THE EXCITATION OPERATOR METHOD
AND
THE VALENCE EXCITED STATES OF ETHYLENE

Thesis by

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To my wife and daughters

Sandra Jane
Angelique de Cameron
Nicole Etienne

"Beauty is truth, truth beauty," -- that is all
Ye know on earth, and all ye need to know.

John Keats in "Ode on a Grecian Urn"

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ABSTRACT

The problem of describing the electronic excited states of an atomic or molecular system can be reduced to one of finding a form for an operator $A^{\dagger}(E)$ such that it satisfies the following equation

$$[\hat{H}, A^{\dagger}(E)]\,|0\rangle \;=\; \Delta E\, A^{\dagger}(E)|0\rangle$$

Four approximations to the excitation operator, $A^{\dagger}(E)$, have been considered: (a) the single transition approximation, corresponding to excitation into virtual orbitals, (b) the improved single transition approximation which allows for the self-consistent field adjustment of the virtual orbital, (c) the Tamm-Dancoff approximation, corresponding to selective configuration interaction in the excited state and (d) the random-phase approximation which attempts to take into account correlation in both ground and excited states.

Analyzing the excitation operator method in terms of the approximations to the excitation operator listed above, we found that the correlation does not always enter in the ground and excited states in a particularly balanced manner and that self-consistent field changes in the core are neglected. In addition, the strong "mixing" of certain doubly excited configurations into the ground state wavefunction, such as ($\pi^*\alpha\pi^*\beta$) in ethylene, is shown to lead to a number of problems in the random-phase approximation, e.g., an instability in the triplet equations.

The excitation operator approach is illustrated by *ab initio* calculations on a number of valence excited states of the ethylene molecule. These calculations indicate that the lowest singlet $\pi \rightarrow \pi^*$ state of ethylene is not a valence state as previously assumed, but that it is significantly more diffuse, e.g., in the improved single transition approximation the $\langle z^2 \rangle$ for the π^*-orbital in the singlet state is 26.3 a.u. compared to 2.8 a.u. in the corresponding triplet state. This behavior is a consequence of the ionic nature of the wavefunction of the singlet state and, thus, is expected to be characteristic of such states in general. We find that σ-π correlation, as included in the above approximations to the excitation operator, does not play an essential role in the description of the excited states, although its effect on the charge distribution of the singlet $\pi \rightarrow \pi^*$ state is substantial.

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1. INTRODUCTION

When electromagnetic radiation of the appropriate wavelength is incident upon a molecule, the molecule can absorb energy from the field and make a transition to a state of higher energy. The specification of the states of a polyatomic molecule requires the assignment of rotational (J), vibrational (υ) and electronic (n) quantum numbers and, thus, such transitions involve a change in one or more of the molecular quantum numbers (n,υ,J). If the radiation has a wavelength in the ultraviolet or visible regions of the spectrum, transitions can be made to excited electronic states. The methods developed here represent one attempt to provide a basis for the theoretical interpretation of the electronic spectra of molecules.

The electronic excited states of atoms and molecules have been of interest to chemists since the advent of modern electronic spectroscopy, but their importance in other areas is now slowly being appreciated.[1,2] The excited states of a system not only determine its spectral characteristics but often they are important in the elucidation of its chemistry,[1] witness the rapid growth in the general area of photochemistry. In addition, our understanding of the exciton structure of molecular crystals is based upon the excited states of the individual molecules which make up the crystal.[3] Thus, an accurate description of the excited states of molecules is important not only to further our general understanding of the electronic structure of molecules, but also to provide a basis for interpreting the interaction of molecules with their environment.

The excited states of an isolated molecule can be categorized into two limiting cases: valence states, of which the ground state is one, and Rydberg states. Valence states are characterized by a compact charge distribution similar in extent to that of the ground state. In an orbital description these states are composed of functions with the same principal quantum numbers as the valence orbitals of the atoms. Rydberg states, on the other hand, have charge distributions similar to that of the corresponding ion plus a very diffuse orbital, the Rydberg orbital. In an orbital description we say that Rydberg states require functions with higher principal quantum numbers than occur in atomic valence states.

The excitation energy is composed of two parts: a change in the Hartree-Fock energy and a change in the correlation energy, i.e.,

$$\Delta E^{ex} = \Delta E^{ex}_{HF} + \Delta E^{ex}_{corr}$$

Since electron pairs are being split up in the excitation process, we might expect the change in the correlation energy to make a significant contribution to the total energy difference. Besides the variations in the charge distributions, Rydberg and valence states can be distinguished by the role that correlation plays in the description of the state.

In Rydberg states the correlation is approximately the same as in the corresponding ion for the Rydberg orbital is spatially quite far from the core. Thus, in such states correlation can be easily taken into account just by referencing the excited state to the ion rather than the neutral molecule. That is, for ionization

$$\Delta E^{\text{ion}} = \Delta E^{\text{ion}}_{\text{HF}} + \Delta E^{\text{ion}}_{\text{corr}}$$

Since for Rydberg states

$$\Delta E^{\text{ex}}_{\text{corr}} \approx \Delta E^{\text{ion}}_{\text{corr}}$$

then

$$\begin{aligned} \text{stability} &= \Delta E^{\text{ex}} - \Delta E^{\text{ion}} \\ &\approx \Delta E^{\text{ex}}_{\text{HF}} - \Delta E^{\text{ion}}_{\text{HF}} \end{aligned}$$

That this is indeed true has been verified by a number of workers,[4,5] although the significance of the result does not always seem to be appreciated and some authors still quote (uncorrected) excitation energies for Rydberg transitions.[6,7]

For valence states no such "zero" of correlation energy exists. We do not expect the correlation energy of the excited state to be as small as that of the ion, which has one less electron, nor do we expect it to be as large as in the ground state, which has all orbitals doubly occupied.

Let us now briefly review the possible approaches to the problem of computing wavefunctions for the excited states of molecules.

The virtual orbital approximation, an approximation which has been widely employed,[8,9,10] merely replaces one of the orbitals occupied in the Hartree-Fock ground state with one of the unoccupied solutions of the ground state Hartree-Fock Hamiltonian, i.e., the so-called virtual orbitals. However, the virtual orbitals of the ground state Hamiltonian experience a potential field due to all of the electrons whereas an occupied orbital experiences only the field due to the other N-1 electrons, as it should. Because of this we expect the virtual orbitals to be far more loosely bound than the variationally correct excited state orbitals. In fact, if we solved the Hartree-Fock equations exactly, the virtual orbitals would all be continuum functions except in those cases in which the molecule has a bound negative ion. In the latter case some of the virtual orbitals should be bound, but they would be appropriate for the negative ion, not for the excited state of the neutral molecule.[5]

In the frozen core approximation[4,5] the excited state wavefunction is again obtained by replacing one of the occupied ground state orbitals with an orbital of higher energy. However, this orbital, called an improved virtual orbital,[5] is obtained by solving for the optimum orbital in the correct N-1 electron potential. Since the remaining orbitals have been taken from the ground state calculation, this method is referred to as the frozen core approximation. The frozen core wavefunction should be considered as the first useful approximation for the excited state.

In the open-shell Hartree-Fock method[11,12] the electrons are assigned to a given orbital configuration and then the orbitals are allowed to self-consistently adjust for the change in the charge distribution. In order to simplify the equations the orbitals are constrained to be orthogonal. The frozen core approximation can be considered an approximation to the open-shell Hartree-Fock wavefunction obtained by restricting the variations to just the (former) virtual orbital. Although simple conceptually, in practice rather severe problems arise in handling the orthogonality constraints and this has prevented all but a limited application of this method to the excited states of molecules.[12] However, recent theoretical work clarifying the role of orthogonality constraints in self-consistent field equations[13] (see also Proposition II) seems promising, so that accurate Hartree-Fock calculations on open-shell states in many systems of chemical interest should soon be possible. Excited state calculations can also be done using the GI method[14] which employs the group operators G_i^γ to insure the correct permutational and spin symmetry for a general product of orbitals. Besides an appealing conceptual picture of the excited states of molecules, the GI wavefunctions for open-shell states satisfy Brillouin's theorem[14] and provide upper bounds on the energies of the states[15] neither of which are accomplished in general by open-shell Hartree-Fock wavefunctions.[16,17]

As stated previously, for the valence excited states of molecules we have no convenient reference point for the correlation energy. The excitation operator method[18,19,20] attempts to deal with this problem by focusing on energy differences between the ground and excited states. Thus, this method is concerned only with the description of the two states relative to one another. The excitation operator, $A^\dagger(E)$, connecting the ground state to the manifold of excited states is defined by

$$A^{\dagger}(E)|0\rangle = |E\rangle$$

so that it satisfies the following commutator

$$[\hat{H}, A^{\dagger}(E)] = \Delta E\ A^{\dagger}(E)$$

Unfortunately, the complexity of the atomic and molecular Hamiltonians prevents the excitation operator from being cast into any simple form. However, it is possible that using chemical intuition we can formulate a new operator $S^{\dagger}(E)$ which contains all the pertinent physical features of the true excitation operator. This method and its application to the ethylene molecule are the topics of the present work.

There are, of course, many ways of going beyond the self-consistent field and excitation operator methods: configuration interaction,[21] the multi-configuration self-consistent field method[22] and perturbation theory in the form of the pair theories proposed by Brueckner,[23] Goldstone,[24] Bethe,[25] Szasz,[26] Sinanoglu[27] and Nesbet.[28] Of these the most promising at the present time appear to be the multi-configuration self-consistent field method and the pair theories put forth in a configuration interaction form by Nesbet and Sinanoglu. Whereas the multi-configuration self-consistent field method seems best suited for alleviating orbital restrictions encountered in the Hartree-Fock method (see Proposition I), the electron pair theories seem amenable to the entire problem. Thus, using the pair method, pair correlation energies could be calculated for both the ground and excited states and the importance of changes in any portion of the correlation energy obtained directly.

As stated above, we are concerned with the application of the excitation operator method to the problem of the electronic excited states of molecules. In particular, calculations are presented on a number of valence excited states of ethylene as well as one $(\pi\pi^*)$ Rydberg state. It is impossible to over-emphasize the importance of understanding the ethylene molecule quantum mechanically. It is the simplest π-electron system and a prototype for larger conjugated molecules, an understanding of which is vital not only in organic chemistry but also in such fields as electronic spectroscopy and molecular biology.

The excitation operator method was chosen because it allows us to concentrate only on energy differences and because it takes into account the effects of electron correlation on the excitation process. Further, while the excitation operator method has found widespread application in the fields of nuclear[29] and solid state[30] physics, its use in atomic and molecular systems has been minimal.[31] It was also our intent to investigate the approximations employed in the excitation operator method as they pertain to molecules and, thus, to assess the general utility of the excitation operator approach in molecular quantum mechanics.

2. THE EXCITATION OPERATOR METHOD

This section begins with a brief review of the formalism of second quantization. The excitation operator "equations of motion" are then derived and the approximations to the excitation operator discussed. Next, the operator formalism is used to derive expressions for the changes in the expectation values of one-electron operators. Finally, the equivalence of some of the approximations for the excitation operator and the more familiar methods used in molecular quantum mechanics is established.

2.1. A brief review of second quantization[32]

As we shall see in the developments in the section which follows, the approximations to the excitation operator are best formulated in the language of second quantization. Use of this particular formalism not only provides insight into certain physical aspects of the problem, but it also provides a straightforward means of correcting the equations when the approximations which have been employed break down. In addition, it allows one to make certain approximations more easily than in the coordinate representation. Assuming that a brief review of second quantization is in order, this section discusses the transformation from the (usual) coordinate representation to the occupation number representation. We shall only deal with fermion systems.

Let us assume that we have a complete set of one-electron functions, $\{\phi_i\}$ (which can be the eigenfunctions of the Hartree-Fock

Hamiltonian or any other convenient set) and that they are ordered according to some convention. A wavefunction for an N-electron system in the coordinate representation constructed from this set might be

$$\Psi_{\text{coord}} = A\,[\,\phi_1(1)\phi_2(2)\ldots\phi_N(N)]$$

where A is the anti-symmetrizer. In terms of occupation numbers we could say that in this wavefunction, orbital levels 1,2,...N have an occupation number of one. Thus, we see that, given a complete set of one-electron functions, any single configuration wavefunction such as the above can be completely specified just by listing the occupation numbers of the various orbitals, e.g.,

$$|\Psi\rangle = |1_1 1_2 \ldots 1_N 0_{N+1} \ldots\rangle \tag{1}$$

To operate on this function in occupation number space, we shall define the annihilation operator for orbital ϕ_i by

$$a_i|1_1 \ldots 1_i \ldots\rangle = (-1)^{\theta}|1_1 \ldots 0_i \ldots\rangle \tag{2}$$

Here θ is an integer which accounts for phase changes between the N and N-1 electron wavefunctions as will become clear later. Thus, the annihilation operator a_i de-populates orbital level i. Because of the orthogonality of the orbitals, the only non-zero matrix elements of a_i are

$$\langle 1_1 \ldots 0_i \ldots|a_i|1_1 \ldots 1_i \ldots\rangle = (-1)^{\theta} \tag{3}$$

The Hermitian conjugate of Eq.(3) defines the Hermitian conjugate of the annihilation operator, the creation operator (denoted by a dagger)

$$\langle 1_1 \ldots 1_i \ldots | a_i^\dagger | 1_1 \ldots 0_i \ldots \rangle = (-1)^\theta \tag{4}$$

so that

$$a_i^\dagger | 1_1 \ldots 0_i \ldots \rangle = (-1)^\theta | 1_1 \ldots 1_i \ldots \rangle \tag{5}$$

Thus, the creation operator $a_i^\dagger$ populates orbital level i. Using these operators we can define the number operator $\hat{n}_i = a_i^\dagger a_i$ with the property

$$\langle \hat{n}_i \rangle = \begin{array}{ll} 0 & \text{if the orbital is unoccupied} \\ 1 & \text{if the orbital is occupied} \end{array} \tag{6}$$

To discover the commutation relations for the creation and annihilation operators, first consider the effect of the product $a_k^\dagger a_i^\dagger$ on the wavefunction $|0_i 0_k\rangle$:

$$a_k^\dagger a_i^\dagger | 0_i 0_k \rangle = a_k^\dagger | 1_i 0_k \rangle = a_k^\dagger | 0_k 1_i \rangle = | 1_k 1_i \rangle \tag{7a}$$

Similarly,

$$a_i^\dagger a_k^\dagger | 0_k 0_i \rangle = | 1_i 1_k \rangle \tag{7b}$$

But, wavefunctions for fermions must be anti-symmetric with respect to interchange of electrons, so

$$| 1_i 1_k \rangle = - | 1_k 1_i \rangle \tag{7c}$$

The zero-electron wavefunction, $|0_i0_k\rangle$, as well as the one-electron wavefunctions, $|1_i0_k\rangle$ and $|1_k0_i\rangle$, are of course symmetric. Note that we have adopted the convention that an annihilation or creation operator always operates on the first position in the number vector. Hence, the orbital level being operated on must be moved to this position by a series of permutations; this is the origin of the phase factors in Eqs.(2), (3), (4) and (5). Combining Eq.(7a) and (7b) and using Eq.(7c), we find that

$$a_k^\dagger a_i^\dagger + a_i^\dagger a_k^\dagger = 0 \tag{8a}$$

Thus, because of the anti-symmetry of fermion wavefunctions, the fermion number operators anti-commute. To distinguish this from the usual commutator notation, Eq.(8a) will be written

$$\{a_i^\dagger, a_k^\dagger\} = 0 \tag{8b}$$

Likewise, it is easily shown that

$$\{a_i, a_k\} = 0 \tag{9}$$

Now consider the product of creation and annihilation operators $a_k^\dagger a_i$ with $i \neq k$:

$$a_k^\dagger a_i|1_i0_k\rangle = |1_k0_i\rangle \tag{10a}$$

$$a_i a_k^\dagger|1_i0_k\rangle = -|1_k0_i\rangle \tag{10b}$$

Therefore, the annihilation and creation operators for different orbital levels also anti-commute:

$$\{a_k^\dagger, a_i\} = 0 \qquad i \neq k \tag{10c}$$

For the case that $i = k$

$$a_i^\dagger a_i |1_i\rangle = |1_i\rangle \tag{11a}$$

$$a_i a_i^\dagger |1_i\rangle = 0 \tag{11b}$$

so

$$\{a_i^\dagger, a_i\} = 1 \tag{11c}$$

The anti-commutation relations for the fermion number operators can be summarized as

$$\{a_i^\dagger, a_k^\dagger\} = \{a_i, a_k\} = 0 \tag{12a}$$

$$\{a_i^\dagger, a_k\} = \delta_{ik} \tag{12b}$$

We must now establish how the usual coordinate operators, such as the kinetic energy or electron repulsion operators, are expressed in terms of the creation and annihilation operators.[33] If $\hat{F}$ is an arbitrary one-electron operator symmetric in the electronic coordinates, i.e.,

$$\hat{F} = \sum_i \hat{f}_i \tag{13}$$

then in terms of the complete set of functions

$$\hat{F}\phi_i = \sum_k \langle \phi_k | \hat{f} | \phi_i \rangle \phi_k \tag{14}$$

But, simplistically,

$$\phi_k = a_k^\dagger a_i \, \phi_i \tag{15}$$

so that Eq.(14) can be written as

$$\hat{F} \, \phi_i = \sum_k \langle \phi_k | \hat{f} | \phi_i \rangle a_k^\dagger a_i \, \phi_i \tag{16}$$

In general then an arbitrary one-electron operator can be expressed as

$$\hat{F} = \sum_i \sum_k \langle \phi_k | \hat{f} | \phi_i \rangle a_k^\dagger a_i \tag{17}$$

In an analogous manner it can be shown that a general two-electron operator is represented by

$$\hat{G} = \sum_i \sum_j \sum_k \sum_\ell \langle \phi_i \phi_j | \hat{g} | \phi_k \phi_\ell \rangle a_j^\dagger a_i^\dagger a_k a_\ell \tag{18}$$

This is essentially all of the formalism of second quantization that we shall require. For a more complete treatment of the subject the reader is referred to Landau and Lifschitz.[32]

2.2. Derivation of the excitation operator "equations of motion"

The derivation of the excitation operator "equations of motion" will closely follow that presented in an earlier paper.[34] More elegant formulations of the equations are possible, however, and for this the reader is referred to the articles by Rowe.[20]

The problem of describing the excited states of a system can be reduced to one of finding a form for an operator $A^\dagger(E)$ such that it satisfies the following equation:

$$[\hat{H}, A^{\dagger}(E)]\,|0\rangle = \Delta E\, A^{\dagger}(E)|0\rangle \qquad (1)$$

where $\hat{H}$ is the complete electronic Hamiltonian for the molecule under consideration. The operator $A^{\dagger}(E)$ contains all the physical information that we need about the excited state. From Eq.(1) we see that the operator $A^{\dagger}(E)$ generates an excited state of the Hamiltonian $\hat{H}$, with excitation energy ΔE, when it operates on the ground state, i.e.,

$$A^{\dagger}(E)|0\rangle = |E\rangle \qquad (2)$$

Note that $A^{\dagger}(E)$ describes a vertical excitation. Taking the Hermitian conjugate of Eq.(1), we can derive a relationship connecting the exact ground state and the Hermitian conjugate of the excitation operator, namely,

$$A(E)|0\rangle = 0 \qquad (3)$$

In practice, the complexity of the molecular Hamiltonian prevents $A^{\dagger}(E)$ from being cast into any convenient form. However, by using chemical and physical intuition, it is possible that an approximation to the excitation operator, $S^{\dagger}(E)$, could be formulated which would reproduce the eigenvalue spectrum of the exact Hamiltonian over some limited range quite satisfactorily. In this case

$$[H, S^{\dagger}(E)] = \Delta E_{\text{approx}}\, S^{\dagger}(E) + R \qquad (4)$$

where R is hopefully small.

The electronic Hamiltonian for a molecular system is, in atomic units,

$$\hat{H} = \sum_i \left(-\tfrac{1}{2}\nabla_i^2 - \sum_\alpha Z_\alpha / r_{\alpha i}\right) + \tfrac{1}{2} \sum_i \sum_j 1/r_{ij} \tag{5a}$$

$$= \sum_i H_i + \tfrac{1}{2} \sum_i \sum_j v_{ij} \tag{5b}$$

In the Hartree-Fock approximation we replace the interaction of electron i with all other electrons, $\sum_j v_{ij}$, by an effective one-particle potential V(i). The lowest N eigenfunctions of the one-particle Hamiltonian[35]

$$(H + V) \left|i\right\rangle = \varepsilon_i \left|i\right\rangle \tag{6}$$

are then combined into a Slater determinant to form the Hartree-Fock wavefunction for the ground state, $\left|HF\right\rangle$. Combining Eqs. (6b) and (7) the total electronic Hamiltonian can be written as

$$\hat{H} = \sum_i (H + V) + \sum_i \left(\tfrac{1}{2} \sum_j v_{ij} - V\right) \tag{7}$$

In the notation of second quantization this becomes

$$\hat{H} = \sum_i \varepsilon_i a_i^\dagger a_i + \tfrac{1}{2} \sum_i \sum_j \sum_k \sum_\ell \underset{\sim}{V}_{ijk\ell}\, a_j^\dagger a_i^\dagger a_k a_\ell$$
$$- \sum_i \sum_k \sum_\beta \left(\underset{\sim}{V}_{\beta i \beta k} - \underset{\sim}{V}_{\beta i k \beta} \right) a_i^\dagger a_k \tag{8}$$

where we have introduced the explicit form of the Hartree-Fock one-particle potential[35]

$$V(i) = \sum_j \left[J_j(i) - K_j(i) \right] \tag{9a}$$

J_j and K_j being the usual coulomb and exchange operators. For the Hartree-Fock orbitals the first term is diagonal since

$$\langle i |\, H + V | j \rangle = \varepsilon_i \delta_{ij} \tag{9b}$$

The integrals $\underset{\sim}{V}_{ijk\ell}$ are defined by

$$\underset{\sim}{V}_{ijk\ell} = \int\int \phi_i^*(1)\phi_j^*(2)\, r_{12}^{-1}\, \phi_k(1)\phi_\ell(2) d\tau_1 d\tau_2 \;; \tag{10}$$

the ϕ's denote molecular spin orbitals. In the above equations and in the ones to follow, we denote by the subscripts

$\alpha, \beta, \gamma, \delta, \ldots$	single particle states occupied in the Hartree-Fock ground state (called hole states when unoccupied)
$m, n, p, q, \ldots$	single particle states not occupied in the Hartree-Fock ground state (called particle states when occupied)
$i, j, k, \ell, \ldots$	any state.

If we define the Fermi level, ε_F, as being the uppermost level occupied in the Hartree-Fock ground state, then for the ground state in the Hartree-Fock approximation the orbital occupation numbers are

$$\begin{array}{ll} n_i = 1 & \varepsilon_i \leq \varepsilon_F \\ n_i = 0 & \varepsilon_i > \varepsilon_F \end{array} \tag{11}$$

These are, of course, just the expectation values of the number operators $\hat{n}_i = a_i^\dagger a_i$ over the Hartree-Fock wavefunction. Let us now define a particle-hole pair creation operator

$$C^\dagger(m\alpha) = a_m^\dagger a_\alpha \qquad (12a)$$

and the corresponding pair annihilation operator

$$C(m\alpha) = a_\alpha^\dagger a_m \qquad (12b)$$

These operators will be the basic building blocks used to construct the approximations to the excitation operator considered here. Thus,

$$C^\dagger(m\alpha)|HF\rangle = |{}^m_\alpha\rangle \qquad (13)$$

is a Slater determinant derived from the Hartree-Fock ground state by destroying a particle in an orbital below the Fermi level (in ϕ_α) and creating a particle in an orbital above the Fermi level (in ϕ_m). Such transitions will be referred to as elementary transitions and are equivalent to the virtual orbital approximation discussed earlier. With the above definitions we find that the particle-hole pair creation and annihilation operators satisfy the following <u>commutation</u> relations

$$[\,C^\dagger(m\alpha),\, C^\dagger(n\beta)\,] = [\,C(m\alpha),\, C(n\beta)\,] = 0 \qquad (14a)$$

$$[\,C(m\alpha),\, C^\dagger(n\beta)\,] = \delta_{\alpha\beta}\delta_{mn} - \delta_{\alpha\beta}\, a_n^\dagger a_m - \delta_{mn}\, a_\alpha a_\beta^\dagger \qquad (14b)$$

The "equations of motion" obeyed by the excitation operator can be obtained by considering the following equation[31]

$$\langle E|\ (E - \hat{H})C^{\dagger}(m\alpha)\ |0\rangle \quad = \quad 0 \tag{15}$$

which after a little manipulation becomes

$$(E - E_0)\langle E|\ C^{\dagger}(m\alpha)|0\rangle \quad - \quad \langle E|\,[\,\hat{H},\ C^{\dagger}(m\alpha)\,]\ |0\rangle \quad = \quad 0 \tag{16}$$

Using the property of the excitation operator, Eq.(2), and its Hermitian conjugate, Eq.(3), the above can be rewritten as

$$\begin{aligned}(E - E_0)\langle 0|\,[\,A(E),\ C^{\dagger}(m\alpha)\,]\ |0\rangle \qquad\qquad\qquad\qquad \\ - \quad \langle 0|\,[\,A(E),\ [\,\hat{H},\ C^{\dagger}(m\alpha)\,]\,]\ |0\rangle \quad = \quad 0\end{aligned} \tag{17}$$

Up to this point the derivation has been completely rigorous, relying only on the definitions and properties of the exact excitation operator. Note that the excitation energy $(E - E_0)$ appears in an equation in which the elements are the ground state expectation values of double commutators, which as we shall later see are less sensitive to the detailed form of the ground state wavefunction.

From Eq.(17) we see that all subsequent derivations will have one thing in common -- the commutator $[\,\hat{H},\ C^{\dagger}(m\alpha)\,]$, which is independent of our approximation to $A^{\dagger}(E)$. Using the second quantized form of the Hamiltonian, Eq.(8), we find that

$$\begin{aligned}[\,\hat{H},\ C^{\dagger}(m\alpha)\,] \quad = \quad & (\varepsilon_m - \varepsilon_\alpha + \underset{\sim}{V}_{m\alpha\alpha m} - \underset{\sim}{V}_{m\alpha m\alpha})\ C^{\dagger}(m\alpha) \\ & + \sum_{(n\beta)}{}' \ (\underset{\sim}{V}_{\alpha n m\beta} - \underset{\sim}{V}_{\alpha n\beta m})\ C^{\dagger}(n\beta)\end{aligned}$$

$$+ \sum_{(n\beta)} (\underset{\sim}{V}_{\alpha\beta mn} - \underset{\sim}{V}_{\alpha\beta nm})\, C(n\beta)$$

$$+ \;\; Q \qquad (18)$$

where

$$\begin{aligned} Q \;=\; & \sum_{\nu}\sum_{\gamma} (\underset{\sim}{V}_{\alpha\nu m\gamma} - \underset{\sim}{V}_{\alpha\nu\gamma m}) a_\nu^\dagger a_\gamma \;+\; \sum_{p}\sum_{r} (\underset{\sim}{V}_{\alpha pmr} - \underset{\sim}{V}_{\alpha prm}) a_p^\dagger a_r \\ & - \tfrac{1}{2} \sum_{i}\sum_{j}\sum_{k} (\underset{\sim}{V}_{ijkm} - \underset{\sim}{V}_{ijmk})\, a_\alpha a_j^\dagger a_i^\dagger a_k \\ & + \tfrac{1}{2} \sum_{j}\sum_{k}\sum_{\ell} (\underset{\sim}{V}_{\alpha jk\ell} - \underset{\sim}{V}_{j\alpha k\ell})\, a_m^\dagger a_j^\dagger a_k a_\ell \qquad (19) \\ & - \sum_{\beta}\sum_{\gamma} (\underset{\sim}{V}_{\beta\gamma\beta m} - \underset{\sim}{V}_{\beta\gamma m\beta}) a_\gamma^\dagger a_\alpha \;-\; \sum_{\beta}\sum_{n} (\underset{\sim}{V}_{\beta n\beta m} - \underset{\sim}{V}_{\beta nm\beta}) a_n^\dagger a_\alpha \\ & + \sum_{\beta}\sum_{\gamma} (\underset{\sim}{V}_{\beta\alpha\beta\gamma} - \underset{\sim}{V}_{\beta\alpha\gamma\beta}) a_m^\dagger a_\gamma \;+\; \sum_{\beta}\sum (\underset{\sim}{V}_{\beta\alpha\beta n} - \underset{\sim}{V}_{\beta\alpha n\beta}) a_m^\dagger a_n \end{aligned}$$

This splits the commutator into two groups: the first group contains all of the single particle-hole terms while the second group, Q, contains no net single particle-hole terms but rather contains interactions which are described as hole-hole, $a_\nu^\dagger a_\gamma$, particle-particle, $a_p^\dagger a_r$, multiple particle-hole, etc. Although it appears that Q does contain single particle-hole terms, we say that the net amount of such terms is zero for if the commutators

$$[\, C^\dagger(n\beta),\, Q \,] \quad \text{and} \quad [\, C(n\beta),\, Q \,]$$

are evaluated over the Hartree-Fock ground state, these terms vanish.[36]

Since we shall confine ourselves to excitation operators which are linear combinations of pair creation and annihilation operators and to expectation values over the Hartree-Fock ground state, we will retain only single particle-hole interactions and "linearize" the commutator to

$$\begin{aligned} [\hat{H}, C^{\dagger}(m\alpha)] \approx\ & (\varepsilon_m - \varepsilon_\alpha + \underset{\sim}{V}_{m\alpha\alpha m} - \underset{\sim}{V}_{m\alpha m\alpha})\ C^{\dagger}(m\alpha) \\ & + \sum_{(n\beta)}{}' (\underset{\sim}{V}_{\alpha n m\beta} - \underset{\sim}{V}_{\alpha n\beta m})\ C^{\dagger}(n\beta) \qquad (20) \\ & + \sum_{(n\beta)} (\underset{\sim}{V}_{\alpha\beta mn} - \underset{\sim}{V}_{\alpha\beta nm})\ C(n\beta) \end{aligned}$$

Note that (1) the above derivation has ignored spin, the resulting equations can be specialized for singlets and triplets in a final step, and (2) the primes on the summations indicate exclusion of the term ($m\alpha$). Eqs. (17) and (20) form the working equations for the approximations to the excitation operator considered here.

In addition to the excitation energy, the transition moment between the ground and excited state

$$\vec{D} = -\langle E |\ \vec{r}\ | 0 \rangle \qquad (21)$$

is also of considerable interest for it relates to the intensity of the absorption.[37] Using Eqs. (2) and (3), Eq. (21) can be rewritten as

$$\vec{D} = -\langle 0 | [A(E), \vec{r}] | 0 \rangle \qquad (22)$$

In second quantization the dipole moment operator is

$$\vec{r} = \sum_{i,j} \vec{r}_{ij} a_i^\dagger a_j$$

[see Eq. (2.1-17)]. To be consistent with the approximations employed in the derivation of the eigenvalue equations, we neglect particle-particle and hole-hole terms and retain for the transition operator only

$$\vec{r} \simeq \sum_{(m\alpha)} \vec{r}_{m\alpha} \left[C^\dagger(m\alpha) + C(m\alpha) \right] \tag{23}$$

For comparison with experiment we also calculate the oscillator strength of a transition. The oscillator strength, f, is defined by[37]

$$f = \frac{2}{3} \Delta E \, |\vec{D}|^2 \tag{24}$$

where ΔE is the theoretically calculated excitation energy and ΔE and $\vec{D}$ are both in atomic units.

We shall now derive the eigenvalue equations for the approximations to the excitation operator.

2.2.1. The single transition approximation[8]

In the single transition approximation (STA), an approximation commonly used by chemists,[8,9,10] the excitation operator is represented by a single particle-hole creation operator, i.e.,

$$S_{STA}^\dagger(E) = C^\dagger(m\alpha) \tag{25}$$

requiring that Eq. (3) be satisfied, we see the corresponding ground state is just the Hartree-Fock ground state. Thus, we speak of $\pi\to\pi^*$, $n\to\pi^*$, etc. transitions. However, this method is much too rigid; not only does it constrain the orbitals to their ground state form, but also the virtual orbital is an eigenfunction of a Hamiltonian which contains interactions with all N electrons. Thus, we expect all the virtual orbitals to be quite diffuse and, in the absense of a stable negative ion of the ground state, to correspond to continuum states. It should be remembered, however, that the use of expansion techniques to solve the Hartree-Fock equations constrains the virtual orbitals to the space described by the chosen set of basis functions. The extreme nature of this approximation will be demonstrated in Section 4.

Using Eqs. (17) and (20) and the commutators for the pair creation and annihilation operators, Eq. (14), we find that the excitation energy is

$$E - E_0 = \varepsilon_m - \varepsilon_\alpha + \underset{\sim}{V}_{m\alpha\alpha m} - \underset{\sim}{V}_{m\alpha m\alpha} \tag{26}$$

making the excited state wavefunctions eigenfunctions of spin, we obtain for <u>singlets</u>

$$\begin{aligned} {}^1E - E_0 &= \varepsilon_m - \varepsilon_\alpha + 2V_{m\alpha\alpha m} - V_{m\alpha m\alpha} \\ &= \varepsilon_m - \varepsilon_\alpha + 2K_{m\alpha} - J_{m\alpha} \end{aligned} \tag{27a}$$

and for <u>triplets</u>

$$^{3}E - E_0 = \varepsilon_m - \varepsilon_\alpha - J_{m\alpha} \qquad (27b)$$

which are just the equations derived by Roothaan in 1951.[8] The $V_{ijk\ell}$ are defined in terms of spatial molecular orbitals; the spin has been integrated out.

