Configuration Interaction Studies of Ground and Excited States of Polyatomic Molecules. I. The CI Formulation and Studies of Formaldehyde

J. L. Whitten and Melvyn Hackmeyer

Articles you may be interested in

Ground and excited states of linked and fused zinc porphyrin dimers: Symmetry adapted cluster (SAC)—configuration interaction (CI) study
J. Chem. Phys. **117**, 11196 (2002); 10.1063/1.1521763

Configuration interaction studies of O3 and O+ 3. Ground and excited states
J. Chem. Phys. **62**, 3912 (1975); 10.1063/1.430306

Reduced Partitioning Procedure in Configuration Interaction Studies. I. Ground States
J. Chem. Phys. **56**, 5467 (1972); 10.1063/1.1677063

Configuration Interaction Studies of Ground and Excited States of Polyatomic Molecules II. The Electronic States and Spectrum of Pyrazine
J. Chem. Phys. **54**, 3739 (1971); 10.1063/1.1675423

Configuration-Interaction Study of the Ground State of the H3 + Molecule
J. Chem. Phys. **41**, 960 (1964); 10.1063/1.1726039

Configuration Interaction Studies of Ground and Excited States of Polyatomic Molecules. I. The CI Formulation and Studies of Formaldehyde*

J. L. Whitten and Melvyn Hackmeyer†

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790

(Received 20 August 1969)

A configuration interaction (CI) procedure which is designed to produce energies and wavefunctions from relatively large scale computations on ground and excited molecular states is presented based on an orthonormal set of molecular orbitals. The method of generating configurations is referenced to the particular state of interest and involves a two-pass procedure: First, the generation of configurations by single and double excitations from selected important configurations (parents), subject to a threshold criterion, followed by diagonalization of the energy to obtain an initial approximation to the wavefunctions of interest; second, the use of these wavefunctions as parents and a repeat of the generation and diagonalization steps to produce the final CI wavefunction. CI studies of the $^{1,3}A_2$ ($n \to \pi^*$), $^{1,3}A_1$ ($\pi \to \pi^*$, $n \to 3p$), $^1B_1$ ($\sigma \to \pi^*$, $\pi \to 3s$), and $^1B_2$ ($n \to 3s$) states of formaldehyde are reported for several large Gaussian basis sets of near atomic Hartree–Fock quality based on molecular orbitals determined from ground and excited state SCF treatments and from certain elementary virtual orbital transformations. Calculated Franck–Condon transition energies are in excellent agreement with experimental results for those transitions which have been observed; of particular interest is the occurrence of a $n \to 3p$ transition on oxygen in the region of the spectrum atound 8 eV.

I. INTRODUCTION

The principles of molecular orbital theory have been widely used to rationalize experimental observations concerning the electronic spectra of polyatomic molecules leading to the well-known concepts of $n \to \pi^*$, $\pi \to \pi^*$, $\sigma \to \pi^*$, etc. type transitions.[1-3] Such transitions, particularly the $\pi \to \pi^*$, have long been treated by semiempirical self-consistent-field (SCF) and configuration interaction (CI) techniques often with exceptionally good agreement with experimental transition energies and polarizations.[4-6] Since interaction matrix elements between multiply excited configurations are not amenable to semiempirical estimation, such treatments of excited states usually involve only a small number of configurations, frequently only single excitations from the ground configuration. On the other hand, numerous *ab initio* CI treatments of atoms and small molecules exist which employ multiply excited configurations and the accurate computation of interaction matrix elements.[7-9] As a result of these studies, it

has been recognized that many multiply excited configurations are extremely important energetically, particularly those involving certain double excitations from the parent (main contributor) configuration of a given ground or excited state. It follows, therefore, that CI treatments of large molecular systems are immediately complicated by the appearance of large numbers of configurations even for fairly modest basis sets and extensive limitations on the number of molecular orbitals allowed to have variable occupancy. Various methods have been proposed and explored for the purpose of selecting the important higher excitation configurations, such as a direct examination of the magnitude of interaction matrix elements and other procedures based on perturbation theory,[10] the assumption of "unlinked cluster" contributions,[11] the optimization of orbitals in multiconfiguration wavefunctions,[12] and more crudely, the examination of diagonal elements or orbital energy arguments. Each of these procedures can be classified as an attempt to establish an adequate level of CI, and thereby to allow errors in the treatment to be ascribed solely to the adequacy of the basis set.

In the present work we present an outline of an SCF–CI formulation which we have found useful in the investigation of $n \to \pi^*$ and $\pi \to \pi^*$ transitions of the fairly large molecules, pyridine, pyrazine, and glyoxal; application to the $n \to \pi^*$, $\pi \to \pi^*$, $\sigma \to \pi^*$, $n \to 3s$, and $n \to 3p$ transitions of formaldehyde are discussed in the present report; studies of the other systems are presented in Part II of this work. The objective in these studies is to achieve a definitive CI treatment which is limited only by the adequacy of the fundamental basis set. According to this point of view, a CI treatment

* Research supported by National Science Foundation Grant GP 7875.

† Graduate student of Michigan State University.

[1] R. S. Mulliken and H. McMurry, Proc. Natl. Acad. Sci. U.S. **26**, 312 (1940).

[2] M. Kasha, Discussions Faraday Soc. **9**, 14 (1950).

[3] K. K. Innes, J. P. Byrne, and I. G. Ross, J. Mol. Spectry. **22**, 125 (1967).

[4] R. Pariser and R. Parr, J. Chem. Phys. **21**, 466, 767 (1953).

[5] L. Goodman and R. W. Harrell, J. Chem. Phys. **30**, 1131 (1959).

[6] R. Hoffmann, Tetrahedron **22**, 539 (1966).

[7] For a discussion of the CI method, see: P.-O. Löwdin, Advan. Chem. Phys. **2**, 207 (1959); and R. K. Nesbet, Advan. Chem. Phys. **9**, 321 (1966); and references contained therein.

[8] For examples of large-scale CI calculations on atoms and diatomic molecules, see: A. W. Weiss, Phys. Rev. **122**, 1826 (1961); C. F. Bender and E. R. Davidson, J. Chem. Phys. **47**, 360 (1967); and H. F. Shaeffer III and F. E. Harris, J. Chem. Phys. **48**, 4946 (1968).

[9] For examples of *ab initio* CI calculations on polyatomic molecules see: (a) J. M. Foster and S. F. Boys, Rev. Mod. Phys. **32**, 296, 300 (1960); (b) F. E. Harris and H. H. Michels, Intern. J. Quantum Chem. **1S**, 329 (1967); (c) S. D. Peyerimhoff, J. Chem. Phys. **47**, 349 (1967); (d) R. J. Buenker, J. L. Whitten, and J. D. Petke, J. Chem. Phys. **49**, 2261 (1968).

[10] A. Pipano and I. Shavitt, Intern. J. Quantum Chem. **2**, 741 (1968); Z. Gershgorn and I. Shavitt, *ibid.* **2**, 751 (1968).

[11] O. Sinanoğlu, J. Chem. Phys. **36**, 706 (1962).

[12] J. Hinze and C. C. J. Roothaan, Progr. Theoret. Phys. (Kyoto) **40**, 37 (1967); N. Sabelli and J. Hinze, J. Chem. Phys. **50**, 684 (1969).

TABLE I. Typical numerical changes in eigenvalues and eigenvectors after successive diagonalization steps, from the 334 configuration pair $^1A_1$ wavefunctions for H_2CO. Six CI wavefunctions are transferred between steps (see text). Only the coefficients of the first six configurations are given.

Eigenvalues number	Eigenvalues	Decrease in eigenvalues on successive diagonalization steps[a]			
	Step 1	Step 2	Step 3	Step 4	Step 5
1	−144.9836	0.0133	0.0033	0.0021	0.0006
2	−144.6664	0.0195	0.0071	0.0042	0.0005
3	−144.5614	0.0093	0.0067	0.0062	0.0009
4	−144.5345	0.0094	0.0073	0.0043	0.0010

	Eigenvector 1		Eigenvector 2	
Configuration	Step 1 coefficient	Step 5 coefficient	Step 1 coefficient	Step 5 coefficient
1	0.9741	0.9698	−0.0037	−0.0029
2	0.0079	0.0054	0.9273	0.9306
3	0.0096	0.0072	−0.0445	−0.0241
4	0.0361	0.0300	−0.0758	−0.0588
5	−0.1165	−0.1145	0.0196	0.0140
6	0.0041	0.0049	0.0214	0.0184

	Eigenvector 3		Eigenvector 4	
Configuration	Step 1 coefficient	Step 5 coefficient	Step 1 coefficient	Step 5 coefficient
1	−0.0674	−0.0650	0.0501	0.0374
2	0.0800	0.0557	−0.0237	−0.0191
3	0.7093	0.6389	0.5987	0.6683
4	0.5364	0.6248	−0.7269	−0.6581
5	−0.1276	−0.1492	0.1743	0.1578
6	−0.1424	−0.1449	0.0658	0.0443

[a] Dimensionality of matrices: Step 1, 86; step 2, 85; step 3, 86; step 4, 85; step 5, 22; including the six wavefunctions transferred between steps. Matrix elements are over pairs of configurations $\varphi \pm \bar{\varphi}$ (see text) in the case of open shell configurations; the number of single configurations present is 654.

employing a Hartree–Fock ground-state atomic orbital basis would provide an assessment of the extent to which valence shell atomic orbitals can be used as a principle for rationalizing electronic spectra. Much of the work to be discussed goes considerably beyond this level, however, by allowing considerable distortion of atomic orbitals in the molecular field and by including higher principal quantum number basis orbitals.

