fect should be measurable in a suitably large magnetic field. The almost vanishing $g_{\perp}$ values for the ^2E states yield somewhat simpler patterns for special directions of the applied field.[28] The anistropy of the ground-state g values is very small, being an order of magnitude less than the small ($\sim 1\%$) departure from the spin-only value. Our calculation gives an anistropy of the correct sign ($g_{||} > g_{\perp}$) but about a factor of 2 too large. In view of the size of this anisotropy and the difficulty in measuring it, this is not a serious disagreement. The g values are relatively insensitive to the exact value of the orbital reduction factor k,[29] (which is a measure of the

delocalization of the d electrons in a crystal) and we have chosen a physically reasonable value of $k = 0.7$.

[28] The g values were calculated by transforming the matrices of **L** and **S** to a basis of the eigenvectors of the zero field Hamiltonian. These eigenvectors were determined for the set of parameters which gave a good fit to the energy levels.

[29] K. W. H. Stevens, Proc. Roy. Soc. London **A219**, 542 (1953).

Nonempirical Calculations on Excited States: The Formaldehyde Molecule

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A series of calculations on the excited states of formaldehyde using excitation operator techniques are presented. As in ethylene, the effect of σ–π interaction on the "$\pi \rightarrow \pi^*$" ($^1A_1$) excitation is rather large, decreasing the calculated excitation energy from 14.89 to 12.03 eV and the oscillator strength from 1.01 to 0.30. The coupling has little effect on the corresponding triplet state ($^3A_1$). The next higher approximation reduces the excitation energy to 11.22 eV and the oscillator strength to 0.21. The effect of the coupling on the "$n \rightarrow \pi^*$" ($^{1,3}A_2$) excitations is not as large as that for the $^1A_1$ state, lowering the excitation energies for both the singlet and triplet by ~ 0.5 eV. Similar results were obtained for the "$\sigma \rightarrow \pi^*$" ($^{1,3}B_1$) excitations. Trends are observed in calculations on corresponding states in ethylene and formaldehyde. Numerous one-electron properties are calculated for the excited states. The results are in moderate agreement with experiment; a major source of error probably arises from the use of an unoptimized, minimum basis set LCAO(STO)–MO–SCF wavefunction.

I. INTRODUCTION

The electronic excited state of molecules are of interest to chemists as a means of interpreting spectra, as reaction intermediates and for numerous other reasons. Unfortunately, a Hartree–Fock treatment of open-shell systems is more complicated than for closed shells and it has only been recently that theoretical work has been started on a Hartree–Fock theory of the excited states of molecules[1] and calculations begun on simple diatomic molecules.[2] This article applies to formaldehyde an alternate approach to problem, based on excitation operator techniques, which was discussed in a previous article and applied there to ethylene.[3]

An excitation operator approach has advantages over a Hartree–Fock theory in that only the ground-state wavefunction, including the virtual orbitals, need be known (thus, eliminating the reoptimization of numerous nonlinear parameters), electronic correlation is put into the ground and excited states in a balanced manner, and energy differences are solved for directly. Also, the problem of nonorthogonal molecular orbitals encountered in a Hartree–Fock theory is avoided by constructing both states out of a set of mutually orthogonal orbitals. This is of particular importance when calculating quantities connecting the two states, such as the transition moment. However, such a method has the disadvantage that only vertical excitations can be described, although in the interpretation of spectra it is just this type of excitation which is of most interest.

* National Science Foundation Predoctoral Fellow 1966–1968.
† Contribution No. 3593.
[1] C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960); S. Huzinaga, Phys. Rev. **120**, 866 (1960); S. Huzinaga, Phys. Rev. **122**, 131 (1961); and C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics* (Academic Press Inc., New York, 1963), Vol. 2, pp. 49–54.
[2] CO: W. M. Huo, J. Chem. Phys. **45**, 1554 (1966); BeO: G. Verhaegen and W. G. Richards, *ibid.* **45**, 1828 (1966), and W. M. Huo, K. F. Freed, and W. Klemperer, *ibid.* **46**, 3556 (1967).

[3] T. H. Dunning and V. McKoy, J. Chem. Phys. **47**, 1735 (1967).

H1(0.0, 1.7320508, +0.5)

y

z

C(0,0,0)   O(0,0,-2.3)
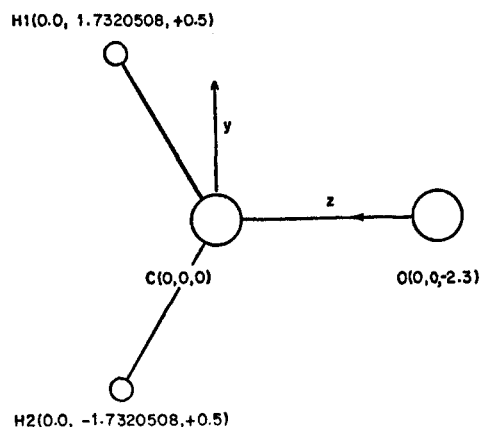
H2(0.0, -1.7320508,+0.5)

FIG. 1. The geometry of formaldehyde.