Using Eqs. (22) and (23) the dipole transition moment is

$$^{1}\vec{D}_{m\alpha} = -\sqrt{2}\,\vec{r}_{m\alpha} \qquad (28a)$$

$$^{3}\vec{D}_{m\alpha} = \vec{0} \qquad (28b)$$

where the left superscript denotes the spin multiplicity.

In this derivation and the ones to follow, it is assumed that the molecular orbitals involved are non-degenerate. If this is not true, the appropriate modifications must be made.

2.2.2. The improved single transition approximation[4,5]

In the improved single transition approximation (ISTA), the excitation operator is written as a linear combination of pair creation operators with the sum restricted to those virtual orbitals accessible from a given ground state orbital, i.e.,

$$S^{\dagger}_{ISTA}(E) = \sum_m g(m\alpha;E)\, C^{\dagger}(m\alpha) \qquad (29)$$

By defining a new orbital

$$\phi_{\bar{m}} = \sum_{m} g(m\alpha;E)\phi_{m} \tag{30}$$

we see that the ISTA wavefunction

$$|E(\mathrm{ISTA})\rangle = \sum_{m} g(m\alpha;E)\, |{}^{m}_{\alpha}\rangle \tag{31}$$

can be written as a single configuration wavefunction. In Section 2.4.2. it is shown that this is equivalent to the frozen core approximation[4,5] and that it allows for the variational adjustment of the virtual orbital. The new orbital is called an improved virtual orbital.[5] Note that we still classify transitions as π→π*, n→π*, etc. with the exception now that the functional form of the orbital $\phi_{\bar{m}}$ (π* in the above) depends on the spin multiplicity of the state as well as the orbital (ϕ_α) that is replaced. This method should be considered the simplest useful approximation for the excited state.

Using Eqs. (17) and (20) and the commutator relations for the pair creation and annihilation operators, the equation for the particle-hole amplitudes, g(mα;E), is

$$[\,\varepsilon_m - \varepsilon_\alpha + \underset{\sim}{V}_{m\alpha\alpha m} - \underset{\sim}{V}_{m\alpha m\alpha} - (E-E_0)\,]\; g(m\alpha;E) + {\sum_{n}}' (\underset{\sim}{V}_{\alpha n m\alpha} - \underset{\sim}{V}_{\alpha n\alpha m})\; g(n\beta;E) = 0 \tag{32}$$

For convenience, hereafter the designation "E" in the particle-hole amplitudes will be dropped. Specializing the above to describe eigenfunctions of spin, we get for singlets

$$[\varepsilon_m - \varepsilon_\alpha + 2V_{m\alpha\alpha m} - V_{m\alpha m\alpha} - ({}^1E - E_0)]\, g(m\alpha) + \sum_n{}' (2V_{\alpha n m\alpha} - V_{\alpha n\alpha m}) g(n\beta) = 0 \tag{33a}$$

and for triplets

$$[\varepsilon_m - \varepsilon_\alpha - V_{m\alpha m\alpha} - ({}^3E - E_0)]\, g(m\alpha) - \sum_n{}' V_{\alpha n\alpha m}\, g(n\beta) = 0 \tag{33b}$$

The transition moment in the improved single transition approximation is

$$\vec{D}_{ISTA} = -\sqrt{2} \sum_m g(m\alpha)\, \vec{r}_{m\alpha} \tag{34}$$

2.2.3. The Tamm-Dancoff approximation[38]

In the Tamm-Dancoff approximation[38] (TDA) we assume that the excited state can be adequately represented by some linear combination of elementary transitions. The net effect of this is to allow, in some restricted way, for the rearrangement of charge density during the excitation by means of the residual electronic interaction. On the basis of chemical experience we would expect that the above linear combination would often have a major component which defines the essentials of the excitation. This allows us to retain in a limited sense the classification of transitions as $\pi \rightarrow \pi^*$, etc. The effect of the minor components on the excitation energy, transition moment and charge distribution of the excited state is a matter which can best be settled by numerical calculation, although it had previously been assumed small unless near degeneracies were involved.

The Tamm-Dancoff approximation to the excitation operator is

$$S^{\dagger}_{TDA}(E) = \sum_{(m\alpha)} g(m\alpha;E)\, C^{\dagger}(m\alpha) \tag{35}$$

requiring that Eq. (3) be satisfied, we see that the appropriate ground state is still just the Hartree-Fock ground state. Using Eqs. (17) and (20) and the commutators, Eqs. (14), the eigenvalue equations for the Tamm-Dancoff approximation to the excited states are

$$\begin{aligned}[] [\,\varepsilon_m - \varepsilon_\alpha + \underset{\sim}{V}_{m\alpha\alpha m} - \underset{\sim}{V}_{m\alpha m\alpha} - (E - E_0)\,]\, g(m\alpha) & \\ + \sum_{(n\beta)}{}' (\underset{\sim}{V}_{\alpha n m\beta} - \underset{\sim}{V}_{\alpha n\beta m})\, g(n\beta) &= 0 \end{aligned} \tag{36}$$

and specializing for spin states, we obtain for <u>singlets</u>

$$\begin{aligned}[] [\,\varepsilon_m - \varepsilon_\alpha + 2V_{m\alpha\alpha m} - V_{m\alpha m\alpha} - ({}^1E - E_0)\,]\, g(m\alpha) & \\ + \sum_{(n\beta)}{}' (2V_{\alpha n m\beta} - V_{\alpha n\beta m}) g(n\beta) &= 0 \end{aligned} \tag{37a}$$

and for <u>triplets</u>

$$[\,\varepsilon_m - \varepsilon_\alpha - V_{m\alpha m\alpha} - ({}^3E - E_0)\,]\, g(m\alpha) - \sum_{(n\beta)}{}' V_{\alpha n\beta m}\, g(n\beta) = 0$$

These are the equations used by Herzenberg, Sherrington and Süveges[39] in their semi-empirical treatment of ethylene. The transition moment in the Tamm-Dancoff approximation is

$$^{1}\vec{D}_{TDA} = -\sqrt{2} \sum_{(m\alpha)} g(m\alpha)\, \vec{r}_{m\alpha} \tag{38}$$

As shown in Section 2.3.2. these equations could also have been obtained by a configuration interaction approach. If we represent the excited state by

$$|E\rangle = \sum_{(m\alpha)} g(m\alpha) \left|{}^{m}_{\alpha}\right\rangle \tag{39}$$

and apply the variational principle to determine the coefficients in the configuration interaction expansion, g(mα), Eqs. (37) would result.

2.2.4. The Random-Phase approximation[18,19,20]

In the language of configuration interaction the ground state wavefunction is better represented by the expansion

$$|0\rangle = C_0 |HF\rangle + \sum_{(m\alpha)} \sum_{(n\beta)} C^{mn}_{\alpha\beta} \left|{}^{mn}_{\alpha\beta}\right\rangle \tag{40}$$

where

$$\left|{}^{mn}_{\alpha\beta}\right\rangle = C^{\dagger}(m\alpha)\, C^{\dagger}(n\beta)\, |HF\rangle$$

is a double excitation from the orbitals occupied in the ground state

$(\phi'_\alpha,\phi'_\beta)$ to the virtual orbitals (ϕ_m,ϕ_n). In fact, such configurations are expected to account for most of the correlation in the ground state.[27] If we were still to represent the excited state as a linear combination of elementary transitions, we see that we could obtain such a transition in two ways: (1) by exciting from the Hartree-Fock ground state

$$\left|{}^{m}_{\alpha}\right\rangle = C^{\dagger}(m\alpha)\ \left|HF\right\rangle$$

or (2) by de-exciting one of the doubly excited components of the true ground state

$$\left|{}^{m}_{\alpha}\right\rangle = C(n\beta)\ \left|{}^{mn}_{\alpha\beta}\right\rangle$$

In view of this we would expect a better approximation to the excitation operator to be

$$S^{\dagger}_{RPA}(E) = \sum_{(m\alpha)} [\ g(m\alpha;E)\ C^{\dagger}(m\alpha) - h(m\alpha;E)C(m\alpha)\ ] \tag{41}$$

where the minus sign has been chosen for convenience. This is the excitation operator for the Random-phase approximation (RPA) to the excited state. Operating on the ground state wavefunction, Eq.(40), with the RPA excitation operator we see that the excited state wavefunction contains, for example,

$$|E\rangle = \sum_{(m\alpha)} [\; g(m\alpha) - \sum_{(n\beta)} h(n\beta)\; C^{mn}_{\alpha\beta} \;]\; |^{m}_{\alpha}\rangle + \sum_{(m\alpha)}\sum_{(n\beta)}\sum_{(p\gamma)} g(m\alpha)\; C^{np}_{\beta\gamma}\; |^{mnp}_{\alpha\beta\gamma}\rangle \qquad (42)$$

In general, the true ground state, $|0\rangle$, could contain all evenly excited configurations and Eq.(3) could still be satisfied. Then, the excited state wavefunction would contain all oddly excited configurations. In fact, it should be noted that the condition

$$A(E)|0\rangle = 0$$

cannot be satisfied exactly unless all such evenly excited configurations are included in the ground state, although the error becomes negligibly small as more and more terms are included (it is of the order of the neglected coefficients).

Using Eqs.(17) and (20) and the analogous equations involving $C(m\alpha)$ with the commutator rules for the pair operators, we obtain the set of coupled equations which describe the random-phase approximation to the excited state:

$$[\; \varepsilon_m - \varepsilon_\alpha + \underset{\sim}{V}_{m\alpha\alpha m} - \underset{\sim}{V}_{m\alpha m\alpha} - (E-E_0) \;]\; g(m\alpha) + \sum_{(n\beta)} (\underset{\sim}{V}_{\alpha n m\beta} - \underset{\sim}{V}_{\alpha n\beta m}) g(n\beta) + \sum_{(n\beta)} (\underset{\sim}{V}_{\alpha\beta mn} - \underset{\sim}{V}_{\alpha\beta nm}) h(n\beta) = 0 \qquad (43a)$$

and

$$\begin{aligned}&[\,\varepsilon_m - \varepsilon_\alpha + \underset{\sim}{V}_{m\alpha\alpha m} - \underset{\sim}{V}_{m\alpha m\alpha} + (E-E_0)\,]\; h(m\alpha)\\ &+ \sideset{}{'}\sum_{(n\beta)} (\underset{\sim}{V}_{\alpha nm\beta} - \underset{\sim}{V}_{\alpha n\beta m})h(n\beta) + \sum_{(n\beta)} (\underset{\sim}{V}_{\alpha\beta mn} - \underset{\sim}{V}_{\alpha\beta nm})g(n\beta) = 0\end{aligned} \tag{43b}$$

Specializing these equations for singlet and triplets in the usual way leads to the following equations for <u>singlets</u>

$$\begin{aligned}&[\,\varepsilon_m - \varepsilon_\alpha + 2V_{m\alpha\alpha m} - V_{m\alpha m\alpha} - ({}^1E-E_0)\,]\; g(m\alpha)\\ &+ \sideset{}{'}\sum_{(n\beta)} (2V_{\alpha nm\beta} - V_{\alpha n\beta m})g(n\beta) + \sum_{(n\beta)} (2V_{\alpha\beta mn} - V_{\alpha\beta nm})h(n\ ) = 0\end{aligned} \tag{44a}$$

and

$$\begin{aligned}&[\,\varepsilon_m - \varepsilon_\alpha + 2V_{m\alpha\alpha m} - V_{m\alpha m\alpha} + ({}^1E-E_0)\,]\; h(m\alpha)\\ &+ \sideset{}{'}\sum_{(n\beta)} (2V_{\alpha nm\beta} - V_{\alpha n\beta m})h(n\beta) + \sum_{(n\beta)} (2V_{\alpha\beta mn} - V_{\alpha\beta nm})g(n\beta) = 0\end{aligned} \tag{44b}$$

and for <u>triplets</u>

$$\begin{aligned}&[\,\varepsilon_m - \varepsilon_\alpha - V_{m\alpha m\alpha} - ({}^3E-E_0)\,]\; g(m\alpha)\\ &\qquad - \sideset{}{'}\sum_{(n\beta)} V_{\alpha n\beta m}\, g(n\beta) - \sum_{(n\beta)} V_{\alpha\beta nm}\, h(n\beta) = 0\end{aligned} \tag{45a}$$

and

$$\begin{aligned}&[\,\varepsilon_m - \varepsilon_\alpha - V_{m\alpha m\alpha} + ({}^3E-E_0)\,]\; h(m\alpha)\\ &\quad - \sideset{}{'}\sum_{(n\beta)} V_{\alpha n\beta m} h(n\beta) - \sum_{(n\beta)} V_{\alpha\beta mn}\, g(n\beta) = 0\end{aligned} \tag{45b}$$

These equations can be written in matrix notation as

$$\begin{pmatrix} \underset{\sim}{A} & \underset{\sim}{B} \\ -\underset{\sim}{B} & -\underset{\sim}{A} \end{pmatrix} \begin{pmatrix} \vec{G} \\ \vec{H} \end{pmatrix} = \Delta E \begin{pmatrix} \vec{G} \\ \vec{H} \end{pmatrix} \tag{46}$$

where, for example, for the singlet state

$$\begin{aligned} \underset{\sim}{A}(m\alpha,m\alpha) &= \varepsilon_m - \varepsilon_\alpha + 2V_{m\alpha\alpha m} - V_{m\alpha m\alpha} \\ \underset{\sim}{A}(m\alpha,n\beta) &= 2V_{\alpha n m\beta} - V_{\alpha n\beta m} \\ \underset{\sim}{B}(m\alpha,n\beta) &= 2V_{\alpha\beta mn} - V_{\alpha\beta nm} \end{aligned} \tag{47}$$

In the random-phase approximation the transition moment to the excited state is

$$^1\vec{D}_{RPA} = -\sqrt{2} \sum_{(m\alpha)} [\, g(m\alpha) + h(m\alpha)]\, \vec{r}_{m\alpha} \tag{48}$$

Comparing the above equations to those derived in the previous sections, we note that the TDA involves only the $\underset{\sim}{A}$ matrix, the ISTA a sub-block of $\underset{\sim}{A}$ and the STA only the diagonal elements of $\underset{\sim}{A}$. It is the $\underset{\sim}{B}$ matrix which allows for the effect of the doubly excited components of the true ground state on the excited state.

From Eq.(46) we see that the RPA excitation energies are the eigenvalues of a non-Hermitian matrix. Because of this the eigenvalues and eigenvectors have some peculiar properties which we will now discuss.[19] The matrix form of the RPA equations indicates that negative eigenvalues will occur with the same magnitude as the positive eigenvalues. To see this, let

$$\vec{G} = \vec{H}' \quad \text{and} \quad \vec{H} = \vec{G}'$$

to obtain

$$\begin{pmatrix} \underset{\sim}{A} & \underset{\sim}{B} \\ -\underset{\sim}{B} & -\underset{\sim}{A} \end{pmatrix} \begin{pmatrix} \vec{H}' \\ \vec{G}' \end{pmatrix} = \Delta E \begin{pmatrix} \vec{H}' \\ \vec{G}' \end{pmatrix}$$

or

$$\begin{pmatrix} \underset{\sim}{A} & \underset{\sim}{B} \\ -\underset{\sim}{B} & -\underset{\sim}{A} \end{pmatrix} \begin{pmatrix} \vec{G}' \\ \vec{H}' \end{pmatrix} = -\Delta E \begin{pmatrix} \vec{G}' \\ \vec{H}' \end{pmatrix} \tag{49}$$

Therefore, $(\vec{G}',\vec{H}') = (\vec{H},\vec{G})$ are solutions of the RPA equations with energy $-\Delta E$, so that the eigenvectors of the negative eigenvalues are identical to those for the positive eigenvalues with the roles of $\vec{G}$ and $\vec{H}$ interchanged. The requirement that the states be orthonormal

$$\langle E|E'\rangle = \delta_{EE'} \tag{50a}$$

leads to

$$\langle 0|\,[\,A(E),\, A^{\dagger}(E)\,]\,|0\rangle = \delta_{EE'} \tag{50b}$$

or in the random-phase approximation

$$\sum_{(m\alpha)} [\, g(m\alpha;E)g(m\alpha;E') - h(m\alpha;E)h(m\alpha;E')\,] = \delta_{EE'} \tag{50c}$$

The particle-hole amplitudes are said to be normalized to an indefinite metric. Last, we note that the excitation energies could be complex in which case the RPA equations are said to be "unstable." However, because of the physical interpretation of these eigenvalues, we are only concerned with those which have $\mathrm{Im}(\Delta E) = 0$.

The above is the random-phase approximation in the form that it is usually presented in the literature.[19,31] We should now pause and elaborate on the derivation of the RPA equations. In this way the origin of the non-Hermiticity of the matrix will become apparent. In deriving the RPA equations the excitation operator was formulated for a ground state such as

$$|0\rangle = C_0|HF\rangle + \sum_{(m\alpha)(n\beta)} \sum C^{mn}_{\alpha\beta} |^{mn}_{\alpha\beta}\rangle$$

However, in evaluating the commutators which occur in Eqs.(17) and (20), and (50) we have assumed that

$$C_o \approx 1 \qquad C^{mn}_{\alpha\beta} << C_0 \tag{51}$$

and thereby used only the Hartree-Fock component. This is the justification of our neglect of Q in the commutator in Eq.(19). This approximation is sometimes called the ground state approximation[31] while other authors refer to it as the quasi-boson approximation.[40] The term quasi-boson approximation arises from the fact that using the true ground state and Eq.(17) the RPA equations can be derived by assuming that

$$[\, C(m\alpha),\ C^{\dagger}(n\beta)\,] \;=\; \delta_{mn}\delta_{\alpha\beta} \tag{52}$$

Thus, the pair creation and annihilation operators commute just as do the boson creation and annihilation operators and, thus, the particle-hole pairs could be termed quasi-bosons. This approximation is directly related to the ground state approximation in that

$$\begin{aligned} \langle 0|\ [\, C(m\alpha),\ C^{\dagger}(n\beta)\,]\ |0\rangle &\simeq \langle HF|\,[\, C(m\alpha),\ C^{\dagger}(n\beta)\,]\ HF\rangle \\ &\simeq \langle HF|\,\delta_{mn}\delta_{\alpha\beta}-a^{\dagger}_{m}a_{n}\delta_{\alpha\beta}-a_{\alpha}a^{\dagger}_{\beta}\delta_{mn}\,|HF\rangle \\ &\simeq \delta_{\alpha\beta}\delta_{mn} \end{aligned} \tag{53}$$

The important point to be noted here is that either of these approximations eliminates any need for the ground state correlation coefficients, $C^{mn}_{\alpha\beta}$, the calculation of which would be quite time consuming. The price that must be paid is that a non-Hermitian matrix whose order is twice that encountered in the TDA must be dealt with. In addition, only if the Hartree-Fock ground state is a good approximation to the true ground state can we expect the RPA results to be valid. The correction of this defect is, of course, quite straightforward: one need only evaluate the commutators using the ground state wavefunction given in Eq.(40) and retain the appropriate terms in Q, i.e., those for which

$$\langle 0|\,[\, A(E),Q\,]\,|0\rangle \;\neq\; 0$$

This approach will be discussed in more detail in Section 3.3.

Although it appears from Eq.(46) that one must diagonalize an unsymmetric matrix in the RPA, this in fact is not the case. If we multiply Eq.(46) by

$$\begin{pmatrix} \underset{\sim}{A} & \underset{\sim}{B} \\ -\underset{\sim}{B} & -\underset{\sim}{A} \end{pmatrix}$$

we obtain

$$\begin{aligned} \begin{pmatrix} \underset{\sim}{A} & \underset{\sim}{B} \\ -\underset{\sim}{B} & -\underset{\sim}{A} \end{pmatrix} \begin{pmatrix} \underset{\sim}{A} & \underset{\sim}{B} \\ -\underset{\sim}{B} & -\underset{\sim}{A} \end{pmatrix} \begin{pmatrix} \vec{G} \\ \vec{H} \end{pmatrix} &= \Delta E \begin{pmatrix} \underset{\sim}{A} & \underset{\sim}{B} \\ -\underset{\sim}{B} & -\underset{\sim}{A} \end{pmatrix} \begin{pmatrix} \vec{G} \\ \vec{H} \end{pmatrix} \\ &= \Delta E^2 \begin{pmatrix} \vec{G} \\ \vec{H} \end{pmatrix} \end{aligned} \tag{54}$$

But

$$\begin{pmatrix} \underset{\sim}{A} & \underset{\sim}{B} \\ -\underset{\sim}{B} & -\underset{\sim}{A} \end{pmatrix}^2 = \begin{pmatrix} \underset{\sim}{A}^2-\underset{\sim}{B}^2 & \underset{\sim}{A}\underset{\sim}{B}-\underset{\sim}{B}\underset{\sim}{A} \\ -\underset{\sim}{B}\underset{\sim}{A}+\underset{\sim}{A}\underset{\sim}{B} & -\underset{\sim}{B}^2+\underset{\sim}{A}^2 \end{pmatrix} \tag{55}$$

is a symmetric matrix of the same order as the original matrix with the same eigenvectors as the RPA matrix but with eigenvalues which are the squares of the RPA eigenvalues. Note that because of Eq.(49) the eigenvalues of the new matrix will be doubly degenerate. Thus, any complex eigenvalues which occur in the solution of the RPA equations must be pure imaginary and the eigenvectors real. So now, we only need solve

$$\begin{pmatrix} \underset{\sim}{A}^2 - \underset{\sim}{B}^2 & \underset{\sim}{A}\underset{\sim}{B} - \underset{\sim}{B}\underset{\sim}{A} \\ \underset{\sim}{A}\underset{\sim}{B} - \underset{\sim}{B}\underset{\sim}{A} & \underset{\sim}{A}^2 - \underset{\sim}{B}^2 \end{pmatrix} \begin{pmatrix} \vec{G} \\ \vec{H} \end{pmatrix} = \Delta E^2 \begin{pmatrix} \vec{G} \\ \vec{H} \end{pmatrix} \tag{56}$$

However, the problem can be simplified even further than this. Writing out the above equations as

$$(\underset{\sim}{A}^2 - \underset{\sim}{B}^2)\vec{G} + (\underset{\sim}{A}\underset{\sim}{B} - \underset{\sim}{B}\underset{\sim}{A})\vec{H} = \Delta E^2 \vec{G}$$

$$(\underset{\sim}{A}\underset{\sim}{B} - \underset{\sim}{B}\underset{\sim}{A})\vec{G} + (\underset{\sim}{A}^2 - \underset{\sim}{B}^2)\vec{H} = \Delta E^2 \vec{H}$$

we see that addition of the two equations leads to

$$(\underset{\sim}{A} - \underset{\sim}{B})(\underset{\sim}{A} + \underset{\sim}{B})(\vec{G} + \vec{H}) = \Delta E^2(\vec{G} + \vec{H}) \tag{57a}$$

while subtraction leads to

$$(\underset{\sim}{A} + \underset{\sim}{B})(\underset{\sim}{A} - \underset{\sim}{B})(\vec{G} - \vec{H}) = \Delta E^2(\vec{G} - \vec{H}) \tag{57b}$$

Note, however that neither $(\underset{\sim}{A} - \underset{\sim}{B})(\underset{\sim}{A} + \underset{\sim}{B})$ nor $(\underset{\sim}{A} + \underset{\sim}{B})(\underset{\sim}{A} - \underset{\sim}{B})$ is symmetric, although their eigenvalues and eigenvectors are insured to be real. Thus, by exploiting the symmetry of the RPA equations we have reduced the problem from one of diagonalizing an un-symmetric matrix of order N to one of diagonalizing a symmetric matrix of the same order <u>or</u> two un-symmetric matrices of order N/2.

It is instructive to note that the RPA equations cannot be derived directly from Eq.(16) if the ground state approximation is employed. To see this note that

$$S_{RPA}(E)\,[H,\ C\,(m\alpha)\,] = \sum A_{n\beta,p\gamma}\, g(p\gamma)C(p\gamma)C^{\dagger}(n\beta)$$

$$+ \sum B_{n\beta,p\gamma}\, h(p\gamma)C^{\dagger}(p\gamma)C(n\beta)$$

(we need not consider the terms involving two creation or annihilation operators) and

$$\langle HF|\ C(p\gamma)C^{\dagger}(n\beta)\ |HF\rangle = \delta_{pn}\delta_{\beta\gamma}$$

as required, but

$$\langle HF|\ C^{\dagger}(p\gamma)C(n\beta)\ |HF\rangle = 0$$

since neither orbitals ϕ_n or ϕ_p are occupied in $|HF\rangle$. Thus, only the TDA is obtained, i.e., the $\underset{\sim}{B}$ matrix and the $\vec{H}$ vector can never contribute. Using Eq.(17) which involves the expectation values of double commutators, however, we find that these terms do contribute even if the ground state approximation is used. This is one illustration of the fact that commutators of operators require less information content than do products.[20]

Before closing this section we should point out that the RPA equations can also be derived via time-dependent Hartree-Fock theory.[41] However, the interpretation of the resulting wavefunctions from that viewpoint is not at all clear.[42] Also, the remedy of the breakdown in the theory, corresponding to the instability discussed here, cannot be implemented as easily as in the present approach.

2.3. The calculation of one-electron properties

Now that we have derived the eigenvalue equations for the approximations to the excitation operator to be considered here, we shall turn to the problem of calculating the changes in the expectation values of one-electron operators, such as dipole moment, forces, etc.

The expectation value of a one-electron operator

$$\hat{F} = \sum_i \sum_j f_{ij} \, a_i^\dagger a_j \tag{1}$$

over an excited state wavefunction can be written as

$$\langle E|F|E\rangle = \langle 0|A(E)FA^\dagger(E)|0\rangle \tag{2}$$

using Eq.(2.2-2). Now,

$$\hat{F}A^\dagger(E) = [\hat{F},A^\dagger(E)] + A^\dagger(E)\hat{F} \tag{3}$$

substituting Eq.(3) into (2) yields

$$\langle E|\hat{F}|E\rangle = \langle 0|A(E)[\hat{F},A^\dagger(E)]|0\rangle + \langle 0|\hat{F}|0\rangle \tag{4}$$

where we have used the relation

$$A(E)A^\dagger(E)|0\rangle = |0\rangle \tag{5}$$

Using Eq.(2.2-3) the above expression can be cast into the convenient form

$$\langle E|\hat{F}|E\rangle - \langle 0|\hat{F}|0\rangle = \langle 0|[A(E),[\hat{F},A^\dagger(E)]]|0\rangle \tag{6}$$

This equation enables one to easily compute the changes in the expectation values of a one-electron operator. Again, the equation has been cast into the convenient form of expectation values of double commutators (see the discussion at the end of Section 2.2.4).

Before evaluating the right hand side of Eq.(6) for the various approximations to the excitation operator, we note that $\hat{F}$ can be decomposed into

$$\hat{F} = \sum_{(m\alpha)} f_{m\alpha} [C^{\dagger}(m\alpha) + C(m\alpha)] + \sum_{(pq)} f_{pq} a_p^{\dagger} a_q + \sum_{(\gamma\nu)} f_{\gamma\nu} a_{\gamma}^{\dagger} a\nu$$

To evaluate the transition moment between the ground and excited state we retained only the particle-hole terms

$$\sum_{(m\alpha)} f_{m\alpha} [C^{\dagger}(m\alpha) + C(m\alpha)]$$

in $\hat{F}$. However, for the types of wavefunctions considered here such terms will make no contribution to the expectation value. Thus, we need only consider the reduced operator

$$\hat{F}^R = \sum_{pq} f_{pq} a_p^{\dagger} a_q + \sum_{\gamma\nu} f_{\gamma\nu} a_{\gamma}^{\dagger} a_{\nu} \tag{7}$$

We shall begin by deriving the equation for the most general operator which we have considered: the RPA excitation operator. The formulas for the remaining operators can then be obtained just by dropping the appropriate terms. The RPA excitation operator is, Eq.(2.2-41),

$$S^{\dagger}_{RPA}(E) = \sum_{(m\alpha)} [\, g(m\alpha)C^{\dagger}(m\alpha) - h(m\alpha)C(m\alpha)\,]$$

Using this and the anti-commutation relations for the annihilation and creation operators, Eqs.(2.1-12), we find that

$$[\, \hat{F}^{R}, S^{\dagger}_{RPA}\,] = \sum_{(m\alpha)} g(m\alpha) \Big\{ \sum_{p} f_{pm} C^{\dagger}(p\alpha) - \sum_{\gamma} f_{\alpha\gamma} C^{\dagger}(m\gamma) \Big\}$$
$$+ \sum_{(m\alpha)} h(m\alpha) \Big\{ \sum_{p} f_{mp} C(p\alpha) - \sum_{\gamma} f_{\gamma\alpha} C(m\gamma) \Big\} \qquad (8)$$

An important point to remember in deriving this expression is that the quasi-boson approximation cannot be used. As explained in the last section, this approximation is appropriate only in the context of an expectation value over the ground state wavefunction. Since we are not evaluating the above commutator over the ground state wavefunction, the quasi-boson approximation must not be used. Evaluating the complete double commutator in Eq.(6) we find that

$$\langle 0 |\, [\, S_{RPA}, [\, \hat{F}^{R}, S^{\dagger}_{RPA}\,]\,]\, | 0 \rangle$$
$$\simeq \sum_{\alpha} \sum_{mm'} [\, g(m\alpha)g(m'\alpha) - h(m\alpha)h(m'\alpha)\,]\, f_{mm'}$$
$$- \sum_{m} \sum_{\alpha\alpha'} [\, g(m\alpha)g(m\alpha') - h(m\alpha)h(m\alpha')\,]\, f_{\alpha\alpha'} \qquad (9)$$

In deriving the final expression we have made use of the ground state or quasi-boson approximation. Combining Eqs.(6) and (9), we find for the changes in a one-electron property on going from the ground to an excited state that in the *random-phase approximation*

$$\langle E|\,\hat{F}\,|E\rangle - \langle 0|\,\hat{F}\,|0\rangle$$

$$= \sum_{\alpha}\sum\sum_{mm'} [\,g(m\alpha)g(m'\alpha) - h(m\alpha)h(m'\alpha)\,]\,f_{mm'}$$

$$- \sum_{m}\sum\sum_{\alpha\alpha'} [\,g(m\alpha)g(m\alpha') - h(m\alpha)h(m\alpha')\,]\,f_{\alpha\alpha'} \qquad (10a)$$

in the *Tamm-Dancoff approximation*

$$\langle E|\,\hat{F}\,|E\rangle - \langle 0|\,\hat{F}\,|0\rangle = \sum_{\alpha}\sum\sum_{mm'} g(m\alpha)g(m'\alpha)\; f_{mm'}$$

$$- \sum_{m}\sum\sum_{\alpha\alpha'} g(m\alpha)g(m\alpha')\; f_{\alpha\alpha'} \qquad (10b)$$

in the *improved single transition approximation*

$$\langle E|\,\hat{F}\,|E\rangle - \langle 0|\,\hat{F}\,|0\rangle = \sum\sum_{mm'} g(m\alpha)g(m'\alpha)\; f_{mm'} - f_{\alpha\alpha'} \qquad (10c)$$

and, finally, in the *single transition approximation*

$$\langle E|\,\hat{F}\,|E\rangle - \langle 0|\,\hat{F}\,|0\rangle = f_{mm} - f_{\alpha\alpha} \qquad (10d)$$

Examining these formulae, we note that since

$$g_{RPA}(m\alpha) \simeq g_{TDA}(m\alpha)$$

and

$$h_{RPA}(m\alpha) \ll g_{RPA}(m\alpha)$$

the expectation values of a one-electron operator over the RPA wavefunction should be approximately equal to those for the TDA wavefunction. This is as it should be for, if the ground and excited states are of different symmetry, the two wavefunctions are completely independent. Since the RPA differs from the TDA primarily in considering a more general form for the ground state wavefunction, the two expectation values should be nearly equal. That any effect at all exists is probably due to the approximations used in the RPA which couple the ground and excited states together, although the presence of the triple excitations in the RPA excited state should be remembered. However, the triple excitations will make no first order contributions to a one-electron property.[43] In addition, we did assume that $C^{mn}_{\alpha\beta} << 1$.

2.4. Relationship of the excitation operator methods to more common approximations

2.4.1. Equivalence of the ISTA and TDA and single excitation configuration interaction

The ISTA and TDA wavefunctions for an excited state have the general form

$$|E\rangle = \sum_{(m\alpha)} g(m\alpha) \, |^{m}_{\alpha}\rangle \tag{1}$$

In this section we shall show that were the excited states represented by the above expansion, application of the variational principle leads to just the ISTA and TDA eigenvalue equations.

