such a way that the EH eigenvalues
for the occupied orbitals denote their ionization energies, then
the same will be true also for the unoccupied orbitals.
3.3. The Relation between Ionization Energies and Electron
Affinities in HAM (and Also in EHT).
The complicated zero, eq 4, can be simplified, again using the orthonormality of
the molecular orbitals (see ref 2, p 98), giving a new form of the zero:
\[ \frac{1}{2} \sum_{\mu \nu} q^\mu(q^\nu - 1) L_{\mu \nu} \]
(13)
with
\[ L_{\mu \nu} = \frac{1}{2} \sum_{\mu \nu} \alpha_\mu^\nu c_\mu^\nu S_{\mu \nu}(\mu|\mu| + (\nu|\nu)) \]
(14)
which has to be added to the Hartree–Fock total energy (ref 2,
p 97).
Although this contribution to the total energy is zero, it will
influence the calculations of ionization energy IP and electron
affinity EA, giving
\[ \text{IP}_A = -q_\mu + \frac{1}{2} L_{\mu \nu} \]
(15)
where $q_\mu$ denotes the orbital energy, belonging to the neutral
molecule (see ref 2, p 103, eq (H.4)). Further,
\[ EA_A = -q_\mu - \frac{1}{2} L_{\mu \nu} \]
(16)
(see ref 2, p 187, eq J.2). These relations are valid independent
of the occupation (orbital charge) $q^\mu$ in orbital $\psi^\nu$ ($q^\nu = 0$ for
an unoccupied and $q^\nu = 1$ for an occupied orbital).
It follows that the difference between IP and EA is simply
$L_{\mu \nu}$, and by adding $L_{\mu \nu}$ to the EHT eigenvalue for the unoccupied

(45) Lindholm, E.; Lundqvist, S. In Density Matrices and Density Func-
(47) Slater, J. C. Quantum Theory of Atomic Structure; McGraw-Hill:
orbital we obtain its EA with negative sign.

In the expression for $L_j$, the integral $\langle \alpha | \mu | \beta \rangle$ denotes the one-center electron-electron repulsion change $\Delta E_{\alpha \beta}$ of the occupied and unoccupied orbitals. Here one could use values from atomic theory where this integral is denoted $F_{\alpha \beta}$ with the following values: H, 12.8 eV; C, 11.1 eV; N, 12.1 eV; O, 13.6 eV; F, 15.6 eV. It is seen that for hydrogen and carbon the $F_{\alpha \beta}$ values are nearly the same. For hydrocarbons eq 14 can then be approximated (see ref 2, p 99):

$$L_j \approx \gamma_{2s,2p} x_2 + \gamma_{2p,x_2} = \gamma_{2s,2p}$$ (17)

This means that for a hydrocarbon $L_j \approx 11.5$ eV. For molecules with heteroatoms we expect larger $L_j$.

3.4. Characteristics of the Extended Hückel Theory. The diagonal elements in the EHT secular determinant are the experimental ionization energies of the valence orbitals of the atoms in the molecule. This means that all one-center correlation energy in the molecule is in principle taken into account, and this means most of the correlation energy in the molecule. In such a situation Koopmans' theorem is not suitable for calculations of ionization energies, since the accuracy of this method rests upon the cancellation of change of correlation energy with the reorganization energy. Since EHT is used to calculate ionization energies of a molecule, it is therefore necessary to calculate the reorganization energy exactly, either by use of a MscF calculation or by use of a transition-state method in which the average of the molecule and the cation is studied. In EHT the transition-state method has been chosen, since the ionization energies, used in EHT, correspond to a $\Delta E_{\text{SCF}}$ procedure. In this way the "eigenvalues" in the output from a EHT calculation give just ionization energies.

4. Experimental Evidence for the Relation between Ionization Energy and Electron Affinity

Equation 17 has been obtained from Hartree–Fock theory by use of the orthonormality of the molecular orbitals. This shows that generally the same $L_j$ can be used for all orbitals (both occupied and unoccupied) in a hydrocarbon molecule.

If we now study a special case (for instance $\pi^*$ in ethylene) by use of well-known experimental data, our finding can be assumed to have general validity.

