

AN AB INITIO PI ELECTRON
HAMILTONIAN

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PREFACE

In this thesis, the canonical transformation approach to quantum chemistry is developed. The pi electron hamiltonian for the ethylene molecule is derived from first principles. The hamiltonian is diagonalized on the valence space and the electronic excitation energies are calculated. We compare our results with experiment and other ab initio calculations. These calculations are only preliminary applications of the canonical transformation technique which promises to be useful for molecular calculations.

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CHAPTER I

INTRODUCTION

This work attempts to transform a many-body problem into a fewer body problem explicitly and legally (canonically). To be more specific we are applying the ideas of the canonical transformation¹ to the problem of calculating electronic excitation spectra of large molecules. Ethylene is the molecule under consideration here but larger molecules are included in our plans for future study.

In considering large molecules, the spectrum of the molecular electronic hamiltonian (with nuclei fixed at $\vec{R}_\alpha, \alpha = 1, \dots, A$),

$$\hat{H}(1, \dots, N) = \sum_{i=1}^N \left\{ \frac{\vec{p}_i^2}{2m} + \sum_{\alpha=1}^A \frac{-Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|} \right\} + \sum_{i < j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad (\text{I-1a})$$

plays a distinct role. The electronic eigenstates $|\Psi_i\rangle$

where

$$\hat{H} |\Psi_i\rangle = E_i |\Psi_i\rangle$$

are in principle, the starting point for considering the dynamic electromagnetic properties of the molecule. We will introduce a new approach based on an old idea for more accurately obtaining these stationary states.

We will generally be considering the equivalent hamiltonian,

$$\hat{H} = \sum_{i=1}^N \left\{ \frac{\hat{p}_i^2}{2m} + \sum_{\alpha=1}^A \frac{-Z_{\alpha} e^2}{|\bar{r}_i - \bar{R}_{\alpha}|} + U_i \right\} + \sum_{i < j} \left\{ \frac{e^2}{|\bar{r}_i - \bar{r}_j|} - \frac{U_i + U_j}{N-1} \right\} \quad (\text{I-1b})$$

which contains the single-particle potential U_i . Note this potential has been both added and subtracted, so this \hat{H} is identical to the preceding \hat{H} . In this work U_i is a molecular Hartree-Fock potential, but any single-particle potential would be applicable. We further introduce notation for the pair potential (the two-body operator in I-1a):

$$g_{12} = \frac{e^2}{|\bar{r}_1 - \bar{r}_2|} - \frac{U_1 + U_2}{N-1}$$

Our attention will ultimately be focused on biological molecules involved in photoreception. These molecules usually are medium to large size containing more than fifty electrons. This size problem is intractable with rigorous quantum chemistry methods. To date there have been a few self-consistent-field calculations on large molecules and complexes, but none of these really approach the Hartree-Fock limit, much less account for electron correlation effects (for instance see Clementi²).

The usual way to tackle these problems is to abandon the rigorous quantum chemistry methods in favor of a semi-empirical approach.³ Here the basic parameters of the theories are defined in terms of rigorous quantum mechanical concepts--most often the matrix elements of an effective hamiltonian over a finite dimensional subspace spanned by atomic valence orbitals. However, most of these matrix elements are

set equal to zero by invoking such approximations as zero-differential overlap, the remaining matrix elements (the non-vanishing parameters of the theory) being evaluated with the help of empirical data. Thus, arise the so-called "semi-empirical" theories such as those of Hückel or Pariser, Parr, and Pople (PPP).

Hückel theory assumes that all of the two-body matrix elements can be eliminated by choosing a suitable U_i . This choice reduces the hamiltonian to a sum of one-body operators

$$\hat{H}^{\text{eff}} = \sum_i h_i^{\text{eff}}$$

Hückel theory treats a reduced number of electrons (e.g., the valence electrons or the pi electrons). Furthermore, matrix elements of h_i^{eff} between atomic orbitals not on the same atom or neighboring atoms are set equal to zero. The remaining one-electron integrals are chosen to reproduce the experimental results (e.g. spectra) of some prototype molecule. Notwithstanding all the approximations used, Hückel theory does produce valuable results.

By not ignoring the two-electron integrals, a higher level of pi electron approximation is achieved. However, the enormous number of integrals required makes it convenient to invoke a zero-differential overlap (ZDO) scheme within the framework of the Pariser-Parr-Pople (PPP) method. In this and other similar schemes the "differential" overlap is set to zero:

$$\int \varphi_\mu(1) \Theta \varphi_\nu(1) = \delta_{\mu\nu} \Theta_{\mu\nu}$$

for all operators, \mathcal{O} , and where $\delta_{\mu\nu}$ is the Kronecker delta symbol. The usefulness of this approximation is found when the two-electron matrix elements are evaluated. If the ZDO scheme were not used, there would be on the order of R^4 integrals like

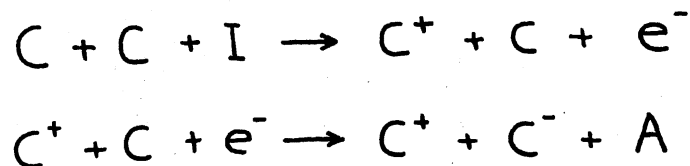
$$(\mu\nu|\sigma\tau) = \iint \varphi_{\mu}^*(1) \varphi_{\nu}^*(2) \frac{1}{r_{12}} \varphi_{\sigma}(1) \varphi_{\tau}(2) d\bar{r}_1 d\bar{r}_2$$

to calculate. Here R is the number of pi orbitals. However, with the ZDO approximation we are left with only R^2 integrals like

$$(\mu\nu|\mu\nu) = \gamma_{\mu\nu}.$$

Other "Neglect of Differential Overlap" theories have been developed.^{4,5,6,7,8} However, in all of these theories introduction of empirical parameters is found to be necessary to make the theory conform with experimental results.

As an example, if a non-empirical calculation of excitation energies is performed using Slater functions, the results are discouraging.⁹ Noting this, Pariser and Parr chose empirical values for some of the integrals and achieved results much closer to experimental values.¹⁰ The reasoning for choosing the semiempirical parameters follows. We consider two chemical reactions



Here I is the ionization potential and A is the electron affinity. Now if we write down the energetics of the above reactions, the energy of the first term equals the energy of the last term:

$$E_c + E_c + I = E_{c^+} + E_{c^-} + A$$

Now from a theoretically naive point of view we can write for the energy of a carbon atom

$$E_c = E_{\text{core}} + E_{\pi}$$

where E_{core} is the energy of the five electron core, and E_{π} is the interaction energy between the core and pi electron. The energy of the carbon-plus ion is given by

$$E_{c^+} = E_{\text{core}}$$

The energy of the carbon-minus ion is given by

$$E_{c^-} = E_{\text{core}} + E_{\pi} + E_{\pi'} + E_{\pi\pi'}$$

That is, the energy of the core plus the energies of the two pi electrons interacting with the core plus the energy of interaction between the two pi electrons equals the energy of the carbon-minus ion.

If we assume $E_{\pi} = E_{\pi'}$, the energy equation balances as follows:

$$2E_{\text{core}} + 2E_{\pi} + I = 2E_{\text{core}} + 2E_{\pi} + E_{\pi\pi'} + A$$

or

$$I - A = E_{\pi\pi'}$$

$E_{\pi\pi'}$ is the interaction energy of two pi electrons on the same carbon atom and is given by

$$E_{\pi\pi'} = (\pi\pi | \pi\pi) = \iint d\vec{r}_1 d\vec{r}_2 \pi^*(1)\pi^*(2) \frac{1}{r_{12}} \pi(1)\pi(2)$$

We have reasoned an experimental value for the theoretical

quantity $(\pi\pi|\pi\pi)$. Considering actual numbers, Mulliken¹¹ found $I = 11.22\text{eV}$ and $A = 0.69\text{eV}$, hence

$$I - A = 10.53\text{eV} = (\pi\pi|\pi\pi)$$

Using integrals evaluated in this empirical fashion, acceptable numbers result for excitation energies. However, the value of $(\pi\pi|\pi\pi)$ using best atomic value Slater functions is found to be 16.93eV .

These purely theoretical numbers lead to poor values for excitation energies.

This discrepancy between experiment and theory is caused by the neglect of correlation effects, and the wrong choice of exponent for the Slater function. From the unitary transformation point of view either an effective (unitarily transformed) operator should be represented or a unitarily transformed basis set should represent the operator. Each statement is equivalent. The operator to be transformed in this case is $1/r_{12}$; the basis to be transformed is the antisymmetrized product of two atomic pi spin orbitals. The unitary transformation mixes the effects of the core and excited orbitals into the operator or basis, depending on the point of view.

When a variational calculation of ζ is performed on the carbon minus ion, a different value is obtained. Intuitively, it would seem more reasonable to use the ζ from such a calculation than the best atom values. In fact, when this ζ is used, the $(\pi\pi|\pi\pi)$ integral is reduced.

The result of this discussion is that it seems the best calculations of excitation spectra of molecules are performed by using empirical data and guesswork as input parameters. When this is done

properly, the results of molecular calculations are quite good.

It appears that these semi-empirical theories will play an ever more important role in discussing biological molecules.¹² Consequently, there have been many valuable efforts put forth in the past few years to place these semi-empirical theories on firmer foundations, and even predict the parameters for the effective hamiltonian on the valence orbital space. Of course, if this could really be carried through, the procedure would cease to be semi-empirical, and one could claim to have a first principles calculation of the electronic states of a large molecule. The past and present programs to justify the semi-empirical procedure include work by Harris¹³, Linderberg and Öhrn¹⁴, Kvasnicka¹⁵, and Freed¹⁶.

Harris' approach focuses on the sigma-pi separability and resulting effective pi electron hamiltonian arising from a unitary (canonical) transformation upon the Coulomb hamiltonian Eq. (I-1). Linderberg and Öhrn tackle the same problem with Green's functions. Kvasnicka generates a model hamiltonian in the framework of Rayleigh-Schrödinger perturbation theory. Recently, Freed has used the cluster decomposition of the wave function due to Sinanoglu and Silverstone¹⁷ to set up formally the matrix elements of an effective hamiltonian in the model space.