II. BASIS SET

The basis set employed in this work has been described previously in an application to the first-row atoms and the ethylene molecule where numerical values of all atomic orbital parameters are tabulated.[13] Atomic orbitals of approximate Hartree–Fock quality are constructed using linear combinations of Gaussian lobe functions; first-row $1s$, $2s$, and $2p$ expansions contain 10, 10, and 5 Gaussian components, respectively. In the present molecular applications, several basis sets are used. The minimal size basis, which is only slightly more flexible than a basis of near Hartree–Fock $1s$, $2s$, and $2p$ atomic orbitals, utilizes three fixed s groups (constrained linear combinations of Gaussians) consisting of 3, 3, and 4 Gaussian components, respectively,

and one 5-term group for each p orbital (see Ref. 13). The second basis set, called a split group basis, is designed to allow considerable distortion of atomic orbitals in the presence of the molecular field and is obtained by treating the longest-range Gaussian component in the s groups and in the p group as independent basis functions to give a final basis set of 4 s groups, (4, 3, 2, and 1 component) and 2 p groups (4 and 1 component) (see Ref. 13). In all cases, on hydrogens, a five-component representation of the $1s$ orbital with scale factor $\eta = \sqrt{2}$ is used.[13] In certain of the molecular calculations, additional basis functions are included to represent atomic $3s$ and $3p$ orbitals, thereby permitting the description of certain low-lying Rydberg-type states. The present basis sets are deficient, however, in the omission of d orbitals, and p-type polarization functions on hydrogens.

III. CONFIGURATION INTERACTION WAVEFUNCTIONS

The N-electron wavefunction for a given electronic state ψ_k is formulated as a linear combination of configurations ϕ_l,

$$\psi_k = \sum_l c_{lk}\phi_l,$$

---

[13] J. L. Whitten, J. Chem. Phys. **44**, 359 (1966).

TABLE II. A comparison of orbital energies from three different SCF calculations on the $^1A_1$ ground state and $^3A_2$ excited state of H₂CO. Energies are in atomic units, 1 a.u. $= 27.21$ eV.[a]

Molecular orbital symmetry, C_{2v}	Ground-state fixed-group basis	Ground-state split-group basis	$^3A_2$ state split-group basis
$11a_1$		1.88	1.86
$5b_2$		1.11	1.07
$10a_1$		0.99	0.99
$4b_1$		0.97	0.91
$9a_1$		0.84	0.83
$4b_2$		0.82	0.77
$8a_1$		0.77	0.77
$7a_1$	0.72	0.54	0.57
$3b_1$		0.50	0.47
$3b_2$	0.78	0.43	0.44
$6a_1$	0.65	0.29	0.29
$2b_1$	0.14	0.11	−0.30
$2b_2$	−0.46	−0.44	−0.54
$1b_1$	−0.55	−0.53	−0.59
$5a_1$	−0.64	−0.64	−0.65
$1b_2$	−0.72	−0.70	−0.66
$4a_1$	−0.88	−0.86	−0.85
$3a_1$	−1.44	−1.42	−1.43
$2a_1$	−11.47	−11.35	−11.28
$1a_1$	−20.59	−20.58	−20.61
Total energy[b]	−113.7048	−113.8094	−113.7151

[a] Nuclear coordinates (in atomic units): C (0, 0, 0); O (0, 0, 2.2864); H (0, ±1.8141, −1.09).

[b] Including nuclear repulsion energy, 31.113780 a.u.

where the ϕ_l are antisymmetrized products of molecular spin orbitals (determinantal functions),

$$\phi_l = \phi_l(a_1^{(l)} a_2^{(l)} \cdots a_N^{(l)})$$
$$= \mathcal{C}[a_1^{(l)}(1) a_2^{(l)}(2) \cdots a_N^{(l)}(N)].$$

The spatial part of each molecular spin orbital $a_k^{(l)}$ is expanded in terms of the fundamental set of basis functions $\{g_k\}$ which in the present work is the set of Gaussian group functions

$$a_k^{(l)} = (\sum_m e_{mk}^{(l)} g_m)\phi_{\mathrm{spin}},$$

where $\phi_{\mathrm{spin}} = \alpha$ or β. Considerations here are restricted to an orthonormal final set of molecular orbitals.

Wavefunctions are determined by a variational minimization of the energy expectation value, $E_k = \langle \psi_k \mid H \mid \psi_k \rangle$, with respect to available parameters subject to the orthogonality constraint, $\langle \psi_k \mid \psi_l \rangle = \delta_{kl}$, where H is the nonrelativistic Hamiltonian

$$H = \sum_i \left[-\tfrac{1}{2}\nabla_i{}^2 - \sum_k (Z_k/r_{ki}) \right] + \sum_{i<j} r_{ij}^{-1}.$$

Matrix elements between configurations reduce to the well-known one- and two-electron integrals over spatial molecular orbitals given elsewhere.[14] These in turn are expressed in terms of integrals over the fundamental basis functions, all of which are computed accurately.

Given a set of basis functions $\{g_k\}$ which for purposes of tractability are assumed invariant in the en-

[14] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), pp. 143–146.

ergy minimization, it is possible to inquire about the remaining parameters which can be varied profitably as follows:

(1) If all configurations $\{\phi_l\}$ derivable from the set $\{a_k\}$ obtained by a linear transformation of the set of functions $\{g_k\}$ are included, only the c_{lk} require variation since the $\{a_k\}$ spans the same space as $\{g_k\}$.

(2) If a truncated set $\{\phi_l\}$ is employed, for example by restricting the occupancy of the $\{a_k\}$, it is meaningful to consider the following:

(a) The direct optimization of the multiconfiguration functions ψ_k by variation of c_{lk} and e_{mk}.

(b) The adequacy of a set of configurations $\{\phi_l\}$ formed from a set of molecular orbitals $\{a_k\}$ determined by some more restrictive formulation, e.g., a ground- or excited-state single determinant SCF treatment, plus additional restrictions on the orbitals allowed to have variable occupancy.

For the large basis sets employed in the present study, both (1) and (2a) generally are intractable; thus we have been forced to restrict the consideration to the formulations of the type described in (2b). Of these we have considered three possibilities for the construction of wavefunctions for an excited electronic state. The first is based on the use of molecular orbitals from a closed-shell ground-state SCF treatment and involves the definition of a core of molecular orbitals which are taken to be unperturbed in all ground and excited states of interest; in addition, certain higher virtual orbitals are excluded in the construction of configurations. The second possibility considered is based on molecular orbitals determined from a triplet-state SCF calculation, followed by core and virtual orbital restrictions. These molecular orbitals are used to construct both singlet and triplet states corresponding to the spatial orbital excitation. A similar use of MO's determined from excited singlet-state SCF calculations is not explored in the present work. The third possibility

TABLE III. A comparison of π and π^* molecular orbitals of H₂CO from ground- and excited-state SCF treatments. Subscripts s and l denote short- and long-range p groups on carbon and oxygen; coefficient ratios of short- and long-range groups on the same nucleus are variable only in the split basis calculations.

C and O p basis groups	Ground-state SCF		Excited-state SCF split s, p basis
	Fixed group basis	Split s, p basis	
$1b_1$ (π) O_s	0.53	0.56	0.65
O_l	0.22	0.26	0.27
C_s	0.43	0.41	0.31
C_l	0.20	0.15	0.09
$2b_1$ (π^*) O_s	−0.63	−0.44	−0.43
O_l	−0.26	−0.53	−0.36
C_s	0.67	0.44	0.66
C_l	0.31	0.74	0.52

considered for constructing a molecular orbital CI basis involves a transformation of the virtual set of orbitals to enhance the convergence of the excited-state CI. Only the most elementary step in this direction is taken in the present work, a thorough investigation of which certainly constitutes an important area for further study.[9a,12,15]

It should be noted that the type of excited-state CI treatment which is most commonly employed is based on the ground-state SCF MO's and the assumption of a relatively large unperturbed core; in fact, single-excitation CI treatments of this type provide a first-order explanation of electronic spectra. To anticipate the results of the present study, however, in case highly flexible basis sets are used, the resulting low-lying ground-state virtual orbitals may be considerably too diffuse as a result of their determination in the negative ion field. As a consequence, the premature truncation of the virtual orbital set is a serious problem which requires careful analysis. To a limited extent this analysis can be accomplished by open-shell SCF or single-excitation CI treatments of the states considered. The studies of formaldehyde reported in subsequent sections provide more quantitative information on this subject.