In ethylene the $\pi^*$ excitation energy (average of singlet at 7.6 eV and triplet at 4.3 eV)49 is 5.9 eV. The ionization energy of $\pi$ is 10.9 eV. It follows that the "ionization energy" of $\pi^*$ is 5.0 eV. Since the electron affinity of $\pi^*$ is $-1.8$ eV, we find that the difference between IP and EA for $\pi^*$ is 6.8 eV. This difference has been denoted as $L_j$ above. The experimental $L_j$ is thus smaller than the spectroscopic value, 11.5 eV, given above.

The difference, 6.8 eV, between IP and EA, which we have obtained from experimental data, is in good agreement with the results from HAM/3 calculations for many molecules. HAM/3 was parametrized long before these general relations were understood, but since both positive and negative ions were used in the parametrization, values for $L_j$ in agreement with experiment are obtained from HAM/3 outputs.

Since our $L_j$ can be assumed to have general validity, we will use $L_j = 7.0$ eV for hydrocarbon molecules.

For molecules with heteroatoms we expect larger $L_j$. We will study the $\sigma^*$ orbital 3$\sigma_2$ in fluorine. Since the $1s_{\text{F}} \rightarrow 3\sigma_2$ excitation energy is 4.1 eV (singlet at 4.6 eV and triplet at 3.6 eV)50,51 and since the ionization energy of $1s_{\text{F}}$ is 15.9 eV, we conclude that the "ionization energy" of $3\sigma_2$ is 11.8 eV. Since the experimental EA is $+2.9$ eV,52 we find $L_j = 8.9$ eV for $\sigma^*$ in $F_2$.

We are not aware of any other molecule for which enough experimental data are available for a similar study.

In the calculations below we will use $L_j = 8.0$ or 9.0 eV when the molecule contains heteroatoms.

A slightly different problem concerns the study of a negative ion. In section 7 we will use the orbital energies of (F-CH$_3$F)~. They are obtained from the EHT eigenvalues by adding $1/2L_j$, which for this problem means about 12.0 eV. (The EH calculation is performed for the neutral molecule, and therefore the negative electron affinities are obtained by adding $L_j$. The HAM/3 calculation is performed for the anion, and according to eq 16 the difference between the eigenvalues for the anion and the negative electron affinities is $1/2L_j$.)

5. The Parameters in EHT

Our preliminary studies using the standard EHT program gave a very reasonable agreement for the electron affinities of several molecules.

It was then reasonable to test whether a small change of the parameters could improve the agreement. It appeared that a change of "exp", the orbital exponent of the Slater orbitals, influenced the energies of the occupied orbitals very little (a few tenths of 1 eV) but influenced the energies of the unoccupied orbitals very much. To illustrate this we give in Table II not only the calculated EA's but also the calculated PES.

The changes were done in the following order.

First, the values of the Slater exponent for carbon 2p and hydrogen 1s were determined so that the correct electron affinity was obtained for methane. This gave a relation between the values for 2p and hydrogen 1s. (The EA of the antibonding orbitals is probably strongly dependent on the overlaps between 2p and hydrogen, and an increased size of 2p requires a diminished size of the hydrogen orbital.)

Second, several molecules, especially acetylene, were tested in order to find reasonable values for the Slater exponents. A difficulty appeared for the carbon orbitals. Their eigenvalue was too low in all molecules. This error could easily be corrected by changing the orbital exponent for 2p in carbon. But then a more serious error appeared. The outermost $\sigma^*$, which also depends on 2p, got a far too high eigenvalue (by tens of 1 eV).

Since the object of the present paper is to study $\sigma^*$ orbitals, we decided to accept erroneous $\pi^*$ eigenvalues.

The reason behind the difficulty is probably that the 2p–2p interaction in $\pi^*$ and the 2p–2p interaction in $\sigma^*$ require different Hückel constants instead of the single value, 1.75, in the EHT program.

Since we compared also the EHT ionization energies with the photoelectron spectra, we found it desirable to change also the energy parameters a little. The change in the carbon 2p energy was valuable since the conventional value gave too high HOMO and LUMO (since the EHT excitation energy is always reasonable, the errors in HOMO and LUMO are usually the same). We could now use nearly the same $L_j$ for LUMO and the $\sigma^*$s, which was not at all possible with the conventional energies for 2p.