Formaldehyde (for the geometry see Fig. 1) was chosen for the present study because of its special interest to spectroscopists and because a theoretical description of its excited states has not been attempted, even at a level comparable to the pi-electron calculations on ethylene,[4] except by semiempirical schemes.[5] Also, although the formaldehyde molecule has been the subject of numerous experimental investigations,[6] some confusion still exists over the assignment of the excited state giving rise to the absorption band at ∼8.0 eV: the two alternatives being that the excited state results

from (a) a $\pi \rightarrow \pi^*$ transition and (b) a Rydberg transition.[7]

Further, many properties of formaldehyde have been measured experimentally, thus providing a stringent test for any theory. When these experimental values are compared with the theoretical values calculated with a recent minimum basis set LCAO–MO–SCF wavefunction, which also provides a basis for the calculations to be presented here, the agreement is rather poor.[8] But, even though we cannot expect any more from the excited state calculations, we can still use the calculated values of these properties to get an idea of the differences in the electronic distributions between the various states. Most important, by comparing the results of the single transition approximation with those of the Tamm–Dancoff approximation (see the following section), we can assess the significance of "core relaxation,"

TABLE I. Experimental vertical excitation energies, oscillator strengths, and dipole moments for the various states of the formaldehyde molecule.

Electronic state	STA Assignment[a]	Energy (eV)[b]	Oscillator strength, f[b]	Dipole moment (D)
$^1A_1$	⋯	0.0	⋯	2.34±0.02[c]
$^3A_2$	$n \rightarrow \pi^*$	3.2	very weak	
$^1A_2$	$n \rightarrow \pi^*$	4.3	∼10⁻⁴	1.56±0.07[d]
$^3B_1$	$\sigma \rightarrow \pi^*$	⋯	⋯	⋯
$^1B_1$	$\sigma \rightarrow \pi^*$	7.1	∼0.02	⋯
$^3A_1$	$\pi \rightarrow \pi^*$	⋯	⋯	⋯
$^1A_1$	$\pi \rightarrow \pi^*$	8.0	∼0.1	⋯
$^3B_2$	$n \rightarrow \sigma^*$	⋯	⋯	⋯
$^1B_2$	$n \rightarrow \sigma^*$	10 ?	⋯	⋯

[a] See text.
[b] See Ref. 6.
[c] J. N. Shoolery and A. H. Sharbaugh, Phys. Rev. **82**, 95 (1951).
[d] See Ref. 17.

[4] R. G. Parr and B. L. Crawford, J. Chem. Phys. **16**, 526 (1948); T. Murai, Progr. Theoret. Phys. (Kyoto) **7**, 345 (1952); and S. Huzinaga, J. Chem. Phys. **36**, 453 (1962).
[5] T. Anno and A. Sadô, J. Chem. Phys. **26**, 1759 (1957); J. W. Sidman, J. Chem. Phys. **27**, 429 (1957); J. A. Pople and J. W. Sidman, *ibid.* **27**, 1270 (1957); R. D. Brown and M. L. Heffernan, Trans. Faraday Soc. **54**, 757 (1958); J. M. Parks and R. G. Parr, J. Chem. Phys. **32**, 1657 (1960); F. L. Pilar, *ibid.* **47**, 884 (1967).
[6] H. Ley and B. Arends, Z. Physik. Chem. **12**, 132 (1931); W. C. Price, J. Chem. Phys. **3**, 156 (1935); J. C. D. Brand, J. Chem. Soc. **1956**, 858; G. W. Robinson and V. E. DiGiorgio, Can. J. Chem. **36**, 31 (1958); J. R. Henderson, J. Chem. Phys. **44**, 3496 (1966), and many others.

TABLE II. The elementary transitions coupled to form the excited states of formaldehyde of symmetry A_1.

Transition[a]		Common designation[b]	Singlet energy STA[c]
Numerical	Symmetry		
7→9	$1b_1 \rightarrow 2b_1$	$\pi \rightarrow \pi^*$	14.89 eV
8→11	$2b_2 \rightarrow 3b_2$	$n(y_0) \rightarrow CH^*$	22.98
6→10	$5a_1 \rightarrow 6a_1$	$\sigma \rightarrow CH^*$	24.09
6→12	$5a_1 \rightarrow 7a_1$	$\sigma \rightarrow \sigma^*$	27.46
5→11	$1b_2 \rightarrow 3b_2$	$CH \rightarrow CH^*$	30.07
4→10	$4a_1 \rightarrow 6a_1$	$CH \rightarrow CH^*$	30.78
4→12	$4a_1 \rightarrow 7a_1$	$CH \rightarrow \sigma^*$	34.47
3→10	$3a_1 \rightarrow 6a_1$	$O_{2s} \rightarrow CH^*$	45.15
3→12	$3a_1 \rightarrow 7a_1$	$O_{2s} \rightarrow \sigma^*$	46.88

[a] The symmetry designation is that with the molecule in the yz plane (see Fig. 1). The numerical designation is used in the following table to denote the transitions (m, α). Note that the numbers refer to the orbitals in order of increasing orbital energy and not as given in S. Aung, R. M. Pitzer, and S. I. Chan, J. Chem. Phys. **45**, 3547 (1966).

[b] Except for the first transition, these descriptions are only approximate since the orbitals are delocalized. The major component of the MO is written without the parenthesis, any minor component within.

[c] Calculated from Eq. (3) of the text. The excitation energies are in electron volts.

i.e., a rearrangement of the electronic density of those electrons not usually associated with a given transition (e.g., the σ electrons in a "π-electron excitation").