We want to generate from first principles the valence shell hamiltonian and use it to determine the electronic excitation spectrum of ethylene. This valence hamiltonian is to operate in a finite dimensional N_v -particle subspace of Fock space. That is, we transform the electronic hamiltonian not only from an infinite dimensional N -particle space to a finite dimensional N -particle space, but also

from the finite dimensional N -particle space to a finite dimensional N_V -particle space (N_V = number of valence electrons). Consequently, the valence hamiltonian must have built into it the effects of the remaining N_c ($N_c = N - N_V$) core electrons, as well as the correlation effects among the valence electrons. If we had explicitly considered the infinite dimensional N_V -particle space, these correlation effects would be treated by configuration interaction (CI) involving virtual excitations from valence to excited orbitals. However, since we only implicitly consider the excited orbitals, the correlation effects must be "built-in" to the valence hamiltonian which operates in the finite subspace defined by all antisymmetrized products of valence orbitals. A CI calculation then yields the eigenvalues and eigenvectors or the effective hamiltonian on this subspace.

In Chapter II we choose an N -electron model space and then use a unitary transformation¹⁸ to eliminate the interaction between this model space and its orthogonal complement. We set forth the conditions imposed on one-, two-, and three-body operators necessary to achieve a partitioning of the effective hamiltonian in N -electron space. These conditions along with certain restrictions on the core orbitals ultimately yield the valence shell hamiltonian.

We then re-examine the unitary transformation in terms of a cluster expansion. The resulting reclassification of terms allows us to impose the partitioning conditions on the one-, two-, and three-body operators.

Finally we develop formulae for the valence shell hamiltonian which are constructed as averages over the matrix elements of the N -electron effective hamiltonian. These explicit formulae involve

the one-, two-, and three-body matrix elements in terms of the core, valence, and excited orbitals.

The procedure introduced is general, but depends in a somewhat arbitrary fashion on the division of the complete set of orbitals into core, valence, and excited sets. However, once this division of one-particle Hilbert space has been achieved, the remaining part of the formalism is well defined and complete. The ultimate result of the procedure is the construction of a valence hamiltonian:

- i) operating on a truncated subspace defined by all anti-symmetrized products of valence orbitals
- ii) yielding the low-lying electronic excitation spectrum of the molecule.

When these points are achieved, the valence hamiltonian will have built into it both the effects of the core and the correlation effects of the excited orbitals.

The method appears applicable to a wide range of problems whenever, on the basis of chemical intuition, a division of the one-electron space into core, valence, and excited orbitals is possible.

In Chapter III we use the formulae for the valence shell hamiltonian to generate an effective pi-electron hamiltonian for large planar conjugated molecules; so this discussion will be framed in the language of sigma and pi orbitals. In the sigma-pi problem certain matrix elements vanish by symmetry considerations beyond what we might hope for in the general case. The sigma-pi problem is of particular importance to our ultimate goal of understanding photo-receptors.

In Chapter IV we discuss the programming involved in performing

the canonical transformation.

Chapter V contains a discussion of work on ethylene by other people and presents the numerical results of our work. The discussions center on the low-lying excited states of ethylene.

Chapter VI contains a discussion of our results and conclusions drawn. Also, we have included suggestions for further work.

REFERENCES

1. For applications of the canonical transformation in nuclear physics see: F. Villars, Nuclear Physics, Proceedings of the International School of Physics, "Enrico Fermi," Course XXIII, 1961, edited by V. F. Weiskopf (Academic Press, Inc., New York, 1963); C. M. Shakin, Y. R. Waghmare, and M. H. Hull, Jr., Phys. Rev., 161, 1006, 1015 (1967); P. Mittlestaedt and M. Ristig, Z. Physik, 193, 349 (1966).
2. E. Clementi, Proc. Nat. Acad. Sci., 27, 493 (1969); E. Clementi, J. M. André, M. Cl. André, D. Klint, D. Hahn, Act. Phys. Acad. Hung., 27, 493 (1969); E. Clementi and D. R. Davis, J. Comp. Phys., 2, 223 (1967)
3. See, for instance, the following well known texts: Robert G. Parr, Quantum Theory of Molecular Electronic Structure (Benjamin, New York, 1964); R. Daudel and C. Sandorfy, Semiempirical Wave Mechanical Calculation on Polyatomic Molecules (Yale U. P., New Haven, 1971).
4. J. A. Pople and G. A. Segal, J. Chem. Phys., 43, 5136 (1965).
5. M. J. S. Dewar and G. Klopman, J. Am. Chem. Soc., 89, 3089 (1967).
6. J. A. Pople, D. L. Bereridge, and P. A. Dobosh, J. Chem. Phys., 47, 2026 (1967).
7. N. C. Baird and M. J. S. Dewar, J. Chem. Phys., 50, 1262 (1969).
8. J. A. Pople, D. P. Santry, and G. A. Segal, J. Chem. Phys., 43, 5129 (1965)
9. R. Pariser and R. G. Parr, J. Chem. Phys. 21, 466 (1953).
10. R. Pariser and R. G. Parr, J. Chem. Phys. 21, 767 (1953).
11. R. S. Mulliken, J. Chem. Phys., 2, 782 (1934).
12. "Quantum Mechanical Investigations of the Electronic Structure of Nucleic Acids and Their Constituents," B. Pullman and A. Pullman in Progress in Nucleic Acid Research and Molecular Biology, edited by J. N. Davidson and Waldo E. Cohn (Academic, New York, 1969), Vol. 9, p. 327.
13. R. A. Harris, J. Chem. Phys. 47, 3967 (1967); 47, 3972 (1967); 48, 3600 (1968).

14. J. Linderberg and Y. Öhrn, J. Chem. Phys. 49, 716 (1968).
15. V. Kvasnicka, Czech. J. Phys. B 24, 605 (1974); V. Kvasnicka, A. Holubec, and I. Hubac, Chem. Phys, Lett. 24, 361 (1974).
16. K. F. Freed, Chem. Phys, Lett. 13, 181 (1972); 15, 331 (1972); 24, 275 (1974); J. Chem. Phys. 60, 1765 (1974); S. Kwata and K. F. Freed, J. Chem. Phys. 61, 1500 (1974).
17. H. J. Silverstone and O. Sinanoglu, J. Chem. Phys. 44, 1899 (1966); *ibid.* 44, 3608 (1966), P. Westhaus and O. Sinanoglu, Int. J. Quantum Chem. IIIs, 391 (1970). P. Westhaus, J. Chem. Phys. 55, 2507 (1971); K. F. Freed, Phys. Rev. 173, 1 (1968); 173, 24 (1973).
18. J. H. VanVleck, Phys. Rev. 33, 467 (1929); S. Fischer, Int. J. Quantum Chem. IIIs, 651 (1970); P. Westhaus, Int. J. Quantum Chem. Viis, 463 (1973); F. Jorgenson and T. Pedersen, Mol. Phys. 27, 33 (1974); 27, 899 (1974); R. Yaris, J. Chem. Phys. 41, 2419 (1964); 42, 3019 (1965).

CHAPTER II

THE EFFECTIVE HAMILTONIAN

The calculation of the electronic states of large molecules begins by introducing a set of spin-orbitals $\phi_1 \phi_2 \dots \phi_i \dots$. In principle, we envision this orbital set to be complete, and thus infinite. In practice, however, we can only introduce a finite set of, say, M spin orbitals. We shall in general denote complete sets by braces $\{\phi_i\}$ and finite sets by brackets, $[\phi_i]$. The orbitals ϕ_i are labeled by four indices

$$\begin{aligned}\phi_i &= \langle \bar{r} \xi | \phi_i \rangle = \langle \bar{r} \xi | \phi_{\eta r \rho m_s} \rangle \\ &= \phi_{\eta r \rho m_s} (xyz \xi)\end{aligned}$$

That is, i stands collectively for four quantum numbers: γ and ρ indicate that the orbital belongs to the ρ th row of the γ th representation; $m_s = \pm \frac{1}{2}$ labels the eigenvalues of S_z ; and η differentiates among the occurrences of the set $(\gamma \rho m_s)$. If one solves some model one-electron problem, then η can be chosen as the single-particle energy.

In this Chapter we will brush aside the precise details of how the orbital basis $\{\phi_i\}$ is to be chosen. Suffice it to say that an elaborate Hartree-Fock calculation or perhaps simply a scattered wave computation using an approximate exchange potential might be done

initially. Even more practically, we can envision introducing a set of atomic orbitals and orthonormalizing them by the Löwdin procedure.

The intuitive physical model motivating our approach is that in the independent particle picture the electrons may be divided into N_c core electrons and $N_v (= N - N_c)$ valence electrons. Of course, we want to go beyond an independent-particle model of the system. Thus, on the basis of chemical intuition we will divide the one-electron space spanned by $\{\phi_i\}$ into three orthogonal subspaces:

$$[c] = [\phi_1 \dots \phi_{M_c}] \quad ; \quad [v] = [\phi_{M_c+1} \dots \phi_{M_c+M_v}]$$

and

$$[e] = [\phi_{M_c+M_v+1} \dots]$$

In terminology similar to other authors, there are M_c core orbitals and M_v valence orbitals; the remaining orbitals outside the "orbital sea" $[c] \cup [v]$ are called excited orbitals. We will take $M_c = N_c$ —i.e., there is only one configuration of the core orbitals—whereas in general, $M_v > N_v$. Strictly speaking, such a division of the basis into core, valence, and excited orbitals is arbitrary. However, chemical intuition usually opts in favor of one or two obvious choices.

With the orbitals $\{\phi_i\}$ we construct the Slater determinants

$$\Phi_{\underline{k}}(x_1 \dots x_N) = \Phi_{k_1 \dots k_N}(x_1 \dots x_N) = Q(N) (\phi_{k_1}(x_1) \dots \phi_{k_N}(x_N))$$

with $\underline{k} \equiv k_1 < k_2 < \dots < k_N$ being an ordered set of N spin-orbitals.