The parameters used in our EHT calculations are given in Table I.

6. Comparison between Calculated and Experimental Electron Affinities for Some Molecules

In Table II the calculated and experimental electron affinities for some molecules are compared. To increase the credibility of our study the calculated and experimental ionization energies from photoelectron spectroscopy are also compared.
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We discuss below the results for some of the molecules. (The numbering is the same as used in Table II.)

1. Methane. The shape resonance with $\text{EA} = -7.5 \text{ eV}$ or $-5 \text{ eV}$\textsuperscript{15} is a $T_2$ state and depends therefore on the C(2p)-H interaction. An Xa study\textsuperscript{26} gives $-6.0 \text{ eV}$ for $\Sigma_T$. It is uncertain whether the feature at $12 \text{ eV}$\textsuperscript{29} corresponds to $\Sigma_A$. If we change the parameters to get improvement for methane, the acetylene results will be impaired.

2. Acetylene. The agreement with the important study by Tronc and Malegat\textsuperscript{7,8} constitutes the basis for the present paper. The errors in our calculated EA values are around $3 \text{ eV}$, but this is not unexpected since the error in one PES value is $2.0 \text{ eV}$. The calculated $\sigma_{xy}$ orbital is strongly C-C bonding and strongly C-H antibonding. It is therefore satisfactory that Dressler\textsuperscript{11} observed only $\text{C}_2\text{H}^-$ at $-6.5 \text{ eV}$ and $\text{C}_2^-$ at $-8 \text{ eV}$ but not $\text{CH}_2^-$ nor $\text{CH}^-$. The ethylene outermost orbital with calculated $\text{EA} = -11.5 \text{ eV}$ is C-C antibonding with small contributions from hydrogen. The broad $\sigma^*_{\text{CH}}$ band, observed by Walker et al.,\textsuperscript{10} must therefore be due to the next four orbitals. In dissociative attachment\textsuperscript{13} formation of $\text{C}_2\text{H}^+$ predominates. The corresponding orbitals must therefore be C-C bonding ($a_1$ and $b_2$). It is then satisfactory that the experimental results show two maxima for this process: one strong at $-11 \text{ eV}$ and one weak at $-7.5 \text{ eV}$. If our interpretations in Table II are correct, our calculated EA's are $3.0 \text{ eV}$ too low. This is not unexpected since two PES values are in error by $1.5 \text{ eV}$.

5. Benzene. The EHT study of benzene is less successful than the study of smaller hydrocarbons. For three occupied orbitals the errors are larger than $2 \text{ eV}$. Since dissociative attachment\textsuperscript{15} gives loss of H at $-8 \text{ eV}$ and cleavage of the ring giving $\text{C}_2\text{H}_3^-$ between $-8$ and $-11 \text{ eV}$, we have looked for orbitals with localized strongly antibonding properties. Orbital $1a_{2g}$ with calculated $\text{EA} = -8.1 \text{ eV}$ is an antibonding chain between the carbons, and ring cleavage is then reasonable if the extra electron enters this orbital.

Orbital $4e_{2u}$ with calculated $\text{EA} = -6.9 \text{ eV}$ is in one of its components strongly antibonding with the hydrogens in the 1- and 4-positions. Attachment of the electron into this orbital could lead to loss of H.

The other empty orbitals in benzene have no pronounced localized antibonding properties.

Our assumption that loss of H or ring cleavage is related to the antibonding property of certain orbitals is supported by similar processes in mass spectrometry. It has been shown that loss of H or $\text{H}_2$ from the cation starts at $13.8 \text{ eV}$, which is the energy of the $\Pi$-H bonding orbital. Further, ring cleavage giving $\text{C}_2\text{H}_3^-$ or $\text{C}_2\text{H}_4^+$ starts at $14.1 \text{ eV}$, which is the energy of the strongly ring-bonding orbital $1b_2$. The $2b_1$ state in Table II has thus never been observed.

Some processes at higher energies\textsuperscript{37} have low intensity.