In Table I, the experimental results on formaldehyde are listed. Note that an $^1A_1$ state has been given at ∼8.0 eV although this assignment at present is questionable.[7]

II. THEORY

The purpose of this section is to give a brief review of the method and to present the necessary formulas. For

[7] See, for example, G. W. Robinson in *Methods of Experimental Physics: Molecular Physics* (Academic Press Inc., New York, 1962), Vol. 3, pp. 155–264.
[8] W. H. Flygare, J. M. Pochan, G. I. Kerley, T. Caves, M. Karplus, S. Aung, R. M. Pitzer, and S. I. Chan, J. Chem. Phys. **45**, 2793 (1966); and S. Aung, R. M. Pitzer, and S. I. Chan, *ibid.* **45**, 3457 (1966). The last article contains the wavefunction used in the calculations presented here.

a more detailed treatment the reader is referred to our previous paper[3] and the references contained therein.

We start by postulating an excitation operator, $S^+(E)$, which we hope will represent the excited states of the system reasonably well. We then examine those terms which are neglected upon forcing the commutator relationship to be satisfied:

$$[\mathcal{K}, S^+(E)] = (E - E_0) S^+(E). \qquad (1)$$

$\mathcal{K}$ is the total electronic Hamiltonian of the system, E is the energy of the excited state, and E_0 is the ground state energy. From Eq. (1) we can see that when the excitation operator, $S^+(E)$, acts on the ground state, $|0\rangle$, it produces an excited state of the Hamiltonian $\mathcal{K}$. The terms which are discarded in Eq. (1) represent the error which arises from the use of such an operator to describe the excited state. In this way we arrive at a set of operators which more or less correspond to the true excited states of the system.

The present technique utilizes excitation operators which give rise to wavefunctions which can be interpreted in terms of configuration interaction. Specifically the operators are chosen to represent excited states which result from single-particle transitions. If this is not the case, then $S^+(E)$ must be generalized to include double-particle transitions, etc.

TABLE III. The lowest excited singlet state of formaldehyde of symmetry A_1 (the "$\pi \rightarrow \pi^*$" transition): excitation energies (in electron volts), transition moments, oscillator strengths and wavefunctions for the various approximations to the excited state.

	STA[a]	TDA[b]	RPA[c]
ΔE	14.89	12.03	11.22
D_z	−1.67	−1.02	−0.88
f	1.01	0.30	0.21
Wavefunctions:			
(m, α)	$g(m\alpha)$	$g(m\alpha)$	$g(m\alpha)$
(9, 7)	1.000000	0.930110	0.966104
(11, 8)		0.161225	0.126608
(10, 6)		0.044100	0.035271
(12, 6)		0.298489	0.243681
(11, 5)		−0.087123	−0.068162
(10, 4)		0.059452	0.045562
(12, 4)		−0.004821	−0.005282
(10, 3)		−0.020318	−0.014553
(12, 3)		−0.079374	−0.063840
			$h(m\alpha)$
(9, 7)			−0.081276
(11, 8)			0.041397
(10, 6)			0.011469
(12, 6)			0.094228
(11, 5)			−0.030992
(10, 4)			0.017562
(12, 4)			−0.007204
(10, 3)			−0.014135
(12, 3)			−0.046865

[a] From Eqs. (3), (4), and (12) of the text.
[b] From Eqs. (6), (7), and (12) of the text.
[c] From Eqs. (10)–(12) of the text. The wavefunction as given is normalized with $\Sigma [g(m\alpha)^2 - h(m\alpha)^2] = 1.000000$, see Eq. (35c) of Ref. 3.

TABLE IV. The lowest triplet state of formaldehyde of symmetry A_1 (the "$\pi \rightarrow \pi^*$" transition): excitation energies and wavefunctions for the various approximations to the excited state.

	STA[a]	TDA[b]
ΔE	3.99	3.88
Wavefunctions:		
(m, α)	$g(m\alpha)$	$g(m\alpha)$
(9, 7)	1.000000	0.997776
(11, 8)		0.001237
(10, 6)		0.000653
(12, 6)		−0.025463
(11, 5)		0.021884
(10, 4)		−0.036564
(12, 4)		−0.004753
(10, 3)		0.021475
(12, 3)		0.038648

[a] From Eqs. (3) and (4) of the text.
[b] From Eqs. (6) and (7) of the text.

It is obvious that if the excitation operator is made completely general by the inclusion of all types of multiple transitions, then the true excited states of the molecule will result. How many terms must be retained in the expansion depends on the single-particle energy level schemes and the symmetry of the states arising from such single, double, etc. excitations. The question of interest is whether the series converges fast enough to be useful. Allowing for the relatively incomplete ground-state wavefunctions, the results of the calculations on ethylene and formaldehyde are encouraging.

In this paper (and the previous one[3]) we choose three approximations to the excitation operator $S^+(E)$. In the *single transition approximation* (STA) the excited state is derived from the Hartree–Fock ground state by removing an electron from an occupied orbital and placing it in a virtual orbital. This approximation assumes that the orbitals for the excited states are the same as those for the ground state, i.e., relaxation is not allowed to occur. In the STA for the excitation $\alpha \rightarrow m$

$$S_{\text{STA}}^+(E) = C^+(m\alpha), \qquad (2)$$

$$\Delta E_{\text{STA}}(m\alpha) = \mathbf{A}_{(m\alpha, m\alpha)}, \qquad (3)$$

and

$$\mathbf{D}_{\text{STA}}(m\alpha) = -\sqrt{2}\langle \phi_m | \mathbf{r} | \phi_\alpha \rangle = -\sqrt{2}\,\mathbf{d}_{m\alpha}, \qquad (4)$$