IV. GENERATION OF CONFIGURATIONS

The main objective of the present work is the determination of wavefunctions for excited electronic states; thus we have sought to develop a procedure for generating configurations which is referenced to the particular excited state of interest, as opposed to a scheme which is organized around certain types of excitations from the ground configurations, i.e., single, double, triple, etc. All such excitation procedures are related, of course, but since configurations which are important contributors to the excited state are accessible by single and double excitations from the major excited-state configurations, it seems advantageous to generate the configurations directly in this way, rather than performing all excitations (at least through triple excitations for the low-lying states of interest) from the ground state.

The procedure used to generate configurations for

TABLE IV. A comparison of energies from constrained SCF calculations on the $^3A_2$ state of H_2CO with single promotion and full SCF energies. In the constrained SCF calculations, all a_1 orbitals are the same as produced by the ground-state SCF treatment and variable numbers of the ground-state b_1 and b_2 orbitals are used as symmetry orbitals.

Symmetry orbital basis	$^3A_2$ energy a.u.
(Single promotion, no SCF)	−144.7722
kb_1, kb_2 ($k=1, 2$)	−144.7849
kb_1, kb_2 ($k=1, 2, 3$)	−144.7984
kb_1, kb_2 ($k=1, 2, 3, 4$)	−144.8189
(full SCF)	−144.8249

[15] R. K. Nesbet, Rev. Mod. Phys. **33**, 28 (1961).

a state of given spatial symmetry and multiplicity (ground or excited states) can be outlined as follows[16,17]:

(1) A set of M parent configurations $\{\psi_k^{(1)}\}$ is chosen, which consists of the configurations expected to be the most important contributors to the state of interest. This set is subject to refinement subsequently based on purely analytical criteria. If several states of the same spatial symmetry and multiplicity are of interest, these must be treated simultaneously to satisfy orthogonality requirements.

(2) A second set of configurations $\{\psi_k^{(2)}\}$ is generated by performing single and double excitations from each parent $\psi_k^{(1)}$ subject to a threshold criterion

$$\left| \frac{|\langle \psi_k^{(2)} | H | \psi_j^{(1)} \rangle|^2}{\langle \psi_k^{(2)} | H | \psi_k^{(2)} \rangle - \langle \psi_j^{(1)} | H | \psi_j^{(1)} \rangle} \right| > \delta$$

for at least one $j = 1, 2 \cdots M$,

where δ is chosen to be small subject to tractability considerations, typically 10^{-3}–10^{-5}.

(3) The combined set of configurations $\{\psi^{(1)}\} \cup \{\psi^{(2)}\}$ is augmented at this point to include all configurations rejected by the interaction criterion which are necessary to obtain precise eigenfunctions of the spin angular momentum operator, S^2, e.g., if the $m_s = 0$ configurations are considered, all $m_s = 0$ permutations of a given open-shell spatial configuration must be included. Assuming the $\{\psi_k^{(2)}\}$ has been so modified, the total wavefunction is expanded

$$\psi = \sum_{i=1}^{2} \sum_k c_{ki} \psi_k^{(i)}$$

and the Hamiltonian matrix is diagonalized to obtain energies E_j and wavefunctions ψ_j.

(4) The M' lowest-energy CI wavefunctions are defined as the parent set $\{\psi_j^{(1)}\}$ and step 2 is repeated using the entire CI wavefunctions for $\psi_j^{(1)}$. The new configurations $\{\psi_k^{(2)}\}$ plus those contained in $\psi_j^{(1)}$ are used, after augmentation to include missing m_s components, as a basis for the final CI expansion.

In the present work, $m_s = 0$ configurations are utilized in order to obtain all possible multiplicities corresponding to a given spatial orbital excitation. In this case, it is convenient to treat configurations in terms of the noninteracting combinations $\phi_l + \bar{\phi}_l$ and $\phi_l - \bar{\phi}_l$, where $\bar{\phi}_l$ is obtained from ϕ_l by replacing spins α by β and β by α. Generally, for the systems studied, the final number of configuration pairs for each state is relatively large, on the order of 200 to 400; thus, the final diagonalization of H requires approximate treatment.

[16] See Ref. 10 for a discussion of a related procedure for generating important configurations based on excitations from improved zeroth-order wavefunctions.

[17] Although the procedure for generating the final set of configurations appears to be somewhat lengthy, it can be accomplished quite economically such that it is insignificantly time consuming compared to the time required to evaluate integrals over molecular orbitals.

TABLE V. Formaldehyde basis orbital parameters. Exponents, coefficients, and lobe displacements for for C, O, and H s- and p-type group functions.[a]

Oxygen

p_1	46.28794670	9.03687108	2.36056691	0.70312221	
	1.00000000	15.79171097	84.93970013	202.77696037	
	0.04170526	0.05005369	0.06414400	0.07559572	
p_2	0.21202128				
	1.00000000				
	0.11778929				
p_3	0.03000000				
	1.00000000				
	0.17320508				
s_1	290.82045364	1424.06427002	4643.44854736		
	1.00000000	0.13444740	0.03226683		
s_2	0.93109988	9.70435202			
	1.15259700	−0.15379070			
s_3	0.28246003				
	1.00000000				
s_4	31.31659460	12.86074781	4.60373884	76.23197079	
	1.00000000	1.87811667	1.08379248	0.62608770	

Carbon

p_1	19.06602335	5.07201254	1.43047583	0.41424804	
	1.00000000	9.21132469	62.76061392	208.05835342	
	0.05909909	0.06466585	0.07498752	0.08456204	
p_2	0.12162199				
	1.00000000				
	0.09899098				
p_3	0.02000000				
	1.00000000				
	0.21213203				
s_1	159.62738037	781.64945874	2548.72558594		
	1.00000000	0.13439400	0.03237879		
s_2	0.47349750	4.93435138			
	1.14118800	−0.15846629			
s_3	0.14804924				
	1.00000000				
s_4	17.18925118	7.05908918	2.52692944	41.84268900	
	1.00000000	1.86506998	1.10902999	0.63078000	

Hydrogen

s_1	2.29560530	0.65169570	0.20594498	9.91954756	64.78691196
	1.00000000	2.47509199	1.89710096	0.22825627	0.03153557

[a] The function p_2 is the principal component of the $3p$ AO; the same value of the exponent is calculated for the s_5 ($3s$) basis function. Basis sets: I. Split group (C and O p_1, p_2, s_1, s_2, s_3, s_4, and H s_1); II. Split group plus O$p_3(\pi)$, O$p_3(b_2)$, and C$p_3(\pi)$ functions; III. Split group plus Os_5 and Cs_5.

V. SUCCESSIVE DIAGONALIZATION PROCEDURE

Generally, for a given $N \times N$ Hamiltonian matrix derived from a set of configurations $\{\phi_k\}$, only the lowest few eigenvalues and corresponding eigenvectors are useful approximations to molecular states; thus, in the present approach, an attempt is made to obtain these lower energy solutions approximately without recourse to diagonalization of the entire matrix. The procedure makes use of the fact that the relative importance of a given configuration $\psi_k^{(2)}$ can be estimated by computing its interaction with each parent

$$\left| \frac{|\langle \psi_k^{2)} | H | \psi_j^{(1)} \rangle|^2}{\langle \psi_k^{(2)} | H | \psi_k^{(2)} \rangle - \langle \psi_j^{(1)} | H | \psi_j^{(1)} \rangle} \right|,$$

where $\psi_j^{(1)}$, $j = 1, 2, 3 \cdots M'$ is a parent. The entire set

of configurations is ordered such that members of the M' parents occur first, followed by the remaining configurations which are ordered according to the above interaction criterion (subject to the condition that each time a configuration is included all $m_s = 0$ spin permuttations of the open-shell orbitals follow sequentially in the list). The approximate diagonalization of the resulting $N \times N$ Hamiltonian matrix is accomplished in a series of p smaller diagonalization steps

$$N_1 \times N_1, \tag{1}$$

$$(N_2 + k) \times (N_2 + k), \tag{2}$$

$$\vdots$$

$$(N_l + k) \times (N_l + k), \tag{l}$$

$$\vdots$$

$$(N_p + k) \times (N_p + k), \tag{p}$$

in which the k lowest energy linear combinations resulting from a particular step are passed on to the next step, and

$$N = \sum_{l=1}^{p} N_l.$$

Thus, the step $l-1$ produces k lowest energy wavefunctions

$$\psi_i = \sum_m c_{mi}\phi_m, \qquad i=1, 2, \cdots k$$

and in the lth step, the wavefunction is constructed as a linear combination of $N_l + k$ terms:

$$\psi = \sum_{i=1}^{k} c_i\psi_i + \sum_{m=1}^{N_l} c_m\phi_{m+q},$$

in which the first k terms are constrained to be the k linear combinations resulting from the $l-1$ step, and $q = N_1 + N_2 + \cdots + N_{l-1}$. At each step, the N_l are chosen to include all necessary $m_s = 0$ spin permutations to insure a proper eigenfunction of S^2. The above diagonalization procedure allows some adjustment of the k lowest energy linear combinations at each step, but only to the extent possible by mixing with the constrained linear combinations actually present. The interest in the present work is only in the one or two lowest energy wavefunctions for each spatial symmetry, and

TABLE VI. Molecular orbital and total energies from ground-state calculations on H_2CO for three basis sets: (I) split group, (II) split group plus C $3p\pi$, O $3p\pi$, and O $3pb_2$, and (III) split group plus C $3s$ and O $3s$. Orbitals allowed to have variable occupancy in CI calculations, performed subsequently, are indicated by an asterisk. Energies are in atomic units.