10. Acetaldehyde. In dissociative attachment\textsuperscript{21,22} a remarkable result was obtained. $\text{CH}_3^-$ is obtained at $-6.5 \text{ eV}$ without any scrambling of the hydrogens and $\text{CH}_2\text{CDO}$ gives pure $\text{CH}_2^-$. This shows that the dissociation of the anion must be extremely fast (cf. mass spectrometry of hydrocarbons, where scrambling is important). If the EHT results are reliable, the explanation should be the existence at $\text{EA} = -6.5 \text{ eV}$ of a molecular orbital which is strongly C-C antibonding.

During our parametrization work such an orbital was observed. When the parameters were improved another orbital got nearly the same energy and mixing took place. To obtain this orbital from the present calculation we have to assume that the calculated EA's $-5.5 \text{ eV}$ for $\varphi_1$ and $-5.2 \text{ eV}$ for $\varphi_2$ are equal. We can then mix them, and it appears that the difference $\varphi_3 - \varphi_2$ is antibonding between the carbons and has negligible contributions from oxygen and the hydrogens.

13. Ammonia. Vibrational excitation\textsuperscript{5} shows a resonance at $-7.3 \text{ eV}$. Its symmetry could not be determined, but from the excitation of $v_1$ vibrations (symmetric NH stretching) we will assume $\Sigma_A$. At lower energy ($-5.6 \text{ eV}$) $\text{H}^-$ and $\text{NH}_2^-$ are formed.\textsuperscript{35} If we attribute this to the $\Sigma_A$ resonance. At about the same energy transmission studies\textsuperscript{26} show a long progression of symmetric bending vibrations. This is interpreted as the Feshbach resonance ($1a_1'' + 3s_1$). At high energy ($-10.5 \text{ eV}$) a fourth state has been observed\textsuperscript{24} giving fragmentation.

14. HCN. Vibrational excitation\textsuperscript{5} shows that the resonance at $-6.7 \text{ eV}$ is C-H antibonding in good agreement with the EHT orbital.

15. Fluorine. The good agreement with the experimental EA is due to the good calculated excitation energy. It can be mentioned that for HF the EHT calculation gives an excitation energy which is incorrect by $4.0 \text{ eV}$.

16. Carbon Tetrafluoride. Dissociative attachment\textsuperscript{25,26} gives $\text{F}^-$ and $\text{CF}_3^-$ with maximum at $-7.0 \text{ eV}$. At about $-0.5 \text{ eV}$ Verhaar et al.\textsuperscript{60} have observed in transmission a feature which could be our calculated $\Sigma_A$ at $-3.0 \text{ eV}$. If so, we expect excitation of symmetric C-F vibrations with reduced energy due to the antibonding orbital. Verhaar's discussion was based upon the assumption that $\Sigma_A$ has no low-lying valence orbitals, and therefore their discussion concerned antisymmetric C-F vibrations. An Xa calculation\textsuperscript{76} gives $2F_2$ at $-3.2 \text{ eV}$ but puts the $\Sigma_A$ at a higher energy ($-5.1 \text{ eV}$).

17. Hexafluoroethane. Dissociative attachment\textsuperscript{27,58} gives $\text{F}^-$ and $\text{CF}_3^-$ at $-4.0 \text{ eV}$. Since the orbital with calculated EA $-3.1 \text{ eV}$ is C-C antibonding, the formation of $\text{CF}_3^-$ is explained.

19. Methyl Fluoride. In transmission Othoff\textsuperscript{24} has recently observed a broad band between $-5$ and $-8 \text{ eV}$. Our calculated values are thus a little too low.

20. Tetrafluoroethene. In our study of fluorinated ethylenes\textsuperscript{33,34} we encountered an unexpected difference between two kinds of molecules. Our results for ethylene, tetrafluoroethylene, and 1,1-difluoroethene are hopefully successful, but for the other ethylenes, which are more unsymmetric, the EHT calculations gave energy values which could not be satisfactorily interpreted. Inspection of the measured curves showed that the “difficult” molecules all show a strong dissociative attachment near $2.0 \text{ eV}$ (shaded areas in ref 33). The dissociations here are due to attachment in the $\pi^*$ orbital, but since they are symmetry forbidden, a geometry change is necessary to mix $\pi^*$ and $\sigma^*$ orbitals.