where

$$C^+(m\alpha) = a_m^+ a_\alpha,$$

and a_m^+ and a_α are the creation and annihilation operators for electrons in molecular orbitals ϕ_m, a virtual orbital, and ϕ_α, an orbital occupied in the Hartree–Fock ground state. The matrix $\mathbf{A}$ is defined by its elements

$$^1\mathbf{A}_{(m\alpha, n\beta)} = (\epsilon_m - \epsilon_\alpha)\delta_{m\alpha, n\beta} + (2V_{anm\beta} - V_{an\beta m})$$

for singlet states and

$$^3\mathbf{A}_{(m\alpha, n\beta)} = (\epsilon_m - \epsilon_\alpha)\delta_{m\alpha, n\beta} - V_{an\beta m}$$

TABLE V. The elementary transitions coupled to form the excited states of formaldehyde of symmetry A_2.[a]

Transition		Common designation	Singlet energy STA
Numerical	Symmetry		
$8 \to 9$	$2b_2 \to 2b_1$	$n(y_0) \to \pi^*$	4.03 eV
$5 \to 9$	$1b_2 \to 2b_1$	$CH \to \pi^*$	13.40
$7 \to 11$	$1b_1 \to 3b_2$	$\pi \to CH^*$	21.97

[a] See comments below Table II.

for triplet states. The ϵ_i denote orbital energies and

$$V_{ijkl} = \iint \phi_i^*(1)\phi_j^*(2) r_{12}^{-1}\phi_k(1)\phi_l(2)\, d\tau_1 d\tau_2.$$

D is the transition moment from the ground to the excited state.

In the Tamm–Dancoff approximation (TDA) the excited state is represented as a linear combination of single particle transitions. This allows for electronic relaxation upon excitation through the residual Coulomb interaction. In this case

$$S_{TDA}^+(E) = \sum_{(m\alpha)} g(m\alpha; E) C^+(m\alpha), \quad (5)$$

the expansion coefficients being solutions of the matrix equation

$$\mathbf{AG} = \Delta E_{TDA}\mathbf{G} \quad (6)$$

with

$$(\mathbf{G})_{(m\alpha)} = g(m\alpha; E).$$

The transition moment is given by

$$\mathbf{D}_{TDA}(E) = -\sqrt{2}\sum_{(m\alpha)} g(m\alpha; E)\,\mathbf{d}_{m\alpha}. \quad (7)$$

In the *random-phase approximation* (RPA) the excited state is still written as a linear combination of single-particle transitions (plus minor contributions from higher order odd excitations, i.e., triplet, etc.), but now we make *implicit* recognition of the fact that the true ground state contains, in addition to the Hartree–Fock wavefunction $|\,HF\,\rangle$, components corresponding to excitations (mainly double) from the Hartree–Fock ground state, $|\,_{\alpha\beta}{}^{mn}\rangle$, i.e., the true ground state is better represented by

$$|\,0\,\rangle = C_0\,|\,HF\,\rangle + \sum_{(m\alpha)}\sum_{(n\beta)} C_{\alpha\beta}{}^{mn}\,|\,_{\alpha\beta}{}^{mn}\rangle$$
$$+\,(\text{higher order excitations}). \quad (8)$$

The RPA then assumes that the $C_{\alpha\beta}{}^{mn}$ are sufficiently small so only terms linear in them need be retained, products being neglected. In this approximation

$$S_{RPA}^+(E) = \sum_{(m\alpha)} [g(m\alpha; E)C^+(m\alpha) - h(m\alpha; E)C(m\alpha)]$$
$$\quad (9)$$

the expansion coefficients being solutions of

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix}\begin{pmatrix} \mathbf{G} \\ \mathbf{H} \end{pmatrix} = \Delta E_{RPA}\begin{pmatrix} \mathbf{G} \\ \mathbf{H} \end{pmatrix}. \quad (10)$$

The matrix **B** is defined by

$$^1\mathbf{B}_{(m\alpha, n\beta)} = 2V_{\alpha\beta mn} - V_{\alpha\beta nm},$$

$$^3\mathbf{B}_{(m\alpha, n\beta)} = -V_{\alpha\beta nm},$$

for the singlet and triplet states, respectively. The transition moment now is

$$\mathbf{D}_{RPA}(E) = -\sqrt{2}\sum_{(m\alpha)} [g(m\alpha; E) + h(m\alpha; E)]\mathbf{d}_{m\alpha}. \quad (11)$$

The energy lowering observed in the RPA is somewhat overestimated and arises from the neglect of products of ground-state correlation coefficients; this can be corrected through the extended RPA.[3] One of the principal successes of the RPA is the effect on the transition moment through the $h(m\alpha)$ coefficients [see Eq. (11)]; this effect is linear in the correlation coefficients and, accordingly, is reasonably well approximated by the RPA. Because of the assumptions about the ground-state correlation coefficients, $C_{\alpha\beta}{}^{mn}$, the RPA becomes unstable (i.e., yields imaginary eigenvalues and eigenvectors) when these become large, as they are for $C_{\pi\pi}{}^{\pi^*\pi^*}$ in both ethylene and formaldehyde.

The oscillator strength, f, which is an experimentally measured quantity, is related to the transition moment and excitation energy by

$$f(E) = \tfrac{2}{3}\Delta E\,|\,\mathbf{D}\,|^2, \quad (12)$$

all quantities being given in atomic units.