Since the orbital basis $\{\phi_i\}$ is complete, the set of all Slater

determinants $\{\Phi_k\}$ constructed from them is complete over the N electron space. In computations the orbitals will comprise a finite set from which a finite and thus necessarily incomplete set of Slater determinants can arise. In virtually all calculations only a subset of this finite set of determinants is actually used, since the total number of N -electron Slater determinants able to be constructed from a total of M orbitals is astronomical even for the most reasonable choices of M . The selection of which determinants to include is the subject of many investigations and the starting point of many formal analyses of electronic correlation effects.

In the approach to be pursued here we assume that there can be a chosen a priori a set of Q N -electron determinants which, within a configuration interaction context, would emerge as the most significant. Intuitively we expect that to compute the ground state and low-lying excited states, all of the chosen determinants will have in common a set of N_c orbitals which, in fact, define the core. The chosen determinants differ from one another in having different sets of $N_v (=N-N_c)$ valence orbitals which are selected from a total of M_v valence orbitals. Thus, there are

$$Q = \frac{M_v!}{N_v!(M_v - N_v)!}$$

determinants in the chosen set and these span a Q dimensional N -particle space designated \mathcal{T}_N . The infinite-dimensional orthogonal complement $\bar{\mathcal{T}}_N$ is spanned by the remaining N -particle Slater determinants in which, if only orbitals from $[c] \cup [v]$ are used, not all core orbitals are occupied, or in which, if all core orbitals are

occupied, at least one excited orbital appears.

Now if the determinantal basis were complete--and for the sake of the formal development of the theory we now envision this to be the case--the set of Q determinants would have the largest coefficients in a CI calculation. However, there still are an "infinite number" of other N -particle determinants which would have to be considered in a complete CI calculation. These additional determinants which are characterized more fully below span the orthogonal complement to \mathcal{T}_N , denoted $\bar{\mathcal{T}}_N$.

We seek an effective hamiltonian \mathcal{H} which does not mix any state in \mathcal{T}_N with those in $\bar{\mathcal{T}}_N$. Thus, the effective hamiltonian can be diagonalized on \mathcal{T}_N and $\bar{\mathcal{T}}_N$ separately, and since \mathcal{T}_N is Q dimensional, the problem of finding Q exact eigenvalues becomes a matrix diagonalization problem. Of course, the difficulty now is explicitly constructing the effective hamiltonian which is partitioned in this way. Assuming we can accomplish this, we want to go further and define an operator acting in the space of valence orbitals and having the same eigenspectrum on this space as does the N -particle effective hamiltonian on \mathcal{T}_N (to within an additive constant). This will be possible for the following reason: all basis functions needed to span \mathcal{T}_N have a common set of core orbitals and differ from one another only in their valence orbital occupation. Consequently, matrix elements of the effective hamiltonian on \mathcal{T}_N need be labeled explicitly only by the bra and ket valence orbitals. That is, we define the valence shell hamiltonian by a one to one correspondence of its matrix elements with those of \mathcal{H} on \mathcal{T}_N . There is, of course, an actual dependence of these matrix elements on the core orbitals

chosen, and consequently a parameterization of the effective valence shell hamiltonian by the core orbitals.

Considering the first part of the partitioning problem, we know in principle the effective hamiltonian in the N-particle space is obtained by a unitary (canonical) transformation on the basic electronic operators of the Schrödinger picture. Thus, we seek to determine S such that the transformed operator \mathcal{H}^{eff} , diagonalized on the space \mathcal{T}_N , where

$$\mathcal{H}^{\text{eff}} = e^{-iS} H e^{iS} \quad (\text{II-1})$$

will yield the exact ground state and low-lying excited states of the system.

We contend that if

$$\mathcal{H}_{mn}^{\text{eff}} \equiv \langle \Phi_m | \mathcal{H}^{\text{eff}} | \Phi_n \rangle \quad m, n = 1, 2, \dots, Q$$

is to be a $Q \times Q$ matrix which yields Q exact eigenvalues of \mathcal{H}^{eff} (and thus of H) by diagonalizing on \mathcal{T}_N , then with $|\chi\rangle$ any vector in \mathcal{T}_N we require

$$\langle \Phi_m | e^{-iS} H e^{iS} | \chi \rangle = 0$$

When we introduce a basis which spans \mathcal{T}_N , say $|\chi_i\rangle$ (note the basis $|\chi_i\rangle$ is infinite though not complete in Hilbert space since it is missing the set of vectors $[\Phi_i]$) we can restate the preceding equations:

$$\langle \Phi_m | \mathcal{H}^{\text{eff}} | \chi_i \rangle = 0 \quad \begin{array}{l} \Phi_m \in \mathcal{T}_N \\ \chi_i \in \bar{\mathcal{T}}_N \end{array}$$

We emphasize that these conditions are among N-particle vectors. The matrix representation of \mathcal{H}^{eff} on the full N-electron Hilbert space spanned by

$$[\Phi_m] U[\chi_i] = \{\Phi_i\}$$

is schematically shown in Figure 1. We now note that we have not determined S (from the e^{-iS} term) uniquely. Indeed, it is obvious that given $[\Phi_i]$ there are many unitarily equivalent \mathcal{H}^{eff} 's which will be of the form shown.

We then can attack the second part of the problem: replacing the effective hamiltonian by one which involves only a subset, N_v , of particles. We want an N_v -particle hamiltonian whose eigenvalues are identical to those of H (to within an additive constant which determines the zero of energy). The possibility of accomplishing this follows from our requirement that all the N-particle wave functions in \mathcal{T}_N contain a specific subset of $[\phi_i]$ called a "core." We will require the core to be "closed shell;" that is, for each occurrence η of a given representation γ all rows and both spin states $M_s = \pm \frac{1}{2}$ appear in the configuration. We have called M_c the number of core orbitals. Note the number of core orbitals equals the number of core electrons (i.e., a single configuration for the core electrons).

The representation of the effective hamiltonian in the space \mathcal{T}_N is

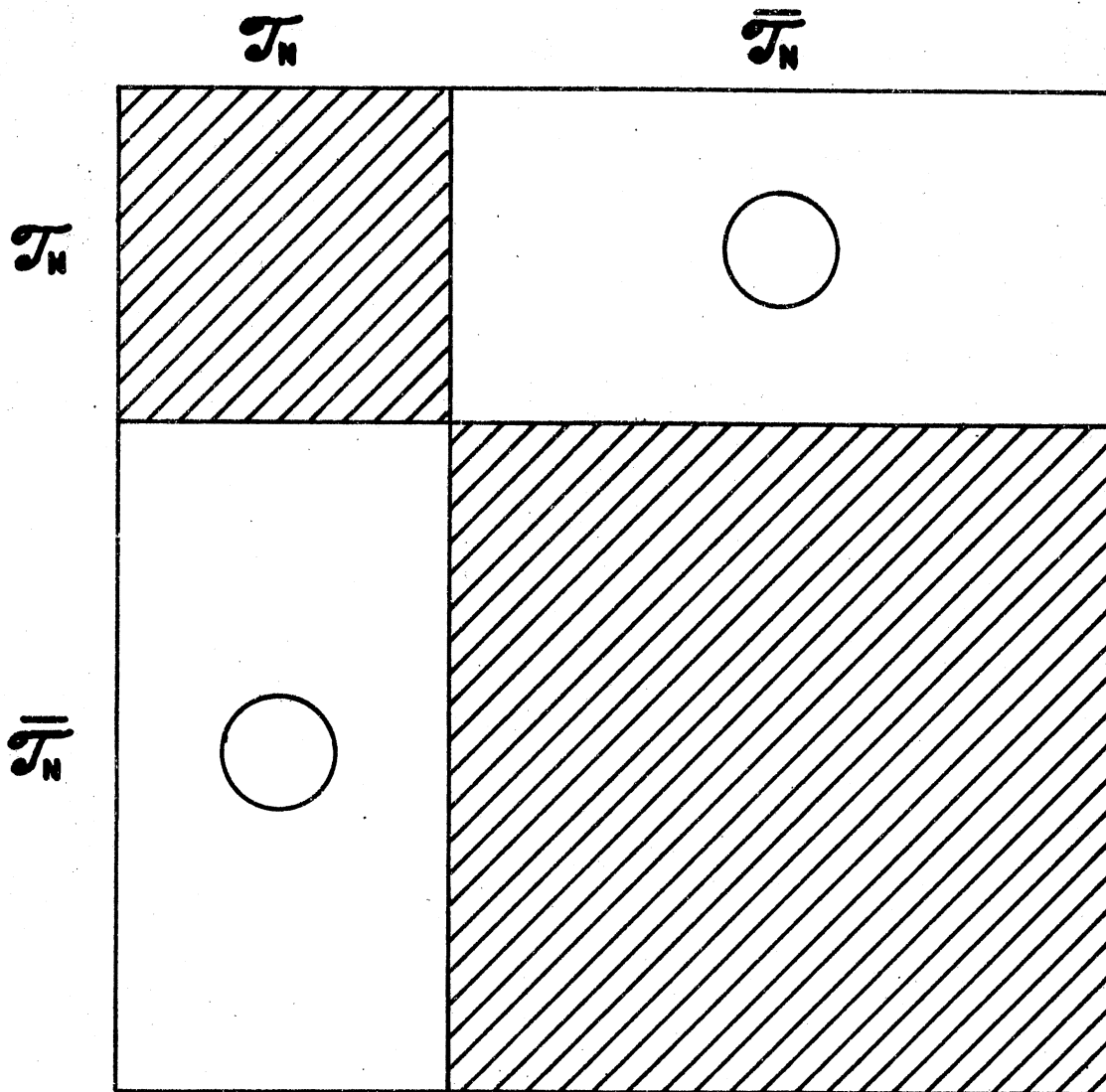


Figure 1. Block Diagonal Form Sought for the Matrix of H^{eff} on N-electron Model Space \mathcal{T}_N and Its Orthogonal Complement $\overline{\mathcal{T}}_N$. Hatch Marks Indicate Nonvanishing Matrix Elements

$$\mathcal{X}_{l_1 \dots l_{N_v}; l'_1 \dots l'_{N_v}} \equiv \langle 1 \dots M_c l_1 \dots l_{N_v} | \mathcal{X}^{\text{eff}} | 1 \dots M_c l'_1 \dots l'_{N_v} \rangle$$

where in labeling the matrix elements we have dropped explicit reference to the core orbitals. This can be done because all wave functions in \mathcal{T}_N have the same set of core orbitals. We define the valence shell hamiltonian H^v by the requirement that to within a constant times the identity its matrix elements obey

$$\begin{aligned} \langle l_1 \dots l_{N_v} | H^v | l'_1 \dots l'_{N_v} \rangle \\ = \langle 1 \dots M_c l_1 \dots l_{N_v} | \mathcal{X}^{\text{eff}} | 1 \dots M_c l'_1 \dots l'_{N_v} \rangle \end{aligned}$$