Basis set[a] I		Basis set[a] II		Basis set[a] III	
$11a_1$	1.88	$11a_1$	1.88	$5b_2$	1.11*
$5b_2$	1.11	$6b_2$	1.11*	$4b_1$	0.97*
$10a_1$	0.99	$6b_1$	1.01*	$4b_2$	0.82*
$4b_1$	0.97*	$10a_1$	0.99	$3b_1$	0.50*
$9a_1$	0.84	$5b_2$	0.85*	$3b_2$	0.43*
$4b_2$	0.82*	$9a_1$	0.84	$2b_1$	0.11*
$8a_1$	0.77*	$8a_1$	0.77	$7a_1$	0.11*
$7a_1$	0.54*	$5b_1$	0.56*	$6a_1$	0.07*
$3b_1$	0.50*	$7a_1$	0.54	$2b_2$	-0.44*
$3b_2$	0.43*	$4b_2$	0.49*	$1b_1$	-0.53*
$6a_1$	0.29*	$6a_1$	0.29	$5a_1$	-0.64*
$2b_1$	0.11*	$4b_1$	0.13*	$1b_2$	-0.70*
$2b_2$	-0.44*	$3b_1$	0.12*	$4a_1$	-0.86
$1b_1$	-0.53*	$3b_2$	0.09*	$3a_1$	-1.42
$5a_1$	-0.64*	$2b_1$	0.04*	$2a_1$	-11.35
$1b_2$	-0.70*	$2b_2$	-0.44*	$1a_1$	-20.58
$4a_1$	-0.86*	$1b_1$	-0.53*	E_T	-113.8094
$3a_1$	-1.42	$5a_1$	-0.64		
$2a_1$	-11.35	$1b_2$	-0.70*		
$1a_1$	-20.58	$4a_1$	-0.86		
E_T	-113.8094	$3a_1$	-1.42		
		$2a_1$	-11.35		
		$1a_1$	-20.58		
		E_T	-113.8097		

[a] SCF calculations were performed for basis sets I and II; for basis III, C $3s$ and O $3s$ orbitals were simply Gram–Schmidt orthogonalized to the MO's obtained from basis set I. The nuclear coordinates and the nuclear repulsion energy are given in Table II.

for this purpose $k=6$ was used; likewise, in order to obtain matrices for which diagonalization would not be unduly time consuming, the N_k were chosen arbitrarily to be ≤ 80. An example showing typical numerical changes in eigenvalues and eigenvectors on successive diagonalization steps is shown in Table I for a $^1A_1$ CI calculation on formaldehyde.

VI. PRELIMINARY REMARKS ON THE DESCRIPTION OF H_2CO EXCITED STATES

The formaldehyde molecule is a sufficiently small system to enable a somewhat detailed investigation of the several points, mentioned previously, which are relevant to a theoretical description of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excited states of the larger molecules to be reported in Part II of this work. Formaldehyde itself is of considerable interest in view of the extensive experimental evidence available on excited electronic states of the molecule[18a-18p] and the corresponding lack of a definitive *ab initio* description of these states.[19-21] There is in fact still some uncertainty experimentally as to the nature of the transition at ~ 8 eV, for which both $\pi \rightarrow \pi^*$ and $n \rightarrow 3p$ (Rydberg) descriptions have been proposed.[18a,18c,18e] The present study of formaldehyde is restricted to an examination of Franck–Condon excitations only (the nuclear geometry of each excited state is taken to be the same as the ground-state equilibrium geometry). Thus, in the case of allowed transitions, the most appropriate experimental quantities for comparison with calculated transition energies are the energies corresponding to band intensity maxima. In this study, the primary question concerns the adequacy of a CI description based on a set of molecular

[18] (a) G. Herzberg, *Molecular Spectra and Molecular Structure: III. Electronic Spectra and Electronic Structure of Polyatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N.J., 1967) and references contained therein; (b) G. W. Robinson *Methods of Experimental Physics: Molecular Physics* (Academic Press Inc., New York, 1962); (c) W. C. Price, J. Chem. Phys. **3**, 256 (1935); (d) A. D. Cohen and C. Reid, J. Chem. Phys. **24**, 85 (1956); (e) A. D. Walsh, Proc. Roy. Soc. (London) **A185**, 176 (1946); (f) J. C. D. Brand, J. Chem. Soc. **1956**, 858; (g) G. W. Robinson and V. E. DiGiorgio, Can. J. Chem. **36**, 31 (1958); (h) V. E. DiGiorgio and G. W. Robinson, J. Chem. Phys. **31**, 1678 (1959); (i) V. Henri and S. A. Schou, Z. Physik **49**, 774 (1928); (j) G. Fleming, M. M. Anderson, A. J. Harrison, and L. W. Pickett, J. Chem. Phys. **30**, 351 (1959); (k) G. W. Robinson, Can. J. Phys. **34**, 699 (1956); (l) J. H. Callomon and K. K. Innes, J. Mol. Spectry. **10**, 166 (1963); (m) J. R. Henderson and M. Muramoto, J. Chem. Phys. **43**, 1215 (1965); (n) H. McMurray, J. Chem. Phys. **9**, 231 (1941); (o) S. E. Hodges, J. R. Henderson, and J. B. Coon, J. Mol. Spectry. **2**, 99 (1958); (p) J. E. Parkin, H. G. Poole, and W. T. Raynes, Proc. Chem. Soc. **1962**, 248.

[19] A number of semiempirical calculations on formaldehyde have been reported: T. Anno and A. Sado, J. Chem. Phys. **26**, 1759 (1957); J. W. Sidman, *ibid.* **27**, 429 (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).

[20] A Hartree–Fock level SCF calculation plus the evaluation of one-electron properties of the ground state of H_2CO is reported by D. B. Neumann and J. W. Moskowitz, J. Chem. Phys. **50**, 2216 (1969).

[21] T. H. Dunning, Jr. and V. McKoy, J. Chem. Phys. **48**, 5263 (1968).

TABLE VII. Energies of H_2CO ground and excited states from CI treatments based on ground-state SCF molecular orbitals and a split-group basis set. The orbitals allowed to have variable occupancy in forming excited configurations are indicated in Table VI. The interaction threshold δ and the total number of configuration pairs (in parentheses) are shown for each calculation. Energies are in atomic units unless otherwise indicated.

Electronic state and orbital promotion	Single configuration energies	Initial step CI energies $\delta = 2 \times 10^{-3}$	Final CI energies $\delta = 2 \times 10^{-4}$	Excitation energies (eV)	Qualitative description of orbital promotion
$^1A_1$					
Ground state	−144.9232	(49) −144.9918	(276)[a] −145.0211	···	Ground state
$1b_1 \rightarrow 2b_1$	−144.4677	−144.5681	−144.6002		$\pi \rightarrow \pi^*$
$^3A_1$					
$1b_1 \rightarrow 2b_1$	−144.7273	(31) −144.7739	(170) −144.8105	5.82	$\pi \rightarrow \pi^*$
$^1A_2$					
$2b_2 \rightarrow 2b_1$	−144.7465	(21) −144.8363	(197) −144.8833	3.84	$n \rightarrow \pi^*$
$^3A_2$					
$2b_2 \rightarrow 2b_1$	−144.7723 [−144.8249][b]	(21) −144.8583 [−144.8844][b]	(187) −144.8977 [−144.9060][b]	3.45	$n \rightarrow \pi^*$

[a] $\delta = 3 \times 10^{-4}$.   [b] Results from a CI treatment based on $^3A_2$ SCF MO's; see Table II.

orbitals in which MO occupancies are restricted by truncation of the set of virtual orbitals and by the definition of an unperturbed core of doubly occupied MO's.