The energy of the above wavefunction is

$$E(\vec{G}) \quad = \quad \frac{\langle E\,|\hat{H}|\,E\rangle}{\langle E|E\rangle} \qquad (2)$$

where we have explicitly noted the fact that the energy is a function of the expansion coefficients in Eq.(1). Minimizing the energy with respect to variations in these coefficients leads to the configuration interaction equations[44]

$$(\langle {}^{m}_{\alpha}|\hat{H}|{}^{m}_{\alpha}\rangle - E)g(m\alpha) + \sum_{(n\beta)}{}^{'} \langle {}^{m}_{\alpha}|\hat{H}|{}^{n}_{\beta}\rangle g(n\beta) \quad = \quad 0 \qquad (3)$$

Evaluating the matrix elements of the total Hamiltonian, with the singlet state as an example, we find

$$\langle {}^{m}_{\alpha}|\hat{H}|{}^{m}_{\alpha}\rangle \quad = \quad E_0 + \varepsilon_m - \varepsilon_\alpha + 2V_{m\alpha\alpha m} - V_{m\alpha m\alpha} \qquad (4a)$$

$$\langle {}^{m}_{\alpha}|\hat{H}|{}^{n}_{\beta}\rangle \quad = \quad 2V_{n\alpha\beta m} - V_{n\alpha m\beta} \qquad (4b)$$

Combining these expressions with Eq.(3) we obtain

$$\begin{aligned}&[\,\varepsilon_m - \varepsilon_\alpha + 2V_{m\alpha\alpha m} - V_{m\alpha m\alpha} - ({}^{1}E - E_0)\,]\,g(m\alpha)\\ &\quad + \sum_{(n\beta)}{}^{'}\,(2V_{n\alpha\beta m} - V_{n\alpha m\beta})g(n\beta) \quad = \quad 0\end{aligned} \qquad (5)$$

which are just the equations satisfied by the expansion coefficients of the excitation operator in the ISTA and TDA, Eqs.(2.2-33a) and (2.2-37a). Thus, the ISTA and TDA are equivalent to a configuration interaction calculation which includes the appropriate singly excited configurations.

2.4.2. Equivalence of the improved single transition and frozen core approximations[16]

In the improved single transition approximation the excited state wavefunction is

$$|E(\mathrm{ISTA})\rangle = \sum_m g(m\alpha)\left|{}^{m}_{\alpha}\right\rangle \tag{6}$$

As shown in the last section, the coefficients g(mα) are obtained by diagonalizing the Hamiltonian in this representation, i.e., by requiring that

$$\langle E\,|\hat{H}|\,E'\rangle = E\delta_{EE'} \tag{7}$$

It is easily seen that the ISTA wavefunctions can be written as single configuration wavefunctions by defining a new orbital

$$\phi_{\bar{m}} = \sum_m g(m\alpha)\phi_m \tag{8}$$

The excited state then can be represented as

$$|E(\mathrm{ISTA})\rangle = \left|{}^{\bar{m}}_{\alpha}\right\rangle \tag{9}$$

Thus, the condition satisfied by the ISTA wavefunctions, Eq.(7), can be written

$$\left\langle {\bar{n} \atop \alpha} \right| \hat{H} \left| {\bar{m} \atop \alpha} \right\rangle = E\delta_{\bar{n}\bar{m}} \tag{10a}$$

or

$$E = \left\langle {\bar{m} \atop \alpha} \right| \hat{H} \left| {\bar{m} \atop \alpha} \right\rangle \tag{10b}$$

and

$$\left\langle {\bar{n} \atop \alpha} \right| \hat{H} \left| {\bar{m} \atop \alpha} \right\rangle = 0 \tag{10c}$$

Using the rules for evaluating the matrix elements between determinantal functions, Eq.(10c) becomes

$$\langle \phi_{\bar{n}} | h + 2J_c - K_c + J_\alpha \pm K_\alpha | \phi_{\bar{m}} \rangle = 0 \tag{11}$$

where J_c and K_c are the total Coulomb and exchange operators for the core, i.e.,

$$J_c = \sum_{\beta \neq \alpha} J_\beta \qquad K_c = \sum_{\beta \neq \alpha} K_\beta$$

and the plus (+) sign refers to the singlet wavefunction and the minus (-) sign to the triplet. Eq.(11) is satisfied only if

$$(h + 2J_c - K_c + J_\alpha \pm K_\alpha)\,\phi_{\bar{m}} = \varepsilon_{\bar{m}}\phi_{\bar{m}} + \sum_\beta \varepsilon_{\bar{m}\beta}\phi_\beta \tag{12}$$

But, Eq.(12) is just the SCF equation that would be obtained if $\phi_{\bar{m}}$

were functionally optimized for the excited state configuration while restricting the remaining orbitals to their ground state forms. Thus, the ISTA allows for changes in the virtual orbital due to the change in the molecular potential upon removing an electron below the Fermi level and placing it above with the correct spin coupling. As only SCF adjustment of the virtual orbital is permitted, this method is commonly called the frozen core approximation.[4] Since it is expected that the largest correction should be associated with the virtual orbital, it is possible that this method corrects for the major SCF changes in the excited state.

Note that the functional form of $\phi_{\bar{m}}$ depends on whether the excited state is a singlet or triplet as well as on which orbital was excited. This will lead to differences in the properties of the singlet and triplet states arising from a given configuration and may account for the major differences arising from a complete SCF treatment of the two multiplicities.

A more complete discussion of the frozen core approximation has been given by Hunt and Goddard.[5]

3. A CRITICAL EXAMINATION OF THE EXCITATION OPERATOR METHOD

3.1. Analysis of the RPA treatment of a simple two electron, two orbital problem

From the arguments given in Section 2. it is obvious that the conceptual basis for the excitation operator method is just configuration interaction. Thus, the ISTA, TDA and RPA should be considered as approximate methods of doing the corresponding configuration interaction calculations. In this regard the ISTA and TDA are quite straightforward, being just limited configuration interaction as shown in Section 2.4. The RPA, on the other hand, deviates from a pure CI treatment by invoking a number of reasonable approximations which, however, have never been tested in atomic and molecular systems. In this section we will analyze a simple two electron, two orbital problem in order to gain some insight into the RPA. As an example, we will consider the π-electron system of ethylene formed from a minimum basis set of Slater orbitals[45] (whether this provides an adequate representation of the states need not concern us here). The information needed for the calculations is given in Table I.

Let us begin by solving the problem exactly and then we shall solve the RPA equations. Only the singlet state will be considered. From the π and π^* orbitals two configurations of A_{1g} symmetry can be constructed. Diagonalizing the Hamiltonian matrix in this representation, we obtain for the ground state

$$|0\rangle = 0.9688\ |\pi\alpha\pi\beta\rangle - 0.2478|\pi^*\alpha\pi^*\beta\rangle$$
$$E_0 = -0.0405 \text{ a.u.} \tag{1}$$

where all energies are given relative to the Hartree-Fock energy of the ground state. Since there are only two orbitals, the exact excited singlet state is simply

$$|^1S\rangle = |\pi\alpha\pi^*\beta\rangle + |\pi^*\alpha\pi\beta\rangle$$
$$E_S = 0.4404 \text{ a.u.} \tag{2}$$

Thus, the excitation energy and transition moment for the excitation from the ground to the excited singlet state are, for the exact wavefunctions,

$$\begin{aligned} E_{\text{exact}} &= 0.4404 - (-0.0405) \\ &= 0.4809 \text{ a.u.} \end{aligned}$$

$$\begin{aligned} D^x_{\text{exact}} &= -\surd 2\ (0.9688 - 0.2478)\ x_{\pi\pi^*} \\ &= -\ 1.35 \text{ a.u.} \end{aligned}$$

Let us now turn to the excitation operator calculations. In the TDA, which in this special case is also the STA, the excitation energy and transition moment are measured with respect to the Hartree-Fock ground state, so we find that

$$\Delta E_{TDA} = 0.4404 \text{ a.u.}$$
$$D^{x}_{TDA} = -1.87 \text{ a.u.} \qquad (4)$$

Comparing the results with the exact results, Eq.(3), we see that the effect of the doubly excited configuration in the exact ground state is to <u>increase</u> the excitation energy and <u>decrease</u> the transition moment.

The RPA attempts to take into account the effect of the doubly excited configuration in the exact ground state. The RPA excitation operator is

$$S^{\dagger}_{RPA} = g(\pi^*\pi)C^{\dagger}(\pi^*\pi) - h(\pi^*\pi)C(\pi^*\pi) \qquad (5)$$

and the RPA "Hamiltonian" matrix for this particular problem has the form, see Eq.(2.2-46),

$$\begin{pmatrix} \Delta E_{TDA} - \Delta E_{RPA} & K_{\pi\pi^*} \\ -K_{\pi\pi^*} & -\Delta E_{TDA} - \Delta E_{RPA} \end{pmatrix} \begin{pmatrix} g \\ h \end{pmatrix} = 0 \qquad (6)$$

The solutions to this equation are

$$\Delta E = \pm 0.4109 \text{ a.u.} \qquad (7a)$$

and the coefficients for the positive energy solution are

$$g(\pi^*\pi) = 1.0178$$
$$h(\pi^*\pi) = -0.1894 \qquad (8)$$

Using Eq.(2.2-48) the transition moment is seen to be

$$D^{x}_{RPA} = -1.54 \text{ a.u.} \tag{7b}$$

Therefore, while the RPA has decreased the transition moment as it should, it has also decreased the excitation energy. In fact, the difference between the exact and RPA excitation energies is 1.90 ev. This is an indication that the decreases in the excitation energies upon going from the TDA to the RPA may be somewhat exaggerated because of the approximations made in deriving the RPA equations. In more general systems the presence of the triply excited components in the RPA excited state, see Eq.(2.2-42), should also lead to a decrease in the excitation energy. The decrease in the transition moment, on the other hand, is consistent with the exact calculations, although it is significantly less.

It should be noted that as the exchange integral $K_{\pi\pi^*}$ approaches zero, the true wavefunction also approaches the Hartree-Fock wavefunction since this integral is just the off-diagonal element in the CI matrix which mixes the two configurations. In the limit that the Hartree-Fock wavefunction closely approximates the exact wavefunction, we see from Eq.(6) that the RPA results approach those of the TDA as do the exact (but from opposite directions). It is the strong mixing of the $|\pi^*\alpha\pi^*\beta\rangle$ component into the ground state which is responsible for the unusually large deviation between the RPA and exact excitation energies. This cautions against too literal an interpretation of the results when applying the RPA to states in which one of the corresponding $C^{mn}_{\alpha\beta}$ is large in the ground state.

Note that the condition

$$S_{RPA} \left|0\right\rangle = 0 \tag{9}$$

provides a means of computing the correlation coefficient in the ground state (for a more general discussion see Section 3.3). This requirement leads to

$$-h(\pi^*\pi)\, C_{\pi\pi} + g(\pi^*\pi)\, C_{\pi^*\pi^*} = 0$$

or

$$\frac{C_{\pi^*\pi^*}}{C_{\pi\pi}} = \frac{h(\pi^*\pi)}{g(\pi^*\pi)} = -0.1861$$

Since the exact ratio of the two coefficients is -0.2558, the RPA consistency condition, Eq.(9), underestimates the amount of correlation in the ground state, although it does significantly better than first order perturbation theory which yields -0.1298.

If we apply the RPA to the triplet state we find that the excitation energy is imaginary and, thus, the RPA solution is unstable. Like the large deviation between the exact and RPA excitation energies for the singlet case, this behavior is a direct result of the large $C^{\pi^*\pi^*}_{\pi\pi}$ coefficient in the exact ground state. Methods of correcting the defects in the random-phase approximation while retaining its conceptual simplicity will be discussed in Section 3.3.

3.2. Correlation energy differences and the excitation operator method

For either the exact wavefunction to all orders in the energy or the first order wavefunction to second order in the energy, the total electronic energy of a closed shell atom or molecule can be written as[27]

$$E_0 = E_{HF} + \sum_{\alpha>\beta} e_{\alpha\beta} \qquad (1)$$

where the $e_{\alpha\beta}$ are pair correlation energies for electrons in orbitals ϕ_α and ϕ_β. The wavefunction for such states are well approximated by[27]

$$|0\rangle = A(123...N) \left[1 + \sum_{\alpha>\beta} \hat{u}_{\alpha\beta}/(\alpha\beta) \right] \qquad (2)$$

where A(123...N) represents a Slater determinant and $\hat{u}_{\alpha\beta}$ is the pair function describing the correlation of two electrons in the orbitals ϕ_α and ϕ_β. In open-shell states, however, correlation effects arise which do not occur if all the shells are completely filled. Sinanoglu and his co-workers[27] have identified these effects as (1) internal correlations which arise from a near degeneracy of zero-order configurations, (2) semi-internal correlations which arise when two electrons are excited, one going into an unoccupied orbital within the Hartree-Fock "sea," (3) orbital corrections which result from the non-symmetric (both spin and space) nature of the open-shell potential as well as (4) the all-external pair correlations which also occur in closed shell systems. If we limit ourselves to the excited singlet and triplet states of molecules which arise from transitions among non-degenerate orbitals, then internal and semi-internal correlations are completely absent. To the extent that many (≥ 3) body effects are negligible, the wavefunction of an excited state obtained by replacing orbital ϕ_α with orbital ϕ_m is then just[27]

$$\Psi_{ex} = A(12\ldots\alpha m)\left[1 + \sum_i \hat{f}_i^p/(i) + \sum_{i>j}\sum \hat{u}_{ij} \right] \tag{3}$$

where the f_i^p's incorporate the effect of symmetry and spin polarizations. If the Hartree-Fock wavefunction contains two or more components, as it does for the excited singlet states, then a term such as Eq.(3) is obtained for each component. Neglecting the cross terms between the $\hat{f}_i$ and $\hat{u}_{k\ell}$, the energy of the above wavefunction is

$$E_{ex} = E_{HF}^{ex} + \sum_i e_i^p + \sum_{\substack{\beta \\ \neq}}\sum_{\substack{\gamma \\ \alpha}} e_{\beta\gamma} + \sum_\beta (e_{\alpha\beta} + e_{m\beta}) + e_{\alpha m} \tag{4}$$

The effect of neglecting the troublesome cross terms has yet to be determined,[27] although it should be noted that to second order they do not contribute at all. The e_i^p correspond to one-electron energy increments resulting from symmetry and spin polarizations of orbital ϕ_i. If the frozen core approximation is used, the Hartree-Fock energy of the excited state becomes

$$E_{HF} = E_{FC} + \sum_i e_i^{SCF} \tag{5}$$

where the e_i^{SCF} refer to energy increments gained upon SCF relaxation of the orbitals. The corresponding $\hat{f}_i^{SCF}$ turns the frozen core orbital ϕ_i into the corresponding Hartree-Fock orbital.

Subtracting the ground state energy, Eq.(1), from the energy of the excited state, Eq.(4), we obtain for the excitation energy

$$\begin{aligned} \Delta E = \Delta E_{HF} &+ \sum_i e_i^{ex} + \sum_\beta \sum_\gamma (e_{\beta\gamma}^{ex} - e_{\beta\gamma}^{gd}) + \sum_\beta [(e_{\beta\alpha}^{ex} - e_{\beta\alpha}^{gd}) \\ &+ (e_{\beta m}^{ex} - e_{\beta\alpha}^{gd})] + e_{\alpha m}^{ex} - e_{\alpha\alpha}^{gd} \end{aligned} \tag{6}$$

In deriving this expression we have made use of the fact that the orbital ϕ_α is doubly occupied in the ground state. This expression isolates in a very effective manner the various components of the correlation energy difference between the ground and excited state.

For true valence excited states, we might expect that the orbitals change only slightly on going from the ground to the excited state (excluding, of course, the virtual orbital for which the frozen core approximation is assumed). Thus, for such states it is probable that

$$\Delta E_{HF} \simeq E_{fc}^{ex} - E_{HF}^{gd} \tag{7a}$$

and

$$e^{ex}_{\beta\gamma} \simeq e^{gd}_{\beta\gamma} \qquad e^{ex}_{\beta\alpha} \simeq e^{gd}_{\beta\alpha} \tag{7b}$$

The expression for the excitation energy then simply reduces to

$$\Delta E \simeq \Delta E_{HF} + \sum_{i} e^{ex}_{i} + \sum_{\beta} (e^{ex}_{\beta m} - e^{gd}_{\beta\alpha}) + e^{ex}_{\alpha m} - e^{gd}_{\alpha\alpha} \tag{8}$$

We also expect

$$|e^{gd}_{\alpha\alpha}| >> |e^{ex}_{\alpha m}| \tag{9a}$$

since $e^{gd}_{\alpha\alpha}$ represents the correlation of two electrons of opposite spin in the same spatial orbital. It is also reasonable that

$$|e^{ex}_{\beta m}| \lesssim |e^{gd}_{\beta\alpha}| \tag{9b}$$

The e_i's are, of course, always negative but in many cases they should be small, e.g., in the carbon atom, Nesbet[28] reports the sum of the e_i's to be -0.002 a.u. which is also approximately the energy difference between the unrestricted and restricted Hartree-Fock energies.[46] In molecules, the e_i's could be more important although in most cases we would not expect their sum to exceed -0.01 a.u. (-0.3 ev). Combining Eqs.(9) with Eq.(8) we predict that the Hartree-Fock excitation energy should always be <u>below</u> the exact excitation energy. As a guideline, then, any theory which attempts to include the effects of correlation upon the description of valence excited states should (1) allow for SCF adjustment of at least the virtual orbital, (2) compute the differences between the way in which orbital

ϕ_m in the excited state and orbital ϕ_α in the ground state correlate with the core and (3) compute the difference between the way in which orbital ϕ_m correlates with ϕ_α in the excited state and the way in which orbital ϕ_α (spin up) correlates with ϕ_α (spin down) in the ground state and (4) calculate the effects of spin and symmetry polarizations of the orbitals although as argued above this may be relatively unimportant.

Let us now see what correlation effects are contained in the TDA and RPA wavefunctions. Given any wavefunction, Sinanoglu[47] has presented a method of analyzing this wavefunction for the orbital corrections, $\hat{f}_i$, which turn the orbitals of a given reference configuration into the appropriate Hartree-Fock orbitals, the pair functions $\hat{u}_{ij}$ and so on. The procedure to be used has been discussed in more detail by Hudson and McKoy.[48] To begin, we first split the wavefunction into a reference configuration and a remainder

$$|E\rangle = |{}^m_\alpha\rangle + \sum_{(n\beta)} \bar{g}(n\beta)|{}^n_\beta\rangle \tag{10}$$

$$= |\Phi_0\rangle + |\chi\rangle$$

where we have chosen the normalization

$$\langle E|{}^m_\alpha\rangle = 1 \tag{11a}$$

and

$$\bar{g}(n\beta) = g(n\beta)/g(m\alpha) \tag{11b}$$

The orbital corrections are given by

$$f_i(\vec{x}_1) = \langle \chi | \, [\, 123\ldots(i-1)(i+1)\ldots\alpha m \,] \rangle_{\vec{x}_1} \tag{12}$$

where the integration does not extend over coordinate $\vec{x}_1$. Thus, for the TDA wavefunction we see that the $\hat{f}_i$ will be non-zero only when (1) orbital ϕ_α is also singly occupied in one of the terms in $|\chi\rangle$; if we represent this class of terms as

$$\sum_n \bar{g}(n\alpha) \, |{}^{n}_{\alpha}\rangle$$

then

$$\hat{f}_m = \sum_n \bar{g}(n\alpha)\phi_n \tag{13}$$

or (2) orbital ϕ_m is singly occupied in one of the terms in $|\chi\rangle$; then, as above

$$\hat{f}_\beta = -g(m\beta)\phi_\alpha \tag{14}$$

Note that there will never be an orbital correction for ϕ_α. In the TDA (and RPA) all virtual levels accessible from a given orbital are used so that the correction for orbital ϕ_m is always included. However, only if no symmetry whatsoever is present will all of the other orbital corrections be included. Even in this case, the $\hat{f}_\beta$

for the core orbitals will contain no virtual orbital contributions, only ϕ_α. In general, depending on the total symmetry of the molecule, some core orbital corrections may be included and others not at all.

To obtain the pair functions, one first removes the $\hat{f}_i$ from $|\chi\rangle$ to obtain $|\chi'\rangle$. The pair function is then obtained by deleting two orbitals from $|\Phi_0\rangle$ and integrating out all coordinates in the integral $\langle\chi'|\Phi_0/(ij)\rangle$ except those depending on two electrons to obtain

$$\hat{u}_{ij}(\vec{x}_1,\vec{x}_2) = \frac{1}{\sqrt{2}}\langle\chi'|\,[123\ldots(i-1)(i+1)\ldots(j-1)(j+1)\ldots\alpha m]\rangle_{\vec{x}_1\vec{x}_2} \tag{15}$$

Using Eq.(10) we see that only the pair functions in which i=m and and j=β (β≠α) will be non-zero and that

$$\hat{\underset{\sim}{u}}_{m\beta} = \frac{1}{\sqrt{2}}\sum_p g(p\beta)\ \phi_p\phi_\alpha$$

The swiggle under $\hat{u}_{m\beta}$ is a reminder that this is only a portion of the pair function, although there is some reason to expect that it may be a sizeable portion of $\hat{u}_{m\beta}$.

In summary, the TDA wavefunction with $|{}^m_\alpha\rangle$ as the reference configuration contains (1) an orbital correction for the virtual orbital ϕ_m and essentially none for the core orbitals and ϕ_α and (2) portions of the pair functions describing the correlation of electrons in $\phi_m(1)\phi_\beta(2)$ ($\beta\neq\alpha$), i.e., correlation between the open-shell orbital

ϕ_m and the doubly occupied core orbitals ϕ_β $(\beta \neq \alpha)$. Thus, the energy of the TDA wavefunction is approximately

$$E_{TDA} = E_{STA} + e_m^{SCF} + \sum_\beta \tilde{e}_{\beta m} \tag{17}$$

The tilde over the pair energy $e_{\beta m}$ denotes that only a portion of the total pair energy is obtained. Comparing this expression with Eq.(8) we see that although the TDA satisfies criterion (1), it contains only a portion of the pair correlations $e_{\beta m}$ and completely neglects $e_{\beta\alpha}$, so that criterion (2) is only partially satisfied. Criteria (3) and (4) are neglected entirely. Since the TDA contains only a portion of $e_{\beta m}$, it is possible, but not very probable, that

$$\sum_\beta (e_{\beta m} - e_{\beta\alpha}) \simeq \sum_\beta \tilde{e}_{\beta m}$$

Confirmation of this appears to be very difficult. It is obvious from this discussion that the fault with the TDA is that it puts all of the correlation into the excited state and none into the ground state.

The RPA attempts to remedy the unbalanced description of ground and excited states by considering the ground state wavefunction

$$|0\rangle = c_0|HF\rangle + \sum_{(n\beta)} \sum_{(p\gamma)} c_{\beta\gamma}^{np}|_{\beta\gamma}^{np}\rangle$$

Proceeding with the analysis as before we find that the RPA ground state contains portions of the pair functions $\hat{u}_{\alpha\beta}$. Thus, for the above ground state, the energy is

$$E^{gd}_{RPA} = E^{gd}_{HF} + \sum_{\beta\gamma} \tilde{e}^{gd}_{\beta\gamma} \; ; \tag{18}$$

again $\tilde{e}_{\beta\gamma}$ is just a portion of $e_{\beta\gamma}$. While this contains the terms $e_{\alpha\alpha}$ and $\sum_\beta e_{\alpha\beta}$ needed to formally balance the energy difference between the ground and excited state, see Eq.(8), it also contains terms such as $\sum_\beta e_{\beta\beta}$ and $\sum_\beta \sum_\gamma e_{\beta\gamma}$ which do not occur in an excited state wavefunction represented as a linear combination of single excitations. However, the RPA excited state wavefunction has the more complicated form given by Eq.(2.2-42) which does include such terms. Quantitatively, it has yet to be shown that these correlations enter in a balanced manner, although intuitive arguments suggest this possibility. Comparing the results of the RPA with Eq.(8) we see that the first three criteria are at least partially satisfied. In addition, it should be noted that the RPA includes such terms as $\tilde{e}_{\beta\gamma}$ $(\beta,\gamma \neq \alpha)$, changes in which are expected to contribute little to the excitation energy. Finally, in reference to the discussion in Section 3.1., it should be remembered that approximations are involved in deriving the RPA equations which assume that the $C^{mn}_{\alpha\beta}$'s are small.

3.3. The extended random-phase approximation

As we have seen in previous sections, the random-phase approximation is a good approximation only when the Hartree-Fock wavefunction is an adequate representation of the exact wavefunction. We shall now consider a scheme which permits the RPA to be used even if the above criterion is not satisfied.

The basic error in the RPA stems from the use of the ground state approximation in deriving the eigenvalue equation. Thus, we should evaluate all of the commutators over the ground state wavefunction

$$|0\rangle = C_0|HF\rangle + \sum_{(m\alpha)} \sum_{(n\beta)} C^{mn}_{\alpha\beta} \left|{}^{mn}_{\alpha\beta}\right\rangle$$

In addition, some of the terms in Q, Eq.(2.2-19), must also be retained for while

$$\langle HF| [A(E), Q] |HF\rangle = 0$$

this need not be true for the above wavefunction. In general, the calculation of the correlation coefficients, $C^{mn}_{\alpha\beta}$, would be a very time-consuming chore. However, an additional constraint was imposed in deriving Eq.(2.2-17), namely,

$$S(E)\,|0\rangle = 0 \tag{1}$$

which will not be satisfied unless there is some relation between the correlation coefficients and the particle-hole amplitudes, $\vec{G}$ and $\vec{H}$. Thus, if

$$S(E) = \sum_{(m\alpha)} [\, g(m\alpha)C(m\alpha) - h(m\alpha)C^{\dagger}(m\alpha) \,] \tag{2}$$

the consistency condition, Eq.(1), is satisfied only if

$$\sum_{(m\alpha)} \left[\sum_{(n\beta)} g(n\beta) C^{mn}_{\alpha\beta} - C_0 h(m\alpha) \right] \left| {}^{m}_{\alpha} \right\rangle = 0 \tag{3}$$

Or, in matrix notation[49]

$$\underset{\sim}{C} = \underset{\sim}{H}\,\underset{\sim}{G}^{-1} \tag{4}$$

where, for example,

$$(\underset{\sim}{C})_{ij} = C^{mn}_{\alpha\beta}/C_0$$

Using this approach an iterative solution of the RPA equations could be adopted: (1) use the ground state approximation to compute an initial set of particle-hole amplitudes, $\underset{\sim}{G}^{(0)}$ and $\underset{\sim}{H}^{(0)}$, (2) calculate $C^{mn}_{\alpha\beta}$ from Eq.(3), (3) use these correlation coefficients to calculate the required expectation values over the ground state, (4) solve the modified RPA equations for a new set of particle-hole amplitudes, $\underset{\sim}{G}^{(1)}$ and $\underset{\sim}{H}^{(1)}$, and (5) re-cycle steps (2)-(4) until the correlation coefficients and particle-hole amplitudes converge. Since the coefficients, $C^{mn}_{\alpha\beta}$, are small, the iterative process can be expected to converge rapidly. In fact, from the calculation on ethylene in Section 3.1, we see that even the first iteration should yield quite satisfactory values for the correlation coefficients. Schemes such as this which treat the ground state in a more consistent fashion are called the extended random-phase approximation.[50] Work in this area is in progress.[51]

An alternate scheme for evaluating the correlation coefficients has been suggested by Sanderson.[52] Using the RPA equations and the fact that the $\underset{\sim}{A}$ matrix is diagonalized by the TDA solutions, he obtains an expression for the correlation coefficients which must also be solved iteratively.

To go beyond the extended RPA, we could formulate a succession of more complex excitation operators.[53] Unfortunately, such higher approximations to the excitation operator lead to eigenvalue equations which rapidly become unwieldy and computationally expensive to solve. Should accuracy beyond that obtainable by the extended RPA be required, it would undoubtedly be best to use a pair theory approach.[27,28]

4. CALCULATIONS ON THE EXCITED STATES OF ETHYLENE

4.1. The ($\pi\pi^*$) states of ethylene

Because of the fundamental importance of conjugated and aromatic molecules in organic chemistry, an accurate theoretical description of such molecules has been a major goal of quantum chemistry since Goeppert-Mayer and Sklar[54] first considered benzene in 1936. In their treatment of benzene, Goeppert-Mayer and Sklar formulated in mathematical terms what is now called the π-electron approximation.[55] The crucial assumption in the π-electron approximation is that the wavefunction describing the σ-core is the same for all of the different π-electron configurations. One by-product of our work will be a rather critical examination of the validity of this assumption.

The ethylene molecule is the simplest unsaturated organic molecule and, thus, it can be considered a prototype for the larger molecules such as butadiene and benzene. Ethylene has the distinct advantage that, because of its small size, rigorous calculations can be done for this molecule which would not be economically feasible for larger molecules. Thus, we can carefully test any approximations before applying them to more complicated systems. Although ethylene is in some respects atypical of larger conjugated systems, it would appear that a method which fails to satisfactorily explain the excited states of such a simple π-electron system as ethylene is unlikely to do well for more complex systems.

The excited states of ethylene which are of most interest both experimentally and theoretically are the singlet and triplet states arising from the ($\pi\pi^*$) configuration. If the molecule lies in the xy-plane with $\hat{x}$ along the CC bond axis as shown in Figure 1.,[34] these states are of B_{3u} symmetry and have been designated $V(^1B_{3u})$ and $T(^3B_{3u})$ by Mulliken.[56] The $(\pi)^2$ ground state is denoted by $N(^1A_{1g})$.[56] The experimental results have been interpreted as involving a vertical excitation energy of 4.6 ev for the $T(^3B_{3u})$ state[57] and 7.6 ev[58] for the $V(^1B_{3u})$ state. The oscillator strength for the transition to the singlet state is ∿0.3.[58]

First, a brief review of three of the more significant π-electron calculations on ethylene is in order. The first non-empirical π-electron calculation on ethylene was by Parr and Crawford.[59] They used a minimum basis set of Slater orbitals with the exponent restricted to be the same in all states and approximately equal to the exponent obtained in atomic calculations. Their results, which are presented in Table II, are typical of such non-empirical π-electron calculations: the location of the triplet state being in reasonable agreement with experiment while the singlet state energy is too high by as much as 3-4 ev. Still within the π-electron approximation, Murai[60] relaxed some of the constraints on the π molecular orbitals by optimizing the orbital exponents of the Slater basis functions for each state. As is evident from Table II, the location of the triplet state is now in much better agreement with experiment, but the excitation energy for the excited singlet state, which was in much need of improvement, has changed hardly at all. Finally, Huzinaga[61] further relaxed the orbital restrictions by permitting the basis functions in the π- and π^*-orbitals to have different exponents and optimizing both exponents for each state of the system. As is illustrated in Table II, the calculated excitation energies now agree very well with experiment. However, a number of troubling facts arose from Huzinaga's calculations. First, the optimum orbital exponent for the π^*-orbital in the V state was quite small, $\zeta_{\pi^*} < 0.4$, and, in fact, Huzinaga notes that the energy was even lower for an exponent of $\zeta_{\pi^*} = 0.2$. However, for $\zeta_{\pi^*} = 0.2$ it appeared that the integrals were inaccurate, so that he discounted this point. In addition to the inexplicably small orbital exponent which we shall discuss later, Huzinaga also obtained an ionization potential far ($\sim$2.0 ev) below the experimentally observed value.

Since 1965 the ethylene molecule has been the subject of numerous all-electron calculations. In that year Moskowitz and Harrison[62] published a series of calculations on the ground state of ethylene with a number of uncontracted Gaussian basis sets. Using the (5s3p/2s) set,[63] which gave an energy of -77.5266 a.u. for the ground state,[64] and the virtual orbital approximation, they obtained excitation energies of 4.32 ev for the $T(^3B_{3u})$ state and 10.43 ev for the $V(^1B_{3u})$ state. While it might have been expected that the spectra of ethylene would be resolved once the σ-core potential was adequately defined, we find that this is not the case. The all-electron calculation gives results no better than those obtainable in the π-electron treatments. In 1967, Schulman, Moskowitz and Hollister[65] published calculations with a very large uncontracted Gaussian basis set, (9s5p/3s),[63] which gave an energy of -78.0062 a.u. for the ground state,[64] and obtained excitation energies only slightly better than before. Again the virtual orbital approximation had been employed for the excited states. In addition, Schulman, Moskowitz and Hollister[65] reported that preliminary open-shell calculations on the singlet and triplet states with the same basis set used for the ground state led to excitation energies essentially the same as those obtained in the virtual orbital approximation. Evidently, the problem is not the neglect of SCF changes in the core. Additional Hartree-Fock calculations have been carried out by Kaldor and Shavitt[66] and Robin et al.[67] with results differing little from those mentioned above. These calculations are summarized in Table III. On the basis of these calculations it would appear that the discrepancy between theory and experiment could only be due to σ-π correlation effects which are neglected in both the π-electron and all-electron SCF calculations.

Working on this assumption, Dunning and McKoy[34] applied the excitation operator method, which is designed to take into account such correlation effects, to ethylene. While the results were far from being quantitatively correct, these calculations indicated that σ-π correlation could account for the observed discrepancies in the excitation energy and oscillator strength for the singlet state. Since this calculation employed only a minimum basis set of Slater orbitals, calculations with more accurate basis sets were deemed necessary.