We now examine the \mathcal{T}_N space in more detail. There are two classes of N particle wave functions in \mathcal{T}_N : those which are constructed only from orbitals in $[c] \cup [v]$ but with one or more core orbitals unoccupied, and those with at least one orbital outside $[c] \cup [v]$. Hence, we divide \mathcal{T}_N into \mathcal{T}'_N and \mathcal{T}''_N corresponding to the two classes of N particle wave functions. To facilitate this examination, we will use the language of second quantization. We begin by expanding the field operators in terms of the orbital creation and destruction operators

$$\begin{aligned} \hat{\psi}(x) &= \sum_{i \in [c]} \phi_i(x) \hat{a}_i + \sum_{i \in [v]} \phi_i(x) \hat{a}_i + \sum_{i \in [e]} \phi_i(x) \hat{a}_i \\ &= \hat{\psi}_{\text{core}}(x) + \hat{\psi}_{\text{valence}}(x) + \hat{\psi}_{\text{excited}}(x) \end{aligned}$$

Subsequently, we will show that

$$\mathcal{K}^{\text{eff}} \equiv e^{-iS} H e^{iS}$$

can be written

$$\mathcal{K}^{\text{eff}} = \sum_{n=1}^N \mathcal{K}^{(n)}$$

where $\mathcal{K}^{(n)}$ is a sum of "linked" n particle terms:

$$\mathcal{K}^{(n)} = \sum_{(i_1 \dots i_n / 1 \dots N)} \mathcal{K}(i_1 \dots i_n) \quad (\text{II-2a})$$

In the language of second quantization this becomes:

$$\begin{aligned} \mathcal{K}^{(n)} &= \frac{1}{n!} \int dx_1 \dots dx_n dx'_1 \dots dx'_n \hat{\psi}^\dagger(x'_n) \dots \hat{\psi}^\dagger(x'_1) \\ &\quad \langle x'_1 \dots x'_n | \mathcal{K}(1 \dots n) | x_1 \dots x_n \rangle \hat{\psi}(x_1) \dots \hat{\psi}(x_n) \\ &= \sum_{\lambda_1 < \dots < \lambda_n} \sum_{\mu_1 < \dots < \mu_n} \langle \lambda_1 \dots \lambda_n | \mathcal{K}(1 \dots n) | \mu_1 \dots \mu_n \rangle a_{\lambda_n}^\dagger \dots a_{\lambda_1}^\dagger a_{\mu_1} \dots a_{\mu_n} \end{aligned} \quad (\text{II-2b})$$

Thus, in second quantized form:

$$\begin{aligned} \mathcal{K}^{\text{eff}} &= \sum_{\lambda_1, \mu_1} \langle \lambda_1 | \mathcal{K}(1) | \mu_1 \rangle a_{\lambda_1}^\dagger a_{\mu_1} \\ &+ \sum_{\lambda_1 < \lambda_2} \sum_{\mu_1 < \mu_2} \langle \lambda_1, \lambda_2 | \mathcal{K}(12) | \mu_1, \mu_2 \rangle a_{\lambda_1}^\dagger a_{\lambda_2}^\dagger a_{\mu_2} a_{\mu_1} \end{aligned}$$

$$\begin{aligned}
& + \sum_{\lambda_1 < \lambda_2 < \lambda_3} \sum_{\mu_1 < \mu_2 < \mu_3} \langle \lambda_1 \lambda_2 \lambda_3 | \mathcal{H}(123) | \mu_1 \mu_2 \mu_3 \rangle a_{\lambda_1}^\dagger a_{\lambda_2}^\dagger a_{\lambda_3}^\dagger a_{\mu_3} a_{\mu_2} a_{\mu_1} \quad (\text{II-2c}) \\
& + \dots
\end{aligned}$$

The basis states $|\mu_1 \dots \mu_n\rangle$ are normalized, antisymmetrized n -particle vectors:

$$\langle x_1 \dots x_n | \mu_1 \dots \mu_n \rangle = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_{\mu_1}(x_1) & \phi_{\mu_2}(x_1) & \dots & \phi_{\mu_n}(x_1) \\ \phi_{\mu_1}(x_2) & & & \\ \vdots & & & \\ \phi_{\mu_1}(x_n) & & & \phi_{\mu_n}(x_n) \end{vmatrix}$$

In the set $\lambda_1 < \lambda_2 < \dots < \lambda_n$ or $\mu_1 < \mu_2 < \dots < \mu_n$ an orbital index may in general stand for either a core, valence, or an excited orbital.

A general orbital label λ may be subscripted with c, v, or e denoting a core, valence, or excited orbital, respectively.

We now make some remarks about the coefficients,

$\langle \lambda_1 \dots \lambda_n | \mathcal{H}(1 \dots n) | \mu_1 \dots \mu_n \rangle$ in the second quantized expansion of $\mathcal{H}^{(n)}$:

$$\mathcal{H}^{(n)} = \sum_{\lambda_1 < \lambda_2 < \dots < \lambda_n} \sum_{\mu_1 < \mu_2 < \dots < \mu_n}$$

$$\langle \lambda_1 \dots \lambda_n | \mathcal{N}(1 \dots n) | \mu_1 \dots \mu_n \rangle a_{\lambda_1}^\dagger \dots a_{\lambda_n}^\dagger a_{\mu_n} \dots a_{\mu_1} \quad (\text{II-2c})$$

From the N-particle condition on the effective hamiltonian

$$\langle \Phi_m | \mathcal{N}^{\text{eff}} | \chi_i \rangle = 0 \quad \begin{cases} \Phi_m \in \mathcal{T}_N \\ \chi_i \in \bar{\mathcal{T}}_N \end{cases}$$

we can reduce the necessary conditions the coefficients,

$$\langle \lambda_1 \dots \lambda_n | \mathcal{N}(1 \dots n) | \mu_1 \dots \mu_n \rangle:$$

- 1) if one or more $\lambda_i \in [e]$ and one or more $\mu_i \in [e]$, then our unitary transformation imposes no restrictions on the matrix element.
- 2) if one or more $\lambda_i \in [e]$ and none of the $\mu_i \in [e]$ then by choice of S the matrix element $\langle \lambda_1 \dots \lambda_n | \mathcal{N}(1 \dots n) | \mu_1 \dots \mu_n \rangle$ must be forced to vanish. Similarly if none of the $\lambda_i \in [e]$ and one or more $\mu_i \in [e]$ then we must require that S be such that the matrix element $\langle \lambda_1 \dots \lambda_n | \mathcal{N}(1 \dots n) | \mu_1 \dots \mu_n \rangle = 0$.

In themselves conditions 1) and 2) will insure \mathcal{N}^{eff} is of the form shown in Figure 2.

The conditions on $\mathcal{N}^{(n)}$ will make blocks $[\mathcal{T}_N, \bar{\mathcal{T}}_N'']$ and $[\bar{\mathcal{T}}_N'', \mathcal{T}_N]$ vanish as required, but they also force blocks $[\bar{\mathcal{T}}_N', \bar{\mathcal{T}}_N'']$ and $[\bar{\mathcal{T}}_N'', \bar{\mathcal{T}}_N']$ to vanish. This latter consequence does not gain anything for us; but, of course, we do not destroy the intended structure of \mathcal{N}^{eff} either. It appears that we could eliminate this superfluous result (namely $[\bar{\mathcal{T}}_N', \bar{\mathcal{T}}_N'']$ vanishes) at the expense of making the conditions on the matrix elements dependent on the configuration of the remaining