On the question of using certain ground-state molecular orbitals to describe excited states, it is reasonable to adopt as a first criterion that the set of MO's utilized be capable of reproducing the excited-state SCF MO's. In Table II, SCF molecular orbital energy diagrams for H_2CO are reported for two different basis set calculations on the $^1A_1$ ground state, and one SCF treatment of the $^3A_2$ $^3(n \rightarrow \pi^*)$ excited state. The fixed-group and split-group basis sets are of the types described in Sec. II, where the latter basis affords considerably more flexibility in adjusting to the molecular field through the increase in number of effective basis functions, i.e., by allowing variable shapes of $2s$ and $2p$ atomic orbitals.

Although the higher virtual orbital energies differ considerably in the two ground-state SCF calculations, the energies of the occupied MO's and the $2b_1$ (π^*) show a close correspondence. In the case of the $2b_1$, however, the similarity of orbital energies is misleading as shown by an analysis of orbital coefficients presented in Table III. In this table, the fixed-group results can be interpreted as resulting from a SCF treatment employing two $p\pi$ basis functions (short- and long-range functions) on each C and O with coefficient ratios constrained to give atomic p orbitals, while in the split-group treatment of the ground state and the $^3A_2$ excited state, these p basis function coefficients plus those of the decomposed long-range s groups are determined at the molecular SCF stage. Two important observations should be made. The first is that the doubly occupied π ($1b_1$) orbital is quite similar in all three calculations, indicating that the flexibility afforded by splitting the p group does not drastically alter the shape of the π MO in either the ground state

or the $^3A_2$ excited state. The second observation concerns the π^* ($2b_1$) orbital. In the ground-state calculation at the split level, the coefficients of the long-range p groups are found to increase considerably as a result of the tendency toward diffuseness of the π^* (virtual) orbital which occurs in the case of a more flexible basis set. Neither of the π^* MO's corresponds closely to the optimum $2b_1$ orbital determined by the $^3A_2$ excited-state SCF treatment; in fact, if a trivial truncation of the virtual spectrum were performed to include only the $2b_1$ orbital in a CI calculation, it is open to question whether the fixed- or split-group ground-state π^* orbital basis would provide the better description of the $^3A_2$ state.

As mentioned previously, the adequacy of a limited number of ground-state-determined MO's as a basis for a CI description of an excited state can be investigated in part by examination of the extent to which the orbitals can be transformed into the occupied excited-state SCF MO's. In order to investigate the number and type of ground-state MO's which must be included to reproduce accurately the occupied excited-state MO's several constrained excited-state SCF calculations were performed. In these calculations a fixed core consisting of all of the doubly occupied MO's except the $1b_2$, $1b_1$ (π), and $2b_2$ (n) was assumed, and the $1b_2$, $1b_1$, $2b_2$, and $2b_1$ orbitals were determined by linear transformation of the ground-state $1b_2$, $1b_1$, and $2b_2$ orbitals plus specified numbers of higher b_1 and b_2 virtual orbitals. The energies from this series of calculations are compared in Table IV with the full $^3A_2$ excited-state SCF limit. These results exhibit two important features. First, there is a significant lowering of the energy at each step up to the inclusion of $4b_1$ and $4b_2$ MO's. This result implies that much of the flexibility needed to reproduce the excited-state b_1 and b_2 MO's is trapped in the higher ground-state virtuals

TABLE VIII. Energies of H_2CO ground and excited states from CI treatments based on ground-state SCF molecular orbitals. A split group plus $3p\pi$ orbitals on C and O and a $3pb_2$ orbital on O basis set is used for the A_1 and A_2 state, and a split group plus $3s$ orbitals on C and O basis set is used for the B_1 and B_2 states; orbitals allowed to have variable occupancy in forming excited configurations are indicated in Table VI. The interaction threshold δ and the total number of configuration pairs (in parentheses) are shown for each calculation. Energies are in atomic units unless otherwise indicated.

Electronic state and orbital promotion	Single configuration energies	Initial step CI energies $\delta = 2.5 \times 10^{-3}$	Final CI energies $\delta = 2 \times 10^{-4}$	Excitation energies (eV)	Qualitative description of orbital promotion
$^1A_1$		(49)	(334)		
Ground state	−144.9235	−144.9695	−145.0029	...	Ground state
$2b_2 \rightarrow 3b_2$	−144.5615	−144.6470	−144.6977	8.30	$n \rightarrow 3pb_2$
$1b_1 \rightarrow 3b_1$	−144.4815	−144.5573	−144.5845	11.39	$\pi \rightarrow \pi^*$
$1b_1 \rightarrow 2b_1$	−144.4625	−144.5274	−144.5565	12.15	$\pi \rightarrow \pi^*$
$^3A_1$		(38)	(299)		
$1b_1 \rightarrow 3b_1$	−144.6354	−144.7685	−144.7906	5.77	$\pi \rightarrow \pi^*$
$2b_2 \rightarrow 3b_2$	−144.5645	−144.6492	−144.6988	8.27	$n \rightarrow 3pb_2$
$1b_1 \rightarrow 2b_1$	−144.4996	−144.5398	−144.5627	11.97	$\pi \rightarrow \pi^*$
$^1A_2$		(35)	(260)		
$2b_2 \rightarrow 3b_1$	−144.6735	−144.8015	−144.8583	3.93	$n \rightarrow \pi^*$
$2b_2 \rightarrow 2b_1$	−144.5847	−144.6545	−144.7014	8.20	$n \rightarrow \pi^*$
$^3A_2$		(35)	(259)		
$2b_2 \rightarrow 3b_1$	−144.6897	−144.8222	−144.8735	3.51	$n \rightarrow \pi^*$
$2b_2 \rightarrow 2b_1$	−144.5867	−144.6546	−144.7011	8.20	$n \rightarrow \pi^*$
$^1B_1$		(24)	(221)		
$5a_1 \rightarrow 2b_1$	−144.5557	−144.6213	−144.6598	9.35	$\sigma \rightarrow \pi^*$
$1b_1 \rightarrow 7a_1$	−144.4946	−144.5508	−144.5910	11.23	$\pi \rightarrow 3sO$
$^1B_2$		(18)	(126)		
$2b_2 \rightarrow 7a_1$	−144.5842	−144.6811	−144.7288	7.48	$n \rightarrow 3sO$

TABLE IX. Optimum $2b_1$ and $3b_1$ (π) molecular orbitals from single excitation $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ calculations. The optimum $2b_1$ and $3b_1$ orbitals are expressed as linear combinations of the ground-state $2b_1$, $3b_1$, $4b_1$, $5b_1$ and $6b_1$ virtual orbitals.

Ground-state virtual orbital	Expansion coefficients							
	$^3(n \rightarrow \pi^*)$		$^1(n \rightarrow \pi^*)$		$^3(\pi \rightarrow \pi^*)$		$^1(\pi \rightarrow \pi^*)$	
	$2b_1$	$3b_1$	$2b_1$	$3b_1$	$2b_1$	$3b_1$	$2b_1$	$3b_1$
$2b_1$	0.336	0.855	0.346	0.854	0.306	0.826	0.912	0.263
$3b_1$	0.784	−0.472	0.786	−0.477	0.791	−0.469	0.273	−0.961
$4b_1$	0.496	0.191	0.489	0.184	0.489	0.282	0.304	0.072
$5b_1$	−0.127	0.098	−0.123	0.096	−0.170	0.130	0.034	0.044
$6b_1$	0.106	0.011	0.095	0.009	0.114	0.026	−0.026	0.034

and that the energy differences (given in Table IV) which are due to truncation of the virtual spectrum would not necessarily be recovered by CI. Examination of the SCF MO coefficients reveals that the π MO's are the ones most significantly altered through mixing with the higher virtuals; the $2b_2$ orbital is not changed appreciably even though this orbital is now singly occupied in the $^3A_2$ state. The second important feature of the series of calculations is the documentation of the adequacy (at least energetically) of a large core of unperturbed MO's, resulting in an energy within 0.006 a.u. of the completely optimized SCF. It is also interesting to note that the $^3A_2 \leftarrow {}^1A_1$ transition energy determined by a split basis SCF calculation on each state is 2.6 eV and, similarly, if the $^3A_2$ SCF MO's are used to construct the $^1A_2$ wavefunction, the

calculated $^1A_2 \leftarrow {}^1A_1$ transition energy is 3.2 eV; thus, both transition energies are lower than experimental values corresponding to the band origins of the transitions, 3.1 and 3.5 eV, respectively. This result implies that the SCF technique using the present basis set affords a somewhat better description energetically of both excited states than of the ground state. Such a situation is reasonable in view of the smaller correlation energy associated with the particular open-shell configuration of the A_2 excited states; this interpretation is borne out by studies, discussed in the next section, in which the energies of the A_2 excited states are lowered less by CI (based on $^3A_2$ SCF MO's) than is the energy of the ground state for a CI treatment based on ground-state SCF MO's.