The above formulas describe transitions among nondegenerate molecular orbitals. If degeneracies exist then the equations must be modified accordingly.

TABLE VI. The lowest singlet state of formaldehyde of symmetry A_2 (the "$n \to \pi^*$" transition): excitation energies (in electron volts) and wavefunctions for the various approximations to the excited state.

	STA[a]	TDA[b]	RPA[c]
ΔE	4.03	3.60	3.47
Wavefunctions:			
(m, α)	$g(m\alpha)$	$g(m\alpha)$	$g(m\alpha)$
$(9, 8)$	1.000000	0.978447	0.983127
$(9, 5)$		−0.206498	−0.211607
$(11, 7)$		0.000804	0.008716
			$h(m\alpha)$
$(9, 8)$			−0.088050
$(9, 5)$			0.025684
$(11, 7)$			−0.054595

[a] From Eqs. (3) and (4) of the text.
[b] From Eqs. (6) and (7) of the text.
[c] From Eqs. (10) and (11) of the text. The wavefunction is normalized with $\sum [g^2(m\alpha) - h^2(m\alpha)] = 1.000000$, see Eq. (35c) of Ref. 3.

III. RESULTS AND DISCUSSION

Tables II–IV give the results of the calculations on the A_1 states. Qualitatively, these states are described as arising from a $\pi \rightarrow \pi^*$ transition.

The results in these tables indicate that the A_1 states of formaldehyde exhibit the same general behavior as the corresponding B_{3u} states in ethylene[3]: the singlet state is quite affected by the coupling of the transitions, the triplet state practically unchanged. It is possible that this type of behavior can, in general, be expected for transitions which have been denoted by Mulliken[9] as $N \rightarrow V$, T, i.e, transitions from bonding to the corresponding antibonding orbitals. Should this prove to be the case, a semiempirical scheme similar to that used by Herzenberg, Sherrington and Süveges[10] could possibly be developed to treat molecules which are out of the range of present LCAO–MO–SCF techniques (and will probably remain so for some time to come).

The effect of the coupling is slightly larger in formaldehyde than in ethylene. It is difficult to say whether this is significant (it probably is not!) except to note that similar results were obtained for ethylene when methane optimized exponents[11] were used in the minimum basis set: the STA guess was worse, the coupling larger.[12]

TABLE VII. The lowest triplet state of formaldehyde of symmetry A_2 (the "$n \rightarrow \pi^*$" transition): excitation energies (in electron volts) and wavefunctions for the various approximations to the excited state.

	STA[a]	TDA[b]	RPA[c]
ΔE	2.88	2.33	2.13
Wavefunctions:			
(m, α)	$g(m\alpha)$	$g(m\alpha)$	$g(m\alpha)$
$(9, 8)$	1.000000	0.974376	0.985927
$(9, 5)$		−0.224803	−0.236076
$(11, 7)$		−0.007391	−0.021384
			$h(m\alpha)$
$(9, 8)$			0.147309
$(9, 5)$			−0.043466
$(11, 7)$			−0.068204

[a] From Eqs. (3) and (4) of the text.
[b] From Eqs. (6) and (7) of the text.
[c] From Eqs. (10) and (11) of the text. The wavefunction is normalized with $\Sigma [g^2(m\alpha) - h^2(m\alpha)] = 1.000000$, see Eq. (35c) of Ref. 3.

[9] R. S. Mulliken, J. Chem. Phys. **7**, 20 (1939).
[10] A. Herzenberg, D. Sherrington, and M. Süveges, Proc. Phys. Soc. (London) **84**, 465 (1964).
[11] R. M. Pitzer, J. Chem. Phys. **46**, 4871 (1967).
[12] For ethylene using methane optimized exponents, it was found that $E_{\text{total}} = -77.8429$ a.u, which is a decrease of 0.0086 a.u. over the energy obtained by using Slater exponents with 1.2 on the hydrogen, and that $^3\Delta E = 3.13$, 2.95 eV for the triplet state and $^1\Delta E = 12.88$, 10.81, 9.96 eV in the STA, TDA, and RPA, respectively: from unpublished calculations by W. E. Palke and T. H. Dunning.

TABLE VIII. The elementary transitions coupled to form the excited states of formaldehyde of symmetry B_1.[a]

Transition		Common designation	Singlet energy STA
Numerical	Symmetry		
$6 \rightarrow 9$	$5a_1 \rightarrow 2b_1$	$\sigma \rightarrow \pi^*$	9.06 eV
$4 \rightarrow 9$	$4a_1 \rightarrow 2b_1$	$CH \rightarrow \pi^*$	20.38
$7 \rightarrow 10$	$1b_1 \rightarrow 6a_1$	$\pi \rightarrow CH^*$	20.46
$7 \rightarrow 12$	$1b_1 \rightarrow 7a_1$	$\pi \rightarrow \sigma^*$	21.18
$3 \rightarrow 9$	$3a_1 \rightarrow 2b_1$	$O_{2s} \rightarrow \pi^*$	31.14

[a] See the comments below Table II.