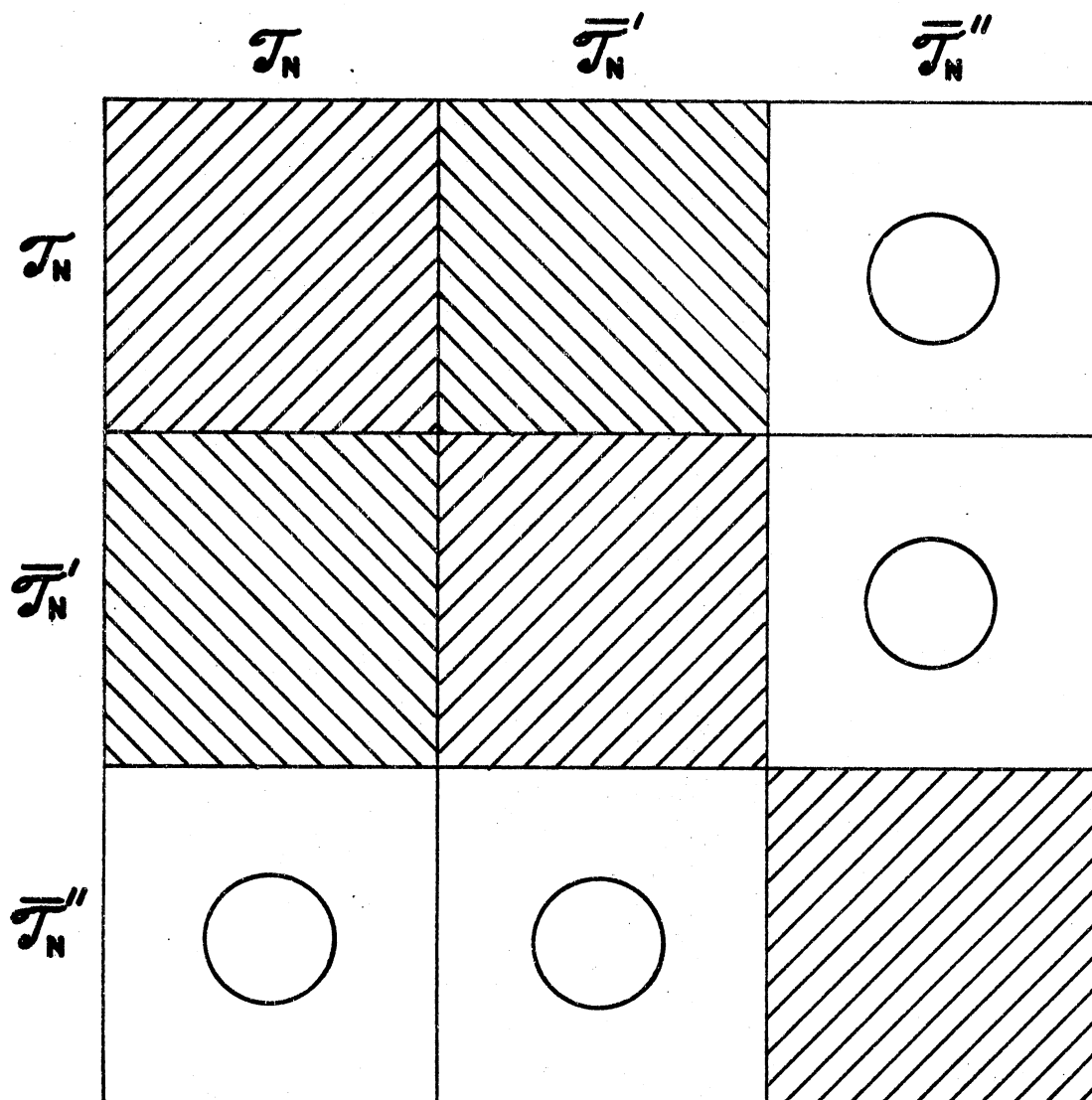


Figure 2. Partial Block Diagonalization of H^{eff} Accomplished by Imposition of Conditions (1) and (2). Without Further Conditions There Remains an Interaction Between \mathcal{T}_N and a Subspace of \mathcal{T}_N , Namely \mathcal{T}'_N

N-n particles. Indeed, such conditions do appear in the formulation due to Freed.⁹ These conditions would imply that the transformed hamiltonian cannot be written as the sum of one-, two-, three-, etc. body operators, that each term is really an N-electron operator. These complications are eliminated if we accept the vanishing of the $[\mathcal{T}'_N, \mathcal{T}''_N]$ and $[\mathcal{T}''_N, \mathcal{T}'_N]$ blocks.

However, we still must make blocks $[\mathcal{T}_N, \mathcal{T}'_N]$ and $[\mathcal{T}'_N, \mathcal{T}_N]$ vanish in order to meet fully the N-particle condition imposed on the effective hamiltonian. We impose a third restriction on the parameters (though more stringent than necessary it clearly achieves the intended result).

- 3) matrix elements off-diagonal in the core orbital indices vanish.

In other words, if a certain subset of core orbitals appears in $\langle \lambda_1 \lambda_2 \dots \lambda_n |$ that same subset must appear in $|\mu_1 \mu_2 \dots \mu_n \rangle$ or the matrix element must be made to vanish. Conditions 1), 2), and 3) imply the structure of the N-particle effective hamiltonian shown in Figure 3.

Recall we are interested in the $[\mathcal{T}_N, \mathcal{T}_N]$ block which, if all conditions on the matrix elements are satisfied, can be diagonalized to yield Q exact eigenvalues of the many-body system. We noted previously that the matrix elements on $[\mathcal{T}_N, \mathcal{T}_N]$ need be labeled only by valence orbitals (since each N-particle basis function in \mathcal{T}_N contains the same set of core orbitals). Hence, in constructing

H^v from \mathcal{H}^{eff} we need consider only that subset of terms in Eq. II-2 which connect Φ_m and Φ_n both in \mathcal{T}_N . Also, we can replace $a_c^\dagger a_c$ in all operators by unity (the occupation number of each

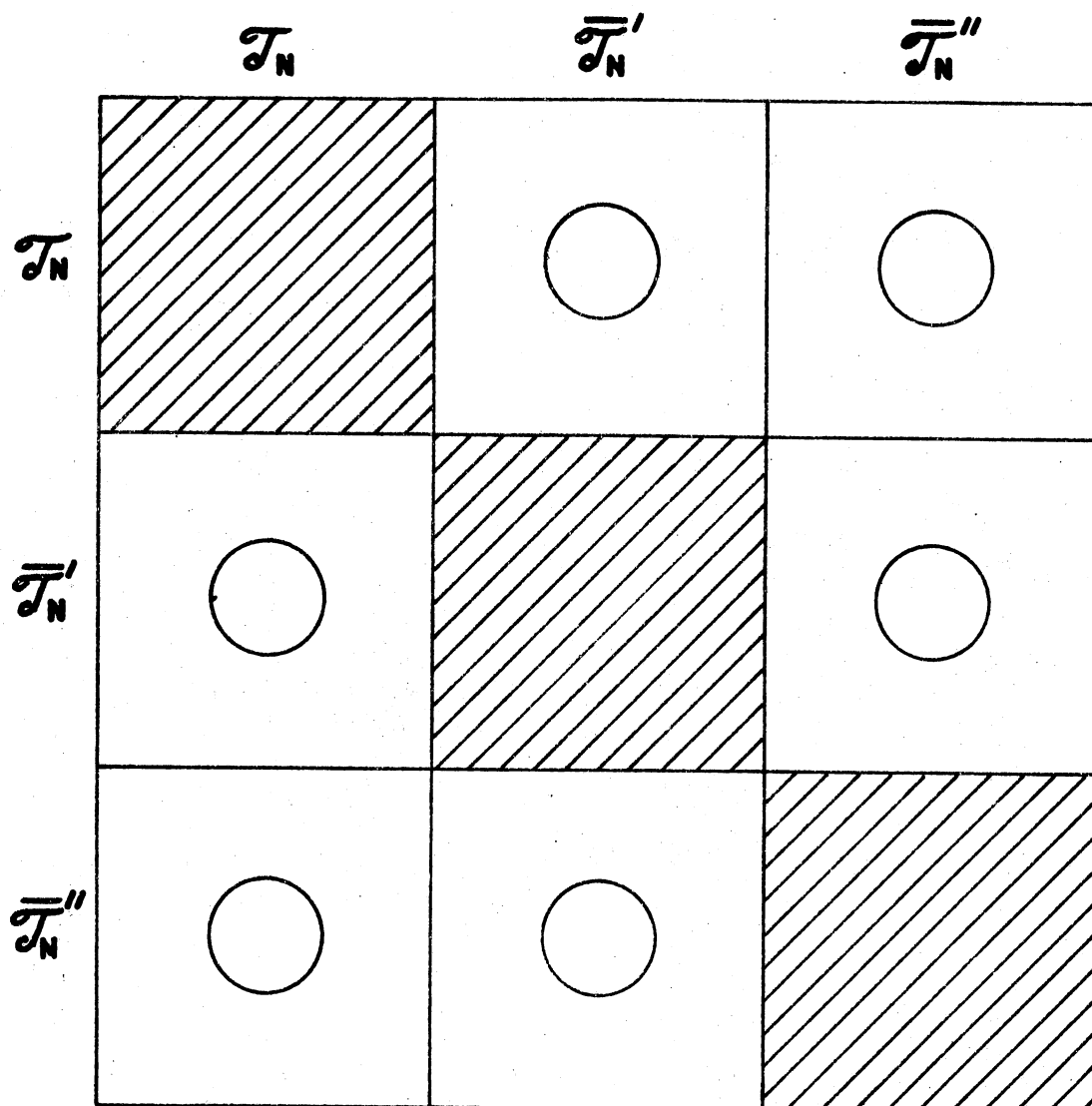


Figure 3. Final Structure of H^{eff} Obtained by Satisfying Conditions (1), (2), and (3)

core orbital in any state in \mathcal{T}_N).

We are now in a position to state the most important result of this work. To within a constant the matrix elements of \mathcal{H}^{eff} between N-electron basis vectors spanning \mathcal{T}_N will be the same as the matrix elements of the valence hamiltonian (for $i, j \in [v]$)

$$H^v = \sum_i \sum_j H_{ij}^{v1} a_i^\dagger a_j + \sum_{i_1 < i_2} \sum_{j_1 < j_2} H_{i_1 i_2 j_1 j_2}^{v2} a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} + \dots \quad (\text{II-3})$$

on the Q dimensional valence space spanned by

$$|l_1 l_2 \dots l_{N_v}\rangle = a_{l_1}^\dagger a_{l_2}^\dagger \dots a_{l_{N_v}}^\dagger |0\rangle$$

Here the parameters $H_{ij}^{v1}, H_{i_1 i_2 j_1 j_2}^{v2}$ are defined as follows: ($i, i_2, j_1, j_2 \in [v]$)

$$H_{ij}^{v1} = \langle i | \mathcal{H}(1) | j \rangle + \sum_c \langle ci | \mathcal{H}(12) | cj \rangle + \sum_{c < c'} \langle cc' i | \mathcal{H}(123) | cc' j \rangle + \dots \quad (\text{II-4a})$$

$$H_{i_1 i_2 j_1 j_2}^{v2} = \langle i_1 i_2 | \mathcal{H}(12) | j_1 j_2 \rangle$$

$$+ \sum_c \langle ci_1 i_2 | \mathcal{H}(123) | cj_1 j_2 \rangle + \dots \quad (\text{II-4b})$$

and in general

$$\begin{aligned}
 H_{i_1 \dots i_n j_1 \dots j_n}^{v_n} &= \langle i_1 \dots i_n | \mathcal{H}(1 \dots n) | j_1 \dots j_n \rangle \\
 &+ \sum_{k=1}^{N_c} \left\{ \sum_{c_1 < \dots < c_k} \langle c_1 \dots c_k i_1 \dots i_n | \mathcal{H}(1 2 \dots n+k) | c_1 \dots c_k j_1 \dots j_n \rangle \right\}
 \end{aligned}
 \tag{II-4c}$$

In the expression for H^v the indices $i_1 i_2 \dots j_1 j_2 \dots$ refer to valence orbitals (all ϕ_k for $k \in [v]$); in the definition of $H_{i_1 \dots i_n j_1 \dots j_n}^{v_n}$ the sums are over all core orbitals, $[c]$. H^v is an operator in the space of antisymmetrized products of N_v valence orbitals and by explicit construction takes into account the effects of the core orbitals and the valence shell correlation effects.