<table>
<thead>
<tr>
<th>Substance</th>
<th>EHT</th>
<th>L - PES</th>
<th>EHT + L</th>
<th>-EA_{exp}</th>
<th>Ref.</th>
<th>EHT</th>
<th>L - PES</th>
<th>EHT + L</th>
<th>-EA_{exp}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Methane (CH₄)</td>
<td>+1.2</td>
<td>7</td>
<td>+0.8</td>
<td>+5.3</td>
<td>+7.5</td>
<td>15</td>
<td>+14</td>
<td>-14.0</td>
<td>-24.4</td>
<td>-25.0</td>
</tr>
<tr>
<td>2. Acetylene (C₂H₂)</td>
<td>+17.7</td>
<td>4aₜ</td>
<td>+24.7</td>
<td>+31.4</td>
<td>7</td>
<td>31</td>
<td>-14.3</td>
<td>-14.0</td>
<td>-12.7</td>
<td>-12.6</td>
</tr>
<tr>
<td>3. Ethylene (C₂H₄)</td>
<td>+10.9</td>
<td>1bₜ</td>
<td>+8.0</td>
<td>+11: C₂H⁻</td>
<td>33</td>
<td>10</td>
<td>-14.3</td>
<td>-14.0</td>
<td>-12.7</td>
<td>-12.6</td>
</tr>
<tr>
<td>4. Allene (C₃H₄)</td>
<td>+10.0</td>
<td>2bₜ</td>
<td>+9.7</td>
<td>+6.4,+6.5</td>
<td>18</td>
<td>-20.1</td>
<td>-37.1</td>
<td>-38.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Benzene (C₆H₆)</td>
<td>+4.5</td>
<td>4bₜ</td>
<td>+11.5</td>
<td>+14.7</td>
<td>-1.1</td>
<td>+1.8</td>
<td>-37.2</td>
<td>-38.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Neopentane (C(CH₃)₃)</td>
<td>+0.2</td>
<td>7</td>
<td>+7.2</td>
<td>+5.3</td>
<td>+7.5</td>
<td>27</td>
<td>+18.4</td>
<td>+18.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Carbon Monoxide (CO)</td>
<td>+1.6</td>
<td>a₁</td>
<td>+9.6</td>
<td>+7.3</td>
<td>9</td>
<td>56</td>
<td>+2.2</td>
<td>+5.8</td>
<td>+5.6</td>
<td>56</td>
</tr>
<tr>
<td>8. Carbon Dioxide (CO₂)</td>
<td>+0.1</td>
<td>a₁</td>
<td>+14.2</td>
<td>+7.0</td>
<td>16</td>
<td></td>
<td>+0.6</td>
<td>+3.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. Water (H₂O)</td>
<td>+11.5</td>
<td>a₁</td>
<td>+4.5</td>
<td>+6.2</td>
<td>8</td>
<td>5</td>
<td>+2.3</td>
<td>+2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10. Acetaldehyde (CH₃CHO)</td>
<td>+1.8</td>
<td>5cₜ</td>
<td>+10.9</td>
<td>+16.4</td>
<td>-0.7</td>
<td>+1.2</td>
<td>+19.5</td>
<td>+19.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11. Nitrogen (N₂)</td>
<td>-11.4</td>
<td>6aₜ</td>
<td>-12.4</td>
<td>-9.7</td>
<td>-0.2</td>
<td>+7.8</td>
<td>+8.4</td>
<td>+8.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12. Nitrous Oxide (N₂O)</td>
<td>-12.0</td>
<td>8bₜ</td>
<td>-12.9</td>
<td>-14.1</td>
<td>-14.1</td>
<td>+7.3</td>
<td>+26.4</td>
<td>+26.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13. Ammonia (NH₃)</td>
<td>+0.4</td>
<td>7</td>
<td>-19.6</td>
<td>-16.5</td>
<td>-16.5</td>
<td>+5.5</td>
<td>+6.5</td>
<td>+6.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14. Hydrogen Cyanide (HCN)</td>
<td>+1.9</td>
<td>7</td>
<td>-24.2</td>
<td>-21.9</td>
<td>-21.9</td>
<td>+5.2</td>
<td>+5.2</td>
<td>+5.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*EA* refers to Electron Affinities, *PES* refers to Potential Energy Surfaces, and *EHT* refers to Extended Hückel Theory.
We suggest therefore that the difficult molecules change their geometry during the attachment, and that therefore an EH calculation on the planar molecule gives inapplicable energies.