Because of the low π^*-orbital exponent which Huzinaga found in his π-electron calculations[61] and because of open-shell Hartree-Fock calculations which became available since this research began[68] (to be discussed later), it was decided to do the excitation operator calculations with two different basis sets: a valence basis set adequate for the ground state and an extended set containing diffuse basis functions in addition to those in the valence set. The valence basis sets for the atoms are the carbon (9s5p) and hydrogen (4s), $\zeta = 1.2$, primitive Gaussian sets of Huzinaga[69] optimally contracted to double zeta size, [4s2p] for carbon and [2s] for hydrogen.[70] This basis set will be denoted as [4s2p/2s] for the molecule.[63] The expanded basis set was obtained by adding to the valence set three low exponent $2p_\pi$ basis functions on each carbon. The additional functions were left uncontracted. This basis set will be denoted as [4s2p/2s] + $R(3p_zC)$ for the molecule.[63] The exponents and contraction coefficients for these basis sets are listed in Table IV.

For the above basis sets the matrix Hartree-Fock equations were solved for the ground state configuration of ethylene which in the present coordinate system is

$$(1a_{1g})^2(1b_{3u})^2(2a_{1g})^2(2b_{3u})^2(1b_{2u})^2(3_{ag})^2(1b_{1g})^2(1b_{1u},\pi)^2$$

The integrals over the Gaussian basis functions were calculated with a program (MOSES) written by M. Geller of the Jet Propulsion Laboratories[71] and modified by N. Winter and the author. The SCF cycling was performed with a set of routines adapted by W. Hunt for the MOSES integral package. The electronic, total and orbital energies obtained from the ground state calculations are presented in Table V. As expected, the diffuse basis functions had little effect on the ground state calculation, lowering the total energy by less than 0.0001 a.u. and the energies of the occupied orbitals by 0.0010 to 0.0005 a.u. Except for the π- and π^*-orbitals, the virtual orbitals were also little affected by the additional $2p_\pi$ basis functions. The most accurate calculation on the ground state of ethylene to date is that of Schulman, Moskowitz and Hollister.[65] However, their ground state energy of -78.0062 a.u. is higher than that of the valence basis set which has considerably fewer basis functions (28 vs. 60). This reinforces our conviction that the contraction schemes used here are close to optimum for the atoms considered.[70] Of course, the quality of a wavefunction should not be judged solely on the energy obtained. A much more sensitive measure of the accuracy of the wavefunction is the expectation values of one-electron operators. In Table VI. we list the expectation values of the following one-electron operators

Second moments r_α^2

Quadrupole moments $\Theta_{\alpha\beta} = \frac{1}{2}(3r_\alpha r_\beta - \delta_{\alpha\beta}r^2)$

Potentials	$1/r$
Electric fields	$f_\alpha = r_\alpha/r^3$
Electric field gradients	$q_{\alpha\beta} = (3r_\alpha r_\beta - \delta_{\alpha\beta} r^2)/r^5$
Densities	$\delta(\vec{r})$

for the two basis sets to be used in the present calculations as well as a more accurate set which is known to yield results very close to those obtainable with a completely uncontracted set.[72] A discussion of these properties can be found elsewhere.[73] The computer program for calculating the one-electron integrals over the Gaussian basis functions is a revised version of a program originally written by D. Neumann and J. Moskowitz at New York University.[74] First, it should be noted that the addition of the diffuse basis functions to the valence set has a negligible effect on all of the properties except those related to the second moments. It is the second moments which are, of course, most sensitive to the detailed form of the wavefunction at large distances. Comparing the expectation values for the [4s2p/2s] basis set with those of the larger [4s3p/2s] set, we note large changes only in the carbon field gradients. This is in agreement with calculations on other molecules which also indicated that more flexibility is needed in the p basis set of first row atoms than is available in the contracted [2p] set.[70]

From the energies and properties quoted above we can safely conclude that the valence basis set should be adequate for describing those excited states of ethylene which arise from the atoms in their ground states. The expanded basis set should then not only be able to describe the valence excited states of ethylene but possibly one or two $(\pi\pi^*)$ Rydberg states as well.

To carry out the excitation operator calculations, a computer program for Caltech's IBM 7040-7094 was written. Starting with the output from the LCAO-MO SCF calculation on the ground state and a list of the coupled elementary transitions, the program assembles the necessary two electron integrals, solves the excitator operator eigenvalue equations and computes the transition moments and oscillator strengths. The program for diagonalizing the unsymmetric RPA matrix was written by S. F. Persselin of the Rocketdyne Division of the North American Aviation Company. An important point which should be mentioned is that the use of symmetry was extremely important in efficiently assembling the two-electron molecular integrals. To make optimum use of symmetry it is necessary to first transform the integrals over the atomic basis functions to integrals over symmetry adapted functions.

Calculations in the ISTA, TDA and RPA were first carried out on the $(\pi\pi^*)$ states of ethylene using just the valence basis set, [4s2p/2s]. The excitation energies, transition moments and oscillator strengths for the lowest singlet and triplet states are listed in Table IX. As with the minimum basis set calculation reported previously, the triplet state in the RPA is unstable, i.e., ΔE is pure imaginary (see reference 34).

A number of important features are evident in this Table. First, these results support the conclusion drawn from the minimum basis set calculation,[34] namely, that σ-π correlation as included in the excitation operator method has a significant effect on both the excitation energy and transition moment for the lowest ($\pi\pi^*$) excited singlet state. As was also found previously, the effect on the triplet state is minimal. Thus, the overall picture which emerges from the accurate valence basis set calculation is unchanged from that drawn from the minimum basis set calculation. The numerical values are, of course, in much better agreement with experiment. However, it should be noted that upon increasing the flexibility of the basis set the excitation energy of the singlet state was lowered by over 2.5 ev in the ISTA. This is due solely to the SCF improvement in the π^*-orbital. With the same change in the basis set the triplet state excitation energies differ by only 0.1 ev. The large decrease in the singlet state excitation energy indicates a marked sensitivity to the functional form of the π^*-orbital and leads one to question whether this orbital is adequately described even in the large valence basis set used here. In the past it has been assumed, either implicitly or explicitly, that the V state is a valence state and, therefore, that a valence basis set should be adequate.[56] As we shall see, this interpretation of the V($^1B_{3u}$) state is inappropriate and more diffuse basis functions than those which occur in the valence set are essential for a correct description of the state.

Tables X and XI contain the results of the excitation operator calculations on the lowest ($\pi\pi^*$) singlet and triplet states of ethylene with the expanded basis set, [4s2p/2s] + R($3p_zC$). Comparing these results with those obtained with just the valence set, the most striking change is the marked improvement in the ISTA description of the excited singlet state: the excitation energy is lowered by nearly 1 ev and the oscillator strength by a factor of over 2. The excitation energy is now only 0.7 ev above the experimental vertical excitation energy[58] and the calculated oscillator strength of 0.41 is in reasonably good agreement with the experimental value of ∿0.3.[58] Although it is not obvious from the particle-hole amplitudes, an examination of Table XII which contains the orbital expansion coefficients for the improved virtual π^*-orbital reveals that this basis set spans the space of the π^*-orbital quite adequately. Again, these changes result strictly from an SCF improvement in the π^*-orbital. From these results it is obvious that a major defect in all of the previous calculations on the singlet state (except for Huzinaga's[61]) was the use of an inadequate basis set for the π^*-orbital.

The triplet state, T($^3B_{3u}$), on the other hand, was little affected by the addition of the diffuse basis functions, so we can conclude that such functions are not essential to the description of the triplet π^*-orbital. An examination of Table XII verifies this conclusion.

To further illustrate the differences in the π^*-orbitals, Table XIII compares the charge distribution of the singlet and triplet π^*-orbitals with that of the ground state π-orbital as revealed by the second moments and the $\langle 1/r_c \rangle$. As can be seen, the spatial extent of the triplet π^*-orbital is comparable to that of the π-orbital in the ground state, being significantly more diffuse only along the CC bond axis as expected from its nodal structure. This is a reflection of the basic similarities in the electronic structure of the lowest (ground) singlet and triplet states as discussed below. In the excited singlet state, on the other hand, the π^*-orbital is quite diffuse $\langle z^2 \rangle$ = 26.2889 a.u. and is bound by only 1.7 ev. These results reveal a basic dissimilarity between the ground and first excited singlet states. As is shown below, the planar $V(^1B_{3u})$ state is just not a "true" valence state but rather it is an ionic state.

To better understand the relationship between the N, T and V states, let us examine the orbital representations of the excited states. First, consider a minimum basis set representation of the π- and π^*-orbitals. Then, in terms of the atomic basis set $\{2p_a, 2p_b\}$, we obtain for the spatial part of the π-electron wavefunctions (neglecting normalization)

$$T(^3B_{3u}) \quad : \quad 2p_a(1)2p_b(2) - 2p_b(2)2p_a(1)$$

$$V(^1B_{3u}) \quad : \quad 2p_a(1)2p_a(2) - 2p_b(1)2p_b(2)$$

Thus, we see that the triplet state is just the anti-bonding state corresponding to the valence bond ground state. Hence, its charge distribution should be somewhat similar to that of the ground state, in agreement with the above calculations. The excited singlet state, on the other hand, is an <u>ionic</u> state and as such would be poorly represented by the above wavefunction; we clearly must allow the orbital exponents of the basis functions in the π- and π*-orbitals to be different. If $\zeta_{\pi *} \neq \zeta_{\pi}$, then the wavefunction for the singlet state is a sum of two terms:

$$V(^1B_{3u}) :$$

$$\{ [2p_a(1)2p_a'(2) + 2p_a'(1)2p_a(2)] - [2p_b(1)2p_b'(2) + 2p_b'(1)2p_b(2)] \}$$

$$+ \{ [2p_a(1)2p_b'(2) + 2p_b'(1)2p_a(2)] - [2p_b(1)2p_a'(2) + 2p_a'(1)2p_b(2)] \}$$

where

$$\pi \sim 2p_a + 2p_b$$

$$\pi * \sim 2p_a' - 2p_b'$$

The first term (enclosed in the first set of braces) is a split-shell ionic component analogous to the previous singlet state wavefunction. The second term is a covalent component which did not appear in the minimum basis set representation of the state. The ionic component will clearly tend to have $\zeta_{\pi *} << \zeta_{\pi}$ in order to minimize the electron repulsion with a static in-out correlation. In addition, upon dissociation the functions in the covalent term asymptotically approach

$$2p_a \rightarrow 2p_a \text{ (atom)}$$
$$2p'_a \rightarrow 3p_a \text{ (atom)}$$

and likewise for the terms on atom b. The excited singlet state wavefunction cannot dissociate to two carbon 2p-orbitals for at infinity the only available states are

$$2p_a(1)2p_b(2) \pm 2p_b(1)2p_a(2)$$

to which the ground and first excited triplet state dissociate. Thus, we expect the covalent terms to also favor $\zeta_{\pi*} << \zeta_{\pi}$.

Since the diffuse nature of the V($^1B_{3u}$) state of ethylene is a consequence of the basic nature of the wavefunction, such behavior is expected to be general. In fact, calculations by Phillipson and Mulliken[75] on the lowest $^{1,3}\Sigma_u^+$ states of H_2 first indicated this trend of T and V states over a decade ago. The Hartree-Fock configuration for the $^{1,3}\Sigma_u^+$ states is $(\sigma_u\sigma_g)$. Phillipson and Mulliken took

$$\sigma_g \propto 1s_a + 1s_b$$
$$\sigma_\xi \propto 1s'_a - 1s'_b$$

and separately optimized the exponents in the σ_g and σ_u orbitals for each state. At the equilibrium internuclear distance for the ground state they found that $\zeta_g = 1.325$ and $\zeta_u = 0.575$ for the T($^3\Sigma_u^+$) state and $\zeta_g = 1.450$ and $\zeta_u = 0.275$ for the $V(^1\Sigma_u^+)$ state in agreement with the results for the analogous states in ethylene. In addition, while relaxing the restriction $\zeta_u = \zeta_g$ lowered the triplet state by 6.6 ev, it lowered the singlet state by 8.8 ev. Referenced to the Hartree-Fock ground state Phillipson and Mulliken obtained an excitation energy and oscillator strength for the singlet-singlet transition of 12.38 ev and 0.275 which are in good agreement with the experimental values (12.27 ev for the excitation energy[76]). The calculated internuclear distance for the $V(^1\Sigma_u^+)$ is 1.15 A° which is longer than that for a Rydberg state, $R_e \sim 1.05$A°,[77] but shorter than the experimentally observed internuclear distance for the V state, $R_e = 1.2927$ A°.[77] While the results obtained by these authors are admittedly rather crude approximations to the exact Hartree-Fock results, the different behavior of the singlet and triplet states is expected to persist at the Hartree-Fock limit. The significance of this calculation had, until the present, been completely overlooked.

As stated previously, in calculations invoking the π-electron approximation, Huzinaga[61] also obtained a diffuse π*-orbital, $\zeta_\pi* < 0.4$, for the $V(^1B_{3u})$ state of ethylene. However, he also found that the energy was lower still for $\zeta_\pi* = 0.2$, which leads to an orbital significantly more diffuse than that found here. To understand these results we recall that Huzinaga used a Goeppert-Mayer-Sklar potential to represent the interaction with the σ-core. Thus, the π*-orbital which he obtained was an eigenfunction of the Hamiltonian

$$H^{GMS} = h + 2J_c + J_\pi + K_\pi$$

whereas the correct SCF Hamiltonian is

$$H^{SCF} = h + 2J_c - K_c + J_\pi + K_\pi$$

The two Hamiltonians differ by the exchange interaction with the core which is an attractive, and therefore binding, potential. Were the orbital to be loosely bound, as it is in the $V(^1B_{3u})$ state, the neglect of such an interaction could cause the orbital to be unbound, in which case the optimum orbital exponent would be zero. In any event, neglect of the core exchange potential would cause the diffuse character of the state to be exaggerated. This character of the excited singlet state casts considerable doubt on the pseudo-potentials chosen in previous π-electron calculations to represent the σ-core.[55]

Robin, Hart and Kuebler[10] have also suggested that diffuse basis functions might be required in calculations on excited states. However, they based their analysis on the virtual orbital approximation. As emphasized earlier, such a representation of the excited state wavefunction is completely inadequate.[5] For example, in the present case the $1\pi^*$-orbital from the ground state calculation with the expanded basis set has $\varepsilon(1\pi^*) = +0.0122$ a.u. and $\langle z^2 \rangle = 224.43$ a.u. and leads to excitation energies of 9.1877 ev and 9.1874 ev for the $V(^1B_{3u})$ and $T(^3B_{3u})$ states respectively.

The all-electron calculations on ethylene by both Schulman, Moskowitz and Hollister[65] and Kaldor and Shavitt[66] used only a valence basis set and, thus, they obtained excitation energies for the $V(^1B_{3u})$

state which are far too high. Basch, Robin and Kuebler,[6,67] in an attempt to circumvent the use of virtual orbitals, proposed that the restricted Hartree-Fock equations be solved for the triplet state and the set of orbitals so obtained used to construct the corresponding singlet wavefunction. This has the advantage that both open-shell orbitals in the triplet state are the eigenfunctions of a single Hamiltonian and, so, the orthogonality of the orbitals is trivially guaranteed and the calculations considerably simplified. However, as we have seen, the spatial distribution of the π^*-orbitals in the singlet and triplet states is markedly different. To see why this is so, we note that the Hartree-Fock Hamiltonians for the π^*-orbital in the T and V states are

$$T(^3B_{3u}) \qquad h_{\pi^*} = h + 2J_c - K_c + J_\pi - K_\pi$$

$$V(^1B_{3u}) \qquad h_{\pi^*} = h + 2J_c - K_c + J_\pi + K_\pi$$

Thus, the singlet and triplet π^* Hamiltonians differ by $2K_\pi$. If this exchange interaction is large, as it is in the lowest ($\pi\pi^*$) states, we expect the singlet orbital to be considerably more diffuse than the triplet orbital since this interaction is repulsive in the singlet Hamiltonian. On the other hand, for some states such as Rydberg states, as well as some valence states, the exchange interaction is quite small and it is a better approximation to assume that the singlet and triplet orbitals are the same.

In summary, we find that a more flexible basis set leads to a much improved orbital description of the lowest ($\pi\pi^*$) singlet state. Let us now see how correlation affects this orbital description. Using the results derived in Section 3.2., we see that the TDA wavefunction contains (1) an orbital correction for the π^*-orbital, f_{π^*}, which turns the reference π^*-orbital into the appropriate SCF orbital and (2) portions of the pair functions which describe the correlation of the π^*-orbital with all the valence σ-orbitals, $\hat{u}_{\sigma\pi^*}$.

Comparing the difference between the ISTA and TDA for the valence and expanded basis sets, we find that the decrease in the excitation energy for the expanded set is less than half of what it is for the valence set (0.52 vs. 1.10 ev). Furthermore, in the expanded basis we find that the addition of σ-π^* correlation actually increases the oscillator strength by $\sim$25% whereas in the valence set it decreased it by more than 30%. Thus, the role played by σ-π^* correlation in the description of the excited state in the TDA is significantly different in the two basis sets. Energetically, we find that σ-π^* correlation is much less dominant, although it is far from being negligible (0.52 ev).

Although σ-π correlation plays a reduced role in the description of the energetics of the excitation process, an equally important question is how it affects the charge distribution of the excited state. From calculations on atomic negative ions, we know that split-shell wavefunctions tend to exaggerate the diffuse nature of the loosely bound orbital. In the atomic case angular correlation must be included for an accurate charge distribution e.g., in the hydride ion, H^-, angular correlation decreases $\langle r^2 \rangle$ by nearly 40%.[78,79] How then do the correlations described by $\hat{u}_{\sigma\pi^*}$ and $\hat{u}_{\pi\pi^*}$ affect the spatial distribution of the π^*-orbital? From π-electron configuration interaction calculations[68] we know that one dominant type of correlation in molecules, that of left-right correlation along a bond, has little effect on the charge distribution. This is a portion of $\hat{u}_{\pi\pi^*}$, i.e., it is strictly a π-electron effect. In analogy to the atomic case it is possible, perhaps even probable, that the "angular" correlation of the π-electrons around the carbon-carbon bond, which is the remainder of $\hat{u}_{\pi\pi^*}$, would lead to a significant contraction in the π^*-orbital. Of course, in molecules correlations other than just those between the two open-shell orbitals can occur. Thus, we have yet to consider σ-π^* correlation effects such as the TDA wavefunction contains.

In Tables XIV and XV the results of the natural orbital analysis of the TDA wavefunctions for the lowest singlet and triplet $(\pi\pi^*)$ states are presented. Note the compact form of the natural orbital wavefunction; only the six "virtual" orbitals in addition to the eight orbitals occupied in the ground state need be considered. Thus, the original twenty-five configuration wavefunction in terms of the regular virtual orbitals has been reduced to just a six term expansion in the natural orbitals.

Comparing the π^* natural orbital from the TDA wavefunction with the frozen core π^*-orbital, see Table XVI, we immediately note a marked contraction of the orbital. Thus, the effect of including the σ-π^* correlation accounted for by the TDA has been to shrink the size of the molecule. While it is reasonable that correlations of this type would cause a contraction in the π^*-orbital, the magnitude of the contraction seems unusually large. Perhaps it is a consequence of the ionic nature of the wavefunction. On the other hand, the basis set could be inadequate for describing the correlation effects in such a diffuse state, e.g., there are no diffuse basis functions other than in the π- and π^*-orbitals, so that all σ^* virtual orbitals are necessarily spatially contracted. An examination of the σ^* natural orbitals reinforces this idea. However, there is insufficient information at this point to draw a sound conclusion.

Before proceeding we should reconsider the results of the TDA calculation on the lowest ($\pi\pi^*$) singlet state with the valence basis set. Knowing only the result of this calculation we might have thought that the description of the excited state was quite adequate: both the excitation energy and oscillator strength were greatly improved over their ISTA values and were in reasonable agreement with experiment. The calculations with the expanded basis set show otherwise, however. It is obvious then that some care must be taken in doing configuration interaction calculations especially if the character of the state of interest is unknown. It is possible, as actually occurs in the present case, that use of an inadequate basis set could increase some portion of the correlation energy and, thereby, obscure any need for a more flexible basis set. It must be realized that no minimum principle exists for any of the components of the correlation energy and, thus, the pair energies calculated with a given basis set are not necessarily an upper bound on the exact pair energies. Before attempting to include correlation effects, it would be best to obtain an accurate orbital description of the excited state if for no other reason than to set some limits on the problem. It should also be noted that such calculations are decidedly less expensive than correlation energy calculations of even the limited type considered here. A natural orbital analysis of the CI wavefunction is also a useful means of monitoring the convergence of the wavefunction, for an examination of the natural orbitals will often indicate any deficiencies in the basis set.

Finally, considering the RPA results for the singlet state given in Table X, we see that, as before, the RPA leads to a significant decrease in both the excitation energy and the oscillator strength, although interestingly enough the oscillator strength is still above that obtained in the ISTA. As was shown in Section 3.1., these changes are due to the strong mixing of the $(\pi^*\alpha\pi^*\beta)$ configuration into the Hartree-Fock ground state; for a basis set such as the one considered here $C_{\pi\pi}^{\pi^*\pi^*} \sim 0.3$. Thus, again the condition for the applicability of the RPA, namely, that

$$C_{\alpha\beta}^{mn} \sim 0$$

is not satisfied. Using the previous calculation on ethylene as a guideline, we expect the neglect of the correlation coefficients to increase the transition moment slightly and to decrease the excitation energies appreciably. To estimate the correction to the RPA excitation energy we must first determine the lowering due to the use of the ground state approximation as separate from any which could be due to the inclusion of triple excitations in the excited state and then we need to correct the ground state energy for the mixing of the $(\pi^*\alpha\pi^*\beta)$ configurations into the ground state Hartree-Fock wavefunction. From π-electron CI calculations[68] we find that the lowering due to the inclusion of the $(\pi^*\alpha\pi^*\beta)$ configurations in the ground state is

$$\begin{aligned} \Delta E_0 &= -0.0322 \text{ a.u.} \\ &= -0.88 \text{ ev} \end{aligned}$$

Determining the lowering of the RPA excitation energy due to the use of the ground state approximation is unfortunately not quite so straightforward. It seems reasonable to assume, however, that the lowering observed in an RPA calculation involving only the $(\pi\pi_i^*)$, $i = 1, n_{\pi^*}$, configurations is an approximation for the decrease in the RPA excitation energy due to the neglect of the correlation coefficients, since we are again dealing with a two particle system. The difference between the RPA and the TDA in this case is 0.17 ev. Thus, the corrected RPA excitation energy referenced to the RPA ground state, Eq.(2.2-40), is

$$\Delta E_{RPA}(V) = 8.51 \text{ ev}$$

This should be a good approximation for the excitation energy which would be obtained upon solving the extended RPA equations. Referencing the TDA result for the triplet state to the same ground state, we obtain

$$\Delta E_{RPA}(T) = 4.25 \text{ ev.}$$

The experimental values are 7.6 ev and 4.6 ev for the V and T states respectively.

There is one major effect which still has not been included in the RPA -- SCF relaxation of the σ-core. Open-shell calculations on the V($^1B_{3u}$) and T($^3B_{3u}$) states[68] have shown that, while core changes are of negligible importance in the triplet state, they lower the energy of the singlet state by 0.6 ev. This is as expected since it is the π^*-orbital in the singlet state which differs significantly in spatial extent from the π-orbital in the ground state. Inclusion of the SCF changes will bring the calculated excitation energy into better agreement with experiment.

In Table XVII we list the one-electron properties of ethylene in the lowest ($\pi\pi^*$) singlet and triplet states and the ground state. Because the triplet state has a charge distribution similar to that of the ground state, we note a marked similarity in the expectation values of the one-electron operators. Any differences are primarily a result of the different "shapes" of the π- and π^*-orbitals. Quite large changes in the one-electron properties are obtained upon (vertical) excitation to the lowest ($\pi\pi^*$) singlet state. The differences between the π^*-orbital in the ISTA and TDA are clearly reflected in the one-electron properties. For the triplet state the difference between the properties in the ISTA and TDA are small and of little importance. Because the ground state approximation is of limited validity in ethylene, the differences in the properties between the TDA and the RPA are exaggerated. For this reason the RPA results have been omitted from the table (see the discussion at the end of Section 2.3.). These expectation values unfortunately have essentially no experimental value for the equilibrium geometry of both the T and V states has the two CH_2 groups rotated 90° relative to each other.[56,58] They do, however, provide a means of displaying the changes in the charge density which occur upon (vertical) excitation.

It has been suggested that changes in the forces on the nuclei[80] upon excitation should correlate with observed changes in the equilibrium geometry. Examining the electric fields given in Table XVII we predict that in both singlet and triplet states the CC bond distance will be lengthened considerably and the $H\hat{C}H$ bond angle compressed slightly. In addition, in the singlet state the CH bond distance is predicted to be somewhat longer. While it is obvious that the CC bond should be longer in the excited states, the predicted changes in the hydrogen positions are probably completely unreliable since they should be strongly coupled to the larger change in the CC bond length. Finally, we note that forces can provide no information whatsoever about the much more interesting rotations around the CC bond, since the components of the forces in this direction vanish by symmetry.

Accurate open-shell Hartree-Fock calculations on the $T(^3B_{3u})$ and $V(^1B_{3u})$ states of ethylene have recently been carried out[68] and the results are given in Table XVIII. The basis set is essentially the expanded set employed here (the valence set is a [4s3p/2s] basis formed from the primitive (9s5p/4s) set and the diffuse functions are identical). We see that the excitation energy is in quite good agreement with experiment although the oscillator strength is too small by a factor of two. It should also be noted that the Hartree-Fock excitation energy is now below the experimental value in distinct contrast to the previous calculations.[66,67] This is in agreement with conclusions drawn in Section 3.3. where it was argued that open-shell states such as the $(\pi\pi^*)$ states of ethylene should inherently have a smaller correlation energy than the ground state so that

$$\Delta E_{HF} < \Delta E_{exp}$$

Since the excitation energy is the sum of the differences of the Hartree-Fock and correlation energies, the SCF calculations indicate that

$$E^{ex}_{corr} - E^{gd}_{corr} \simeq 0.23 \text{ ev}$$

Considering the diffuse nature of the π^*-orbital, a difference this small is somewhat puzzling. This could be due to other changes which accompany excitation, e.g., the contraction of the σ- and π-orbitals. Since this same phenomena occurs in hydrogen, however, it is likely that this is an intrinsic property of such "ionic" states.[75,81]

We see that the open-shell Hartree-Fock calculations also give a diffuse π^*-orbital. In fact, we see that the π^*-orbital in the SCF approximation is significantly more diffuse than the frozen core π^*-orbital, e.g., $\langle\pi^*|z^2|\pi^*\rangle$ = 42.1 a.u. vs. 26.3 a.u. This is caused by the relaxation of the core orbitals (both σ and π) which upon self-consistency become more contracted than in the ground state. Combining this observation with the fact that SCF relaxation of the core also lowers the energy of the $V(^1B_{3u})$ state by $\sim$0.6 ev, it is obvious that an accurate description of the $V(^1B_{3u})$ state of ethylene cannot be obtained if such self-consistency is neglected. However, we do find that the essential physical characteristics of the excited state are contained in the frozen core, TDA and RPA wavefunctions.

For the triplet state, self-consistency has a much smaller effect on the charge distribution and, thus, the frozen core approximation is more reliable. In fact, one might expect this to be the general trend in most "true" valence states.

As was noted previously, the σ-π^* correlation effects contained in the TDA causes a significant contraction in the π^*-orbital, e.g., in the TDA $\langle\pi^*|z^2|\pi^*\rangle$ = 10.7 a.u. Judging from the open-shell Hartree-Fock calculations, the charge distribution in the TDA is too contracted spatially, since the TDA does not include any SCF relaxation of the core.

Both the excitation operator and open-shell Hartree-Fock calculations lead to a V($^1B_{3u}$) state which is considerably more diffuse than a valence state. Since this conclusion is at odds with the interpretation of the experimental results as well as with previous theoretical discussions about the nature of this state, it would seem necessary to briefly discuss the experimental facts known about the V($^1B_{3u}$) state of ethylene.[82]

The $\pi \rightarrow \pi^*$ (N→V) electronic transition of ethylene[58] consists of a single, slightly irregular progression of diffuse bands of rapidly increasing intensity. The origin of the bands (0→0 transition) is thought to be near 2650 $\mathring{A}$ with absorption beginning in the gas phase at ∿2100 $\mathring{A}$ and merging into a continuum at 1750 $\mathring{A}$ which reaches a flat maximum at 1620 $\mathring{A}$. The maximum in the absorption curve is thus at 7.65 ev which according to the Franck-Condon principle corresponds to a vertical excitation. Since the excited state has three bonding CC orbitals ($\sigma^2\pi$) and one anti-bonding orbital (π^*), excitation of the carbon-carbon stretching vibration is expected to occur. On this basis Wilkinson and Mulliken[58] assigned the observed bands as progressions in the upper state carbon-carbon stretching vibration, obtaining a frequency of 852 cm^{-1}. Although Wilkinson and Mulliken[58] recognized that the equilibrium geometry of the V($^1B_{3u}$) state had the two CH_2 groups rotated at 90° relative to each other,[56] they neglected any effect torsional oscillation might have on the spectrum. Later, McDiarmid and Charney[83] re-interpreted the spectrum as progressions in the V state twisting vibration, obtaining a frequency of 807 cm^{-1} compared to 1027 cm^{-1} in the ground state, and Ogilvie[84] has even attributed them to the CH_2 wagging vibration. Finally, in 1969 Merer and Mulliken[85] put forth the argument that both stretching and twisting vibrations must be taken into account and claim that reasonable agreement between the calculated and observed band structure can be obtained in this way. However, pending further work, they did not give the stretching and twisting frequencies so obtained. At this time then, reliable estimates of the vibrational frequencies of any of the modes in the V state are not available.

If the planar $V(^1B_{3u})$ state of ethylene is actually as diffuse as the calculations predict, it might be expected that the stretching frequency would be nearly that of a Rydberg state,[58] $\sim$1300 cm^{-1}. Mulliken[58,85] has estimated the carbon-carbon bond length in the $V(^1B_{3u})$ state to be 1.70-1.80 A^o (in analogy with the "corresponding" states in the oxygen molecule[77]) whereas the equilibrium bond length for the first Rydberg state is $\sim$1.45 A^o. Clearly, however, these simple deductions are complicated by the fact that, unlike Rydberg states, the $V(^1B_{3u})$ state has an equilibrium geometry with the planes of the two CH_2 groups at right angles. In addition, although the π^*-orbital is considerably more diffuse than a valence orbital, it is not as diffuse as a typical Rydberg orbital, e.g., the first Rydberg

π^*-orbital in the triplet series has an $\langle z^2 \rangle$ = 69.6 a.u. vs. 26.3 a.u. for the π^*-orbital in the V state. Unlike Rydberg states we also might expect the ionic component of the wavefunction, which in a minimum basis set description was the only component, to be an integral part in the description of the state. Thus, although a formal analogy exists between the Rydberg states and the V($^1B_{3u}$) state because of the diffuse nature of the π^*-orbital, one should be cautioned against any broad generalities until a more thorough investigation has been completed.

Information on the spatial extent of a state can also be obtained from the spectrum of the molecule in either the solid phase, in a matrix or under extremely high pressure. In such a situation the diffuse orbital is strongly perturbed by the neighboring atoms or molecules resulting in a marked change in the spectra. Lubezky and Kopelman[86] obtained the spectrum of a molecular crystal of ethylene 1-mm thick. The only "positive" results which they obtained were two weak and relatively sharp transitions at 2044 A° and 2079 A° which they assigned to the N→V transition. Because of the lack of data this assignment must be considered tenative. Robin et al.[67] report the spectra of ethylene in both a Krypton matrix and in the gas phase with 2200 psi of N_2 added. Although they were interested in the first Rydberg transition, and therefore the spectra is somewhat incomplete as concerns the V($^1B_{3u}$) state, the underlying vibrational structure which is attributed to the V state does not differ radically from that in the gas phase. In summary, the experimental data on the physical characteristics of the V($^1B_{3u}$) state are quite incomplete and attest to the difficulty in interpreting the spectra of a molecule even as simple as ethylene. Of all of the experimental work done on ethylene only that of Robin et al.[67] has provided any information on the extent of the excited state charge distribution and even there the data at present are quite incomplete. The basic question, of course, is not whether the state is perturbed on going to the solid phase but is how diffuse a state has to be before it is perturbed significantly by the neighboring atoms and molecules and how does the perturbation depend on the angular characteristics of the diffuse orbital, the composition of the matrix, etc.,[87] although certainly the disappearance of the first Rydberg state of ethylene sets some limits.[67]

Of course, the spatial extent of the V state in its equilibrium configuration with the two groups rotated 90° relative to each other need not be as diffuse as it is for the planar configuration.

In addition to the lowest singlet and triplet ($\pi\pi^*$) states of ethylene, the expanded basis set is sufficiently flexible so as to adequately describe the first ($\pi\pi^*$) Rydberg state. The excitation energies, transition moments, oscillator strengths and particle-hole amplitudes for these states are given in Tables IXX and XX.