The problem now turns to computing the $\langle \lambda_1 \dots \lambda_n | \mathcal{H}(1 \dots n) | \mu_1 \dots \mu_n \rangle$ parameters to fulfill conditions 1), 2), and 3) by an appropriate choice of S . According to these conditions the one-, two-, and three-body matrices of \mathcal{H}^{eff} must have the structures shown in Figure 4, 5, and 6. For instance, in Figure 5 the label (cv) denotes the space spanned by all possible two particle kets made up of one core and one valence orbital. The subspaces (ce), (ve), and (ee) are, of course, infinite dimensional. In these figures, the conditions are to be imposed in order to yield explicit zeroes; further, the subblocks indicate the representation is block diagonal in the core indices. This means a matrix element such as

$$\langle c v_1 v_2 | \mathcal{H}(123) | c' v_1' v_2' \rangle$$

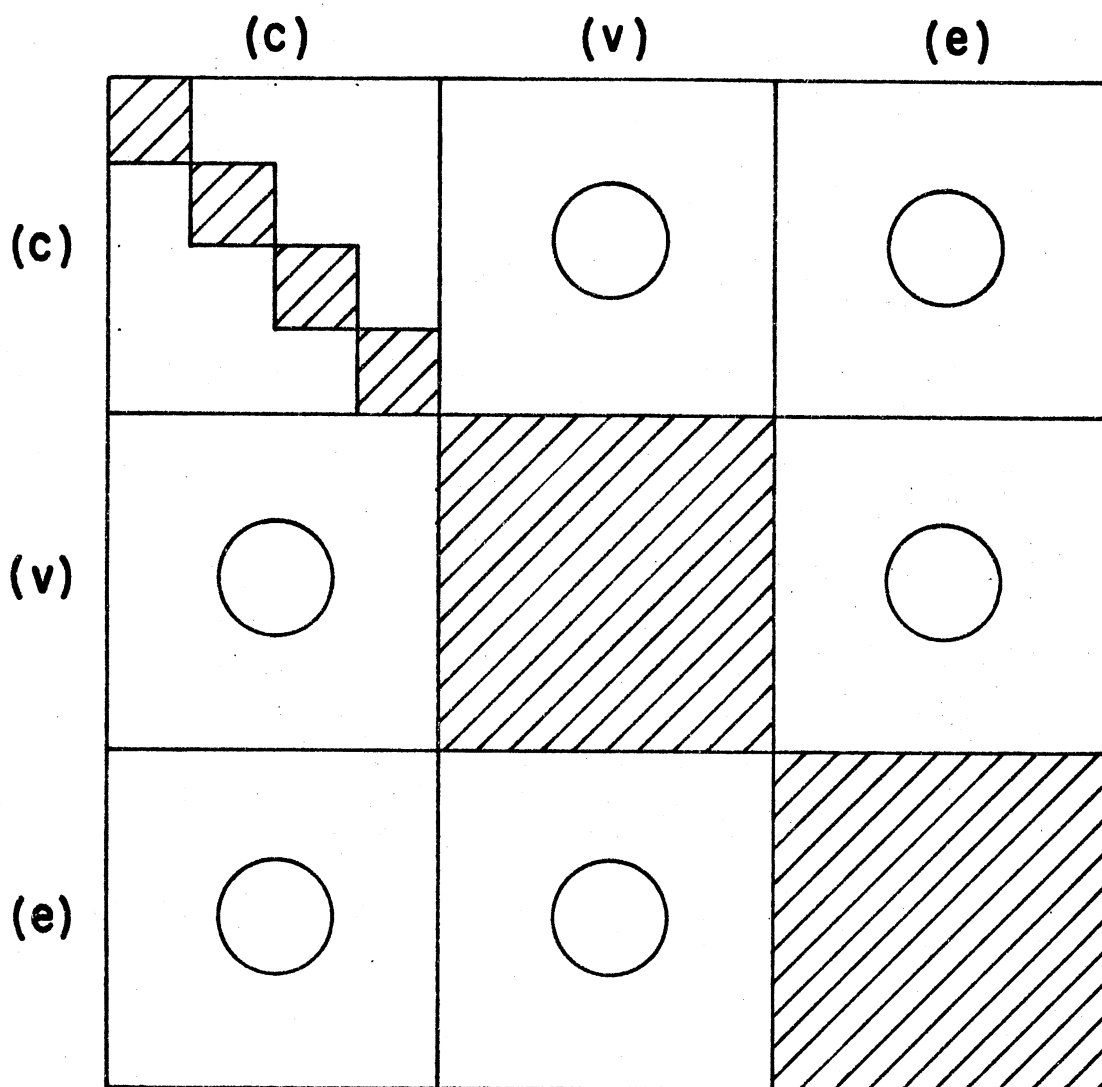


Figure 4. Explicit Form Required of the Matrix Elements of $\mathcal{H}(1)$ to Satisfy Conditions (1), (2), and (3). "C" Denotes Core Orbitals, "V" Denotes Valence Orbitals, and "e" Denotes Excited Orbitals. The "e" Space is in Principle Infinite. The Hatching in This and Subsequent Figures Denote Nonvanishing Matrix Elements

	(cc)	(cv)	(vv)	(ce)	(ve)	(ee)
(cc)		○	○	○	○	○
(cv)	○		○	○	○	○
(vv)	○	○		○	○	○
(ce)	○	○	○			
(ve)	○	○	○			
(ee)	○	○	○			

Figure 5. Explicit Form of Matrix Elements of $\mathcal{H}(12)$ in Order That Conditions (1), (2), and (3) be Fulfilled. (cc), (cv), etc. Represent the Spaces Spanned by All Antisymmetrized Products of Two Spin Orbitals of the Type Denotes

	(ccc)	(ccv)	(cvv)	(vvv)	(cce)	(cve)	(cee)	(vve)	(vee)	(eee)
(ccc)		○	○	○	○	○	○	○	○	○
(ccv)	○		○	○	○	○	○	○	○	○
(cvv)	○	○		○	○	○	○	○	○	○
(vvv)	○	○	○		○	○	○	○	○	○
(cce)	○	○	○	○						
(cve)	○	○	○	○						
(cee)	○	○	○	○						
(vve)	○	○	○	○						
(vee)	○	○	○	○						
(eee)	○	○	○	○						

Figure 6. Explicit Form of Matrix Elements of $\mathcal{H}(123)$ in Order That Conditions (1), (2), and (3) be Fulfilled. (cve), etc. Represent Antisymmetrized Products of Three Spin-Orbitals

vanishes unless $c = c'$. Finally diagonal hatches indicate no conditions need be imposed on the matrix elements on these subspaces.

We can now write down the form of the n -body matrix element $\langle \lambda_1 \dots \lambda_n | \mathcal{H}(1 \dots n) | \mu_1 \dots \mu_n \rangle$. There are $(n+1)$ different types of n -body basis kets with c and v orbitals but no e orbitals. For instance, for one-body kets there are types: $|c\rangle$ and $|v\rangle$; for two-body kets there are three types: $|cc'\rangle$, $|cv\rangle$, and $|vv'\rangle$; etc. The n -particle matrix elements with m core orbitals and $n-m$ valence orbitals must have the form:

$$\begin{aligned} & \langle c_1 \dots c_m v_1 \dots v_{n-m} | \mathcal{H}(1 \dots n) | c'_1 \dots c'_m v'_1 \dots v'_{n-m} \rangle \\ & = \delta_{c_1 c'_1} \dots \delta_{c_m c'_m} \langle c_1 \dots v_{n-m} | \mathcal{H}(1 \dots n) | c'_1 \dots v'_{n-m} \rangle \end{aligned}$$

That is, they must be diagonal in the core orbitals. We now turn to the problem of the cluster expansion of \mathcal{H}^{eff} in order to exhibit the one-, two-, three-, . . . body operators.

Cluster Expansion of \mathcal{H}^{eff}

In the preceding section, we set up the conditions that certain matrix elements of the effective hamiltonian, \mathcal{H}^{eff} , should vanish. These conditions should determine our choice of \mathcal{S} . However, there remains the problem of explicitly determining the operators, $\mathcal{H}(i)$, $\mathcal{H}(ij)$, $\mathcal{H}(ijk)$, Since \mathcal{S} is originally defined only by conditions on the N -electron space, the operators on subsets of

particles cannot be uniquely defined in any rigorous sense. However, the adoption of the following form for S

$$\begin{aligned} S &= S_1 + S_2 + \dots + S_N + S_{12} + S_{13} + \dots + S_{123} + \dots + S_{12\dots N} \\ &= \sum_{n=1}^N \sum_{1 \leq i_1 < i_2 < \dots < i_n} S_{i_1 i_2 \dots i_n} \end{aligned} \quad (\text{II-6})$$

leads to a well defined expansion for \mathcal{H}^{eff} .

The problem, then, is to arrange and classify (according to the number of interacting particles) the terms of the unitarily transformed hamiltonian:

$$\mathcal{H}^{\text{eff}} = e^{-iS} H e^{iS} = H - i[S, H] + \frac{(-i)^2}{2!} [S, [S, H]] + \dots \quad (\text{II-7})$$

Although the original hamiltonian, H , contains only one- and two-particle operators, the transformed hamiltonian contains many-particle interactions. Each commutator in the preceding equation contains one-, two-, . . . N -body terms due to the nature of S .

We want to re-express equation (II-7) in the following form:

$$\begin{aligned} \mathcal{H}^{\text{eff}} &= \mathcal{H}^{(1)} + \mathcal{H}^{(2)} + \dots + \mathcal{H}^{(N)} \\ &= \sum_{i_1=1}^N \mathcal{H}(i_1) + \sum_{i_1 < i_2} \mathcal{H}(i_1 i_2) + \dots \\ &= \sum_{n=1}^N \sum_{i_1 < \dots < i_n} \mathcal{H}(i_1 \dots i_n) \end{aligned} \quad (\text{II-8})$$

That is, we want \mathcal{H}^{eff} to be expressed as a sum of one-body operators ($\mathcal{H}^{(1)} = \sum_i \mathcal{H}^{(1)}$), two-body operators ($\mathcal{H}^{(2)} = \sum_{i_1 < i_2} \mathcal{H}^{(2)}(i_1, i_2)$), etc.