Concerning the general feasibility of the procedure

TABLE X. Energies of H_2CO ground and excited states from CI treatments based on molecular orbitals determined by single-excitation CI calculations, (see text). A split group plus 3 $p\pi$ orbitals on C and O and a $3pb_2$ orbital on O basis set is used. The same orbitals are allowed to have variable occupancy as in the calculation reported in Table VIII. The interaction threshold δ and the total number of configuration pairs (in parentheses) are shown for each calculation. Energies are in atomic units unless otherwise indicated.

Electronic state and orbital promotion	Single configuration energies	Initial step CI energies $\delta = 2.5 \times 10^{-3}$	Final CI energies $\delta = 2 \times 10^{-4}$	Excitation energies (eV)	Qualitative description of orbital promotion
$^1A_1$		(41)	(342)		
Ground state	-144.9235	-144.9626	-145.0026	$\cdots$	Ground state
$2b_2 \rightarrow 3b_2$	-144.5652	-144.6439	-144.6975	8.30	$n \rightarrow 3pb_2$
$1b_1 \rightarrow 2b_1$	-144.4920	-144.5430	-144.5869	11.31	$\pi \rightarrow \pi^*$
$1b_1 \rightarrow 3b_1$	-144.4618	-144.5220	-144.5568	12.13	$\pi \rightarrow \pi^*$
$^3A_1$		(28)	(269)		
$1b_1 \rightarrow 2b_1$	-144.7590	-144.7681	-144.7946	5.66	$\pi \rightarrow \pi^*$
$2b_2 \rightarrow 3b_2$	-144.5705	-144.6641	-144.7049	8.10	$n \rightarrow 3pb_2$
$1b_1 \rightarrow 3b_1$	-144.4876	-144.5368	-144.5682	11.82	$\pi \rightarrow \pi^*$
$^1A_2$		(22)	(226)		
$2b_2 \rightarrow 2b_1$	-144.7650	-144.8287	-144.8628	3.80	$n \rightarrow \pi^*$
$2b_2 \rightarrow 3b_1$	-144.5702	-144.6646	-144.7088	7.99	$n \rightarrow \pi^*$
$^3A_2$		(23)	(211)		
$2b_2 \rightarrow 2b_1$	-144.7937	-144.8436	-144.8783	3.38	$n \rightarrow \pi^*$
$2b_2 \rightarrow 3b_1$	-144.5706	-144.6649	-144.7085	8.00	$n \rightarrow \pi^*$

outlined above in investigating the excited states of large molecules, it should be mentioned that such constrained SCF calculations are not prohibitively difficult and can be used to advantage, before starting the CI treatment, to investigate the adequacy of a proposed core and the point at which to truncate the virtual spectrum. It is also possible, of course, to base the CI formulation on the molecular orbitals produced by such limited SCF treatments. Since the major defect of the ground-state MO's is in the virtual spectrum, these SCF treatments could be limited to a transformation of the virtual MO's only.

Likewise, it should be noted that a transformation of the virtual MO's could be accomplished by single-excitation CI procedures which could be performed advantageously before generation of the full set of MO integrals needed in the final CI treatment. For example, for the $^1A_1$ states of H_2CO, the set of ground-state virtual orbitals $2b_1$, $3b_1$, and $4b_1$, could be replaced by the transformed set, $2b_1'$, $3b_1'$, and $4b_1'$, determined by a CI calculation involving only the single excitation configurations $1b_1 \rightarrow 2b_1$, $1b_1 \rightarrow 3b_1$, and $1b_1 \rightarrow 4b_1$. That is, if the resulting three CI wavefunctions, denoted by index k, have coefficients c_{lk} for the configuration $\phi(lb_1)$ $(1b_1 \rightarrow lb_1)$ the kb_1' orbital is given by

$$kb_1' = \sum_{l=1}^{3} c_{lk}\phi(lb_1), \qquad k = 1, 2, 3.$$

Similarly, the b_2' and a_1' MO's could be determined by separate CI calculations on configurations resulting from a specified choice of ground-state orbital from which single excitations would be performed. While it is true that the diffuseness of the lower virtuals would

be reduced by such transformations, and that initial convergence of CI expansions based on the new MO's presumably would be enhanced, the orbital optimizations outlined are definitely limited in scope and are not clearly highly advantageous. A numerical investigation of the merits of the over-all procedure is presented in the next section.

VII. CALCULATION OF H_2CO EXCITED STATES

Configuration interaction treatments of the low-lying excited states of H_2CO, many of which have been observed experimentally and have been qualitatively described as $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $n \rightarrow 3s$, and $n \rightarrow 3p$ excitations, are discussed in this section. The treatments are based in part on the findings of Sec. VI concerning the $^3A_2$ state, mainly, the adequacy of a relatively large core of doubly occupied MO's and the importance of including essentially all ground-state virtual b_1 orbitals in the CI formulation. Since these conclusions have not been established for the other states of interest, a somewhat larger number of MO's is allowed to have variable occupancy in the present CI treatments. In addition, in certain of the calculations, the split basis set is augmented by the inclusion of additional basis functions which provide a representation of $3p$ and $3s$ atomic orbitals on carbon and oxygen. These functions were determined by atomic calculations in which a one-component Gaussian orbital was added to the basis set, followed by exponent optimization to minimize the energy of the $^3(2p \rightarrow 3p)$ or $^3(2p \rightarrow 3s)$ configurations of carbon and oxygen. The complete basis set for H_2CO is listed in Table V. This basis is somewhat minimal for the investigation of spectral excita-

tions and specifically does not include d-type polarization functions. Such functions are known to be important in the computation of ground-state molecular properties[20] and are likely also important in the evaluation of transition moments.

Configuration interaction treatments based on ground state SCF MO's are presented for three basis sets: a split-group basis (described in Sec. II), a split-group basis plus $3p\pi$ orbitals on carbon and oxygen and a $3p$ nonbonding (b_2) orbital on oxygen, and a split-group basis plus $3s$ orbitals on carbon and oxygen. Molecular orbital and total energies resulting from ground-state SCF calculations employing these basis sets are given in Table VI; those molecular orbitals which are allowed to have variable occupancy in the CI calculations performed subsequently are also indicated in the table. Ground- and excited-state energies from CI treatments, performed in the manner outlined previously in Secs. III–V, are reported in Tables VII and VIII. The first step in these CI treatments involves the selection of the principal single excitation configurations (parents) from which a relatively small number of additional configurations is generated by performing single and double excitations, subject to the interaction threshold criterion. The resulting lower energy CI wavefunctions (including up to four expansions per state) are then treated as parents and additional configurations are generated to form a basis for the final CI calculation. The lowering of energies which occurs in the final CI step, as shown in the tables, partly is due to the lowering of the interaction threshold and partly to the inclusion of configurations which interact strongly with configurations not present in the initial set of parents. In comparing the CI treatment based on the split-group basis set (Table VII) with the CI treatment based on the split group plus $3p$ or $3s$ basis set (Table VIII), it should be noted that the former allows variable occupancy of the $4a_1$ to $8a_1$ MO's, which is not the case in the latter treatment. This fact is responsible for the lower total energies for comparable states obtained in the former treatment, although the differences between ground and excited states are approximately the same in both CI treatments. Also given in Table VII are $^3A_2$ energies obtained from a CI treatment using $^3A_2$ SCF MO's; these energies are lower than the previous results at the single-excitation and initial CI levels, but the final CI energy of the $^3A_2$ state is only 0.008 a.u. lower than the result obtained using ground-state SCF MO's.

For purposes of comparison with the above CI treatments, elementary studies along the lines mentioned previously were conducted to investigate the transformation of virtual orbitals by single-excitation CI calculations to enhance the convergence of the CI expansions. Although the technique could be applied specifically to each state of a given symmetry and multiplicity, in the present work, an attempt was made

TABLE XI. Major contributions to the ground- and excited-state CI wavefunctions for H_2CO. Only those configurations with coefficients >0.09 in magnitude in the final CI wavefunctions are included in the list; in the case of open-shell configurations, the coefficient listed is for the pair of configurations $2^{-1/2}(\varphi\pm\bar{\varphi})$; see text. Configurations are described in terms of orbital promotions from the ground configuration based on MO's numbered according to increasing orbital energy as given in Table VI.