The dissociative attachment spectra of C\textsubscript{2}F\textsubscript{4} show strong bands around -3.5 eV (F\textsuperscript{-} and CF\textsubscript{2}\textsuperscript{-}). They could be due to π\textsuperscript{*}, but the formation of CF\textsubscript{2}\textsuperscript{-} indicates attachment to an orbital which is strongly C-C antibonding. We suggest therefore that these bands are due to the σ\textsuperscript{*} orbital 6b\textsubscript{1u} with calculated EA = -1.9 eV, and that the molecule remains planar during the attachment. This means that no dissociation, which we observe, is due to F\textsuperscript{-}.

It is thus possible that the lowest σ\textsuperscript{*} orbital is lower than π\textsuperscript{*}. This agrees with findings from EPR studies which show that the C\textsubscript{2}F\textsubscript{4} radical anion is a σ\textsuperscript{*} radical.

Also orbital 5b\textsubscript{2u} with calculated EA = -10.4 eV is strongly C-C antibonding and can therefore explain the formation of CF\textsubscript{2}\textsuperscript{-} at -11.5 eV.

21. Hexafluorobenzene. Orbital 1a\textsubscript{2u} with calculated EA = -8.6 eV is the antibonding chain, which is shown for benzene at EA = -8.1 eV. It is localized on the carbons, and its energy is therefore not much influenced by the F atoms. After the ring cleavage dissociations giving loss of F or F\textsuperscript{-} may take place.

Orbital 7e\textsubscript{1u} with calculated EA = -5.0 eV is also shown for benzene (at -6.9 eV). Loss of F or F\textsuperscript{-} is obvious.

20. Tetrafluoroethylene (C\textsubscript{2}F\textsubscript{4}).

<table>
<thead>
<tr>
<th>EHT</th>
<th>L</th>
<th>-PES</th>
<th>EHT + L</th>
<th>-EA\textsubscript{exp}</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>-13.0 σ\textsubscript{a}</td>
<td>9</td>
<td>15. Fluorine (F\textsubscript{2})</td>
<td>-17.2</td>
<td>e</td>
<td>-17.0</td>
</tr>
<tr>
<td>-16.3 π\textsubscript{a}</td>
<td>-15.9</td>
<td>-18.8</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>-18.6 σ\textsubscript{a}</td>
<td>-21.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-38.0 σ\textsubscript{a}</td>
<td>-37.5</td>
<td></td>
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<tr>
<td>-40.1 σ\textsubscript{a}</td>
<td>-41.8</td>
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<tr>
<td>-0.5 t\textsubscript{2}</td>
<td>8</td>
<td>+3.0</td>
<td>+1</td>
<td>60</td>
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<td>-17.4</td>
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<tr>
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<td></td>
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</tr>
<tr>
<td>-7.3 e</td>
<td>-18.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-17.8 t\textsubscript{1}</td>
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<td>-43.8</td>
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<tr>
<td>+0.3 e</td>
<td>8</td>
<td>+8.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1.2 σ\textsuperscript{*}C-C</td>
<td>8</td>
<td>+6.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1.6 e</td>
<td>8</td>
<td>+6.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-2.1 e</td>
<td>8</td>
<td>+5.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-4.9 σ\textsuperscript{*}C-C</td>
<td>8</td>
<td>+3.1</td>
<td>+4</td>
<td>57, 58</td>
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</tr>
<tr>
<td>-13.8</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-16.7 e</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-7.2 e</td>
<td>9</td>
<td>+1.8</td>
<td>+1.7</td>
<td>57</td>
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<tr>
<td>-8.0 a\textsubscript{1}</td>
<td>9</td>
<td>+1.0</td>
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<td>-13.8</td>
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</tr>
<tr>
<td>-16.8 e</td>
<td>-16.4</td>
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<td></td>
</tr>
<tr>
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<td>-15.9</td>
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</tr>
<tr>
<td>-17.2 e</td>
<td>-17.5</td>
<td></td>
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<tr>
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<td>-19.8</td>
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</tr>
<tr>
<td>-18.2 e</td>
<td>-21.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+0.3 a\textsubscript{1}</td>
<td>CH\textsubscript{3}</td>
<td>+7.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1.6 a\textsubscript{1}</td>
<td>CH\textsubscript{3}</td>
<td>+5.4</td>
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<tr>
<td>-3.4 σ\textsuperscript{*}C-F</td>
<td>8</td>
<td>+4.6</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>-14.3 e</td>
<td>-13.1</td>
<td></td>
<td></td>
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<tr>
<td>-16.9 a\textsubscript{1}</td>
<td>-17.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The column EHT gives the eigenvalues and EHT + L after addition of L\textsubscript{ij} which in the table is denoted L. PES gives the experimental ionization energies and EA\textsubscript{exp} gives the experimental electron affinities. In some cases the degenerate orbitals are denoted e. The two references correspond to the first and second values in the -EA\textsubscript{exp} column.