This problem is attacked by cluster expansion techniques.^{12,13}

It is essential to keep in mind that various cluster expansions are based upon different resolutions of the identity operator. Thus, if completely summed, a cluster decomposition of the operator is guaranteed to yield the original operator. It is in this spirit that defining the N-body operator \mathcal{H}^{eff} does not uniquely determine $\mathcal{H}^{(1)}$, $\mathcal{H}^{(2)}$, $\mathcal{H}^{(3)}$, etc.

On the other hand, only those expansions which can be meaningfully truncated in low order ($\mathcal{H}^{\text{eff}} \approx \mathcal{H}^{(1)} + \mathcal{H}^{(2)} + \mathcal{H}^{(3)}$) and thus presumably lead to a tractable computational procedure are worthwhile considering. We now argue that the Van Kampen cluster decomposition¹³ leads to a practical scheme for generating "linked terms" in expanding the effective hamiltonian. Our definition for "linked terms" and their importance will be discussed shortly.

We begin by introducing the following set of operators: N one-body operators,

$$\begin{aligned}
 J_i &= e^{-iS_i} \left[\frac{\vec{p}_i^2}{2m} + \sum_{\alpha} \frac{-Z_{\alpha} e^2}{|\vec{r}_i - \vec{R}_{\alpha}|} + U_i \right] e^{iS_i} \\
 &= e^{-iS_i} h_i e^{iS_i}
 \end{aligned}$$

$N \cdot (N-1)/2$ two-body operators,

$$J_{ij} = e^{-i(s_i + s_j + s_{ij})} [h_i + h_j + g_{ij}] e^{i(s_i + s_j + s_{ij})}$$

and, in general $N! / \{n!(N-n)!\}$ n-body operators

$$J_{i_1 \dots i_n} = e^{-i\mathcal{S}(i_1 \dots i_n)} \left[\sum_{p=1}^n h_{i_p} + \sum_{p < q} g_{i_p i_q} \right] e^{i\mathcal{S}(i_1 \dots i_n)} \quad (\text{II-9a})$$

where

$$\mathcal{S}(i_1 \dots i_n) = \sum_{p=1}^n \left\{ \sum_{\{l_1, l_2, \dots, l_p / i_1, i_2, \dots, i_n\}} S_{l_1, l_2, \dots, l_p} \right\} \quad (\text{II-9b})$$

Here the notation $\Sigma\{l_1 \dots l_p / i_1 \dots i_n\}$ implies our summing over all terms with p ordered indices $l_1 < l_2 < \dots < l_p$ chosen from the given set $i_1 < i_2 < \dots < i_n$. In these equations the subscripts are particle labels and all the operators are assumed to be symmetric functions of the particle labels.

Each operator $J_{i_1 \dots i_n}$ is defined in terms of a unitary transformation on the n -particle subspace. Thus, it may be expanded in a commutator series:

$$\begin{aligned}
\mathcal{J}_{i_1 \dots i_n} &= \left\{ \sum_{p=1}^n h_{i_p} + \sum_{p < q} g_{i_p i_q} \right\} \\
&- i \left[\mathcal{S}(i_1 \dots i_n), \left\{ \sum_{p=1}^n h_{i_p} + \sum_{p < q} g_{i_p i_q} \right\} \right] \\
&+ \frac{(-i)^2}{2!} \left[\mathcal{S}(i_1 \dots i_n), \left[\mathcal{S}(i_1 \dots i_q), \left\{ \sum_{p=1}^n h_{i_p} + \sum_{p < q} g_{i_p i_q} \right\} \right] \right] + \dots
\end{aligned} \tag{II-9c}$$

The basic insight of the Van-Kampen¹³ cluster development is that we can write a hierarchal series of equations:

$$\mathcal{J}_{i_1 \dots i_n} = \sum_{p=1}^n \left\{ \sum_{\{l_1 \dots l_p / i_1 \dots i_n\}} \mathcal{K}(l_1 \dots l_p) \right\} \tag{II-10}$$

which implicitly define the operators, $\mathcal{K}(l_1 \dots l_p)$ in terms of the \mathcal{J} 's. Explicitly, we write

$$\mathcal{J}_i = \mathcal{K}(i) \quad , \quad i = 1, \dots, N$$

$$\mathcal{J}_{ij} = \mathcal{K}(i) + \mathcal{K}(j) + \mathcal{K}(ij), \quad i < j = 1, \dots, N$$

$$\begin{aligned}
\mathcal{J}_{ijk} &= \mathcal{K}(i) + \mathcal{K}(j) + \mathcal{K}(k) + \mathcal{K}(ij) + \mathcal{K}(ik) + \mathcal{K}(jk) \\
&+ \mathcal{K}(ijk)
\end{aligned}$$

etc. Note that in the equation for $\mathcal{J}_{i_1 \dots i_n}$, all the $\mathcal{H}(\ell_1 \dots \ell_p)$ operators with $p < n$ have already been defined in terms of previous equations in the hierarchy, with the $\mathcal{J}_{i_1 \dots i_n}$ itself having been explicitly defined (in terms of S) in equation (II-9c). Thus, the equations implicitly define $\mathcal{H}(i_1 \dots i_n)$.

The transformed hamiltonian \mathcal{H}^{eff} is itself the N-body operator $\mathcal{J}_{1\dots N}$, the cluster expansion of which implicitly defines $\mathcal{H}(1\dots N)$. However, an essential characteristic of a useful cluster expansion of

$$\mathcal{H}^{\text{eff}} = \mathcal{J}_{1\dots N} = \sum_{i=1}^N \mathcal{H}(i) + \sum_{i < j} \mathcal{H}(ij) + \dots \mathcal{H}(1\dots N) \quad (\text{II-11})$$

is that we are able to truncate it after two or three sums:

$$\mathcal{H}^{\text{eff}} \approx \sum_{i=1}^N \mathcal{H}(i) + \sum_{i < j} \mathcal{H}(ij) + \sum_{i < j < k} \mathcal{H}(ijk)$$

In such a case, the required operators $\mathcal{H}(i)$, $\mathcal{H}(ij)$, and $\mathcal{H}(ijk)$ would be expressed in terms of the one-, two-, and three-body \mathcal{J} 's.

In general, the equation implicitly defining $\mathcal{H}(\ell_1 \dots \ell_q)$, can be inverted to yield the explicit formula

$$\mathcal{H}(i_1 \dots i_q) = \sum_{p=1}^q (-1)^{q-p} \left\{ \sum_{\{l_1 \dots l_p / i_1 \dots i_q\}} \mathcal{J}_{l_1 \dots l_p} \right\} \quad (\text{II-12})$$

In particular we have that

$$\mathcal{N}(i) = \mathcal{J}_i$$

$$\mathcal{N}(ij) = \mathcal{J}_{ij} - \mathcal{J}_i - \mathcal{J}_j$$

$$\mathcal{N}(ijk) = \mathcal{J}_{ijk} - \mathcal{J}_{ij} - \mathcal{J}_{ik} - \mathcal{J}_{jk} + \mathcal{J}_i + \mathcal{J}_j + \mathcal{J}_k$$

While it is obvious that $\mathcal{N}(i_1 \dots i_q)$ depends only upon operators acting upon the kets in the q -particle space labeled $i_1 \dots i_q$, the precise structure of these operators is not yet clear.

We now seek to establish the theorem that a given cluster operator (equation II-12) is composed of terms in which: i) all factors are "linked" and, ii) all q -particle labels ($i_1 \dots i_q$) occur. A "linked" term is one in which each factor in the term contains at least one particle label which appears in another factor. For example, terms like $S_{12} g_{13}$, $S_{13} h_3$, $S_{123} g_{12}$ are linked, whereas $S_{12} h_3$, $S_{12} g_{34}$, $S_{13} g_{24}$ are not linked. Thus, all terms in the expansion for $\mathcal{N}(ijk)$ will contain i , j , and k and will be linked.

The proof of these assertions is straight forward. First, since each $\mathcal{J}_{1 \dots p}^l$ in equation (II-12) may be written as a sum of nested commutators (recall definitions in equation (II-9)) no unlinked terms appear, for clearly, two factors having no particle labels in common commute. Second an n^{th} order commutator such as

$$\frac{(-i)^n}{n!} \left[S_{k_1 k_2}, \left[S_{k_2 k_3}, \dots \right] \right]$$

in which $k_1 \dots k_t$ is a proper subset of $i_1 \dots i_q$ occurs in all $\mathcal{J}^{\ell_1 \dots \ell_p}$'s for which the set $k_1 \dots k_t$ is contained in $\ell_1 \dots \ell_p$. Because each $\mathcal{J}^{\ell_1 \dots \ell_p}$ enters with a factor ± 1 in equation (II-12), we find the overall coefficient of such a commutator to be given by

$$\sum_{p=t}^q (-1)^{q-p} \frac{(q-t)!}{(q-p)!(p-t)!} = \sum_{r=0}^{q-t} (-1)^{q-t-r} \frac{(q-t)!}{(q-t-r)! r!} = \begin{cases} 0 & t < q \\ 1 & t = q \end{cases}$$

Hence, all terms containing only a proper subset of the particle labels $i_1 \dots i_q$ cancel from the expansion of $\mathcal{H}(i_1 \dots i_q)$. Thus, the theorem is established.

The result derived here leads us to argue on physical grounds that the many-particle terms in the cluster expansion

$$\mathcal{H}^{\text{eff}} = \sum_{i=1}^N \mathcal{H}(i) + \sum_{i_1 < i_2}^N \mathcal{H}(i_1, i_2) + \dots + \sum_{i_1 < i_2 < \dots < i_n} \mathcal{H}(i_1, i_2, \dots, i_n) + \dots$$

contain only the linked-parts of the interaction among many particles and may be neglected in comparison with, say, the one-, two-, and three-particle terms. Of course, any blanket statement such as this must be tempered by calculations on the particular system.