A_1 states

| | State and coefficient | | | | |
Configuration	$^1A_1$	$^1A_1$	$^1A_1$	$^3A_1$	$^3A_1$
Ground	0.97				
$8\rightarrow10$		0.93			0.94
$7\rightarrow9$			0.64	0.31	
$7\rightarrow11$			0.62	0.79	
$7^2\rightarrow11^2$	0.11		0.15		
$8\rightarrow19$			0.14		
$7^2\rightarrow11, 12$	0.10		0.10		
$7^2\rightarrow9, 12$			0.09		
$7, 8\rightarrow11, 10$		0.09			
$7^2\rightarrow9, 11$			0.13		
$5\rightarrow10$		0.12			0.12
$7\rightarrow12$			0.25	0.47	
$7\rightarrow16$				0.16	
$7, 8\rightarrow10, 12$		0.10			0.09
$7\rightarrow21$				0.11	
$8\rightarrow14$					0.10

A_2 states

| | State and coefficient | | | |
Configuration	$^1A_2$	$^1A_2$	$^3A_2$	$^3A_2$
$8\rightarrow11$	0.76	0.40	0.76	0.41
$8\rightarrow9$	0.33	0.84	0.33	0.84
$8\rightarrow12$	0.42	0.11	0.44	0.10
$8\rightarrow16$	0.11		0.11	
$7, 8\rightarrow11^2$	0.14		0.12	
$5\rightarrow11$	0.14		0.12	
$7, 8\rightarrow9, 12$		0.09		

B_1 states

| | State and coefficient | |
Configuration	$^1B_1$	$^1B_1$
$7\rightarrow10$		0.78
$6\rightarrow11$	0.94	
$7\rightarrow9$		0.56
$6, 7\rightarrow11^2$	0.22	
$7^2\rightarrow10, 11$		0.15
$6\rightarrow14$	0.15	
$7^2\rightarrow9, 11$		0.14

B_2 state

| | State and coefficient |
Configuration	$^1B_2$
$8\rightarrow10$	0.85
$8\rightarrow9$	0.39
$7, 8\rightarrow10, 11$	0.12
$5\rightarrow10$	0.11
$7^2, 8\rightarrow11^2, 10$	0.09

TABLE XII. A comparison of calculated transition energies and other properties of H_2CO with experimental results. All energies are in electron volts.

Electronic state and orbital promotion	Transition energy calculated[a]	Experimental range[b]	Band origin[b]	Oscillator strength		Dipole moment		References
				Calc[c]	Exptl	Calc (D)	Exptl (D)	
$^1A_1\ \pi\rightarrow\pi^*$	11.31			0.40				
$^1B_1\ \pi\rightarrow 3s$	11.23							
$^1B_1\ \sigma\rightarrow\pi^*$	9.35			0.002				
$^1A_1\ n\rightarrow 3pb_2$	8.30	7.97	7.97	0.03				18(a), 18(c)
$^3A_1\ n\rightarrow 3pb_2$	8.10							
$^3A_2\ n\rightarrow\pi^*$	8.00							
$^1A_2\ n\rightarrow\pi^*$	7.99							
$^1B_2\ n\rightarrow 3sO$	7.48	7.08–7.51	7.08	0.0005	~0.04			18(a), 18(c), 18(j)
$^3A_1\ \pi\rightarrow\pi^*$	5.66							
$^1A_2\ n\rightarrow\pi^*$	3.80	3.51–5.39	3.49		~2×10⁻⁴	1.92	1.56[d]	18(a), 18(f), 18(i), 18(l), 22
$^3A_2\ n\rightarrow\pi^*$	3.38	3.13–3.44	3.12		~7×10⁻³	2.07		18(a), 18(d), 18(f), 18(g), 18(h), 22
$^1A_1$ ground	⋯	⋯	⋯			3.13	2.34[e]	

[a] Franck–Condon excitation, from Table X.
[b] Reference 18(a).
[c] Computed from $f=\frac{2}{3}\Delta E|\ R\ |^2$, where ΔE and R are the calculated transition energy and transition moment, respectively, in atomic units.
[d] D. E. Freeman and W. Klemperer, J. Chem. Phys. **45**, 52 (1966).
[e] J. M. Schoolery and A. H. Sharbaugh, Phys. Rev. **82**, 95 (1951).

to obtain a single set of virtual orbitals to be used insofar as possible for all A_1 and A_2 states. In these states, it is the singly occupied $2b_1$ (π) orbital which requires the most attention. The differences in the optimum $2b_1$ orbital (in the single configuration, virtual only transformation sense) in the various states is investigated by performing single-excitation CI calculations on the states, $^1A_2$ ($n\rightarrow\pi^*$), $^3A_2$ ($n\rightarrow\pi^*$), $^1A_1$ ($\pi\rightarrow\pi^*$), and $^3A_1$ ($\pi\rightarrow\pi^*$). The mixing of the single-excitation configurations is reported in Table IX. Since all configurations for a given state are produced by a single excitation from the same ground-state orbital, the CI result is precisely the same as would be obtained by a restricted SCF calculation in which all occupied orbitals except the $2b_1$ (π) are constrained to be the same as produced by the ground-state SCF. The results shown in Table IX indicate that the optimum $2b_1$ orbitals are quite similar in the $^3A_2$, $^1A_2$, and $^3A_1$ states, but differ considerably from the optimum $2b_1$ orbital in the $^1A_1$ excited state, the latter being rather similar to the ground-state virtual $2b_1$ orbital.

The final CI treatment of the $^1A_1$ states is based on the $2b_1$ to $6b_1$ MO's determined by the interaction of the $^1A_1$ configurations, $1b_1\rightarrow 2b_1$, $3b_1$, $4b_1$, $5b_1$, $6b_1$, and on the $3b_2$ to $6b_2$ MO's determined by the interaction of the $^1A_1$ configurations, $2b_2\rightarrow 3b_2$, $4b_2$, $5b_2$, $6b_2$. For the $^1A_2$, $^3A_2$, and $^3A_1$ states, the CI is based on the $2b_1$ to $6b_1$ MO's determined by the interaction of the $^1A_2$ configurations, $2b_2\rightarrow 2b_1$, $3b_1$, $4b_1$, $5b_1$, $6b_1$, and on the above $3b_2$ to $6b_2$ MO's. Since the new orbitals are only linear transformations of the original MO's, the CI treatment of course does not contain in principle any additional capability over the former CI; thus, the only possible advantage would be a reduction in the number of configurations for comparable numerical accuracy. The results of the CI treatment are reported in Table X. A comparison of these results with the

results in Table VIII shows the expected considerable improvement in the energy at the single configuration level, moderate improvement in the energy of most states for generally fewer configurations at the initial CI step, and essentially no significant change in the final CI results. Those differences in energy which do exist are most significant for those states in which the $2b_1$ orbital differs most significantly from the ground-state virtual $2b_1$ MO. For all states, however, the agreement between the two CI calculations must be considered quite close, particularly since the use of the same interaction threshold might tend to favor the CI based on the transformed set of MO's; thus, these results provide some numerical evidence to support the reliability of the over-all CI procedure outlined in Secs. III–V.

In Table XI, the main contributions to the calculated ground- and excited-state CI wavefunctions are reported, and in Table XII, calculated transition energies are compared with experimental values. In certain cases, calculated oscillator strengths and dipole moments are also reported; however, as mentioned previously, these quantities are not expected to be well described in view of the d-orbital deficiency of the basis set.

Concerning the comparisons with experiment, four of the excited states have been observed experimentally and have been classified as $^1A_2$, $^3A_2$, $^1B_2$, and $^1A_1$ based on the C_{2v} point group of the ground state. The $^1A_2$ and $^3A_2$ states are the ones most definitely established and these are known to have nonplanar equilibrium geometries[18]; qualitatively, the states have been described as $n\rightarrow\pi^*$ excitations, involving a promotion from the nonbonding (b_2) orbital of oxygen to the CO π^* orbital. Transitions to these states from the $^1A_1$ ground state are forbidden to first order, but can occur in the $^1A_2$ case by a magnetic dipole or vibronic mecha-

nism, and in $^3A_2$ case by spin–orbit mixing with excited singlet states.[22] In neither case does the available experimental information correspond directly to the Franck–Condon transition energy calculated; however, for both states the calculated transition energies (3.38 eV for $^3A_2\leftarrow{}^1A_1$ and 3.80 for $^1A_2\leftarrow{}^1A_1$) are within 0.3 eV of the band origins of the transitions, and as such, the agreement with experiment must be considered excellent. The calculated dipole moment of the $^1A_2$ state is in moderate agreement with experiment which is as satisfactory as can be expected from the present basis set. The principal contributions to the wavefunction, reported in Table XI, confirm the description of the $^{1,3}A_2$ states as involving $n\rightarrow\pi^*$ promotions.

The next excited state for which experimental evidence is available is the $^1B_2$, where the calculated transition energy of 7.48 eV for the transition $^1B_2\leftarrow{}^1A_1$ (ground) is within the reported experimental range and differs by only 0.4 eV from the reported band origin. As seen in Table XI, this state involves mainly a $n\rightarrow3s$ excitation on oxygen, and thus the agreement with experiment is perhaps surprisingly good in view of the simple description of the $3s$ atomic orbital. The exceedingly small calculated oscillator strength is likely unreliable, however.[23]

The experimentally observed transition at 7.97 eV has been described variously as a $\pi\rightarrow\pi^*$ or a $n\rightarrow3p$ (Rydberg) transition to a $^1A_1$ state. The lowest $^1A_1$ state calculated is at 8.30 eV which would identify quite satisfactorily with a state with a band origin at 7.97 eV. From the wavefunction reported in Table XI, this state is seen to be principally $n\rightarrow3pb_2$ on oxygen; the mixing with the $\pi\rightarrow\pi^*$ configurations, although substantial, is insufficient to produce a large value for the $^1A_1\leftarrow{}^1A_1$ (ground) oscillator strength which is calculated as 0.03. The next $^1A_1$ state calculated, which is principally $\pi\rightarrow\pi^*$ is quite high in energy at 11.31 eV with an oscillator strength of 0.4. Thus, the present calculations on formaldehyde clearly favor the existence of a $n\rightarrow3p$, A_1, state at $\sim$8 eV, but do not show a $\pi\rightarrow\pi^*$ singlet state in this region of the spectrum.