In the frozen core approximation the excitation energy for the Rydberg singlet state is 9.12 ev. Since the Koopmans's theorem ionization potential for this basis set is 10.15 ev, the stability of the Rydberg state is -1.03 ev. Correcting the excitation energy for the difference between the Koopmans's theorem[88] and experimental ionization potentials (0.37 ev), we predict a singlet ($\pi\pi^*$) Rydberg state at 9.49 ev and the corresponding triplet state at 9.14 ev. Since the oscillator strength is predicted to be rather large, f ∿ 0.16-0.05, this transition should be observable in the optical spectra.

Wilkinson[89] has observed four Rydberg series in the ultraviolet spectra of ethylene. Of these, three have their first members in the region of the strong N→V transition, so that they cannot be attributed to $\pi \rightarrow n\pi^*$ excitations. The fourth Rydberg series has its origin at 9.05 ev and Wilkinson has tenatively assigned this as a $\pi \rightarrow \pi^*$ transition with n = 4 and a quantum defect of 0.95. The theoretical calculations presented here locate the first Rydberg ($\pi\pi^*$) state of ethylene at ∿9.5 ev. As was discussed previously, the lowest singlet ($\pi\pi^*$) state dissociates to atoms in a (2p,3p) configuration, so the appropriate quantum number for the first Rydberg level should be n = 4 in agreement with Wilkinson. The calculated quantum defect is 0.47. The fact that the $2\pi^*$ orbital has an effective quantum number of four can also be understood by noting that the $1\pi^*$ orbital is nominally a 3d-orbital of the positive ion and, thus, the $2\pi^*$ orbital will be the 4d-orbital. Because of the nature of the lower ($1\pi 1\pi^*$) state, we expect the ($1\pi 2\pi^*$) state to be somewhat perturbed from an atomic-like structure. This is reflected in the quantum defect; d-orbitals usually have $\delta \sim 0$.

Examining these tables in more detail we see that the difference in the ISTA and TDA excitation energies are considerably smaller for the second ($\pi\pi^*$) state than for the first: 0.18 ev vs. 0.52 ev for the singlet state and 0.01 ev vs. 0.11 ev for the triplet state. Since the TDA wavefunction is primarily accounting for σ-π^* correlation, this is direct evidence for the decreased importance of such effects in Rydberg states. As a result, the correlation energy of a Rydberg state is similar to that of the positive ion as was discussed in the Introduction. The decrease in the oscillator strength by a factor of more than three is indicative of significant changes in the electronic structure of the excited state which are not, however, reflected in the energy changes.

The difference between the description of the state in the TDA and in the RPA is much smaller than for the lowest ($\pi\pi^*$) state and the triplet state is now stable. The decrease in the oscillator strength for the singlet state is again more than might have been expected. The smaller effect of the RPA on the excitation energies is not an indication of a smaller effect of the ($\pi^*\alpha\pi^*\beta$) configurations on the ground state, that is a constant which is independent of the excited state under consideration, but reflects a decreased sensitivity of the equations to the ground state approximation.

The orbital expansion coefficients for the π^*-orbitals from both the ISTA and TDA wavefunctions are given in Table XXI. A reasonably accurate description of the singlet or triplet excited state can be obtained just by combining the appropriate frozen core (ISTA) π^*-orbital with the remaining ground state orbitals. The effect of the TDA upon the (singlet) π^*-orbital is evident both in this Table and in Table XXII, which contains expectation values of the second moments and $1/r_C$. Just as in the lowest ($\pi\pi^*$) state the additional configurations in the TDA has caused a substantial contraction in the $2\pi^*$-orbital. In fact, if the overlaps of the ISTA and TDA orbitals are any criterion, the differences are even greater in this case than in the lowest ($\pi\pi^*$) state. This result is at present inexplicable, although it could be an indication that the basis set in not sufficiently flexible to describe the correlations in such a diffuse Rydberg state.

Open-shell Hartree-Fock calculations have also been carried out on the second ($\pi\pi^*$) state.[68] These calculations predict the second Rydberg state to be at 9.61 ev with an oscillator strength of 0.06, in good agreement with the excitation operator calculations. As for the lowest ($\pi\pi^*$) state the SCF π^*-orbital is considerably more diffuse than the frozen core orbital (186.7 a.u. vs. 137.7 a.u.).

In summary, both the excitation operator and open-shell Hartree-Fock calculations predict a Rydberg ($\pi\pi^*$) state at ∿9.5 ev with an oscillator strength in the range 0.16 - 0.02. Tentatively, this is correlated with the R''' state observed by Wilkinson in the optical spectra.

4.2. Other valence excited states of ethylene

Excitation operator calculations were also carried out on a number of other singly excited states of ethylene. Only those transitions terminating in the π*-orbital were found to be valence states. Because these states are true valence states, the [4s2p/2s] set was found to be adequate and the results reported here are for that set. All other excited states involved Rydberg σ*-orbitals which cannot be adequately described by our basis set (the expanded set contains only diffuse π and π*-orbitals).

The lowest (σπ*) states arise from the transitions

$$1b_{1g} \rightarrow \pi^* \qquad {}^{1,3}B_{3g}$$

$$3a_{ag} \rightarrow \pi^* \qquad {}^{1,3}B_{2g}$$

Neither of these transitions is dipole allowed and, hence, they will appear only weakly in the optical spectrum if at all. In fact, no such states have even been reported, all of the observed lines in the spectra above the V($^1B_{3u}$) state being attributed to Rydberg transitions.[89] It is possible that such states could be detected in electron impact work[90,91] where the usual selection rules are no longer valid and where the intensity of forbidden transitions has identifiable characteristics.

Tables XXIII, XXIV, XXV and XXVI list the excitation energies and particle-hole amplitudes for the singlet and triplet B_{3g} and B_{2g}

states. The effect of σ-π^* correlation as contained in the TDA and RPA is seen to be of minor importance in all four states. Even though the ($\pi^*\alpha\pi^*\beta$) configurations are quite important in the exact ground state wavefunction, they have no effect on these excited states since they do not occur in the corresponding RPA ground states. See Eq.(2.2-40) and (3.3-3).

In 1963 Berry[92] suggested that $\sigma\rightarrow\pi^*$ transitions could have low excitation energies in ethylene in analogy to the $n\rightarrow\pi^*$ transition in formaldehyde. He chose the $1b_{1g}\rightarrow\pi^*$ transition as a most likely candidate on the basis that the $1b_{1g}$-orbital most closely resembles the n-orbital of formaldehyde (it is also highest in energy of the σ-orbitals). Since the excitation energy for the singlet $n\rightarrow\pi^*$ transition in formaldehyde is ∿4 ev, we see that the analogy is far from complete. This result is due to the lower energy of the $1b_{1g}$-orbital (2 ev) and the reduced Coulombic interaction between the $1b_{1g}$- and π^*-orbitals (4 ev); it should be remembered that the n- and π^*-orbitals in formaldehyde are both predominantly on the oxygen. At the time this explanation was put forth to explain the so-called "mystery band" of ethylene.[93] However, recent experimental work[90,91,94] has failed to confirm the existence of this transition, although Ross and Lassettre[91] have attributed small irregularities in their electron impact spectra of ethylene in the region around 7 ev to a quadrupole transition.

In Table XVII we list the orbital expansion coefficients for the

π^*-orbital in the singlet and triplet B_{3g} and B_{2g} states from the ISTA or frozen core wavefunctions. Because of the small changes associated with higher approximations to the excitation operator, these improved virtual orbitals when combined with the appropriate ground state orbitals (see Table V) should provide a reasonable approximation to the excited state wavefunctions. Note that the expansion coefficients illustrate quite effectively the valence-like nature of the π^*-orbitals (compare with the coefficients in the expansion of the π^*-orbital in the V state, Table XII).

Just for the sake of completeness, a number of one-electron properties of the $\sigma\rightarrow\pi^*$ excited states are given in Table XVIII. The second moments indicate that both states involve the removal of a predominantly carbon-hydrogen bond orbital from the σ-core. Examination of the expansion coefficients of the $1b_{1g}$- and $3a_{1g}$-orbitals given in Table V support this conclusion. If the forces are any indication of the equilibrium geometry, we would predict that the carbon-carbon bond length will be smaller than the ground state in the $^{1,3}B_{3g}$ states and longer in the $^{1,3}B_{2g}$ states. In addition, in all four excited states the $\widehat{HCH}$ bond angle is predicted to be significantly smaller and the CH bond length longer than in the ground state. The larger changes in the forces associated with the hydrogens again indicate carbon-hydrogen character in the σ orbital. Note the small differences between the charge distributions in the singlet and triplet states of the same orbital configuration.

5. CONCLUSIONS

Although the Tamm-Dancoff and random-phase approximations have been actively discussed for many years, especially in reference to solid state[18,30] and nuclear physics,[19,20,29] the use of these methods in atomic and molecular systems has been suggested only recently.[31,34,39] Because of the indeterminate form of the interaction potential in solids and nuclei, the work in these areas tested the ability of the TDA and RPA to provide a semi-empirical framework for the interpretation of experimental results more than their effectiveness as ab initio methods. In addition, the phenomena which occur in the infinite electron gas and in infinite nuclear matter are inherently different in nature from those which occur in atoms and molecules, e.g., the states of interest often correspond to collective modes.[30] Because of the known interaction potential ($1/r_{ij}$) in atomic and molecular systems and because it is now possible to carry out rigorous calculations on molecules as large as ethylene, we were able to carefully examine some of the approximations involved as they pertain to atoms and molecules.

Unfortunately, the analysis of the TDA and RPA was complicated by the discovery that the ($\pi\pi^*$) excited singlet state of ethylene has a much different character than had been expected. Thus, it is likely that ethylene is too stiff a test case and that the TDA and RPA could lead to more consistent results for larger systems where the basic approximations may be more valid.

For ethylene the TDA and RPA lead to reasonable values for the excitation energies and oscillator strengths. However, we found that the correlation introduced by these methods does not always enter in the ground and excited states in a particularly balanced manner and that SCF changes in the core are neglected. In addition, the strong mixing of the ($\pi^*\alpha\pi^*\beta$) components into the ground state of ethylene led to a number of problems in the RPA, e.g., instability of the triplet, T($^3B_{3u}$), equations and too low an excitation energy for the V($^1B_{3u}$) state. Comparing the results of calculations with a valence and an extended basis set we found that the role of σ-π^* correlation varied considerably. In the valence set such correlation was an essential part of the description of the excited state. In the more flexible set, however, σ-π^* correlation was reduced to the auxiliary role of modifying a much improved orbital representation of the state. While causing small changes in the excitation energy and oscillator strength for the V state, the σ-π^* correlation effects caused a substantial contraction in the spatial extent of the charge distribution of the excited state. While this could be due to basis set limitations, it is also possible that it is an intrinsic property of such "ionic" wavefunctions.

It is not expected that the diffuse character of the V state is limited to ethylene, but rather such states should also be present in such molecules as butadiene, benzene and napthalene. In the larger systems it is expected that some $\pi\rightarrow\pi^*$ singlet transitions will involve valence π^*-orbitals while others will make use of expanded orbitals as in ethylene.

The diffuse nature of the V states has extensive implications in many areas of chemistry. Thus, because of the extended size of the molecule and the low binding energy of the π^*-orbital, ethylene in its V($^1B_{3u}$) state might be expected to be rather reactive, especially in reactions which involve electron transfer. In addition, the exciton structure of a molecular crystal of ethylene would be decidedly different than would be expected for a valence state. Although there has been little experimental interest in crystalline ethylene, as mentioned above such diffuse states are also expected to occur in molecules such as benzene and naphthalene which are more accessible experimentally.

6. APPENDIX

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Nonempirical Calculations on Excited States: The Ethylene Molecule

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A series of nonempirical calculations are reported on the excited states of the ethylene molecule using a recent minimum basis set LCAO MO SCF wavefunction. For the lowest excited singlet state of ethylene (${}^1B_{3u}$) the coupling between the π electrons and σ electrons is significant: the excitation energy being decreased from 11.98 to 10.17 eV and the oscillator strength from 1.03 to 0.73. This coupling has little effect on the triplet state. In the next higher approximation (the random-phase approximation) the excitation energy is further decreased to 9.44 eV and the transition moment to 0.51. With the use of accurate LCAO MO SCF wavefunctions, it is felt that the methods presented here will provide a basis for the theoretical interpretation of electronic spectra.

I. INTRODUCTION

A. General

Now that the application of the Hartree–Fock–Roothaan treatment of the electronic structure of molecules is practical for many molecules of chemical interest,[1–3] one of the more important problems in molecular quantum mechanics is assessing the effect of electronic correlation particularly for observables other than the total energy. To obtain even a simple approximate Hartree–Fock wavefunction for a relatively small molecule requires a fair amount of effort and computer time. Very accurate Hartree–Fock wavefunctions for the ground state would demand a prohibitively large investment. If one is interested in properties related to two states, the problem becomes even more formidable, and correlation effects have still not been included. What we show in this paper is that correlation effects are significant in locating an important excited state of ethylene (for both excitation energy and oscillator strength for the singlet state located at 7.6 eV experimentally), but that it can be described quite economically from a simple ground-state Hartree–Fock calculation by applying, among others, the theory of the random-phase approximation (RPA) for electronic correlation. We chose the methods for their conceptual usefulness and potential for future applications, but they are certainly not the only ones which would yield these results.

The methods to be employed have been widely used both in nuclear and solid-state physics[4–7] and more recently in the study of electronic correlation in atoms[8] and molecules.[9] The theory as applied here is not very difficult and the physical concepts are simple. In keeping with the usual procedure in these fields, we derive the equations using the formalism of second quantization. In this representation we can make reasonable approximations which are difficult to formulate in the coordinate representation. All of the equations derived in this paper are obtainable from appropriate variational procedures, but the method employed here has the advantage that the approximations are explicitly displayed and the removal of any difficulties is a conceptually straightforward matter.

We chose ethylene as our example as its spectrum is of considerable interest. It is not necessary to stress the importance of understanding the ethylene molecule quantum mechanically. It is the simplest π-electron system and a prototype for larger π-electron molecules. If we want to know the properties of some of its excited states, we need to have some physical idea as to how "to get" this state from the ground state. The problem is one of finding a form for an operator $A^+(E)$ such that it satisfies the following equation:

$$[\mathcal{H}, A^+(E)]\,|0\rangle = \Delta E A^+(E)\,|0\rangle, \tag{1}$$

where $\mathcal{H}$ is the complete electronic Hamiltonian for the molecular system under consideration. The operator $A^+(E)$ contains whatever physical information we have about the excited state of the system. We see that the operator $A^+(E)$ generates an excited state of the Hamiltonian $\mathcal{H}$, with excitation energy ΔE, when it operates on the ground state; i.e.,

$$A^+(E)\,|0\rangle = |E\rangle. \tag{2}$$

Note that the above describes a vertical excitation. In practice, because of electronic interaction, $A^+(E)$ cannot be determined such that the above equation is exactly satisfied, but rather we have

$$[\mathcal{H}, S^+(E)] = \Delta E S^+(E) + R \tag{3a}$$

$$\approx \Delta E S^+(E), \tag{3b}$$

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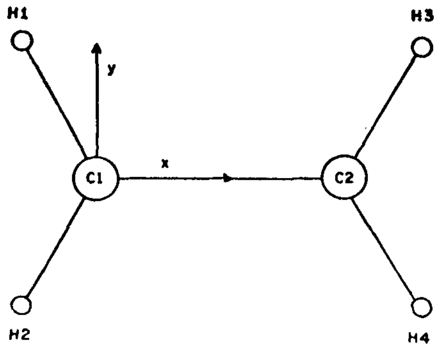

FIG. 1. The geometry of ethylene.

where R represents all the terms which cannot be reduced into a form consistent with $S^+(E)$. The operator $S^+(E)$ generates an approximate excited state of the system when it acts on the ground state. It is one of the variables of the problem in whose formulation we may utilize our chemical intuition.

In this paper we consider the following three approximations for the excited states created by the excitation operator $S^+(E)$.

(1) The single-transition approximation (STA)[10] is the approximation most frequently used by chemists. It assumes that the excited state can be represented by a single particle above the set of levels occupied in the ground state coupled with a hole within that set, e.g., the ${}^1B_{3u} \leftarrow {}^1A_{1g}$ transition in ethylene would correspond to an electron going from a π-bonding to a π-antibonding orbital.

(2) In the Tamm–Dancoff approximation (TDA)[4,9] the excited state is represented as a linear combination of single-particle transitions. This method is encountered quite frequently in molecular quantum mechanics, e.g., in the study of the spectra of aromatic molecules by Pople.[11] Again, with ethylene as an example, we now include in the excited-state wavefunction configurations corresponding to moving an electron from the "σ" and "CH" bonding orbitals (the σ core) into antibonding levels.

(3) In the random-phase approximation (RPA)[5,8] the excited state is still represented by a linear combination of single-particle transitions except that now we allow the ground state to include configurations other than just the Hartree–Fock (HF) component, i.e., the effects of configuration interaction (CI) are, to some extent, taken into account. We still solve an eigenvalue equation for ΔE directly. This, as expected, is an improvement on Method (2).

In the above a "hole" state corresponds to an unoccupied level within the normal HF ground state while a "particle" state denotes an occupied virtual orbital. Excitation of the type considered here creates "particle–hole" pairs, each such pair having its own frequency (excitation energy). By diagonalizing the Hamiltonian matrix within this set we find the normal modes of the assembly of coupled oscillators. Surprisingly, such coupling is not negligible in ethylene as it reduces the oscillator strength given by the STA by a factor of 2.

B. The Ethylene Molecule

To provide a concrete foundation for the above approximations, we have done the complete set of calculations on the ethylene molecule utilizing the recent minimum basis set LCAO MO SCF calculation by Palke and Lipscomb.[12] The excited state in which we are most interested is the one which arises from the so-called $\pi \rightarrow \pi^*$ transitions which, if we define the coordinate system as shown in Fig. 1, is of symmetry B_{3u} with the emitted radiation polarized along the x axis. Since some new concepts have arisen from this work, especially in regard to the π-electron approximation, we briefly review three of the more significant π-electron calculations on ethylene in order to gain the proper perspective.

The first nonempirical π-electron calculation on ethylene was by Parr and Crawford[13] using the formalism developed by Goeppert-Mayer and Sklar.[14] Their results are typical of nonempirical π-electron calculations: the predicted spectra being in qualitative, but not quantitative, agreement with experiment. The results of this calculation, as well as the following two, are listed in Table I along with the experimentally observed excitation energies and oscillator strengths. Still within the π-electron approximation, Murai[15] relaxed the constraints on the π-molecular orbitals by allowing the orbital exponents of the atomic Slater orbitals to be a function of the state of the system. As is evident from Table I, the triplet state is now in better agreement with experiment while the singlet

TABLE I. π-Electron calculations on the excited B_{3u} state of ethylene: excitation energies (in electron volts), oscillator strengths, and ionization potential.[a]

	Parr and Crawford	Murai	Huzinaga	Exptl
${}^3B_{3u}$ (T)	3.10	4.60	4.45	4.6
${}^1B_{3u}$ (V)	11.50	11.20	7.28	7.6
$f({}^1B_{3u})$				$\sim$0.3[b]
I.P.	11.90	8.80	8.52	10.52

[a] Except as noted, see text Ref. 28.

[b] M. Zelikoff and K. Watanabe, J. Opt. Soc. Am. 43, 756 (1953).

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[10] C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

[11] J. A. Pople, Proc. Phys. Soc. (London) A68, 81 (1955).

[12] W. E. Palke and W. N. Lipscomb (private communication).

[13] R. G. Parr and B. L. Crawford, J. Chem. Phys. 16, 526 (1948).

[14] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938).

[15] T. Murai, Progr. Theoret. Phys. (Kyoto), 7, 345 (1952).

state, which was in much need of improvement, has hardly changed. Finally, Huzinaga[16] carried the π-electron approximation to its fullest by permitting the bonding and antibonding π-molecular orbitals to have different exponents as well as allowing the exponents to vary with the state. The predicted spectra now agree very well with experiment. However, the calculated ionization potential is far below the experimental.

The π-electron treatment of ethylene has attained a refinement which cannot be approached in larger π-electron systems and still all the experimental facts cannot be adequately explained. An improvement in the theoretically calculated value of one observable is attained only at the expense of poor values for other observables. We feel that the calculations presented in this paper go a long way towards resolving these difficulties. We can see the role played by electronic correlation in the excitation process and discuss a simple method of taking it into account.

One may have expected that the problem of the spectra of ethylene would be resolved once an accurate 16-electron Hartree–Fock treatment of the molecule was available, for then the core potential would be adequately defined. However, the locations of the excited states obtained from Palke and Lipscomb's LCAO MO SCF wavefunction are comparable to those obtained by π-electron theory (compare the STA results in Tables V and VI with those for the Parr and Crawford calculation given in Table I) and therefore the trouble with predicting the spectra does not arise completely from the π-electron approximation for the ground-state calculation.

The source of the trouble is the neglect of the change in the σ core upon excitation; the π electrons being coupled by the residual electronic interaction to the σ electrons. In fact, this coupling is sufficiently strong to cause a decrease of about 2 eV in the excitation energy and a decrease of 30% in the oscillator strength for the ${}^1B_{3u}\leftarrow{}^1A_{1g}$ transition compared to the $\pi\rightarrow\pi^*$ approximation. As expected, the RPA further decreases the excitation energy to 9.44 eV and the oscillator strength to 0.51.

A word of caution is appropriate at this point. Our calculations are based on a minimum basis set LCAO MO SCF calculation and as such we have not reached the Hartree–Fock molecular-orbital limit. As a remedy for this we could enlarge the basis set, for example, see the results of Moskowitz and Harrison[17] using a large set of Gaussian orbitals which predict values for the excitation energies using the $\pi\rightarrow\pi^*$ approximation which are almost as good as ours using the RPA.

The methods discussed here are not the only ones relevant to the problem. One could use the LCAO MO SCF results as a basis for an extensive configuration-interaction calculation on both the ground state and excited states. Besides being uneconomical (for a large number of molecular integrals must be assembled), the following consideration must be taken into account. In the usual CI calculation one mixes in components corresponding to double excitations from electrons in the same spatial orbital. These are usually the most important. However, the lowering that we observe while essentially being a correlation effect is due to correlations between electrons in orbitals that are quite different spatially, i.e., as Herzenberg *et al.*[9] state "correlations extending from bond to bond."

Alternately, one could do an open-shell LCAO MO SCF calculation on the excited states with the hope that correlation effects would cancel. This method would allow for some relaxation of the σ electrons and should give an excitation energy lower than the STA. However, preliminary open-shell calculations in this Laboratory and others (e.g., see Ref. 17) indicate that the relaxation of the core electrons has a small effect on the excitation energy and the oscillator strength. These results emphasize that the important coupling is due to the residual σ–π interaction, i.e., it is a correlation effect.

As a brief outline of the remainder of the paper, in Sec. II we discuss the main ideas of second quantization and then derive the equations related to the various approximations to $A^+(E)$. In Sec. III the results of the calculations on ethylene are presented in detail. In Sec. IV we discuss the results and comment on their interpretation.

II. THEORY

The electronic Hamiltonian for the molecular system is, in atomic units,

$$\mathcal{H}=\sum_i[-\tfrac{1}{2}\nabla_i^2-(\sum_\alpha Z_\alpha/r_{\alpha i})]+\tfrac{1}{2}\sum_i\sum_j r_{ij}^{-1} \quad (4a)$$

$$=\sum_i H_i+\tfrac{1}{2}\sum_i\sum_j v_{ij}. \quad (4b)$$

In the Hartree–Fock approximation we replace the electronic interaction term, $\frac{1}{2}\sum_j v_{ij}$, by an effective one-particle potential, V_i. The lowest N eigenfunctions of the new Hamiltonian

$$(H+V)\mid i\rangle=\epsilon_i\mid i\rangle \quad (5)$$

are then combined into a Slater determinant in order to form the Hartree–Fock molecular wavefunction, $\mid \mathrm{HF}\rangle$.

For molecular systems explicit numerical solution of the Hartree–Fock equations is intractable and an additional approximation is required; namely, that the molecular orbital, $\mid i\rangle$, can be satisfactorily approximated by a linear combination of atomic orbitals centered on the various nuclei (the LCAO approximation). The Hartree–Fock, or molecular-orbital, limit can, thus, be achieved only through the use of large basis sets.

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[16] S. Huzinaga, J. Chem. Phys. 36, 453 (1962).

[17] J. W. Moskowitz and M. C. Harrison, J. Chem. Phys. 42, 1726 (1965); J. S. Schulman, J. W. Moskowitz, and C. Hollister, J. Chem. Phys. 46, 2759 (1967).

Combining Eqs. (4b) and (5) the complete electronic Hamiltonian can be written as

$$\mathcal{H}=\sum_i(H_i+V_i)+\sum_i(\tfrac{1}{2}\sum_j v_{ij}-V_i). \qquad (6)$$

The last two terms comprise the residual interaction and give rise to electronic correlation.

In the notation of second quantization[18] the Hamiltonian is

$$\mathcal{H}=\sum_i \epsilon_i a_i^+ a_i+\tfrac{1}{2}\sum_{ijkl}\mathbf{V}_{ijkl}a_j^+a_i^+a_ka_l - \sum_{jk\beta}(\mathbf{V}_{\beta j\beta k}-\mathbf{V}_{\beta jk\beta})a_j^+a_k, \qquad (7)$$

where we have introduced the explicit form of the Hartree–Fock one-particle potential, V_i. The operators a_i^+ and a_i are the creation and annihilation operators. The operator a_i^+ acting on a state puts an electron into level i while a_i does just the reverse. The usefulness of this "occupation number" representation is in part due to the fact that in this new representation we can make reasonable approximations which are very difficult to formulate in the coordinate representation.

The integrals $\mathbf{V}_{ijkl}$ are defined by

$$\mathbf{V}_{ijkl}=\iint\phi_i^*(1)\phi_j^*(2)r_{12}^{-1}\phi_k(1)\phi_l(2)dv_1dv_2,$$

the ϕ_i's denoting the molecular spin orbitals. In this equation and the ones to follow, we denote by the subscripts

$\alpha, \beta, \gamma, \delta, \cdots$	single-particle states occupied in the Hartree–Fock ground state (i.e., hole states),
$m, n, p, q, \cdots$	single-particle states unoccupied in the Hartree–Fock ground state (i.e., particle states),
$i, j, k, l, \cdots$	any state (either particle or hole).

If we define the Fermi level, ϵ_F (we use it just for vocabulary purposes), as being the uppermost level which is occupied in the Hartree–Fock ground state, then in the Hartree–Fock approximation the orbital occupation numbers are given by

$$n_i=1, \qquad \epsilon_i\leq\epsilon_F;$$

$$n_i=0, \qquad \epsilon_i>\epsilon_F.$$

These are just the expectation values of the number operators $\hat{n}_i=a_i^+a_i$ over the HF ground state. A transition will then be defined as removing an electron from below the Fermi level and placing it above.

We now need the precise form of the excitation operator, $S^+(E)$, in second quantization. But, before doing this we require a further property of the exact excitation operator. Denoting the eigenstates of the Hamiltonian H by $|0\rangle$, $|E\rangle$, etc., the equations defining the excitation operator $A^+(E)$ are just Eqs. (1a) and (1b). Taking the Hermitian conjugate of Eq. (1), we can derive a relationship connecting the true ground state and the Hermitian conjugate of the excitation operator, namely,

$$A(E)\ |0\rangle=0. \qquad (8)$$

This property of $A(E)$ will be used frequently and places restrictions on the choice of the approximate excitation operator, $S^+(E)$; i.e., given an approximate $|0\rangle$, $S^+(E)$ must be such that its Hermitian conjugate satisfies the above equation and vice versa.

Let us now define a particle–hole creation operator

$$C^+(m\alpha)=a_m^+a_\alpha \qquad (9a)$$

and the corresponding destruction operator

$$C(m\alpha)=a_\alpha^+a_m. \qquad (9b)$$

These operators will be the basic building blocks used to construct the various approximations to the excited-state operator; for example,

$$C^+(m\alpha)\ |\mathrm{HF}\rangle=\left|{}^{m}_{\alpha}\right\rangle,$$

a Slater determinant derived from the HF ground state by replacing the orbital $|\alpha\rangle$ by the virtual orbital $|m\rangle$. With these definitions, the particle–hole creation and destruction operators satisfy the following commutation relations:

$$[C^+(m\alpha),C^+(n\beta)]=[C(m\alpha),C(n\beta)]=0, \qquad (10a)$$

$$[C(m\alpha),C^+(n\beta)]=\delta_{mn}\delta_{\alpha\beta}-\delta_{\alpha\beta}a_n^+a_m-\delta_{mn}a_\beta^+a_\alpha, \qquad (10b)$$

whereas the operators a_i^+ and a_i satisfy the anticommutation relation

$$\{a_i^+, a_j^+\}=\{a_i, a_j\}=0, \qquad (11a)$$

$$\{a_i^+, a_j\}=\delta_{ij}. \qquad (11b)$$

The eigenvalue equations for the various forms of $S^+(E)$ can all be derived from a consideration of the equation[19]

$$\langle E\,|\,(E-\mathcal{H})C^+(m\alpha)\ |0\rangle=0, \qquad (12)$$

which after a little manipulation becomes

$$(E-E_0)\langle E\,|\,C^+(m\alpha)\ |0\rangle-\langle E\,|\,[\mathcal{H},C^+(m\alpha)]\,|0\rangle=0. \qquad (13)$$

Using the property of the excitation operator, Eq. (1), and its Hermitian conjugate, Eq. (8), the above can

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[18] A concise discussion of the formalism of second quantization may be found in L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory* (Pergamon Press Ltd., London, 1958), pp. 215–223.

[19] The derivation given here follows closely that of Altick and Glassgold, Ref. 8.

be rewritten as

$$(E-E_0)\langle 0\,|\,[A(E),C^+(m\alpha)]\,|\,0\rangle$$
$$-\langle 0\,|\,\{A(E),[\mathcal{H},C^+(m\alpha)]\}\,|\,0\rangle=0. \quad (14)$$

Note the way in which the pertinent eigenvalues appear, as $\Delta E=E-E_0$. One need only postulate an approximate excitation operator and a consistent ground state; the above then provides the necessary equations for calculating the wavefunction and excitation energy of the excited state.

From Eq. (14) we see that all of the subsequent derivations will have one thing in common—the commutator $[\mathcal{H}, C^+(m\alpha)]$, which is independent of our choice of $S^+(E)$. Using the second quantized form of the Hamiltonian, we find that

$$[\mathcal{H},C^+(m\alpha)]=(\epsilon_m-\epsilon_\alpha+\mathbf{V}_{m\alpha\alpha m}-\mathbf{V}_{m\alpha m\alpha})C^+(m\alpha)+\sum_{(n\beta)}{}'(\mathbf{V}_{\alpha nm\beta}-\mathbf{V}_{\alpha n\beta m})C^+(n\beta)+\sum_{(n\beta)}(\mathbf{V}_{\alpha\beta mn}-\mathbf{V}_{\alpha\beta nm})C(n\beta)+Q, \quad (15)$$

where[20]

$$\begin{aligned}Q=&\sum_{(\delta,\gamma)}(\mathbf{V}_{\alpha\delta m\gamma}-\mathbf{V}_{\alpha\delta\gamma m})C^+(\delta\gamma)+\sum_{(p,r)}(\mathbf{V}_{\alpha pmr}-\mathbf{V}_{\alpha prm})C^+(pr)\\&-\tfrac{1}{2}\sum_{ijk}(\mathbf{V}_{ijkm}-\mathbf{V}_{ijmk})a_\alpha a_j{}^+a_i{}^+a_k+\tfrac{1}{2}\sum_{jkl}(\mathbf{V}_{\alpha jkl}-\mathbf{V}_{j\alpha kl})a_m{}^+a_j{}^+a_ka_l\\&-\sum_{(\beta\delta)}(\mathbf{V}_{\beta\delta\beta m}-\mathbf{V}_{\beta\delta m\beta})C^+(\delta\alpha)-\sum_{(\beta n)}(\mathbf{V}_{\beta n\beta m}-\mathbf{V}_{\beta nm\beta})C^+(n\alpha)\\&+\sum_{(\beta\delta)}(\mathbf{V}_{\beta\alpha\beta\delta}-\mathbf{V}_{\beta\alpha\delta\beta})C^+(m\delta)+\sum_{(\beta n)}(\mathbf{V}_{\beta\alpha\beta n}-\mathbf{V}_{\beta\alpha n\beta})C^+(mn).\end{aligned} \quad (16)$$

This splits the commutator into two groups: the first group contains all the single particle–hole terms while Q contains no net single particle–hole terms but contains interactions which might be described as hole–hole $[C^+(\delta\gamma)]$, particle–particle $[C^+(pr)]$, multiple particle–hole $[C^+(n\beta)C^+(p\gamma)]$, etc. In this paper we are only interested in excited states which can adequately be represented by an elementary transition or a linear combination of elementary transitions. Thus, in the above commutator only single particle–hole interactions are retained. We may now neglect Q and linearize the commutator to

$$\begin{aligned}[\mathcal{H},C^+(m\alpha)]\approx&(\epsilon_m-\epsilon_\alpha+\mathbf{V}_{m\alpha\alpha m}-\mathbf{V}_{m\alpha m\alpha})C^+(m\alpha)\\&+\sum_{(n\beta)}{}'(\mathbf{V}_{\alpha nm\beta}-\mathbf{V}_{\alpha n\beta m})C^+(n\beta)\\&+\sum_{(n\beta)}{}'(\mathbf{V}_{\alpha\beta mn}-\mathbf{V}_{\alpha\beta mn})C(n\beta).\end{aligned} \quad (17)$$

Note that (1) the above derivation has ignored spin, the resulting equations can be specialized for singlets and triplets in a final step and (2) the prime on the summations indicate exclusion of the term $(m\alpha)$.