In formaldehyde the doubly excited $| _{\pi\pi}\pi^*\pi^* \rangle$ state lies 19.25 eV above the ground state and is of the appropriate symmetry to mix with the singly excited $| _\pi\pi^* \rangle$ state (and the ground state). Hence, the question arises as to whether the excited state of $^1A_1$ symmetry is well represented by a single-particle transition (or some suitable linear combination). To answer this question we did a configuration–interaction calculation[13] "mixing" the $| _\pi\pi^* \rangle$ and $| _{\pi\pi}\pi^*\pi^* \rangle$ states and found that (a) the energy of the first excited state was lowered by 0.02 eV, (b) the transition moment with the Hartree–Fock ground state changed from −1.67 to −1.66, and (c) the dipole moment of the excited state decreased from 0.352 a.u. to 0.096 a.u.[14] From this we can conclude that for properties connecting the two states, we might approximate the excited state by a single-particle transition, but for the relatively sensitive expectation values we definitely cannot! In this paper we are primarily interested in properties which relate to both the ground- and excited states (excitation energies and oscillator strengths), so we will not concern ourselves with the above except to point it out. However, in the future, for more accurate calculations, this interaction will have to be taken into account and the excitation operator modified accordingly.

If we assume that the difference $\Delta E_{\text{calc}} - \Delta E_{\text{exptl}}$ is the same for the $^1A_1$ state of formaldehyde as for the $^1B_{3u}$ state of ethylene, which is not unreasonable in view of the observed trends, then we would predict an excitation energy of 9.4 eV for the so-called $\pi \rightarrow \pi^*$ transition in formaldehyde. It is thus possible that the $^1A_1$ state does give rise to the band at ~ 8.0 eV. In view of the effect on ΔE_{STA} as a result of improvements in the wavefunction for ethylene,[15] calculations of formaldehyde employing excitation operator techniques on analogous wavefunctions should provide a definite answer to this question.

[13] For the form of the matrix elements see: J. Cizek, Theoret. Chim. Acta **6**, 292 (1966).
[14] To convert from atomic units to debyes multiply by 2.541603.
[15] For the excitation energies (STA) for ethylene calculated from various Gaussian wavefunctions see: J. W. Moskowitz and M. C. Harrison, J. Chem. Phys. **42**, 1726 (1965) and J. M. Schulman, J. W. Moskowitz, and C. Hollister, *ibid.* **46**, 2759 (1967).

TABLE IX. The lowest singlet state of formaldehyde of symmetry B_1 (the "$\sigma \rightarrow \pi^*$" transition): excitation energies (in electron volts), transition moments (in atomic units), oscillator strengths, and wavefunctions for the various approximations to the excited state.

	STA[a]	TDA[b]	RPA[c]
ΔE	9.06	8.85	8.56
D	−0.17	−0.22	−0.22
f	0.006	0.011	0.010

Wavefunctions:

(m, α)	$g(m\alpha)$	$g(m\alpha)$	$g(m\alpha)$
(9, 6)	1.000000	0.993979	0.999448
(9, 4)		0.073172	0.072425
(10, 7)		−0.002842	0.001395
(12, 7)		0.002421	0.017584
(9, 3)		−0.081468	−0.081868
			$h(m\alpha)$
(9, 6)			−0.051212
(9, 4)			−0.018942
(10, 7)			−0.011221
(12, 7)			−0.088920
(9, 3)			−0.011903

[a] From Eqs. (3), (4), and (12) of the text.
[b] From Eqs. (6), (7), and (12) of the text.
[c] From Eqs. (10)–(12) of the text. The wavefunction is normalized with $\Sigma [g^2(m\alpha) - h^2(m\alpha)] = 1.000000$, see Eq. (35c) of Ref. 3.

The A_2 states, qualitatively described as arising from an $n \rightarrow \pi^*$ transition (or $N \rightarrow Q$ in Mulliken's notation[16]), are of much interest since they are prototypes for such states in larger molecules and because they are out of the realm of pi-electron theory. In an elementary picture n is taken as a $2p$-lone pair orbital on oxygen. From the LCAO–MO–SCF wavefunction,[8] however, we see that the corresponding molecular orbital has a significant amplitude on the hydrogens and carbon. In fact, as Freeman and Klemperer[17] point out, this molecular orbital has its centroid 0.12 Å from the midpoint of the CO bond rather than at the oxygen as would be the case if the orbital were pure $2p$. Just as a point of interest, consider the following. If we use the LCAO–MO–SCF π^* orbital and orbital energies for n[18] and π^*, but let n be an oxygen $2p_y$ orbital, we find that in the STA the triplet excitation energy is 1.09 eV and the singlet 2.33 eV in marked contrast to both the LCAO–MO–SCF STA calculation (see below) and the experimental results. Thus, just as Freeman and Klemperer[17] found that the change in dipole moment upon excitation was better rationalized by the LCAO–MO–SCF orbital, we find that the LCAO–MO–SCF results represent the excited state better than the simpler picture.

Tables V–VII list results of the calculations on the

[16] R. S. Mulliken, Phys. Rev. 50, 1017 (1936); H. L. McMurry and R. S. Mulliken, Proc. Natl. Acad. Sci. U.S. 26, 312 (1940); and H. L. McMurry, J. Chem. Phys. 9, 231 (1941).
[17] D. E. Freeman and W. Klemperer, J. Chem. Phys. 45, 52 (1966).
[18] The SCF orbital energy is 10.49 eV, which compares quite well with the ionization potential of the "lone pair" oxygen electrons in formaldehyde, 10.83 eV [W. C. Price, Phys. Rev. 46, 529 (1934)].