Although we have no evidence which would suggest that the above conclusions regarding the $^1A_1$ states are not reliable, several areas of uncertainty in the present treatment should be noted. The first is obviously at the basis function level where, although a split-group basis plus carbon and oxygen $3p\pi$ orbitals is used, the present basis might be incapable of providing a sufficiently accurate representation of molecular orbitals in the $\pi\rightarrow\pi^*$ excited state. A second area of uncertainty would be the possibility of a CI deficiency

which is peculiar to the $\pi\rightarrow\pi^*$ state. Conceptually, for example, double excitation from the π to the low-lying π^* orbital, $\pi^2\rightarrow\pi^{*2}$, is quite important energetically in stabilizing the ground configuration. In the singly excited $\pi\rightarrow\pi^*$, $^1A_1$ state, such an excitation is no longer possible; thus, if a similar type of correlation effect is important in the excited state, the only orbitals to which excitation could be performed are the higher p-type virtual components since d functions are not included in the basis set. Finally, the possibility also exists that the excited state has an equilibrium geometry which is sufficiently different from that of the ground state to cause extension of the $\pi\rightarrow\pi^*$ transition (in C_{2v}) down to the 8-eV region; however, significant intensity in this region would likely also require a Franck–Condon excitation considerably lower than the 11.31-eV value calculated.

The remaining states for which the basis could be expected to be reasonably adequate are the $^3A_1$ and the $^1B_1$ which are calculated at 5.66 and 9.35 eV, respectively. Unlike the lowest $^1A_1$ excited state, the lowest $^3A_1$ state is almost entirely $\pi\rightarrow\pi^*$, as shown in Table XI. Also shown in the table, is the $^1B_1$ composition which is mainly $\sigma\rightarrow\pi^*$ as opposed to $\pi\rightarrow3s$. The remaining states listed in Table XII are not clearly meaningful since they are, to a large measure, only low-lying orthogonal complements to the lower energy states of the same symmetry and multiplicity. Likewise, at most, only the lower two or three wavefunctions of a particular symmetry and multiplicity are listed in the table; for the present basis sets, a proliferation of additional states occurs starting around 8 eV.

VIII. SUMMARY

A CI procedure which is designed to produce energies and wavefunctions from relatively large-scale computations on ground and excited molecular states is presented based on an orthonormal set of molecular orbitals. The method of generating configurations is referenced to the particular state of interest and involves a two-pass procedure: first, the generation of configurations by single and double excitations from selected important configurations (parents), subject to a threshold criterion, followed by diagonalization of the energy to obtain an initial approximation to the wavefunctions of interest; second, the use of these wavefunctions as parents and a repeat of the generation and diagonalization steps to produce the final CI wavefunction, which in the present work typically contains on the order of 500 configurations.

CI studies of the $^{1,3}A_2$ $(n\rightarrow\pi^*)$, $^{1,3}A_1$ $(\pi\rightarrow\pi^*, n\rightarrow3p)$, $^1B_1$ $(\sigma\rightarrow\pi^*, \pi\rightarrow3s)$, and $^1B_2$ $(n\rightarrow3s)$ states of formaldehyde are reported for several Gaussian basis sets of near atomic Hartree–Fock quality based on molecular orbitals determined from ground- and excited-state SCF treatments and from certain elementary virtual-orbital transformations. Calculated Franck–Condon transition energies, which are in excellent agreement

[22] J. A. Pople and J. W. Sidman, J. Chem. Phys. **27**, 1270 (1957); J. R. Henderson, *ibid.* **44**, 3496 (1966); J. W. Sidman, *ibid.* **29**, 644 (1958); J. H. Callomon and K. K. Innes, J. Mol. Spectry. **10**, 166 (1963).

[23] The final value of the $^1B_2\leftarrow{}^1A_1$ oscillator strength is the result of many numerical cancellations, and thus is likely strongly dependent on the precise form of the $3s$ AO.

with experimental results in the case of the observed transitions are 3.38, 3.80, 5.66, 7.48, 8.30, 9.35, and 11.31 eV for transitions to the $^3A_2$, $^1A_2$, $^3A_1$ ($\pi \rightarrow \pi^*$), $^1B_2$, $^1A_1$ ($n \rightarrow 3p$), $^1B_1$ ($\sigma \rightarrow \pi^*$), and $^1A_1$ ($\pi \rightarrow \pi^*$) states, respectively. Of particular interest is the existence of a $n \rightarrow 3p$ transition on oxygen in the region of the spectrum around 8 eV.

Simple Bond-Charge Model for Symmetric Stretching Vibrations of XY_n Molecules

RAYMOND F. BORKMAN

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

(Received 7 July 1969)

A bond-charge model, previously applied to homonuclear and heteronuclear diatomic species has been extended to symmetric XY_n polyatomic molecules. The chief theoretical tool is the scaled form of the molecular virial theorem. Using this theorem, we relate the force constant for symmetric breathing vibrations to model expressions for the electronic kinetic and potential energies. As in the diatomic case, the kinetic energy is modeled as a particle in a box and the potential energy as a classical system of point charges. Using experimental force constants and bond lengths as input we have evaluated the model bond-charge and path-length parameters for 30 polyatomic species. The bond-charge parameter q is reasonably interpreted as a measure of bond order while the free-electron path-length parameter ν is a measure of atomic core radii. Values of q and ν are given for ground-state and electronically excited-state molecules as well as charged molecular ions, in symmetries $D_{\infty h}, D_{3h}, C_{2v}, C_{3v}$, and T_d. The path-length parameter ν is shown to correlate with position of the constituent atoms in the periodic chart. It is then shown that polyatomic ν values can be predicted accurately from ν values of homonuclear diatomic molecules. This latter result permits the possibility of predicting force constants from input of bond lengths only, and some results of this type are presented.

I. INTRODUCTION

In earlier papers,[1,2] a "bond-charge" model for molecular vibrations was developed and applied to homonuclear[1] and heteronuclear[2] diatomic molecules. For diatomic systems the vibrational potential function, $W(R)$, was taken to be of the form of a Fues potential[3]

$$W(R) = W_0 + (W_1/R) + (W_2/R^2). \tag{1}$$

Application of the diatomic-molecular virial theorem to Eq. (1) revealed that the term W_1/R was purely potential energy, while the term W_2/R^2 was purely kinetic energy. The R-dependent parts of the potential and kinetic energies were modeled, respectively, as a system of point charges obeying Coulomb's Law, and as a "particle-in-a-box." This modeling led to an interpretation of the vibrational properties (equilibrium internuclear distance, and quadratic and higher potential constants) in terms of two new parameters: first, a quantity q, which appeared to measure the amount of electron density in the bonding region of the molecule (bond order), and second, a quantity ν which measured

the effective free-electron path length for the particle-in-a-box model, and which could be related to the "core radii" of the constituent atoms. This interpretation of ν suggested that ν values for heteronuclear diatomic molecules might be related to the corresponding homonuclear ν values. Such a relationship was found [Ref. 2, Eq. (15)], and thus the force constant or, equivalently, the vibration frequency for a heteronuclear diatomic could be predicted from its equilibrium internuclear distance and homonuclear parameters.[2] The method was applied to over 50 different diatomic species (including ions and neutrals) in over 100 different electronic states.

More recently, progress has been made in extending the bond-charge method to polynuclear systems. In particular, Martin has given an application to the vibrations of covalent crystals,[4] and Parr and Brown[5] and Nelander[6] have presented a general form of the virial theorem, suitable for extending the method to polyatomic molecules. In addition, Parr and Brown[5] have given an application of the method to interpreting the observed potential constants in the CO_2 molecule, through quartic degree.

[1] R. G. Parr and R. F. Borkman, J. Chem. Phys. **49**, 1055 (1968).

[2] R. F. Borkman, G. Simons, and R. G. Parr, J. Chem. Phys. **50**, 58 (1969).

[3] See R. F. Borkman and R. G. Parr, J. Chem. Phys. **48**, 1116 (1968), and references cited therein.

[4] R. M. Martin, Chem. Phys. Letters **2**, 268 (1968).

[5] R. G. Parr and J. E. Brown, J. Chem. Phys. **49**, 4849 (1968).

[6] B. Nelander, J. Chem. Phys. **51**, 469 (1969).