In second quantization the dipole moment operator is

$$\mathbf{r}=\sum_{i,j}\mathbf{d}_{ij}a_i{}^+a_j,$$

where

$$\mathbf{d}_{ij}=\langle i\,|\,\mathbf{r}\,|\,j\rangle=\int\phi_i{}^*\mathbf{r}\phi_jdv.$$

Again, retaining only the particle–hole interactions, this reduces to

$$\mathbf{r}\approx\sum_{(m\alpha)}\mathbf{d}_{m\alpha}[C^+(m\alpha)+C(m\alpha)].$$

The dipole transition moment is defined as

$$\mathbf{D}=-\langle E\,|\,\mathbf{r}\,|\,0\rangle$$

or, using Eqs. (2) and (8),

$$\mathbf{D}=-\langle 0\,|\,[A(E),r]\,|\,0\rangle. \quad (18)$$

We are now in a position to derive the equations relating to the various approximations to the excited-state operator.

A. The Single-Transition Approximation[10]

In this approximation, the one most commonly used by chemists, the excited-state operator is represented by a single particle–hole creation operator, i.e.,

$$S^+(E)=C^+(m\alpha). \quad (19)$$

Thus, we speak of $\pi\rightarrow\pi^*$ transitions, $n\rightarrow\pi^*$ transitions, etc. However, this method, frequently called the frozen core approximation is too rigid; it constrains the orbitals to retain their ground-state form. It is hardly likely that the molecular orbitals which are consistent for the excited state are the same as those for the ground state.[21]

Using Eq. (17) and the commutators Eqs. (10a) and (10b), we find that Eq. (14) becomes

$$E-E_0=\epsilon_m-\epsilon_\alpha+\mathbf{V}_{m\alpha\alpha m}-\mathbf{V}_{m\alpha m\alpha}. \quad (20)$$

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[20] As given, it appears that Q contains single particle–hole interactions. However, when the commutator $[A(E),Q]$ is evaluated over the HF ground state, these particle–hole interactions are canceled by corresponding ones in the third and fourth terms of Eq. (16). Equation (16) was retained in its present form for convenience.

[21] S. R. LaPaglia and O. Sinanoğlu, J. Chem. Phys. 44, 1888 (1966).

Making the excited states eigenfunctions of spin, we get *for singlets*

$$
\begin{aligned}
{}^1E-E_0&=\epsilon_m-\epsilon_\alpha+2V_{m\alpha\alpha m}-V_{m\alpha m\alpha}\\
&=\epsilon_m-\epsilon_\alpha+2K_{m\alpha}-J_{m\alpha},
\end{aligned}
\tag{21a}
$$

and *for triplets*

$$
{}^3E-E_0=\epsilon_m-\epsilon_\alpha-J_{m\alpha},
\tag{21b}
$$

which are the equations derived by Roothaan in 1951.[10] Note that the V_{ijkl} are defined in terms of molecular orbitals.

Using Eqs. (18) and (19) the dipole transition moment is

$$
{}^1\mathbf{D}_{m\alpha}=-\sqrt{2}\langle m\mid \mathbf{r}\mid \alpha\rangle=-\sqrt{2}\,\mathbf{d}_{m\alpha},
\tag{22a}
$$

$$
{}^3\mathbf{D}_{m\alpha}=0,
\tag{22b}
$$

where the superscript denotes the spin multiplicity.

In the derivation of the excitation energies and transition moments for the singlet and triplet states, we have assumed that the molecular orbitals involved are nondegenerate, which is the case for ethylene. If this is not true, say for acetylene, then the appropriate modifications must be made. In any case Eq. (19) is the starting point.

B. The Tamm–Dancoff Approximation[1,9]

In this approximation we assume that the excited state can be adequately represented by some linear combination of single-particle excitations of the appropriate symmetry. The net effect of this is to allow, in some restricted way, for the rearrangement of the total charge density during the excitation. On the basis of chemical intuition we would expect that the above linear combination would have a major component which defines the essentials of the excitation. This allows us to retain in a limited sense the classification of transitions as being π→π* etc., but this is certainly not required. The effect of the minor components on the excitation energy and transition moment is a matter which can best be settled by numerical calculation, although they had previously been assumed small unless degeneracy was involved. Certainly on the basis of the one-electron levels one might not have expected these minor components to have the effect we soon find. It is the coupling together of many of these excitations that leads to a modification of the lowest-lying state of ethylene.

The excitation operator is

$$
S^+(E)=\sum_{(m\alpha)}g(m\alpha;E)C^+(m\alpha).
\tag{23}
$$

Use of Eqs. (17) and (14) and the commutator relations for the particle–hole operators gives the eigenvalue equation to be satisfied by the particle–hole amplitudes, $g(m\alpha;E)$,

$$
[\epsilon_m-\epsilon_\alpha+\mathbf{V}_{m\alpha\alpha m}+\mathbf{V}_{m\alpha m\alpha}-(E-E_0)]g(m\alpha;E)+\sum_{(n\beta)}{}'(\mathbf{V}_{\alpha nm\beta}-\mathbf{V}_{\alpha n\beta m})g(n\beta;E)=0.
\tag{24}
$$

For convenience the designation "E" in the particle–hole amplitudes is dropped. Specializing the above to describe eigenfunctions of spin as before, we get

for singlets:

$$
[\epsilon_m-\epsilon_\alpha+2V_{m\alpha\alpha m}-V_{m\alpha m\alpha}-({}^1E-E_0)]g(m\alpha)+\sum_{(n\beta)}{}'(2V_{\alpha nm\beta}-V_{\alpha n\beta m})g(n\beta)=0
\tag{25a}
$$

and *for triplets*:

$$
[\epsilon_m-\epsilon_\alpha-V_{m\alpha m\alpha}-({}^3E-E_0)]g(m\alpha)-\sum_{(n\beta)}{}'(V_{\alpha n\beta m})g(n\beta)=0.
\tag{25b}
$$

These are just the equations derived by Herzenberg *et al.*[9] in their semiempirical calculation, including the σ electrons, on the spectra of ethylene.

The transition moment in this approximation is

$$
{}^1\mathbf{D}_{\mathrm{TDA}}=\sqrt{2}\sum_{(m\alpha)}g(m\alpha)\,\mathbf{d}_{m\alpha}.
\tag{26}
$$

These results could also have been obtained by a linear variational procedure. If we represent the excited state by

$$
|E\rangle=\sum_{(m\alpha)}g(m\alpha)\left|\begin{matrix}m\\ \alpha\end{matrix}\right\rangle
\tag{27}
$$

and apply the variational principle to determine the amplitudes $g(m\alpha)$, Eq. (24) would result.

C. The Random-Phase Approximation[5,8]

Using the language of CI, the ground-state wavefunction to first order is represented by the expansion

$$
|0\rangle=C_0\,|\,\mathrm{HF}\rangle+\sum_{(m\alpha)}\sum_{(n\beta)}C^{mn}_{\alpha\beta}\left|\begin{matrix}mn\\ \alpha\beta\end{matrix}\right\rangle,
\tag{28}
$$

where

$$
\left|\begin{matrix}mn\\ \alpha\beta\end{matrix}\right\rangle
$$

is a double excitation from the orbitals occupied in the HF ground state ($\alpha\beta$) to the virtual orbitals (mn). We still represent the excited state as being a linear combination of single-particle transitions except that now, using the above ground state, a single-particle transition may be "obtained" in two ways: (1) by exciting from the HF ground state [the associated operator being $C^+(m\alpha)$] or (2) by de-exciting from one of the doubly excited components of the true ground state [the associated operator being $C(n\beta)$]. In view of this we would expect that a better approximation to the excitation operator would be

$$S^{\dagger}(E)=\sum_{(m\alpha)}[g(m\alpha;E)C^{+}(m\alpha)-h(m\alpha;E)C(m\alpha)]. \tag{29}$$

Examination of the commutators in Eqs. (3a) and (17) shows that this approximation takes into account all of the single particle-hole terms. In this case, also, there will be an equation analogous to Eq. (14) involving $C(m\alpha)$.

Using the resulting Eqs. (14) and the commutators for the particle-hole operators, we get the set of coupled equations

$$[\epsilon_m-\epsilon_\alpha+\mathbf{V}_{m\alpha\alpha m}-\mathbf{V}_{m\alpha m\alpha}-(E-E_0)]g(m\alpha)+\sum_{(n\beta)}{}'(\mathbf{V}_{\alpha nm\beta}-\mathbf{V}_{\alpha n\beta m})g(n\beta)+\sum_{(n\beta)}(\mathbf{V}_{\alpha\beta mn}-\mathbf{V}_{\alpha\beta nm})h(n\beta)=0, \tag{30a}$$

$$[\epsilon_m-\epsilon_\alpha+\mathbf{V}_{m\alpha\alpha m}-\mathbf{V}_{m\alpha m\alpha}+(E-E_0)]h(m\alpha)+\sum_{(n\beta)}{}'(\mathbf{V}_{\alpha nm\beta}-\mathbf{V}_{\alpha n\beta m})h(n\beta)+\sum_{(n\beta)}(\mathbf{V}_{\alpha\beta mn}-\mathbf{V}_{\alpha\beta nm})g(n\beta)=0. \tag{30b}$$

Specializing these equations for singlets and triplets in the usual way leads to

for singlets:

$$[\epsilon_m-\epsilon_\alpha+2V_{m\alpha\alpha m}-V_{m\alpha m\alpha}-({}^1E-E_0)]g(m\alpha)+\sum_{(n\beta)}{}'(2V_{\alpha nm\beta}-V_{\alpha n\beta m})g(n\beta)+\sum_{(n\beta)}(2V_{\alpha\beta mn}-V_{\alpha\beta nm})h(n\beta)=0, \tag{31a}$$

$$[\epsilon_m-\epsilon_\alpha+2V_{m\alpha\alpha m}-V_{m\alpha m\alpha}+({}^1E-E_0)]h(m\alpha)+\sum_{(n\beta)}{}'(2V_{\alpha nm\beta}-V_{\alpha n\beta m})h(n\beta)+\sum_{(n\beta)}(2V_{\alpha\beta mn}-V_{\alpha\beta nm})g(n\beta)=0, \tag{31b}$$

and *for triplets*:

$$[\epsilon_m-\epsilon_\alpha-V_{m\alpha m\alpha}-({}^3E-E_0)]g(m\alpha)-\sum_{(n\beta)}{}'V_{\alpha n\beta m}g(n\beta)-\sum_{(n\beta)}V_{\alpha\beta nm}h(n\beta)=0, \tag{31c}$$

$$[\epsilon_m-\epsilon_\alpha-V_{m\alpha m\alpha}+({}^3E-E_0)]h(m\alpha)-\sum_{(n\beta)}{}'V_{\alpha n\beta m}h(n\beta)-\sum_{(n\beta)}V_{\alpha\beta nm}g(n\beta)=0. \tag{31d}$$

These equations can be written in matrix notation as

$$\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ -\mathbf{B} & -\mathbf{A}\end{pmatrix}\begin{pmatrix}\mathbf{G}\\ \mathbf{H}\end{pmatrix}=\Delta E\begin{pmatrix}\mathbf{G}\\ \mathbf{H}\end{pmatrix}, \tag{32}$$

where for the singlet state

$$\mathbf{A}(m\alpha,m\alpha)=\epsilon_m-\epsilon_\alpha+2V_{m\alpha\alpha m}-V_{m\alpha m\alpha}, \tag{33a}$$

$$\mathbf{A}(m\alpha,n\beta)=2V_{\alpha nm\beta}-V_{\alpha n\beta m}, \tag{33b}$$

$$\mathbf{B}(m\alpha,n\beta)=2V_{\alpha\beta mn}-V_{\alpha\beta nm}, \tag{33c}$$

and a corresponding set for the triplet.

Comparing the above equations to those derived in the previous section, we note that the TDA involves only the matrix **A**, and the STA only the diagonal elements of A. The **B** matrix allows for the effect of the doubly excited components of the true ground state on the singly excited state.

From Eq. (32) we see that the excitation energies are the eigenvalues of a non-Hermitian matrix. Because of this the eigenvalues and eigenvectors have some peculiar properties which we now discuss.

The matrix form of the RPA equations indicates that negative eigenvalues occur with the same magnitude as the positive eigenvalues. To see this, take the Hermitian conjugate of Eq. (32) to get

$$\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ -\mathbf{B} & -\mathbf{A}\end{pmatrix}\begin{pmatrix}\mathbf{H}\\ \mathbf{G}\end{pmatrix}=-\Delta E\begin{pmatrix}\mathbf{H}\\ \mathbf{G}\end{pmatrix}. \tag{34}$$

Thus, the eigenvectors for the negative eigenvalues are identical to those of the positive eigenvalues with the roles of **H** and **G** interchanged. The requirement that the excited states be orthonormal

$$\langle E\mid E'\rangle=\delta_{EE'} \tag{35a}$$

leads to

$$\langle 0\mid[A(E),A^{+}(E')]\mid 0\rangle=\delta_{EE'} \tag{35b}$$

or

$$\sum[g(m\alpha;E)g(m\alpha;E')-h(m\alpha;E)h(m\alpha;E')]=\delta_{EE'}. \tag{35c}$$

The particle-hole amplitudes are, thus, normalized to an indefinite metric. Last, we note that the excitation energies could be complex. However, because of the physical interpretation of these eigenvalues we are only concerned with those which have $\operatorname{Im}(\Delta E)=0$.

The above is the random-phase approximation as it usually is presented in the literature.[5,6,9] We would now like to pause and elaborate on the derivation of the RPA equations. The origin of the non-Hermiticity of the matrix then becomes apparent.

In deriving the RPA equations we have assumed for the ground state to first order

$$\mid 0\rangle=C_0\mid \mathrm{HF}\rangle+\sum C_d\mid d\rangle, \tag{36a}$$

that

$$C_0\approx 1,\qquad C_d\ll 1. \tag{36b}$$

This allows us to use the ground-state approximation,

TABLE II. Wavefunction of ethylene.[a]

MO[b]	Orbital energy	Coefficients H1 $2p_x$C1	 H2 $2p_y$C1	 H3 $1s$C2	 H4 $2s$C2	 $1s$C1 $2p_z$C2	 $2s$C1 $2p_x$C2	 $2p_z$C1 $2p_y$C2
$1a_g(1a_g)$	−11.3391	−0.004420 0.	−0.004420 0.	−0.004420 0.703982	−0.004420 0.014810	0.703982 0.002067	0.014810 0.	−0.002067 0.
$1b_{1u}(1b_{3u})$	−11.3384	−0.004461 0.	−0.004461 0.	0.004461 −0.703805	0.004461 −0.023659	0.703805 0.003673	0.023659 0.	0.003673 0.
$2a_g(2a_g)$	− 1.0419	0.080301 0.	0.080301 0.	0.080301 −0.161837	0.080301 0.479569	−0.161837 −0.110549	0.479569 0.	0.110549 0.
$2b_{1u}(2b_{3u})$	− 0.8025	0.206081 0.	0.206081 0.	−0.206081 0.126147	−0.206081 −0.431860	−0.126147 −0.203934	0.431860 0.	−0.203934 0.
$1b_{3u}(1b_{2u})$	− 0.6661	0.251413 0.399054	−0.251413 0.	0.251413 0.	−0.251413 0.	0. 0.	0. 0.399054	0. 0.
$3a_g(3a_g)$	− 0.5908	−0.207729 0.	−0.207729 0.	−0.207729 −0.011250	−0.207729 0.025045	−0.011250 −0.512543	0.025045 0.	0.512543 0.
$1b_{2g}(1b_{1g})$	− 0.5292	0.367882 0.408586	−0.367882 0.	−0.367882 0.	0.367882 0.	0. 0.	0. −0.408586	0. 0.
$1b_{2u}(1b_{1u})$	− 0.4047	0. 0.	0. 0.628564	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.628564
$1b_{3g}(1b_{2g})$	0.2056	0. 0.	0. 0.825081	0. 0.	0. 0.	0. 0.	0. 0.	0. −0.825081
$4a_g(4a_g)$	0.4344	−0.669375 0.	−0.669375 0.	−0.669375 −0.101083	−0.669375 0.955990	−0.101083 0.515356	0.995990 0.	−0.515356 0.
$2b_{3u}(2b_{2u})$	0.4409	0.711080 −0.756979	−0.711080 0.	0.711080 0.	−0.711080 0.	0. 0.	0. −0.756979	0. 0.
$3b_{1u}(3b_{3u})$	0.4711	0.725739 0.	0.725739 0.	−0.725739 −0.132831	−0.725739 1.153837	0.132831 0.270117	−1.153837 0.	0.270117 0.
$2b_{2g}(2b_{1g})$	0.7179	0.727053 −1.019986	−0.727053 0.	−0.727053 0.	0.727053 0.	0. 0.	0. 1.019986	0. 0.
$4b_{1u}(4b_{3u})$	0.8037	0.105834 0.	0.105834 0.	−0.105834 0.094518	−0.105834 −0.992343	−0.094518 1.210833	0.992343 0.	1.210833 0.

[a] This table is from unpublished calculations by W. E. Palke and W. N. Lipscomb. To facilitate comparison with their previously published results, Ref. 3, the molecule here lies in the *xz* plane. For the remainder of this work the molecule has been rotated into the *xy* plane to agree with the usual spectroscopic notation.

[b] The symmetry of the orbitals for the molecule rotated into the *xy* plane are enclosed in parentheses. Note that in Ref. 3, the b_{1u} orbitals were incorrectly labeled as a_{1u} (private communication from W. E. Palke).

i.e., ignore products of the C_d's while retaining the terms linear in C_d. To evaluate the commutators in Eq. (14) over the state $|0\rangle$, we can then effectively use the Hartree–Fock ground state. Thus, only if the HF ground state closely represents the true ground state can we expect the RPA results to be valid.

From the form of the singlet and triplet RPA equations, we can see that the RPA is more likely to fail in locating a triplet than a singlet excited state. Specifically, for molecular calculations the appearance of this "instability" will depend on how closely the LCAO expansion approaches the HF limit; although in some pathological cases of strong mixing of the ground state with a doubly excited configuration, it may never disappear. Fortunately, the correction of this defect is straightforward: one need merely evaluate the commutators using the ground-state wavefunction to first order. This, however, assumes that the correlation coefficients, C_d, are known—just the difficulty that we were trying to bypass when we used the ground-state approximation. There is another, and more interesting, approach to the problem. From the definition of the excitation operator, we find that there is a mutual constraint which this operator and the ground-state wavefunction must satisfy, namely,

$$A(E)\,|0\rangle=0. \tag{8}$$

Given the form of the excitation operator, we merely look for a ground state which satisfies the above relation. For the RPA excitation operator the ground state is as given in Eq. (28) and equations can be derived which permit the calculation of the correlation coefficients, $C_{\alpha\beta}{}^{mn}$.[22] In nuclear physics this is known as the extended RPA.[23] Its applicability to molecular systems is presently under study.

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[22] E. A. Sanderson, Phys. Letters **19**, 141 (1965).

[23] K. Hara, Progr. Theoret. Phys. Kyoto **32**, 88 (1964); K. Ikeda, T. Udagawa, and H. Yamaura, *ibid.* **33**, 22 (1965).

TABLE III. The molecular integrals, V_{ijkl}, required for the treatment of the B_{3u} state of ethylene.[a]

i	j	k	l	V_{ijkl}	i	j	k	l	V_{ijkl}
9	9	8	8	0.486677	12	6	12	6	0.025382
11	9	8	7	−0.006293	14	6	12	6	0.010080
12	9	8	6	−0.000596	12	6	10	4	0.029903
14	9	8	6	0.018200	13	5	12	6	−0.016009
10	9	8	4	0.024901	12	6	12	3	−0.014651
13	9	8	5	−0.011451	14	3	12	6	−0.009848
12	9	8	3	−0.046558	14	6	14	6	0.089809
14	9	8	3	0.043314	14	6	10	4	0.045175
11	11	7	7	0.358632	14	6	13	5	−0.039177
12	11	7	6	−0.034885	14	6	12	3	−0.039565
14	11	7	6	−0.002028	14	6	14	3	0.047390
11	10	7	4	−0.055069	10	4	10	4	0.050754
13	11	7	5	0.117438	13	5	10	4	−0.034288
12	11	7	3	0.037165	12	3	10	4	−0.033584
14	11	7	3	−0.014081	14	3	10	4	0.009595
12	12	6	6	0.360222	13	5	13	5	0.048769
14	12	6	6	−0.015710	11	7	11	7	0.044318
12	10	6	4	0.109642	12	6	11	7	−0.020512
13	12	6	5	−0.027352	11	8	9	7	−0.007751
12	12	6	3	0.009487	12	8	9	6	0.006714
14	12	6	3	−0.035274	14	8	9	6	0.008209
14	13	6	5	−0.007745	10	8	9	4	0.027503
14	12	6	3	−0.035274	13	8	9	5	−0.009673
14	14	6	3	0.111471	12	8	9	3	−0.030172
10	10	4	4	0.359020	14	8	9	3	0.024716
13	10	5	4	−0.039745	12	7	11	6	−0.023760
12	10	4	3	−0.094796	14	7	11	6	−0.017414
14	10	4	3	−0.036816	11	4	10	7	−0.022275
13	13	5	5	0.391534	13	7	11	5	0.061154
13	12	5	3	0.055546	12	7	11	3	0.015003
14	13	5	3	−0.033708	14	7	11	3	−0.018506
12	12	3	3	0.359503	12	4	10	6	0.042439
14	12	3	3	−0.040165	13	6	12	5	−0.013004
14	14	3	3	0.537546	12	6	12	3	−0.014651
9	8	9	8	0.158394	14	6	12	3	−0.039565
11	7	9	8	−0.014897	14	4	10	6	0.016506
12	6	9	8	0.009200	14	5	13	6	−0.009401
14	6	9	8	0.092648	14	3	12	6	−0.009848
10	4	9	8	0.056091	14	6	14	3	0.047390
13	5	9	8	−0.050457	13	5	12	3	0.032140
12	3	9	8	−0.055192	14	3	13	5	−0.034339
14	3	9	8	0.060550	12	3	12	3	0.029072
14	14	6	6	0.499948	14	3	12	3	−0.025136
14	10	6	4	0.048800	14	3	14	3	0.060354
14	6	11	7	−0.014189	13	4	10	5	−0.016829
11	7	10	4	−0.027126	12	4	10	3	−0.030548
13	5	11	7	0.039152	14	4	10	3	−0.009334
12	3	11	7	0.023518	13	3	12	5	0.014030
14	3	11	7	−0.019405	14	5	13	3	−0.015973

[a] In this table,

$$V_{ijkl}=\iint \phi_i^*(1)\phi_j(1)r_{12}^{-1}\phi_k^*(2)\phi_l(2)dv_1dv_2.$$

This arrangement was chosen to coincide with that of the atomic integrals obtained from the LCAO MO SF calculation. The integrals are in atomic units.

For the RPA, the transition moment is

$$^1\mathbf{D}_{\mathrm{RPA}}=-\sqrt{2}\sum_{(m\alpha)}[g(m\alpha)+h(m\alpha)]\mathbf{d}_{m\alpha}. \tag{37}$$

For comparison with experiment we also calculate the oscillator strength of a transition. The oscillator strength, f, is defined by

$$f=\tfrac{2}{3}\Delta E\,|\,\mathbf{D}\,|^2, \tag{38}$$

where ΔE is the theoretically calculated excitation energy, and ΔE and $\mathbf{D}$ are both in atomic units.

Before closing this section we should point out that the RPA equations can be derived via time-dependent Hartree–Fock theory (TDHF).[24,25] However, the interpretation of the resulting wavefunctions from that viewpoint is not at all clear.[26] Also, the remedy of a breakdown in the theory, corresponding to the instability discussed here, cannot be implemented so easily as in the present approach.

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[24] M. A. Ball and A. D. McLachlan, Mol. Phys. **7**, 501 (1964).

[25] A. D. McLachlan, Rev. Mod. Phys. **36**, 844 (1964).

[26] D. J. Rowe, Nucl. Phys. **80**, 209 (1966).

TABLE IV. The single-particle transitions coupled to form the excited B_{3u} states of ethylene.

Transition[a] Symmetry	Transition[a] Numerical	Approximate description[b]	Singlet transition energy[c]
$1b_{1u}\rightarrow 1b_{2g}$	$8\rightarrow 9$	$\pi\rightarrow\pi^*$	11.98
$1b_{1g}\rightarrow 2b_{2u}$	$7\rightarrow 11$	CH→CH*	19.05
$3a_g\rightarrow 3b_{3u}$	$6\rightarrow 12$	CH$(\sigma)\rightarrow$CH*(σ^*)	20.47
$3a_g\rightarrow 4b_{3u}$	$6\rightarrow 14$	CH$(\sigma)\rightarrow\sigma^*$	29.23
$2b_{3u}\rightarrow 4a_g$	$4\rightarrow 10$	CH$(\sigma^*)\rightarrow$CH*(σ)	26.65
$1b_{2u}\rightarrow 2b_{1g}$	$5\rightarrow 13$	CH→CH*	29.66
$2a_g\rightarrow 3b_{3u}$	$3\rightarrow 12$	$\sigma\rightarrow$CH*(σ^*)	32.97
$2a_g\rightarrow 4b_{3u}$	$3\rightarrow 14$	$\sigma\rightarrow\sigma^*$	38.88

[a] The symmetry designation is that with the molecule in the *xy* plane. The numerical designation is used in the following table to identify the two-electron integrals.

[b] Except for the first transition, these descriptions are only qualitative since the orbitals are delocalized. The designation enclosed in parentheses refers to the minor component of the orbital.

[c] Calculated with Eq. (21a) of the text. The excitation energies are in electron volts.

III. RESULTS

To provide a concrete foundation for the theories discussed in this paper, we have carried out the full set of calculations on the ethylene molecule using the recent LCAO MO SCF wavefunction of Palke and Lipscomb (unpublished results, see Table II). The purposes of the calculation are: (1) to check the relevance of these theories for the calculation of the electronic spectra of molecular systems and (2) to rigorously investigate the proposal of Herzenberg *et al.*[9] that the coupling between the σ and π electrons in ethylene could have a profound effect on the lowest-lying excited states of that molecule. Their results were obtained in the TDA with a dipole–dipole approximation for $1/r_{12}$ and a semiempirical evaluation of the integrals which caused some skepticism about the strength of the observed coupling.

In Table II the wavefunction obtained by Palke and Lipscomb[12] for ethylene is given. The basis functions are Slater orbitals with orbitals exponents chosen by Slater's rules; this is in contrast to their published work[3] in which a hydrogen exponent of 1.2 was used. Table III lists the two-electron molecular integrals, V_{ijkl}, required for the calculation on the B_{3u} state. The atomic integrals are available upon request.

In Table IV are listed the eight excitations which are coupled together to form the excited B_{3u} states of ethylene. We have ignored any excitation of the 1*s* electrons as being energetically unfavorable; calculations on the other states showed that the contribution from the 1*s* electrons was indeed negligible.

Tables V and VI give the results of the calculations on the singlet and triplet states of symmetry B_{3u}. Excitation energies, transition moments, oscillator strengths, and wavefunctions (particle–hole amplitudes) for the STA, TDA, and RPA are given.

The STA values are comparable to those presented earlier for the π-electron calculations for the same assumptions are inherent in both, namely, a neglect of the effect of the excitation of a π electron on the remaining electrons in the molecule (the σ electrons in this case). The only difference is that in the LCAO MO SCF calculation the core potential is generated exactly (within the limited basis set used) in the ground-state calculation.

From the TDA results we immediately note the profound effect that the inclusion of the σ electrons has on both the excitation energy and the oscillator strength. It is just not possible to ignore the rearrangement of the σ core as is done in π-electron theory. It is quite polarizable. From the wavefunctions we can see why this interaction was not detected earlier. In the previous calculations which attempted to answer the question of σ–π separability,[27] the σ electrons which were considered were those of the carbon–carbon bond. Clearly, the electrons to be considered are those in the CH bonds for these are the ones most strongly coupled to the $\pi\rightarrow\pi^*$ transition.

As expected, the RPA results are merely a refinement of those of the TDA, bringing the calculated excitation

TABLE V. The lowest singlet state of ethylene of symmetry B_{3u}: 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	11.98	10.17	9.44
D[d]	1.87	1.71	1.49
f	1.03	0.73	0.51
Wavefunctions			
(m, α)	$g(m\alpha)$	$g(m\alpha)$	$g(m\alpha)$[e]
(9, 8)	1.000000	0.960329	0.966983
(11, 7)		0.056820	0.036436
(12, 6)		−0.033354	−0.023823
(14, 6)		−0.206246	−0.160605
(10, 4)		−0.119678	−0.087569
(13, 5)		0.093880	0.067878
(12, 3)		0.062356	0.041913
(14, 3)		−0.062177	−0.045988
			$h(m\alpha)$
(9, 8)			−0.098574
(11, 7)			0.006566
(12, 6)			0.000955
(14, 6)			−0.083727
(10, 4)			−0.032685
(13, 5)			0.032538
(12, 3)			0.029633
(14, 3)			−0.036484

[a] From Eqs. (21a), (22a), and (38) of the text.

[b] From Eqs. (25a), (26), and (38) of the text.

[c] From Eqs. (31a), (31b), (37), and (38) of the text.

[d] In atomic units. The dipole matrix elements were computed using the dipole-moment program of M. D. Newton and F. P. Boer as modified by R. Frank.

[e] Unnormalized, $\Sigma[g^2(m\alpha)-h^2(m\alpha)]=0.957\,785$; see Eq. (35c) of the text.

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[27] C. M. Moser, Trans. Faraday Soc. 49, 1239 (1953).

energy and oscillator strength into better agreement with experiment.

Because of the large

$$\begin{pmatrix} \pi^* & \bar{\pi}^* \\ \pi & \bar{\pi} \end{pmatrix}$$

component in the ground state, see Table VII, the conditions for the application of the RPA were not strictly satisfied and, as a result, the excitation energy of the triplet state became pure imaginary. The remedy of this situation, if it is worthwhile since the properties of triplet states are relatively easy to predict with just the STA, has been discussed previously and is not commented on further here. It is instructive to note, however, that the wavefunction of Moskowitz and Harrison,[17] which they believe approaches the (sp) limit, does not exhibit this instability.

Table VI. The lowest triplet state of ethylene of symmetry B_{3u}: excitation energies (in electron volts) and wavefunctions for the various approximations to the excited state.

	STA[a]	TDA[b]
ΔE	3.36	3.19
Wavefunctions		
(m, α)	$g(m\alpha)$	$g(m\alpha)$
(9, 8)	1.000000	0.995423
(11, 7)		−0.029092
(12, 6)		0.005806
(14, 6)		0.034536
(10, 4)		0.043743
(13, 5)		−0.024380
(12, 3)		−0.053773
(14, 3)		0.040760

[a] From Eq. (21b) of the text.
[b] From Eq. (25b) of the text.

In these calculations we did not make the assumptions and approximations that Herzenberg *et al.*[9] did. But, our results indicate that their conclusions are essentially correct. As a further test of their suggestion[9] that the effect of the particle–hole scattering terms is negligible, the calculation for the B_{3u} state was done neglecting those terms. The results were essentially the same as those obtained previously: the contribution from the σ core being appreciable.

The effect obtained for the transition moments is particularly striking. It has long been known that transition moments calculated by the simple MO method (STA) are off by a factor of 2 or so—the explanation being electronic correlation. As evidenced by this calculation, the inclusion of all particle–hole terms provides an adequate explanation of the above phenomena. The discrepancy is a result of neglecting the "unexcited" electrons in the molecule, e.g., the σ electrons in ethylene during a π-electron transition.

Table VII. Configuration interaction: inclusion of the

$$\begin{pmatrix} \pi^* & \bar{\pi}^* \\ \pi & \bar{\pi} \end{pmatrix}$$

component in the ground state of ethylene.

Required integrals (in a.u.)

$\epsilon_\pi = -0.4047$ $\epsilon_{\pi^*} = 0.2056$

$J_{\pi\pi} = 0.487271$

$J_{\pi^*\pi^*} = 0.500717$

$J_{\pi\pi^*} = 0.486677$ $K_{\pi\pi^*} = 0.158394$

Results

$E - E_{\mathrm{HF}} = -0.040518$ a.u.

Coefficients

C_0	0.968805
$C\begin{pmatrix} \pi^* & \bar{\pi}^* \\ \pi & \bar{\pi} \end{pmatrix}$	−0.247825

The program for diagonalizing the unsymmetric RPA matrix was provided by S. F. Persselin of Rocketdyne Division of the North American Aviation Company. With this program we were able to reproduce the required symmetry of the eigenvectors to eight significant figures by suitable adjustment of the optimization parameters and, hence, we feel that the performance of the program is satisfactory.