7. Applications to Chemical Reactions

7.1. Photochemistry of Ethane. For all other molecules in this paper our calculations have been compared with electron affinities. It is, of course, possible to use these data for estimation of excitation energies.

It is known that photolysis of ethane with 1400-A light gives loss of H\textsubscript{2}. Studies of partially deuteriated ethane show that both hydrogen atoms come from the same methyl group in ethane. Theoretical studies have been performed under the assumption that the low-lying excited states of ethane are entirely Rydberg in nature. We will now try to explain the process using the excited valence orbitals from the EH calculation (see "22. Ethane" in Table II).

Excitation from 1e\textsubscript{g} (orbital 10 with calculated energy -12.0 eV) to 2e\textsubscript{g} (orbital 5 with calculated value -3.0 eV) requires 9.0 eV.

*The column EHT gives the eigenvalues and EHT + L after addition of L\textsubscript{ij} which in the table is denoted L. PES gives the experimental ionization energies and EA\textsubscript{exp} gives the experimental electron affinities. In some cases the degenerate orbitals are denoted e. The two references correspond to the first and second values in the -EA\textsubscript{exp} column.

---


TABLE III: Study of (F-CH$_3$-F) at the Transition Geometry of an S$_2$2 Reaction$^{a}$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>EHT</th>
<th>L</th>
<th>EHT + 1/2L</th>
<th>HAM/3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$ +</td>
<td>-0.8</td>
<td>e</td>
<td>CH$_3^*$</td>
<td>7</td>
</tr>
<tr>
<td>F</td>
<td>-1.2</td>
<td>e</td>
<td>CH$_3^*$</td>
<td>7</td>
</tr>
<tr>
<td>F</td>
<td>-8.4</td>
<td>e</td>
<td>C$_2$</td>
<td>8</td>
</tr>
<tr>
<td>F</td>
<td>-14.6</td>
<td>e</td>
<td>CH$_3^*$</td>
<td>7</td>
</tr>
<tr>
<td>F</td>
<td>-16.8</td>
<td>e</td>
<td>F</td>
<td>9</td>
</tr>
<tr>
<td>F</td>
<td>-17.0</td>
<td>e</td>
<td>F + F</td>
<td>9</td>
</tr>
<tr>
<td>F</td>
<td>-17.1</td>
<td>e</td>
<td>F + F</td>
<td>9</td>
</tr>
<tr>
<td>F</td>
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<td>F</td>
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</tr>
<tr>
<td>F</td>
<td>-22.4</td>
<td>e</td>
<td>C$_2$F</td>
<td>8</td>
</tr>
<tr>
<td>F</td>
<td>-39.0</td>
<td>e</td>
<td>F</td>
<td>9</td>
</tr>
</tbody>
</table>

$^{a}$C-F distance = 1.878 Å. Eigenvalues from an EH calculation are given. The orbital energies of the anion are then obtained by adding $1/2J_{ij}$ (see section 4). Since most of the orbitals are strongly localized, we have used $J_{ij}$ values according to eq 15 and the rules above. The orbital energies of the occupied orbitals are then compared with the orbital energies from a HAM/3 calculation, since no experimental results are available for a comparison.