A_2 states. When compared to the previous $N \rightarrow V$, T results, we see that the magnitude of the effect is not as large as that observed in the $N \rightarrow V$ case but larger than for the $N \rightarrow T$ case. Also, the effect of the coupling is slightly larger for the triplet state than for the singlet. Such behavior may be indicative of $n \rightarrow \pi^*$ transitions. Since the transition to the $^1A_2$ state is magnetic dipole[6] rather than electric dipole allowed, no transition moment has been calculated.

The results for the B_1 states are given in Tables VIII–X. The transition to this state is electric dipole allowed, polarized in the x direction, and can qualitatively be described as arising from a $\sigma \rightarrow \pi^*$ transition. The coupling has an effect similar to that for the corresponding transitions in ethylene (B_{1u} or B_{2u}). In fact, in all cases investigated, the effect of the coupling is nearly the same for corresponding transitions in ethylene[3] and formaldehyde. In this case the coupling increases the transition moment, which is toward better agreement with experiment.

The excitation energies for the B_2 states are found to be rather high (15–18 eV), so we will not discuss them anymore at present. We will mention that the coupling is much larger in the triplet, decreasing the energy by 2.4 eV, than in the singlet, decreasing the energy by only 0.4 eV; this is similar to that for the corresponding B_{2u} state of ethylene.

In the STA the charge distribution in singlet and triplet states derived from the same orbital configuration is identically the same. However, in the TDA, as in Hartree–Fock theories, this is not so. Thus, by computing the expectation values of various one-electron operators, we can compare not only the changes in the electronic density from one state to the next,

TABLE X. The lowest triplet state of formaldehyde of symmetry B_1 (the "$\sigma \rightarrow \pi^*$" transition): excitation energies (in electron volts) and wavefunctions for the various approximations to the excited state.

	STA[a]	TDA[b]	RPA[c]
ΔE	7.28	6.99	6.53

Wavefunctions:

(m, α)	$g(m\alpha)$	$g(m\alpha)$	$g(m\alpha)$
(9, 6)	1.000000	0.986418	0.995786
(9, 4)		0.159971	0.164044
(10, 7)		−0.015612	−0.026983
(12, 7)		−0.030052	−0.056657
(9, 3)		−0.015582	−0.027327
			$h(m\alpha)$
(9, 6)			0.086910
(9, 4)			0.035876
(10, 7)			−0.024582
(12, 7)			−0.116694
(9, 3)			0.011093

[a] From Eqs. (3) and (4) of the text.
[b] From Eqs. (6) and (7) of the text.
[c] From Eqs. (10) and (11) of the text. The wavefunction is normalized with $\Sigma [g^2(m\alpha) - h^2(m\alpha)] = 1.000000$, see Eq. (35c) of Ref. 3.

TABLE XI. One-electron properties of formaldehyde in various states (in atomic units).

Property[a]		Ground state $^1A_1$[b]	Excited states[c]					
			$^3A_1$	$^1A_1$	$^3A_2$	$^1A_2$	$^3B_1$	$^1B_1$
$q_{zz}(O)$	STA	0.8365	1.1545		0.5832		3.4569	
	TDA		1.1502	1.0489	0.6298	0.6225	3.4115	3.4386
$q_{yy}(O)$	STA	−2.9294	−2.6556		0.4286		−2.7966	
	TDA		−2.6553	−2.6182	0.3390	0.3532	−2.7767	−2.7875
$r_0 \cos\theta_0$	STA	0.3964	0.3520		0.1436		−0.2344	
	TDA		0.3482	0.2241	0.1964	0.1882	−0.1847	−0.2237
r_0^2	STA	83.3788	83.6995		82.8990		84.1396	
	TDA		83.7138	83.9258	82.7473	82.7709	83.9680	84.1162
$f_z(O)$	STA	−2.6481	−3.1395		−2.4596		−1.0676	
	TDA		−3.1355	−2.7861	−2.4949	−2.4894	−1.1034	−1.0963
$f_z(C)$	STA	0.2507	0.5333		0.4037		0.6392	
	TDA		0.5345	0.5265	0.3861	0.3888	0.6036	0.6365
$f_\alpha(H)$	STA	−0.1238	−0.1179		−0.0769		−0.0997	
	TDA		−0.1182	−0.1189	−0.0813	−0.0806	−0.1017	−0.1001
$f_\beta(H)$	STA	−0.0008	−0.0079		−0.0160		0.0131	
	TDA		−0.0079	−0.0070	−0.0169	−0.0168	0.0142	0.0131
$1/r_H$	STA	6.4983	6.5061		6.4399		6.5114	
	TDA		6.5066	6.5177	6.4340	6.4349	6.5064	6.5105
$q_{\alpha\alpha}(D)$	STA	0.4498	0.4452		0.4220		0.4374	
	TDA		0.4452	0.4411	0.4254	0.4249	0.4388	0.4377
$q_{\alpha\beta}(D)$	STA	0.0055	0.0124		0.0174		−0.0113	
	TDA		0.0124	0.0104	0.0188	0.0186	−0.0123	−0.0112
$q_{\beta\beta}(D)$	STA	−0.2204	−0.2135		−0.1834		−0.1852	
	TDA		−0.2136	−0.2132	−0.1850	−0.1847	−0.1860	−0.1853

[a] For definitions of the operators see: W. H. Flygare, J. M. Pochan, G. I. Kerley, T. Caves, M. Karplus, S. Aung, R. M. Pitzer, and S. I. Chan, J. Chem. Phys. **45**, 2793 (1966) and the text.