Finally, in Table VIII the lowest excitation energies for states of various symmetries are listed. Of particular interest are the two low-lying states of symmetry B_{2g} and B_{3g} which are also in the same region of the spectrum as the singlet B_{3u} state.

IV. DISCUSSION AND CONCLUSIONS

These results indicate that most of the essential features of an excitation are contained in the TDA with the RPA merely altering these values by small, but far from negligible, amounts. Within the scope of the TDA

Table VIII. Excitation energies for other low-lying excited states of ethylene.

	Excitation energies (in eV)		
State	STA[a]	TDA[b]	RPA[c]
$^3B_{2g}$	9.99	9.73	9.43
$^1B_{2g}$	10.76	10.47	10.32
$^3B_{3g}$	9.82	9.81	9.79
$^1B_{3g}$	10.46	10.44	10.44
$^3B_{1u}$	13.23	13.10	12.96
$^1B_{1u}$	14.24	14.11	14.10
$^3B_{2u}$	17.78	14.54	14.22
$^1B_{2u}$	19.58	18.69	18.67

[a] From Eqs. (21a) and (21b) in the text.
[b] From Eqs. (25a) and (25b) in the text.
[c] From Eqs. (31a), (31b), (32a), (32b) in the text.

we may draw an analogy between the excited molecule and a set of interacting oscillators. Calculation of the lowest excitation energy of a given symmetry then corresponds to a search for the lowest mode of the set of coupled oscillators, which, as expected on classical grounds, occurs at a lower frequency than that of any one of the oscillators.

As Herzenberg *et al.*[9] pointed out, the coupling together of many particle–hole excitations leads to a significant modification of the low-lying excited states of ethylene which can be interpreted in terms of a reduction in the effective interaction between the π electrons by the dynamic polarization of the other electrons. This reduction is primarily a result of long-range, interbond, correlations as is evidenced by the fact that the dipole approximation for the Coulomb potential was sufficient to reproduce the significant features of this effect. They also estimated that there may be a collective state of ethylene at about 50 eV. No indication of such a state was found in this calculation (one excitation corresponding to an excitation energy of 32 eV did have a heavy weighting in several elementary transitions; however, the oscillator strength was only 0.25).

On the basis of chemical intuition we would expect that many excitations would have a major component which essentially defines the excitation, thus allowing us to retain, in a limited sense, the classifications of excitations as being $\pi \rightarrow \pi^*$ etc. This is indeed the case for the lowest state of symmetry B_{3u} in ethylene, the $\pi \rightarrow \pi^*$ component comprising about 92% of the total wavefunction. However, the effect of the minor components of the excitation are far from being insignificant.

One of the assumptions of π-electron theory is that the σ core is invariant to the disposition of the π electrons, i.e., the σ electrons are little affected by the precise form of the π-electron wave-function. However, the π electrons are strongly coupled to the σ electrons such that a rearrangement of one causes a corresponding rearrangement of the other. Allowing in some crude fashion for the polarization of the σ core decreases the excitation energy by $\sim$15% and the oscillator strength by $\sim$30%. At the same time the TDA results provide a theoretical justification for the success of the Pariser–Parr–Pople method.[28] The net effect of the coupling between the particle–hole pairs is to decrease the interaction between the π electrons and justifies the use of empirical values for the matrix elements of π-electron theory smaller than the theoretical ones. By lowering the value of a certain integral, γ_{pp}, using spectroscopic arguments, Pariser[29] achieved this required decrease in the electronic interaction. Thus, the downgrading of certain integrals is justified by molecular considerations as well as the proposed atomic considerations.[30] From the above we note that in a molecule, the π electrons may be pictured as being immersed in a polarizable medium corresponding to the σ-electron density.[31] It might thus be possible to describe the effect of this polarizable medium on the π electrons by means of a microscopic dielectric constant. Herzenberg *et al.*[9] showed that within the set of approximations adopted by them, i.e., a dipole–dipole approximation for the Coulombic potential, that this indeed was the case—both the decrease in the excitation energy and the transition moment being explicable in terms of such a concept. This model can be rigorously justified by a selective summation of Feynman diagrams[32] or by a series of appropriate transformations on the Hamiltonian.[33] Investigation of the feasibility of this approach for the study of the spectra of larger π-electron systems is presently under way.

In contrast to the π-electron calculations, we note that the methods presented here have no effect on the calculated ionization potential. The calculated value of 10.82 eV is in excellent agreement with experiment (see Table I).

Also, of considerable interest is the application of the techniques presented here for the study of other molecules, e.g., acetylene, numerous diatomics,[34] etc. At the present time, the set of calculations presented herein is being rerun using the Gaussian wavefunction for ethylene which was calculated by Moskowitz and Harrison.[17] This will provide information on the sensitivity of the method to the accuracy of the ground-state wavefunction and, if the effects which have been shown to be operative here persist in the more detailed wavefunction, the results should provide a limit for the theoretical excitation energy and oscillator strength.

From a study of Table VIII in the last section, we see that in the STA four states lie below the $^1B_{3u}$ state while in the RPA no singlet state lies below it.[35] This

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[28] R. G. Parr, *Quantum Theory of Molecular Electronic Structure* (W. A. Benjamin, Inc., New York, 1963), Chap. 3.

[29] R. Pariser, J. Chem. Phys. **21**, 568 (1953).

[30] M. Orloff and O. Sinanoğlu, J. Chem. Phys. **43**, 49 (1965).

[31] Contrary to the traditional viewpoint, the π electrons are deeply immersed in the σ-electron density. See, for example, C. A. Coulson, N. H. March, and S. Altmann, Proc. Natl. Acad. Sci. (U.S.) **38**, 372 (1952); M. D. Newton, F. P. Boer, and W. N. Lipscomb, J. Am. Chem. Soc., **88**, 2367 (1966); A. C. Wahl, "Pictorial Studies of Molecules," Argonne National Lab. Tech. Rept. July, 1965. In these works it is shown that the σ-electron density exceeds that of the π electrons throughout most of the bonding region, including the region in which the π-electron density is greatest.

[32] D. Falkoff, in *Lecture Notes on the Many-Body Problem from the First Bergen International School of Physics—1961* (W. A. Benjamin, Inc., New York, 1962).

[33] R. Harris (private communication).

[34] For application of the STA see C. W. Sherr, J. Chem. Phys. **23**, 569 (1955); N_2; J. W. Richardson, *ibid.* **35**, 1829 (1961), N_2; H. Brion and C. Moser, *ibid.* **32**, 1194 (1960); CO; B. J. Ransil, *ibid.* **35**, 669 (1961); F_2, HF, Li_2, LiH, N_2, and others; and R. K. Nesbet, *ibid.* **43**, 4403 (1966); N_2, CO, BF. For applications of the TDA see H. Lefebvre-Brion, C. Moser, and R. K. Nesbet, *ibid.* **35**, 1702 (1961); CO.

[35] Note that this is in disagreement with the CI results of R. Polak and J. Paldus, Theoret. Chim. Acta **5**, 422 (1966), who obtained a reversal of the energy levels and found an excited singlet state ($^1B_{2g}$) much below $^1B_{3u}$. However, their use of the Mulliken approximation to evaluate the multicenter integrals negates much of the quantitative significance of the calculation.

is in contrast to the results of Robin *et al.*[36] who, with a set of Guassians augmented with expanded orbital exponents, find two states below $^1B_{3u}$, namely, $^1B_{1u}$ and $^3B_{1u}$. In our calculations the four states lying closest to the $^1B_{3u}$ state are of symmetry B_{3g} and B_{2g}, the former corresponding to the Berry[37] assignment of the mystery band of ethylene. The state proposed by Robin *et al.* for the mystery band, B_{1u}, is found to lie at rather high energies, ~14 eV, even in the RPA. Thus, our calculations cannot account for a mystery band lying below the $^1B_{3u}$ state. To prevent misinterpretation, however, it should be pointed out that because of the nature of the ground-state calculation (i.e., the use of a minimum basis set), the above results cannot provide a definitive answer to the question of the mystery band of ethylene.

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[36] M. B. Robin, R. R. Hart, and N. A. Kuebler, J. Chem. Phys. **44**, 1803 (1966).

[37] R. S. Berry, J. Chem. Phys. **38**, 1934 (1963).

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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 $\sim$0.5 eV. Similar results were obtained for the "$\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.

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* 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).

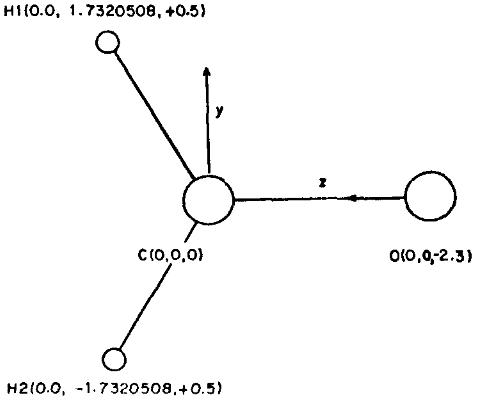

FIG. 1. The geometry of formaldehyde.

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]

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	$\sim10^{-4}$	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.

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," 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").

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

Transition[a] Numerical	Transition[a] Symmetry	Common designation[b]	Singlet energy STA[c]
7→9	$1b_1\rightarrow2b_1$	$\pi\rightarrow\pi^*$	14.89 eV
8→11	$2b_2\rightarrow3b_2$	$n(y_0)\rightarrow$CH*	22.98
6→10	$5a_1\rightarrow6a_1$	$\sigma\rightarrow$CH*	24.09
6→12	$5a_1\rightarrow7a_1$	$\sigma\rightarrow\sigma^*$	27.46
5→11	$1b_2\rightarrow3b_2$	CH→CH*	30.07
4→10	$4a_1\rightarrow6a_1$	CH→CH*	30.78
4→12	$4a_1\rightarrow7a_1$	CH→σ^*	34.47
3→10	$3a_1\rightarrow6a_1$	$O_{2s}\rightarrow$CH*	45.15
3→12	$3a_1\rightarrow7a_1$	$O_{2s}\rightarrow\sigma^*$	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.

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

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[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).

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[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:

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

$\mathcal{H}$ 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 $\mathcal{H}$. 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 $\alpha\rightarrow m$

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

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

and

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

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

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

for singlet states and

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

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		
$8\rightarrow9$	$2b_2\rightarrow2b_1$	$n(y_0)\rightarrow\pi^*$	4.03 eV
$5\rightarrow9$	$1b_2\rightarrow2b_1$	$\mathrm{CH}\rightarrow\pi^*$	13.40
$7\rightarrow11$	$1b_1\rightarrow3b_2$	$\pi\rightarrow\mathrm{CH}^*$	21.97

[a] See comments below Table II.

for triplet states. The ϵ_i denote orbital energies and

$$V_{ijkl}=\iint\phi_i^*(1)\phi_j^*(2)r_{12}^{-1}\phi_k(1)\phi_l(2)d\tau_1d\tau_2.$$

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

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

the expansion coefficients being solutions of the matrix equation

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

with

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

The transition moment is given by

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

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 $|\mathrm{HF}\rangle$, 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

$$|0\rangle=\mathrm{Co}\,|\mathrm{HF}\rangle+\sum_{(m\alpha)}\sum_{(n\beta)}C_{\alpha\beta}{}^{mn}\,|{}_{\alpha\beta}{}^{mn}\rangle$$

$$+(\text{higher order excitations}).\qquad(8)$$

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

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

the expansion coefficients being solutions of

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

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

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

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

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

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 "$n\rightarrow\pi^*$" transition): excitation energies (in electron volts) and wavefunctions for the various approximations to the excited state.

	STA[a]	TDA[b]	RPA[c]
ΔE	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 $\Sigma[g^2(m\alpha)-h^2(m\alpha)]=1.000000$, 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 $\pi \to \pi^*$ 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 $N \to V$, 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 "$n \to \pi^*$" transition): excitation energies (in electron volts) and wavefunctions for the various approximations to the excited state.

	STA[a]	TDA[b]	RPA[c]
ΔE	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.

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→9	$5a_1 \to 2b_1$	$\sigma \to \pi^*$	9.06 eV
4→9	$4a_1 \to 2b_1$	$\mathrm{CH} \to \pi^*$	20.38
7→10	$1b_1 \to 6a_1$	$\pi \to \mathrm{CH}^*$	20.46
7→12	$1b_1 \to 7a_1$	$\pi \to \sigma^*$	21.18
3→9	$3a_1 \to 2b_1$	$\mathrm{O}_{2s} \to \pi^*$	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 $\Delta E_{\mathrm{calc}} - \Delta E_{\mathrm{exptl}}$ 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 $\pi \to \pi^*$ 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.

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[12] For ethylene using methane optimized exponents, it was found that $E_{\mathrm{total}} = -77.8429$ 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.

[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 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.

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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.

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[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]:

$$\begin{aligned} q_{zz}(\mathrm{O}) &= (3z_{\mathrm{O}}^2 - r_{\mathrm{O}}^2)/r_{\mathrm{O}}^5, \\ q_{yy}(\mathrm{O}) &= (3y_{\mathrm{O}}^2 - r_{\mathrm{O}}^2)/r_{\mathrm{O}}^5, \\ r_{\mathrm{O}} \cos\theta_{\mathrm{O}} &= z_{\mathrm{O}}, \\ &r_{\mathrm{O}}^2, \\ f_z(\mathrm{O}) &= z_{\mathrm{O}}/r_{\mathrm{O}}^3, \\ f_z(\mathrm{C}) &= z_c/r_c^3, \\ f_\alpha(\mathrm{H}) &= \alpha_{\mathrm{H}}/r_{\mathrm{H}}^3, \\ f_\beta(\mathrm{H}) &= \beta_{\mathrm{H}}/r_{\mathrm{H}}^3, \\ &1/r_{\mathrm{H}}, \\ q_{\alpha\alpha}(\mathrm{D}) &= (3\alpha_{\mathrm{D}}^2 - r_{\mathrm{D}}^2)/r_{\mathrm{D}}^5, \\ q_{\alpha\beta}(\mathrm{D}) &= 3\beta_{\mathrm{D}}\alpha_{\mathrm{D}}/r_{\mathrm{D}}^5, \\ q_{\beta\beta}(\mathrm{D}) &= (3\beta_{\mathrm{D}}^2 - r_{\mathrm{D}}^2)/r_{\mathrm{D}}^5. \end{aligned} \tag{13}$$

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 $|_{\pi\pi}{}^{\pi*\pi*}\rangle$ 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.

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TABLES

Table I. A minimum Slater basis set representation of the π-electron system of ethylene.[a] The σ-core is the LCAO-MO SCF core for the ground state. All integrals are in atomic units.

Orbitals

$$\pi = 0.6286(2p_a) + 0.6286(2p_b)$$

$$\pi^* = 0.8251(2p_a) - 0.8251(2p_b)$$

Required integrals

$$\varepsilon_{\pi} = -0.4047 \qquad \varepsilon_{\pi^*} = 0.2056$$

$$J_{\pi\pi} = 0.4873$$

$$J_{\pi^*\pi^*} = 0.5007$$

$$J_{\pi\pi^*} = 0.4867 \qquad K_{\pi\pi^*} = 0.1584$$

$$X_{\pi\pi^*} = 1.32$$

[a] See reference 34.

Table II. Pi-electron calculations on the lowest $^{1,3}B_{3u}(\pi\pi^*)$ excited states of ethylene. Excitation energies and ionization potentials are given in electron volts (evs).

	Parr and Crawford[a]	Murai[b]	Huzinaga[c]	Expt'l
$E(^3B_{3u},T)$	3.10	4.60	4.45	4.6[d]
$E(^1B_{3u},V)$	11.50	11.20	7.28	7.6[e]
$f(^1B_{3u})$				∿0.3[e]
I.P.	11.90	8.80	8.52	10.52[e]

[a] Reference 59.

[b] Reference 60.

[c] Reference 61.

[d] Reference 57.

[e] Reference 58.

Table III. All-electron calculations on the lowest $^{1,3}B_{3u}(\pi\pi^*)$ states of ethylene. Excitation energies and ionization potentials are given in electron volts (evs).

	Moskowitz-Harrison[a]	Schulman-Moskowitz-Hollister[b]	Dunning-McKoy[c]			Kaldor-Shavitt[d]	Robin et al[e]	Expt'l[f]
			STA	TDA	RPA			
$\Delta E(^3B_{3u})$	3.67	4.19	3.36	3.19	—	3.40	—	4.6
$\Delta E(^1B_{3u})$	9.79	9.30	11.98	10.17	9.44	12.10	9.40	7.6
f	—	0.74	1.03	0.73	0.51	1.03	∿0.75	∿0.3
I.P.	10.35	10.17		10.82		10.04	10.20	10.52
Basis set	(5s3p/2s) Gaussian	(9s5p/3s) Gaussian		(2s1p/1s) Slater		(2s1p/1s) Slater	[4s2p/2s] Gaussian	

[a] Reference 9. [b] Reference 65. [c] Reference 34. [d] Reference 66.

[e] References 57 and 58.

Table IV. Contracted basis sets for the carbon atom in a (9s5p) primitive basis and the hydrogen atom in a (4s) primitive basis (ζ=1.2).[a] Contracted basis functions are separated by solid lines.

Carbon atom

Exponents	Coefficients 4s	Label	Exponents	Coefficients 2p	Label
4232.6100	0.002029	1s	18.1557	0.018534	2p
634.8820	0.015535		3.9864	0.115442	
146.0970	0.075411		1.1429	0.386206	
42.4974	0.257121		0.3594	0.640089	
14.1892	0.596555		0.1146	1.000000	2p'
1.9666	0.242517				
5.1477	1.000000	1s'	0.0365	1.000000	2p''
0.4962	1.000000	2s	0.0116	1.000000	2p'''
0.1533	1.000000	2s'	0.0037	1.000000	$2p^{iv}$

Table IV. 'continued'

Hydrogen atom

Exponents	Coefficients 2s	Label
19.2406	0.032828	
2.8992	0.231208	1s
0.6534	0.817238	
0.1776	1.000000	1s'

Table V. The orbital,energies and molecular orbital expansion coefficients for the occupied orbitals from the LCAO-MO SCF calculation on the ground state of ethylene.

Basis set: [4s2p/2s]

Orbital	$1a_{1g}$	$1b_{3u}$	$2a_{1g}$	$2b_{3u}$	$1b_{2u}$	$3a_{1g}$	$1b_{1g}$	$1b_{1u}(\pi)$
ε_i	-11.24107	-11.23955	-1.03863	-0.79604	-0.65547	-0.58022	-0.51483	-0.37260
Function								
1sH1	0.00034	0.00041	0.08790	0.14820	0.15395	0.12050	0.19239	0.0
1s'H1	0.00005	0.00000	0.01531	0.06906	0.09845	0.09728	0.14273	0.0
1sH2	0.00034	0.00041	0.08790	0.14820	-0.15395	0.12050	-0.19239	0.0
1s'H2	0.00005	0.00000	0.01531	0.06906	-0.09845	0.09728	-0.14273	0.0
1sH3	0.00034	-0.00041	0.08790	-0.14820	0.15395	0.12050	-0.19239	0.0
1s'H3	0.00005	0.00000	0.01531	-0.06906	0.09845	0.09728	-0.14273	0.0
1sH4	0.00034	-0.00041	0.08790	-0.14820	-0.15395	0.12050	0.19239	0.0
1s'H4	0.00005	0.00000	0.01531	-0.06906	-0.09845	0.09728	0.14273	0.0
1sC1	0.42481	0.42498	-0.09632	-0.07518	0.0	0.00607	0.0	0.0
1s'C1	0.30921	0.30946	-0.12960	-0.10219	0.0	0.00860	0.0	0.0
2sC1	0.00353	0.00308	0.35296	0.28115	0.0	-0.02481	0.0	0.0
2s'C1	-0.00021	-0.00118	0.20824	0.24543	0.0	0.02610	0.0	0.0
$2p_x$C1	0.00049	-0.00026	0.11893	-0.19284	0.0	-0.47970	0.0	0.0
$2p'_x$C1	-0.00012	-0.00036	-0.01497	-0.01063	0.0	-0.06520	0.0	0.0
$2p_y$C1	0.0	0.0	0.0	0.0	0.38004	0.0	0.37681	0.0
$2p'_y$C1	0.0	0.0	0.0	0.0	0.05888	0.0	0.12595	0.0

Table V. 'continued'

Orbital	$1a_{1g}$	$1b_{3u}$	$2a_{1g}$	$2b_{3u}$	$1b_{2u}$	$3a_{1g}$	$1b_{1g}$	$1b_{1u}(\pi)$
$2p_zC1$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.46063
$2p_z'C1$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.21710
1sC2	0.42481	-0.42498	-0.09632	0.07518	0.0	0.00607	0.0	0.0
1s'C2	0.30921	-0.30946	-0.12960	0.10219	0.0	0.00860	0.0	0.0
2sC2	0.00353	-0.00308	0.35296	-0.28115	0.0	-0.02481	0.0	0.0
2s'C2	-0.00021	0.00118	0.20824	-0.24543	0.0	0.02610	0.0	0.0
$2p_xC2$	-0.00049	-0.00026	-0.11893	-0.19284	0.0	0.47970	0.0	0.0
$2p_x'C2$	0.00012	-0.00036	0.01497	-0.01063	0.0	0.06520	0.0	0.0
$2p_yC2$	0.0	0.0	0.0	0.0	0.38004	0.0	-0.37681	0.0
$2p_y'C2$	0.0	0.0	0.0	0.0	0.05888	0.0	-0.12595	0.0
$2p_zC2$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.46063
$2p_z'C2$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.21710

Table VI. The orbital energies and molecular orbital expansion coefficients for the occupied orbitals from the LCAO-MO SCF calculation on the ground state of ethylene.

Basis set: [4s2p/2s] + R($3p_zC$)

Orbital	$1a_{1g}$	$1b_{3u}$	$2a_{1g}$	$2b_{3u}$	$1b_{2u}$	$3a_{1g}$	$1b_{1g}$	$1b_{1u}(\pi)$
ε_i	-11.24189	-11.24037	-1.03958	-0.79681	-0.65633	-0.58110	-0.51559	-0.37314
Function								
1sH1	0.00034	0.00041	0.08785	0.14819	0.15392	0.12053	0.19239	0.0
1s'H1	0.00005	0.00000	0.01527	0.06894	0.09817	0.09715	0.14252	0.0
1sH2	0.00034	0.00041	0.08785	0.14819	-0.15392	0.12053	-0.19239	0.0
1s'H2	0.00005	0.00000	0.01527	0.06894	-0.09817	0.09715	-0.14252	0.0
1sH3	0.00034	-0.00041	0.08785	-0.14819	0.15392	0.12053	-0.19239	0.0
1s'H3	0.00005	0.00000	0.01527	-0.06894	0.09817	0.09715	-0.14252	0.0
1sH4	0.00034	-0.00041	0.08785	-0.14819	-0.15392	0.12053	0.19239	0.0
1s'H4	0.00005	0.00000	0.01527	-0.06894	-0.09817	0.09715	0.14252	0.0
1sC1	0.42481	0.42498	-0.09633	-0.07520	0.0	0.00602	0.0	0.0
1s'C1	0.30922	0.30946	-0.12963	-0.10223	0.0	0.00853	0.0	0.0
2sC1	0.00354	0.00309	0.35312	0.28130	0.0	-0.02463	0.0	0.0
2s'C1	-0.00022	-0.00118	0.20812	0.24576	0.0	0.02632	0.0	0.0
$2p_xC1$	0.00049	-0.00026	0.11915	-0.19284	0.0	-0.47980	0.0	0.0
$2p_x'C1$	-0.00012	-0.00037	-0.01496	-0.01048	0.0	-0.06501	0.0	0.0
$2p_yC1$	0.0	0.0	0.0	0.0	0.38028	0.0	0.37708	0.0
$2p_y'C1$	0.0	0.0	0.0	0.0	0.05897	0.0	0.12588	0.0

Table VI. 'continued'

Orbital	$1a_{1g}$	$1b_{3u}$	$2a_{1g}$	$2b_{3u}$	$1b_{2u}$	$3a_{1g}$	$1b_{1g}$	$1b_{1u}(\pi)$
$2p_z$C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.46125
$2p_z'$C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.21102
$2p_z''$C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00809
$2p_z'''$C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00422
$2p_z^{iv}$ C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.00156
1sC2	0.42481	-0.42498	-0.09633	0.07520	0.0	0.00602	0.0	0.0
1s'C2	0.30922	-0.30946	-0.12963	0.10223	0.0	0.00853	0.0	0.0
2sC2	0.00354	-0.00309	0.35312	-0.28130	0.0	-0.02463	0.0	0.0
2s'C2	-0.00022	0.00118	0.20812	-0.24576	0.0	0.02632	0.0	0.0
$2p_x$C2	-0.00049	-0.00026	-0.11915	-0.19284	0.0	0.47980	0.0	0.0
$2p_x'$C2	0.00012	-0.00037	0.01496	-0.01048	0.0	0.06501	0.0	0.0
$2p_y$C2	0.0	0.0	0.0	0.0	0.38028	0.0	-0.37708	0.0
$2p_y'$C2	0.0	0.0	0.0	0.0	0.05897	0.0	-0.12588	0.0
$2p_z$C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.46125
$2p_z'$C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.21102
$2p_z''$C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00809
$2p_z'''$C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00422
$2p_z^{iv}$ C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.00156

Table VII. Electronic energies, total energies and orbital energies from the LCAO-MO SCF calculations on ethylene. All quantities are in atomic units.[a]

Basis set	[4s2p/2s] + R($3p_zC$)	[4s2p/2s]
Electronic energy	-111.3936	-111.3934
Total energy	-78.0111	-78.0109
$\varepsilon(1a_{1g})$	-11.2420	-11.2411
$\varepsilon(1b_{3u})$	-11.2405	-11.2395
$\varepsilon(2a_{1g})$	-1.0397	-1.0387
$\varepsilon(2b_{3u})$	-0.7969	-0.7961
$\varepsilon(1b_{2u})$	-0.6565	-0.6555
$\varepsilon(3a_{1g})$	-0.5812	-0.5802
$\varepsilon(1b_{1g})$	-0.5187	-0.5148
$\varepsilon(1b_{1u})$, 1π	-0.3731	-0.3726
$\varepsilon(2b_{1u})$, 2π	0.0088	0.4918
$\varepsilon(1b_{2g})$, $1\pi^*$	0.0122	0.1440
$\varepsilon(3b_{1u})$, 3π	0.0392	—
$\varepsilon(2b_{2g})$, $2\pi^*$	0.0456	0.6132
$\varepsilon(3b_{2g})$, $3\pi^*$	0.1141	—
$\varepsilon(4b_{1u})$, 4π	0.1503	—
$\varepsilon(4b_{2g})$, $4\pi^*$	0.2124	—
$\varepsilon(3b_{3u})$	0.2607	0.2611
$\varepsilon(4a_{1g})$	0.2862	0.2868
$\varepsilon(2b_{2u})$	0.3838	0.3844
$\varepsilon(4b_{3u})$	0.4004	0.4010
$\varepsilon(5a_{1g})$	0.4177	0.4182
$\varepsilon(3b_{2u})$	0.4351	0.4358
$\varepsilon(2b_{1g})$	0.4545	0.4549
$\varepsilon(5b_{1u})$, 5π	0.6580	—
$\varepsilon(3b_{1g})$	0.7048	0.7053

Table VII. 'continued'

$\varepsilon(5b_{2g})$, $5\pi^*$	0.7150	—
$\varepsilon(6a_{1g})$	0.7325	0.7333
$\varepsilon(5b_{3u})$	0.8911	0.8922
$\varepsilon(6b_{3u})$	1.1294	1.1302
$\varepsilon(7a_{1g})$	1.3051	1.3058
$\varepsilon(4b_{2u})$	1.4115	1.4122
$\varepsilon(7b_{3u})$	1.4406	1.4413
$\varepsilon(4b_{1g})$	1.7320	1.7326

[a] 1 a.u. of energy = 27.2107 e.v.

Table VIII. The one-electron properties of ethylene: the ground state in the [4s2p/2s], [4s2p/2s] + R($3p_zC$) and [4s3p/2s] Gaussian basis sets. All expectation values are in atomic units.

Basis set Properties[a,b]	[4s2p/2s]	[4s2p/2s] + R($3p_zC$)	[4s3p/2s]
$\langle x^2 \rangle_{CM}$	49.5867	49.6160	49.6435
$\langle y^2 \rangle_{CM}$	21.2688	21.2965	21.3057
$\langle z^2 \rangle_{CM}$	12.0636	12.1718	12.0172
$\langle r^2 \rangle_{CM}$	82.9191	83.0843	82.9664
Θ_{xx}(CM)	1.3859	1.4246	1.3244
Θ_{yy}(CM)	1.6025	1.6435	1.5708
Θ_{zz}(CM)	-2.9884	-3.0681	-2.8952
$\langle 1/r_H \rangle$	6.2531	6.2522	6.2538
$\langle 1/r_C \rangle$	18.5744	18.5737	18.5801
E_x(H1)	-0.0426	-0.0427	-0.0428
E_y(H1)	0.0672	0.0672	0.0685
E_x(C)	-0.0062	-0.0065	-0.0126
$q_{\alpha\alpha}$(H)	-0.3749	-0.3747	-0.3738
$q_{\beta\beta}$(H)	0.1805	0.1805	0.1791
q_{zz}(H)	0.1944	0.1942	0.1947
ϕ	0°22'	0°23'	0°18'
q_{xx}(C)	0.1424	0.1420	0.2359
q_{yy}(C)	0.1461	0.1472	0.1293
q_{zz}(C)	-0.2885	-0.2893	-0.3652
$\langle \delta(r-H) \rangle$	0.4274	0.4274	0.4285
$\langle \delta(r-C) \rangle$	119.5868	119.5879	119.5715

[a] See the text for a definition of the operators.

[b] The following abbreviations have been adopted CM = center of mass, H1 = hydrogen 1 and C = carbon

Table IX. The lowest singlet and triplet ($\pi\pi^*$) states of ethylene in the ISTA, TDA and RPA: excitation energies, transition moments and oscillator strengths.

Basis set: [4s2p/2s]

	ISTA	TDA	RPA
Singlet state: $V(^1B_{3u})$			
ΔE(ev)	9.29	8.19	7.71
D_x(a.u.)	-2.03	-1.79	-1.59
f	0.94	0.65	0.48
Triplet state: $T(^3B_{3u})$			
ΔE(ev)	3.47	3.36	—

Table X. The lowest singlet ($\pi\pi^*$) state of ethylene, V($^1B_{3u}$), in the ISTA, TDA and RPA: excitation energies, transition moments, oscillator strengths and particle-hole amplitudes.

Basis set: [4s2p/2s] + R($3p_zC$)

	ISTA	TDA	RPA	
ΔE(ev)	8.34	7.82	7.46	
D_x(a.u.)	-1.42	-1.67	-1.55	
f	0.41	0.54	0.44	
(m,α)[a]	g(mα)	g(mα)	g(mα)	h(mα)
(10,8)	-0.250468	-0.105781	-0.071451	0.000806
(12,8)	0.691152	0.448533	0.364520	-0.008731
(13,8)	0.676696	0.832210	0.856938	-0.051499
(15,8)	-0.023941	-0.248508	-0.339084	0.047914
(25,8)	0.032926	-0.011189	-0.036234	0.011959
(18,7)		-0.035701	-0.033288	-0.017173
(21,7)		0.084469	0.068970	0.027848
(30,7)		-0.006859	-0.006124	-0.004053
(16,6)		0.030111	0.028121	0.016077
(19,6)		0.037379	0.032260	0.009365
(27,6)		-0.101015	-0.087859	-0.055767
(28,6)		0.022247	0.020329	0.013639
(31,6)		0.011744	0.010409	0.005248
(22,5)		0.055212	0.044927	0.019576
(24,5)		-0.028736	-0.022554	-0.013156
(32,5)		-0.004129	-0.003072	-0.002580
(17,4)		-0.052889	-0.044262	-0.017811
(20,4)		-0.030509	-0.024493	-0.006061
(26,4)		-0.029806	-0.024493	-0.021823
(29,4)		0.010178	0.007933	0.005220
(16,3)		-0.039046	-0.031772	-0.017716
(19,3)		0.005008	0.001645	0.006630
(27,3)		0.021589	0.017119	0.020281
(28,3)		-0.030203	-0.025572	-0.015391
(31,3)		-0.007168	-0.007121	-0.002380

[a] The numerical designation refers to the position of the orbital in Table VII.

Table XI. The lowest triplet ($\pi\pi^*$) state of ethylene, T($^3B_{3u}$), in the ISTA and TDA: excitation energies and particle-hole amplitudes.

Basis set: [4s2p/2s] + R($3p_zC$)

	ISTA	TDA
ΔE(ev)	3.48	3.37
(mα)[a]	g(mα)	g(mα)
(10,8)	-0.016665	-0.016326
(12,8)	0.154796	0.152582
(13,8)	0.767107	0.762290
(15,8)	-0.601313	-0.602733
(25,8)	-0.160405	-0.163701
(18,7)		-0.016335
(21,7)		-0.010337
(30,7)		-0.006439
(16,6)		-0.006975
(19,6)		-0.011952
(27,6)		0.020961
(28,6)		-0.007095
(31,6)		-0.006355
(22,5)		-0.006861
(24,5)		0.014544
(32,5)		0.006472
(17,4)		0.027613
(20,4)		0.012879
(26,4)		-0.005034
(29,4)		-0.012764
(16,3)		0.025164
(19,3)		-0.028212
(27,3)		-0.032879
(28,3)		0.010230
(31,3)		-0.010327

[a] The numerical designation refers to the position of the orbital in Table VII.