In other words, the two electrons are simultaneously on one of the methyl groups, and since all three hydrogens on this group have the same sign in the excited state, we do not believe that this reaction can leave as H$_2$, taking with them two electrons. The CH$_3$CH molecule is then formed in its ground state.

The description here is not quite correct, since in orbital 10 the hydrogens are bonded whereas in orbital 5 they are antibonded. The description must therefore be completed by addition of a covalent component.$^{67}$

Excitation from $\sigma$ (orbital 8 at $-12.6$ eV) to $\sigma^*$ (orbital 7 at $-3.1$ eV) can be discussed in the same way, but since CH$_3$CH is now formed in an excited state, we do not believe that this reaction takes place.

This is speculative. Only the calculated excitation energy 9.0 eV and the fact that all hydrogens have the same sign in the excited state after an allowed transition are direct results from the EH study.

7.2. The $S_p$2 Reaction $\text{F}^+ + \text{CH}_3\text{F} = \text{FCH}_3 + \text{F}^-$: A problem in the theory for $S_p$2 reactions is to understand to what extent the $\sigma^*$ orbital takes part in the reaction by mixing with the $\sigma$ orbitals. This has been discussed much (for references see ref 72), but no definite answer has been given since the energies of $\sigma^*$ orbitals have been unknown. An EH calculation might give an approximate answer.

In Table III the molecule (F-CH$_3$-F)$^+$ is studied at the transition geometry. Before any conclusions concerning $\sigma^*$ can be drawn we must show that the EH calculation is reasonable. In the absence of experimental information we compare with the results from a HAM/3 calculation,$^{68}$ which is probably more accurate. It is seen that our addition of $1/2J_{ij}$ (for proof see section 4) is reasonably successful. The deviations are not larger than one can expect from an EH calculation.

The difference between the orbital energies of $\sigma^*$ and $\sigma$ in the anion is thus $3.6 + 3.3 = 6.9$ eV. Since the matrix element for the interaction is small, we can to a reasonable approximation neglect the interaction with $\sigma^*$ in this $S_p$2 reaction.

8. Summary and Conclusions

The results for several small molecules show that extended Hückel calculations, in combination with HAM theory, can be used to predict the energies of $\sigma^*$ orbitals in a molecule. The errors for the molecules studied here are not larger than a few eV, which corresponds to the errors in the calculations of ionization energies by use of the EH method.

It follows that the extended Hückel method, which is the most simple and most primitive of all all-valence quantum-chemical methods, can be used to study both occupied and unoccupied orbitals of a molecule, since it is directly useful for the calculation of excitation energies.

The extended Hückel method has been derived from first principles, i.e., from Hartree–Fock theory, by use of the HAM method as an intermediate.

It should be stressed that conventional uses of the extended Hückel theory, e.g., deduction of Woodward–Hoffmann's rules, require only calculated ionization energies of electrons in occupied orbitals together with calculated excitation energies. These uses are very little influenced by the suggested changes of some parameters in this paper, and for such uses the conventional parameters$^{1,18}$ are recommended for the future. Only when $\sigma^*$ orbitals are studied the new parameters might be useful.

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Registry No. CH$_4$, 74-82-8; C$_2$H$_6$, 74-86-2; C$_3$H$_8$, 74-85-1; CH$_5$, 463-49-0; C$_4$H$_{10}$, 71-43-2; C(CH$_3$)$_4$, 463-82-1; CO, 630-08-0; CO$_2$, 124-38-9; H$_2$O, 7732-18-5; CH$_3$CHO, 75-07-0; N$_2$, 7727-37-9; N$_2$O, 10024-97-2; NH$_3$, 7664-41-7; HCN, 74-90-8; F$_2$, 7782-41-4; CF$_4$, 75-73-0; C$_2$F$_2$, 76-16-4; NF$_3$, 7783-54-2; CH$_2$F, 593-53-3; C$_2$F$_{2}$, 116-14-3; C$_2$F$_{3}$, 392-56-3; C$_2$H$_4$, 74-84-0.