[b] S. Aung, R. M. Pitzer, and S. I. Chan, J. Chem. Phys. **45**, 3457 (1966).
[c] The upper number is the expectation value in the STA, the lower two the expectation values in the TDA.

but also we can assess the differences between the electronic density in singlet and triplet states. Further, by comparing the STA and TDA we can determine the significance of any "core relaxation." A word of caution though: this is not the same relaxation effect which would be observed in an LCAO–MO–SCF calculation on the excited state, for the relaxation observed here also contains some of the effects of electron correlation. We shall not be concerned with the absolute magnitudes of the various quantities, since the agreement between ground state expectation values and experiment was poor, but shall attach some significance only to differences. Anyway, the wavefunctions obtained here describe vertical excitations, so care must be taken when comparing quantities which strongly depend on the internuclear distance with experiment.

In Table XI we list the values of various one-electron properties for the ground and excited states. The symbols have the following meaning[8]:

$$q_{zz}(O) = (3z_O{}^2 - r_O{}^2)/r_O{}^5,$$

$$q_{yy}(O) = (3y_O{}^2 - r_O{}^2)/r_O{}^5,$$

$$r_O \cos\theta_O = z_O,$$

$$r_O{}^2,$$

$$f_z(O) = z_O/r_O{}^3,$$

$$f_z(C) = z_c/r_c{}^3,$$

$$f_\alpha(H) = \alpha_H/r_H{}^3,$$

$$f_\beta(H) = \beta_H/r_H{}^3,$$

$$1/r_H,$$

$$q_{\alpha\alpha}(D) = (3\alpha_D{}^2 - r_D{}^2)/r_D{}^5,$$

$$q_{\alpha\beta}(D) = 3\beta_D\alpha_D/r_D{}^5,$$

$$q_{\beta\beta}(D) = (3\beta_D{}^2 - r_D{}^2)/r_D{}^5. \tag{13}$$

The α axis is along the CH axis and the β axis is perpendicular to α in the plane of the molecule.

Examination of the table shows that for the A_1 states the triplet state is well represented in the STA while the singlet varies considerably. Thus, relaxation is significant for the $^1A_1$ state but negligible for the $^3A_1$ state, a fact which was predicted earlier from a consideration of the expansion coefficients, $g(m\alpha)$, alone.

For the A_2 states the singlet state relaxes less than the triplet, but in both cases this change is appreciable. Of special interest is the dipole moment of formaldehyde in the $^1A_2$ state for this has recently been measured by Freeman and Klemperer.[17] They found that the dipole moment changes by 0.7 D upon excitation. We predict 0.6 and 0.5 D in the STA and TDA, respectively.[14] Thus, in this case the effect of core relaxation is small and of no particular importance.

For the B_1 states the amount of relaxation is again larger for the triplet state than for the singlet, but in both cases it is relatively small and resembles that for the A_2 states.

As in ethylene ($^3B_{3u}$) the RPA treatment of the $^3A_1$ state of formaldehyde is unstable. Again this instability is caused by the large $\mid \pi_\pi\pi^*\pi^* \rangle$ component in the true ground state. We shall not discuss this further at present for it will be treated in later papers.

IV. CONCLUSIONS

Considering the inadequacy of the wavefunctions which have been employed, i.e., unoptimized, minimum basis set LCAO–MO–SCF wavefunctions, the results of the ethylene[3] and formaldehyde calculations demonstrate the utility of an excitation operator approach to the excited-state problem. To fully assess the capabilities and limitations of the method, we now need to do calculations on molecules for which accurate Hartree–Fock wavefunctions are known, e.g., diatomic[19] or simple linear polyatomic molecules.[20] However, because of the interest in and importance of ethylene and formaldehyde, calculations have begun on these molecules using wavefunctions, constructed from large Gaussian basis sets, which are considered to be near the (sp) limit.[21] These calculations, while not at the Hartree–Fock level, should provide an adequate representation of the low-lying valence excited states of these molecules.

Examination of the ethylene[3] and formaldehyde results shows that transitions denoted as $N \rightarrow V$, T have a definite and predictable behavior: the triplet state is well represented by the STA while the singlet state, because of the large relaxation effect, is not. It is quite possible that $N \rightarrow Q$ transitions will also follow the pattern observed here. If such trends persist, this could provide a means of empiricizing calculations, such as those presented here, for molecules beyond the reach of SCF techniques. This possibility argues for calculations on other large molecules, such as propene and acetaldehyde.

[19] F$_2$: A. C. Wahl, J. Chem. Phys. **41**, 2600 (1964); CO and BF: W. M. Huo, *ibid.* **43**, 624 (1965); N$_2$: P. E. Cade, K. D. Sales, and A. C. Wahl, *ibid.* **44**, 1973 (1966); the first- and second-row hydrides, AH: P. E. Cade and W. M. Huo, *ibid.* **47**, 614, 649 (1967).

[20] A. D. McLean and M. Yoshimine, "Tables of Linear Molecule Wave Functions," IBM J. Res. Develop. (to be published, private distribution).

[21] For the ethylene wavefunction in a (955/3) Gaussian basis see: J. M. Schulman, J. W. Moskowitz, and C. Hollister, J. Chem. Phys. **46**, 2759 (1967); for formaldehyde see: N. W. Winter, T. H. Dunning, and J. H. Letcher, "The Formaldehyde Molecule in a Gaussian Basis," *ibid.* (to be published).