Table XII. Orbital expansion coefficients for the π^*-orbital from the ISTA or frozen core wavefunctions.

Basis set: [4s2p/2s] + R($3p_z$C)

Orbital	$^1\pi^*$	$^3\pi^*$
Basis functions[a]		
$2p_z$C1	0.196536	0.564740
$2p'_z$C1	0.317532	0.528518
$2p''_z$C1	0.930933	0.066389
$2p'''_z$C1	1.608963	0.041982
$2p^{iv}_z$C1	0.042753	-0.026140
$2p_z$C2	-0.196536	-0.564740
$2p'_z$C2	-0.317532	-0.528518
$2p''_z$C2	-0.930933	-0.066389
$2p'''_z$C2	1.608963	-0.041982
$2p^{iv}_z$C2	0.042753	0.026140

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[a] See Table IV

Table XIII. A comparison of the singlet and triplet π^*-orbitals from the ISTA or frozen core wavefunction and the ground state π-orbital.

Basis set: $[4s2p/2s] + R(3p_zC)$

Property[a]	Ground state	Excited states	
	π	$^3\pi^*$	$^1\pi^*$
$\langle x^2 \rangle_{CM}$	2.1847	3.8852	27.2726 (6.8469)[b]
$\langle y^2 \rangle_{CM}$	0.9089	0.9265	8.7630 (1.4006)
$\langle z^2 \rangle_{CM}$	2.7268	2.7795	26.2889 (4.2019)
$\langle 1/r_C \rangle$	0.5303	0.5287	0.2164 (0.4355)
ε	-0.3731	-0.2454	-0.0665 (-0.0311)

[a] CM refers to the center of mass of ethylene and C refers to carbon 1.

[b] The values in parentheses are for the valence basis set.

Table XIV. The natural orbitals and natural orbital occupation numbers for the lowest ($\pi\pi^*$) singlet state of ethylene, $V(^1B_{3u})$.

Basis set: [4s2p/2s] + $R(3p_zC)$

Orbital	$1a_{1g}$	$1b_{3u}$	$2a_{1g}$	$2b_{3u}$	$1b_{2u}$	$3a_{1g}$	$1b_{1g}$	$1b_{1u}(\pi)$
Occ. no.	2.00000	2.00000	1.99835	1.99527	1.99610	1.98551	1.99153	1.03318
Function								
1sH1	0.00034	0.00041	0.12208	0.14819	0.15392	0.08570	0.19239	0.0
1s'H1	0.00005	0.00000	0.04583	0.06894	0.09817	0.08700	0.14252	0.0
1sH2	0.00034	0.00041	0.12208	0.14819	-0.15392	0.08570	-0.19239	0.0
1s'H2	0.00005	0.00000	0.04583	0.06894	-0.09817	0.08700	-0.14252	0.0
1sH3	0.00034	-0.00041	0.12208	-0.14819	0.15392	0.08570	-0.19239	0.0
1s'H3	0.00005	0.00000	0.04583	-0.06894	0.09817	0.08700	-0.14252	0.0
1sH4	0.00034	-0.00041	0.12208	-0.14819	-0.15392	0.08570	0.19239	0.0
1s'H4	0.00005	0.00000	0.04583	-0.06894	-0.09817	0.08700	0.14252	0.0
1sC1	0.42481	0.42498	-0.08922	-0.07520	0.0	0.03682	0.0	0.0
1s'C1	0.30922	0.30946	-0.11992	-0.10223	0.0	0.04994	0.0	0.0
2sC1	0.00354	0.00309	0.32623	0.28130	0.0	-0.13738	0.0	0.0
2s'C1	-0.00022	-0.00118	0.20546	0.24576	0.0	-0.04231	0.0	0.0
$2p_xC1$	0.00049	-0.00026	-0.04222	-0.19284	0.0	-0.49257	0.0	0.0
$2p_x'C1$	-0.00012	-0.00037	-0.03517	-0.01048	0.0	-0.05669	0.0	0.0
$2p_yC1$	0.0	0.0	0.0	0.0	0.38028	0.0	0.37708	0.0
$2p_y'C1$	0.0	0.0	0.0	0.0	0.05897	0.0	0.12588	0.0

Table XIV. 'continued'

Orbital	$1a_{1g}$	$1b_{3u}$	$2a_{1g}$	$2b_{3u}$	$1b_{2u}$	$3a_{1g}$	$1b_{1g}$	$1b_{1u}(\pi)$
$2p_z$C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.46125
$2p_z'$C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.21102
$2p_z''$C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00809
$2p_z'''$C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00422
$2p_z^{iv}$ C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.00156
1sC2	0.42481	-0.42498	-0.08922	0.07520	0.0	0.03682	0.0	0.0
1s'C2	0.30922	-0.30946	-0.11992	0.10223	0.0	0.04994	0.0	0.0
2sC2	0.00354	-0.00309	0.32623	-0.28130	0.0	-0.13738	0.0	0.0
2s'C2	-0.00022	0.00118	0.20546	-0.24576	0.0	-0.04231	0.0	0.0
$2p_x$C2	-0.00049	-0.00026	0.04222	-0.19284	0.0	0.49257	0.0	0.0
$2p_x'$C2	0.00012	-0.00037	0.03517	-0.01048	0.0	0.05669	0.0	0.0
$2p_y$C2	0.0	0.0	0.0	0.0	0.38028	0.0	-0.37708	0.0
$2p_y'$C2	0.0	0.0	0.0	0.0	0.05897	0.0	-0.12588	0.0
$2p_z$C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.46125
$2p_z'$C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.21102
$2p_z''$C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00809
$2p_z'''$C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00422
$2p_z^{iv}$ C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.00156

Table XIV. 'continued'

Orbital	$1b_{2g}(\pi^*)$	$3b_{3u}$	$2b_{2u}$	$4a_{1g}$	$2b_{1g}$	$4b_{3u}$
Occ. no.	0.96681	0.01448	0.00846	0.00472	0.00389	0.00164
Function						
1sH1	0.0	0.00252	-0.15873	-0.00627	0.00351	0.03330
1s'H1	0.0	-0.28899	-0.67549	0.64299	0.07056	-0.39426
1sH2	0.0	0.00252	0.15873	-0.00627	-0.00351	0.03330
1s'H2	0.0	-0.28899	0.67549	0.64299	-0.07056	-0.39426
1sH3	0.0	-0.00252	-0.15873	-0.00627	-0.00351	-0.03330
1s'H3	0.0	0.28899	-0.67549	0.64299	-0.07056	0.39426
1sH4	0.0	-0.00252	0.15873	-0.00627	0.00351	-0.03330
1s'H4	0.0	0.28899	0.67549	0.64299	0.07056	0.39426
1sC1	0.0	0.06990	0.0	0.07376	0.0	-0.09524
1s'C1	0.0	0.10560	0.0	0.12734	0.0	-0.15244
2sC1	0.0	-0.47382	0.0	-0.74747	0.0	0.98091
2s'C1	0.0	-0.83447	0.0	-0.35228	0.0	-0.90266
$2p_x$C1	0.0	-0.96654	0.0	0.31829	0.0	-0.39070
$2p'_x$C1	0.0	-0.67393	0.0	0.24091	0.0	-0.13548
$2p_y$C1	0.0	0.0	-0.35468	0.0	0.72737	0.0
$2p'_y$C1	0.0	0.0	1.19237	0.0	-1.42251	0.0

Table XIV. 'continued'

Orbital	$1b_{2g}(\pi^*)$	$3b_{3u}$	$2b_{2u}$	$4a_{1g}$	$2b_{1g}$	$4b_{3u}$
$2p_z$C1	0.35358	0.0	0.0	0.0	0.0	0.0
$2p_z'$C1	0.48755	0.0	0.0	0.0	0.0	0.0
$2p_z''$C1	0.80192	0.0	0.0	0.0	0.0	0.0
$2p_z'''$C1	0.62066	0.0	0.0	0.0	0.0	0.0
$2p_z^{iv}$ C1	-0.07966	0.0	0.0	0.0	0.0	0.0
1sC2	0.0	-0.06990	0.0	0.07976	0.0	0.09524
1s'C2	0.0	-0.10560	0.0	0.12734	0.0	0.15244
2sC2	0.0	0.47382	0.0	-0.74747	0.0	-0.98091
2s'C2	0.0	0.83447	0.0	-0.35228	0.0	0.90266
$2p_x$C2	0.0	-0.96654	0.0	-0.31829	0.0	-0.39070
$2p_x'$C2	0.0	-0.67393	0.0	-0.24091	0.0	-0.13548
$2p_y$C2	0.0	0.0	-0.35468	0.0	-0.72737	0.0
$2p_y'$C2	0.0	0.0	1.19237	0.0	1.42251	0.0
$2p_z$C2	-0.35358	0.0	0.0	0.0	0.0	0.0
$2p_z'$C2	-0.48755	0.0	0.0	0.0	0.0	0.0
$2p_z''$C2	-0.80192	0.0	0.0	0.0	0.0	0.0
$2p_z'''$C2	-0.62066	0.0	0.0	0.0	0.0	0.0
$2p_z^{iv}$ C2	0.07966	0.0	0.0	0.0	0.0	0.0

Table XV. The natural orbitals and natural orbital occupation numbers for the lowest ($\pi\pi^*$) triplet state, T($^3B_{3u}$), of ethylene.

Basis set: [4s2p/2s] + R($3p_zC$)

Orbital	$1a_{1g}$	$1b_{3u}$	$2a_{1g}$	$2b_{3u}$	$1b_{2u}$	$3a_{1g}$	$1b_{1g}$	$1b_{1u}(\pi)$
Occ. no.	2.00000	2.00000	1.99713	1.99887	1.99969	1.99940	1.99957	1.00527
Function								
1sH1	0.00034	0.00041	-0.05593	0.14819	0.15392	0.13827	0.19239	0.0
1s'H1	0.00005	0.00000	0.00879	0.06894	0.09817	0.09795	0.14252	0.0
1sH2	0.00034	0.00041	-0.05593	0.14819	-0.15392	0.13827	-0.19239	0.0
1s'H2	0.00005	0.00000	0.00879	0.06894	-0.09817	0.09795	-0.14252	0.0
1sH3	0.00034	-0.00041	-0.05593	0.14819	0.15392	0.13827	-0.19239	0.0
1s'H3	0.00005	0.00000	0.00879	0.06894	0.09817	0.09795	-0.14252	0.0
1sH4	0.00034	-0.00041	-0.05593	0.14819	-0.15392	0.13827	0.19239	0.0
1s'H4	0.00005	0.00000	0.00879	0.06894	-0.09817	0.09795	0.14252	0.0
1sC1	0.42481	0.42498	0.09491	-0.07520	0.0	-0.01756	0.0	0.0
1s'C1	0.30921	0.30946	0.12781	-0.10223	0.0	-0.02322	0.0	0.0
2sC1	0.00354	0.00309	-0.34852	0.28130	0.0	0.06190	0.0	0.0
2s'C1	-0.00022	-0.00118	-0.19548	0.24576	0.0	0.07610	0.0	0.0
$2p_xC1$	0.00049	-0.00026	-0.23216	-0.19284	0.0	-0.43648	0.0	0.0
$2p'_xC1$	-0.00012	-0.00037	-0.00127	-0.01048	0.0	-0.06670	0.0	0.0
$2p_yC1$	0.0	0.0	0.0	0.0	0.38028	0.0	0.37708	0.0
$2p'_yC1$	0.0	0.0	0.0	0.0	0.05898	0.0	0.12588	0.0

Table XV. 'continued'

Orbital	$1a_{1g}$	$1b_{3u}$	$2a_{1g}$	$2b_{3u}$	$1b_{2u}$	$3a_{1g}$	$1b_{1g}$	$1b_{1u}(\pi)$
$2p_z$C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.46125
$2p_z'$C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.21102
$2p_z''$C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00809
$2p_z'''$C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00422
$2p_z^{iv}$ C1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.00156
1sC2	0.42481	-0.42498	0.09491	0.07520	0.0	-0.01756	0.0	0.0
1s'C2	0.30921	-0.30946	0.12781	0.10223	0.0	-0.02322	0.0	0.0
2sC2	0.00354	-0.00309	-0.34852	-0.28130	0.0	0.06190	0.0	0.0
2s'C2	-0.00022	0.00118	-0.19548	-0.24576	0.0	0.07610	0.0	0.0
$2p_x$C2	-0.00049	-0.00026	0.23216	-0.19284	0.0	0.43648	0.0	0.0
$2p_x'$C2	0.00012	-0.00037	0.00127	-0.01048	0.0	0.06670	0.0	0.0
$2p_y$C2	0.0	0.0	0.0	0.0	0.38028	0.0	-0.37708	0.0
$2p_y'$C2	0.0	0.0	0.0	0.0	0.05898	0.0	-0.12588	0.0
$2p_z$C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.46125
$2p_z'$C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.21102
$2p_z''$C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00809
$2p_z'''$C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00422
$2p_z^{iv}$ C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.00156

Table XV. 'continued'

Orbital	$1b_{2g}(\pi^*)$	$3b_{3u}$	$4a_{1g}$	$4b_{3u}$	$2b_{2u}$	$2b_{1g}$
Occ. no.	0.99472	0.00286	0.00112	0.00059	0.00042	0.00030
Function						
1sH1	0.0	0.24438	0.29372	-0.26436	-0.26849	-0.28089
1s'H1	0.0	0.48876	0.70227	-0.72828	-0.52528	-1.21585
1sH2	0.0	0.24438	0.29372	-C.26436	0.26849	0.28089
1s'H2	0.0	-0.48876	0.70227	0.72828	-0.52528	1.21585
1sH3	0.0	-0.24438	0.29372	0.26436	0.26849	-0.28089
1s'H3	0.0	-0.48876	0.70227	0.72828	0.52528	-1.21585
1sH4	0.0	-0.24438	0.29372	0.26436	0.26849	-0.28089
1s'H4	0.0	-0.48876	0.70227	0.72828	0.52528	-1.21585
1sC1	0.0	0.09116	0.05444	0.01603	0.0	0.0
1s'C1	0.0	0.13152	0.07778	0.03118	0.0	0.0
2sC1	0.0	-0.40658	-0.25201	-0.34823	0.0	0.0
2s'C1	0.0	-2.19657	-1.11132	1.05802	0.0	0.0
$2p_x$C1	0.0	-0.58464	0.40942	-0.77609	0.0	0.0
$2p'_x$C1	0.0	-0.31445	0.37083	-0.46102	0.0	0.0
$2p_y$C1	0.0	0.0	0.0	0.0	0.68158	0.87106
$2p'_y$C1	0.0	0.0	0.0	0.0	0.15026	1.68776

Table. XV. 'continued'

Orbital	$1b_{2g}(\pi^*)$	$3b_{3u}$	$4a_{1g}$	$4b_{3u}$	$2b_{2u}$	$2b_{1g}$
$2p_z$C1	0.56796	0.0	0.0	0.0	0.0	0.0
$2p_z'$C1	0.52434	0.0	0.0	0.0	0.0	0.0
$2p_z''$C1	0.05940	0.0	0.0	0.0	0.0	0.0
$2p_z'''$C1	0.04306	0.0	0.0	0.0	0.0	0.0
$2p_z^{iv}$ C1	-0.02687	0.0	0.0	0.0	0.0	0.0
1sC2	0.0	-0.09116	0.05444	-0.01603	0.0	0.0
1s'C2	0.0	-0.13152	0.07778	-0.03118	0.0	0.0
2sC2	0.0	0.40658	-0.25201	0.34823	0.0	0.0
2s'C2	0.0	2.19657	-1.11132	-1.05802	0.0	0.0
$2p_x$C2	0.0	-0.58464	-0.40942	-0.77609	0.0	0.0
$2p_x'$C2	0.0	-0.31445	-0.37083	-0.46102	0.0	0.0
$2p_y$C2	0.0	0.0	0.0	0.0	0.68158	-0.87106
$2p_y'$C2	0.0	0.0	0.0	0.0	0.15026	-1.68776
$2p_z$C2	-0.56796	0.0	0.0	0.0	0.0	0.0
$2p_z'$C2	-0.52434	0.0	0.0	0.0	0.0	0.0
$2p_z''$C2	-0.05940	0.0	0.0	0.0	0.0	0.0
$2p_z'''$C2	-0.04306	0.0	0.0	0.0	0.0	0.0
$2p_z^{iv}$ C2	0.02687	0.0	0.0	0.0	0.0	0.0

Table XVI. A comparison of the π^*-orbital from the ISTA and TDA wavefunctions for the lowest ($\pi\pi^*$) singlet state of ethylene.

Basis set: [4s2p/2s] + R($3p_zC$)

Property[a]	ISTA	TDA
$\langle x^2 \rangle_{CM}$	27.2726	11.7286
$\langle y^2 \rangle_{CM}$	8.7630	3.5615
$\langle z^2 \rangle_{CM}$	26.2889	10.6845
$\langle 1/r_C \rangle$	0.2164	0.3499
$\langle \pi^*_{ISTA} \vert \pi^*_{TDA} \rangle$	0.9206	

[a] CM refers to the center of mass of ethylene and C to carbon 1.

Table XVII. The one-electron properties of ethylene in the lowest ($\pi\pi^*$) singlet, V($^1B_{3u}$), and triplet, T($^3B_{3u}$), states.

Basis set: [4s2p/2s] + R($3p_zC$)

	Ground State	Excited States			
		V($^1B_{3u}$)		T($^3B_{3u}$)	
Property[a]	$^1A_{1g}$	ISTA	TDA	ISTA	TDA
$\langle x^2 \rangle_{CM}$	49.6160	74.7039	58.8365	51.3165	51.2811
$\langle y^2 \rangle_{CM}$	21.2965	29.1506	23.9287	21.3141	21.3100
$\langle z^2 \rangle_{CM}$	12.1718	35.7338	19.8973	12.2245	12.1891
$\langle r^2 \rangle_{CM}$	83.0843	139.5883	102.6625	84.8551	84.7802
$\langle 1/r_H \rangle$	6.2522	6.1135	6.1843	6.2538	6.2544
$\langle 1/r_C \rangle$	18.5744	18.2598	18.3995	18.5721	18.5741
E_x(H1)	- 0.0427	- 0.0928	- 0.0766	- 0.0530	- 0.0529
E_z(H1)	0.0672	0.1144	0.0919	0.0603	0.0603
E_z(C1)	- 0.0065	- 0.0714	- 0.0664	- 0.0558	- 0.0557
$\langle \delta(r-H) \rangle$	0.4274	0.4274	0.4263	0.4274	0.4276
$\langle \delta(r-O) \rangle$	119.5879	119.5879	119.5950	119.5879	119.5865

[a] For the definition of the operators, see the text. CM refers to the center of mass of ethylene, H1 to hydrogen 1 and C1 to carbon 1.

Table XVIII. The results of accurate open-shell Hartree-Fock calculations on the $^{1,3}B_{3u}(\pi\pi^*)$ state of ethylene.[a] Except as noted, all quantities are in atomic units.

Basis set: [4s3p/2s] + R($3p_z$C)

	Ground state[b]	Excited states	
	$^1A_{1g}$	$V(^1B_{3u})$	$T(^3B_{3u})$
E_{HF}(a.u.)	-78.0140	-77.7415	-77.8917
ΔE(ev)	—	7.41	3.33
f	—	0.15	—
$\varepsilon(\pi)$	-0.3729	-0.5995	-0.5175
$\varepsilon(\pi^*)$	—	-0.0593	-0.2419
$\langle\pi\|x^2_{CM}\|\pi\rangle$ [c]	2.1540	2.0294	2.0634
$\langle\pi\|y^2_{CM}\|\pi\rangle$ [c]	0.8809	0.7246	0.7559
$\langle\pi\|z^2_{CM}\|\pi\rangle$ [c]	2.6428	2.1739	2.2678
$\langle\pi^*\|x^2_{CM}\|\pi^*\rangle$ [c]	—	43.0190	3.8468
$\langle\pi^*\|y^2_{CM}\|\pi^*\rangle$ [c]	—	14.0272	0.9149
$\langle\pi^*\|z^2_{CM}\|\pi^*\rangle$ [c]	—	42.0815	2.7446

[a] T. H. Dunning, W. J. Hunt and W. A. Goddard, Chem. Phys. Letters (to be published).

[b] T. H. Dunning and V. McKoy, unpublished results.

[c] CM refers to the center of mass of ethylene.

Table XIX. The first Rydberg $^1B_{3u}(\pi\pi^*)$ state of ethylene in the ISTA, TDA and RPA: excitation energies, transition moments, oscillator strengths and particle-hole amplitudes.

Basis set: [4s2p/2s] + R($3p_zC$)

	ISTA	TDA	RPA	
ΔE(ev)	9.12	8.94	8.89	
D_x(a.u.)	-0.85	-0.49	-0.30	
f	0.16	0.05	0.02	
(mα) [a]	g(mα)	g(mα)	g(mα)	h(mα)
(10,8)	-0.838459	-0.705474	-0.670474	-0.000201
(12,8)	0.190221	0.583394	0.658043	0.002245
(13,8)	-0.500052	-0.315662	-0.230962	0.013689
(15,8)	0.101730	0.234586	0.247937	-0.013406
(25,8)	-0.020029	0.015110	0.023331	-0.003943
(18,7)		0.010862	0.006818	0.003529
(21,7)		-0.041949	-0.028298	-0.009209
(30,7)		0.002365	0.001521	0.001042
(16,6)		-0.011783	-0.008402	-0.003795
(19,6)		-0.018717	-0.013309	-0.003121
(27,6)		0.044911	0.031028	0.017617
(28,6)		-0.009093	-0.006379	-0.004109
(31,6)		-0.005236	-0.003672	-0.001786
(22,5)		-0.026218	-0.017393	-0.006833
(24,5)		0.014947	0.010133	0.004903
(32,5)		0.002128	0.001370	0.001040
(17,4)		0.025406	0.017325	0.005552
(20,4)		0.014194	0.009141	0.002785
(26,4)		0.012995	0.008425	0.006985
(29,4)		-0.004802	-0.003074	-0.001837
(16,3)		0.015191	0.008886	0.005930
(19,3)		-0.003708	-0.002141	-0.002073
(27,3)		-0.009953	-0.006493	-0.006478
(28,3)		0.013244	0.008823	0.005248
(31,3)		0.003255	0.002575	0.000816

[a] The numerical designation refers to the position of the orbital in Table VII.

Table XX. The first Rydberg $^3B_{3u}(\pi\pi^*)$ state of ethylene in the ISTA, TDA and RPA: excitation energies and particle-hole amplitudes.

Basis set: [4s2p/2s] + R($3p_z$C)

	ISTA	TDA	RPA	
ΔE(ev)	8.77	8.76	8.75	
(mα)[a]	g(mα)	g(mα)	g(mα)	h(mα)
(10,8)	-0.561044	-0.557396	-0.547054	0.000182
(12,8)	0.788200	0.789794	0.796049	-0.002315
(13,8)	0.031565	0.037578	0.060549	-0.015910
(15,8)	0.247207	0.248424	0.247188	-0.017845
(25,8)	0.043169	0.044807	0.047575	-0.010755
(18,7)		0.007461	0.012612	0.003273
(21,7)		0.005943	0.008635	0.002050
(30,7)		0.001253	0.002319	0.001340
(16,6)		-0.003709	-0.005545	-0.000694
(19,6)		0.002776	0.005529	0.001903
(27,6)		-0.004924	-0.006477	-0.002735
(28,6)		0.000580	0.000310	0.000069
(31,6)		0.001230	0.002073	0.001151
(22,5)		0.005054	0.007103	0.001859
(24,5)		-0.003674	-0.005859	-0.002442
(32,5)		-0.001345	-0.002118	-0.001202
(17,4)		-0.005728	-0.008509	-0.003226
(20,4)		-0.006426	-0.008639	-0.002575
(26,4)		-0.001685	-0.001717	0.000046
(29,4)		0.002547	0.003746	0.002040
(16,3)		-0.009598	-0.011162	-0.002834
(19,3)		0.002979	0.003912	0.002238
(27,3)		0.004067	0.004620	0.002602
(28,3)		-0.003507	-0.004597	-0.002096
(31,3)		0.001366	0.001612	0.000845

[a] The numerical designation refers to the position of the orbital in Table VII.

Table XXI. The π^*-natural orbital from the ISTA and TDA wavefunctions for the first Rydberg $B_{3u}(\pi\pi^*)$ state of ethylene.

Basis set: $[4s2p/2s] + R(3p_zC)$

	ISTA		TDA	
	$^1\pi^*$	$^3\pi^*$	$^1\pi^*$	$^3\pi^*$
Basis functions[a]				
$2p_z$C1	-0.152934	-0.086796	-0.164770	-0.086819
$2p'_z$C1	-0.248965	-0.087344	-0.233127	-0.084082
$2p''_z$C1	-0.661197	0.379847	-0.182901	0.391247
$2p'''_z$C1	1.260439	2.833696	2.582962	2.829064
$2p^{iv}_z$ C1	4.661401	1.276134	2.606347	1.253484
$2p_z$C2	0.152934	0.086796	0.164770	0.086819
$2p'_z$C2	0.248965	0.087344	0.233127	0.084082
$2p''_z$C2	0.661197	-0.379847	0.182901	-0.391247
$2p'''_z$C2	-1.260439	-2.833696	-2.582962	-2.829064
$2p^{iv}_z$ C2	-4.661401	-1.276134	-2.606347	-1.253484

[a] See Table IV.

Table XXII. The spatial extent of the π^*-natural orbitals from the ISTA and TDA wavefunctions for the first Rydberg $B_{3u}(\pi\pi^*)$ state of ethylene.

Basis set: [4s2p/2s] + R($3p_z$C)

	$^1\pi^*$		$^3\pi^*$	
	ISTA	TDA	ISTA	TDA
$\langle x^2 \rangle$ CM[a]	138.5613	95.7734	70.4704	69.9248
$\langle y^2 \rangle$ CM[a]	45.9043	31.6333	23.1947	23.0127
$\langle z^2 \rangle$ CM[a]	137.7128	94.8998	69.5841	69.0380
$\langle r^2 \rangle$ CM[a]	322.1784	222.3065	163.2492	161.9755
$\langle 1/r_C \rangle$	0.1187	0.1185	0.0998	0.1002
$\varepsilon(\pi^*)$	-0.0380	--	-0.0510	--
$\langle \pi^*_{ISTA} \mid \pi^*_{TDA} \rangle$	0.8870		0.9999	

[a] CM refers to the center of mass of ethylene.

Table XXIII. The lowest excited $^1B_{3g}(\sigma_{CH}\pi^*)$ state of ethylene in the ISTA, TDA and RPA: excitation energies and particle-hole amplitudes.

Basis set: [4s2p/2s]

	ISTA	TDA	RPA	
ΔE(ev)	9.50	9.45	9.41	
(m,α)[a]	g(mα)	g(mα)	g(mα)	h(mα)
(10,7)	0.98909	0.98487	0.98556	-0.01372
(12,7)	-0.14731	-0.15432	-0.15575	0.00509
(18,8)		-0.05744	-0.05526	-0.01643
(21,8)		0.00639	0.01060	-0.03494
(30,8)		0.00699	0.00687	0.00555
(9,5)		-0.05323	-0.05422	0.00344

[a] For uniformity the numerical designation of the virtual orbitals corresponds to that for the expanded set (see Table VII).

Table XXIV. The lowest excited $^3B_{3g}(\sigma_{CH}\pi^*)$ state of ethylene in the ISTA, TDA and RPA: excitation energies and particle-hole amplitudes.

Basis set: [4s2p/2s]

	ISTA	TDA	RPA	
ΔE(ev)	8.92	8.87	8.82	
(m,α)[a]	$g(m\alpha)$	$g(m\alpha)$	$g(m\alpha)$	$h(m\alpha)$
(10,7)	0.98745	0.98357	0.98384	0.01693
(12,7)	-0.15796	-0.16750	-0.16955	-0.00640
(18,8)		0.02092	0.02148	-0.00529
(21,8)		-0.01817	-0.02418	-0.04035
(30,8)		-0.00490	-0.00517	0.00052
(9,5)		-0.06241	-0.06514	-0.00458

[a] For uniformity the numerical designation of the virtual orbitals corresponds to that for the expanded set (see Table VII).

Table XXV. The lowest excited $^{1}B_{2g}(\sigma_{CH}\pi^{*})$ state of ethylene in the ISTA, TDA and RPA: excitation energies and particle-hole amplitudes.

Basis set: [4s2p/2s]

	ISTA	TDA	RPA	
ΔE(ev)	10·22	9.96	9.84	
(m,α)[a]	g(mα)	g(mα)	g(mα)	h(mα)
(10,6)	0.97863	0.95652	0.96237	-0.01358
(12,6)	-0.20561	-0.21145	-0.21697	0.00718
(16,8)		0.14756	0.11242	0.01163
(19,8)		-0.06689	-0.06167	0.00746
(27,8)		-0.01092	-0.00439	-0.05863
(28,8)		0.00712	0.00396	0.00980
(31,8)		-0.00885	-0.00881	0.00460
(9,4)		0.02898	0.03032	-0.00633
(10,3)		0.10088	0.10211	0.00188
(12,3)		-0.05328	-0.05374	-0.00072

[a] For uniformity the numerical designation of the virtual orbitals corresponds to that for the expanded set (see Table VII).

Table XXVI. The lowest excited $^3B_{2g}(\sigma_{CH}\pi^*)$ state of ethylene in the ISTA, TDA and RPA: excitation energies and particle-hole amplitudes.

Basis set: [4s2p/2s]

	ISTA	TDA	RPA	
ΔE(ev)	9.50	9.29	9.05	
$(m,\alpha)^a$	$g(m\alpha)$	$g(m\alpha)$	$g(m\alpha)$	$h(m\alpha)$
(10,6)	0.97623	0.94838	0.94301	0.02797
(12,6)	-0.21672	-0.22399	-0.23142	-0.01153
(16,8)		0.18318	0.20876	0.02296
(19,8)		-0.02187	-0.02903	0.01280
(27,8)		-0.04830	-0.06182	-0.07874
(28,8)		0.02735	0.03348	0.02203
(31,8)		0.00148	0.00136	0.00944
(9,4)		0.02737	0.02424	-0.00827
(10,3)		0.09286	0.10463	0.00884
(12,3)		-0.06266	-0.07054	-0.01312

[a] For uniformity the numerical designation of the virtual orbitals corresponds to that for the expanded set (see Table VII).

Table XXVII. The π^*-natural orbitals for the lowest $^{1,3}B_{3g}$ and $^{1,3}B_{2g}$ excited states of ethylene from the ISTA (or frozen core) wavefunctions.

Basis set: [4s2p/2s]

	Excited states			
	B_{3g}		B_{2g}	
	$^1\pi^*$	$^3\pi^*$	$^1\pi^*$	$^3\pi^*$
Basis function[a]				
$2p_z C1$	0.51320	0.52106	0.55566	0.56360
$2p_z' C1$	0.64359	0.62966	0.56608	0.55097
$2p_z C2$	-0.51320	-0.52106	-0.55566	-0.56360
$2p_z' C2$	-0.64359	-0.62966	-0.56608	-0.55097

[a] See Table IV

Table XXVIII. Selected one-electron properties of ethylene in the lowest $^{1,3}B_{3g}$ and $^{1,3}B_{2g}$ states. All quantities are in atomic units.

Basis set: [4s2p/2s]

	Ground State	Excited States			
Property[a,b]	$^1A_{1g}$	$^1B_{3g}$	$^3B_{3g}$	$^1B_{2g}$	$^3B_{2g}$
$\langle x^2\rangle_{CM}$	49.5867	49.1994	49.1407	49.0574	48.9989
$\langle y^2\rangle_{CM}$	21.2688	19.3266	19.3060	20.9758	20.9552
$\langle z^2\rangle_{CM}$	12.0636	14.5373	14.4753	14.2503	14.1886
$\langle r^2\rangle_{CM}$	82.9191	83.0633	82.9220	84.2835	84.1427
$\langle 1/r_{H1}\rangle$	6.2531	6.1168	6.1179	6.1800	6.1811
$\langle 1/r_{C1}\rangle$	18.5744	18.6185	18.6202	18.5290	18.5339
$f_x(H1)$	-0.0426	-0.0659	-0.0652	-0.0284	-0.0277
$f_y(H1)$	0.0672	0.0663	0.0655	0.0966	0.0959
$f_x(C1)$	-0.0062	0.0142	0.0147	-0.0441	-0.0436
$\langle \delta(r-H1)\rangle$	0.3974	0.3974	0.3974	0.3551	0.3551
$\langle \delta(r-C1)\rangle$	119.5868	119.5868	119.5868	119.5816	119.5816

[a] See the text for the definition of the operators.

[b] The following abbreviations have been adopted: CM = center of mass, H1 = hydrogen 1 and C1 = carbon.