Implicit in this proof is an assumption which must be more fully explored. We have assumed, for example, that the two-particle

operators, such as g_{12} and S_{12} are linked. Yaris¹¹ has argued that the generators of the unitary transformation are themselves linked in the sense that, for example, S_{12} does not contain terms such as $(S_1 + S_2)$ or $S_1 S_2$. On the other hand, it is clear that g_{12} is unlinked in this very sense since, by definition

$$g_{12} = \frac{e^2}{r_{12}} - \frac{U_1 + U_2}{N-1}$$

Therefore, the three-body commutator in $\mathcal{H}(123)$, $[S_{13}, g_{12}]$, contains a term

$$\frac{S_{13} U_1 - U_1 S_{13}}{N-1}$$

depending on only two, rather than all three, particle indices.

Generally, if g_{12} is "split-up," then clearly linked terms enter n-body operators which have only n-1 particle indices. Note that such terms are multiplied by $(N-1)^{-1}$.

It is evident that if the operators g_{ij} are considered to be split-up, the statement that the n-body $\mathcal{H}(i_1 \dots i_n)$ contains only terms with all n indices $(i_1 \dots i_n)$ cannot apply to certain terms containing the U_i 's. One can easily show, however, that these (n-1)-particle terms can be combined with identical terms arising from (n-1)-particle clusters. Such a splitting up and rearrangement of terms results in one linked expansion for

$$e^{-iS} \left(\sum_{i < j} \frac{e^2}{r_{ij}} \right) e^{iS}$$

and a second linked expansion for

$$e^{-iS} \left(\sum_{i=1}^N U_i \right) e^{iS}$$

The factor $(N-1)^{-1}$ has disappeared, a fact which formally follows from the regrouping of n -body and $(n-1)$ -body cluster terms. A little reflection indicates this result is obvious since the original operator can be written:

$$\begin{aligned} \sum_{i < j} g_{ij} &= \sum_{i < j} \left[\frac{e^2}{r_{ij}} - \frac{U_i + U_j}{N-1} \right] \\ &= \sum_{i < j} \frac{e^2}{r_{ij}} - \sum_i U_i \end{aligned}$$

Thus, instead of transforming $\sum_{ij} g_{ij}$, we may transform $\sum_{i < j} e^2/r_{ij}$ and $-\sum_i U_i$ separately, expanding the results in two linked cluster series. The proof that each series is linked goes through exactly as above.

However, we can look on g_{ij} formally as the basic two-body interaction in the sense of a pair potential. Consequently, we will keep g_{ij} intact. The matrix elements that enter for the "dressed" two-body potential, g_{ij} , will therefore have an explicit dependence on the potential U_i and the total number of electrons, N , in the system.

Effective Hamiltonian Operators

We can now return to the construction of the valence shell hamiltonian, \mathbb{H}^v . For our purposes we take the orbitals in which we expand $\Phi(x)$ to be eigenfunctions of h :

$$\hat{h}_1 |\phi_j\rangle = \epsilon_j |\phi_j\rangle$$

The one-body operator is thus already diagonal in the orbital indices and, hence, we take $S_i = 0$. Our problem is to choose S_{12} , S_{123} , etc. so the matrices in Figures 5 and 6 will have the required structure.

We begin by considering the two-body term. In second quantized form they are

$$\mathcal{X}^{(2)} = \sum_{\lambda_1 < \lambda_2} \sum_{\mu_1 < \mu_2} \langle \lambda_1, \lambda_2 | \mathcal{X}(12) | \mu_1, \mu_2 \rangle a_{\lambda_1}^\dagger a_{\lambda_2}^\dagger a_{\mu_2} a_{\mu_1}$$

where

$$|\lambda_1, \lambda_2\rangle = \frac{1}{\sqrt{2!}} \left\{ |\lambda_1\rangle_1 |\lambda_2\rangle_2 - |\lambda_1\rangle_2 |\lambda_2\rangle_1 \right\}$$

In principle, we can choose S_{12} so that the matrix representation of $\mathcal{X}^{(2)}$ has the form shown in Figure 5. That is, we would like,

$$\begin{aligned} \langle cc' | \mathcal{H}(12) | pp' \rangle & \quad \text{either } \rho = c'' (\neq c, c') \\ & = \langle pp' | \mathcal{H}(12) | cc' \rangle = 0 \quad \text{unless or } \rho' = c'' (\neq c, c') \quad (\text{II-14a}) \\ & \quad \text{or } |pp'\rangle = |cc'\rangle \end{aligned}$$

$$\begin{aligned} \langle cv | \mathcal{H}(12) | cp \rangle \\ & = \langle cp | \mathcal{H}(12) | cv \rangle = 0 \quad \text{unless } \rho = v' \quad (\text{II-14b}) \end{aligned}$$

$$\begin{aligned} \langle vv' | \mathcal{H}(12) | pp' \rangle \\ & = \langle pp' | \mathcal{H}(12) | vv' \rangle = 0 \quad \text{unless } |pp'\rangle = |v''v'''\rangle \quad (\text{II-14c}) \end{aligned}$$

It is impossible in practice to impose these conditions and solve for S . By approximating $\mathcal{H}(12)$, we can develop a tractable approach to the problem.

$$\begin{aligned} \mathcal{H}(12) & = e^{-iS_{12}} [h_1 + h_2 + g_{12}] e^{iS_{12}} - h_1 - h_2 \\ & = g_{12} + (-i) [S_{12}, h_1 + h_2 + g_{12}] \\ & \quad + \frac{(-i)^2}{2!} [S_{12}, [S_{12}, h_1 + h_2 + g_{12}]] + \dots \quad (\text{II-15}) \end{aligned}$$

We also partition g_{12} into the sum of a "diagonal" part and an "off-diagonal" part, writing

$$g_{12} = g_{12}^{\text{diag}} + g_{12}^{\text{off-diag}}$$

where

$$g_{12}^{\text{diag}} = \sum_{\lambda_1 < \lambda_2} |\lambda_1, \lambda_2\rangle \langle \lambda_1, \lambda_2 | g_{12} | \lambda_1, \lambda_2 \rangle \langle \lambda_1, \lambda_2 |$$

and

$$g_{12}^{\text{off-diag}} = g_{12} - g_{12}^{\text{diag}}$$

Now, we define the operator W_{12} over all two-particle space as

$$W_{12} \equiv g_{12} - i [S_{12}, h_1 + h_2 + g_{12}^{\text{diag}}] \quad (\text{II-16})$$

This could be an approximation to the transformed two-body operator $\mathcal{H}(12)$. Inserting this definition into equation (II-15), we find:

$$\begin{aligned} \mathcal{H}(12) &= W_{12} - i [S_{12}, g_{12}^{\text{off-diag}}] \\ &+ \frac{(-i)^2}{2!} [S_{12}, i \{ W_{12} - g_{12}^{\text{diag}} - g_{12}^{\text{off-diag}} \}] \\ &+ \frac{(-i)^2}{2!} [S_{12}, [S_{12}, g_{12}^{\text{off-diag}}]] + \dots \\ &= W_{12} - \frac{i}{2} [S_{12}, g_{12}^{\text{off-diag}}] \\ &- \frac{1}{2} [S_{12}, i \{ W_{12} - g_{12}^{\text{diag}} - i [S_{12}, g_{12}^{\text{off-diag}}] \}] + \dots \end{aligned}$$

$$\begin{aligned}
&= W_{12} - \frac{i}{2} [S_{12}, g_{12}^{\text{off-diag}}] - \frac{1}{2} [S_{12}, i \{W_{12} - g_{12}^{\text{diag}}\}] \\
&\quad - \frac{1}{2} [S_{12}, [S_{12}, g_{12}^{\text{off-diag}}]] + \dots \quad (\text{II-17})
\end{aligned}$$

We will approximate $\mathcal{N}(12)$ as the sum of W_{12} plus the first order commutators. However, we still cannot impose conditions (II-14) on this approximation and find a tractable equation for S_{12} . Consequently, we impose conditions analogous to (II-14) on the first term in the approximation, W_{12} . The resulting S_{12} can be substituted into our approximation for $\mathcal{N}(12)$. The corresponding matrix elements of S_{12} are then given by:

$$\begin{aligned}
&\langle \lambda_1, \lambda_2 | S_{12} | \mu_1, \mu_2 \rangle \\
&= \frac{i \langle \lambda_1, \lambda_2 | g_{12} | \mu_1, \mu_2 \rangle}{\epsilon_{\lambda_1} + \epsilon_{\lambda_2} + \langle \lambda_1, \lambda_2 | g_{12} | \lambda_1, \lambda_2 \rangle - \epsilon_{\mu_1} - \epsilon_{\mu_2} - \langle \mu_1, \mu_2 | g_{12} | \mu_1, \mu_2 \rangle}
\end{aligned}$$

This result follows immediately from inserting a complete set of two-body states between the operator factors in

$$W_{12} = g_{12} - i \left\{ S_{12} (h_1 + h_2 + g_{12}^{\text{diag}}) - (h_1 + h_2 + g_{12}^{\text{diag}}) S_{12} \right\}$$

and recognizing that, for example:

$$(h_1 + h_2 + g_{12}^{\text{diag}}) |\mu_1, \mu_2\rangle = (\epsilon_{\mu_1} + \epsilon_{\mu_2} + \langle \mu_1, \mu_2 | g_{12} | \mu_1, \mu_2 \rangle) |\mu_1, \mu_2\rangle$$

We shall choose the remaining matrix elements of S_{12} equal to zero. The structures of W_{12} and S_{12} are shown in Figures 7 and 8.

In general, the symmetry operators for the Coulomb hamiltonian commute with $h_1 + h_2$, but not with g_{12}^{diag} . Imposing the conditions (Eq.'s II-14) on W_{12} then leads to an effective hamiltonian that does not possess the original symmetry. The problem arises with our choice of the two particle states with respect to which g_{12}^{diag} is defined. These two-particle vectors are antisymmetrized products of spin orbitals and, therefore, they are basis vectors for reducible representations of the symmetry group.

The result of this broken symmetry is that when CI calculations are performed, the ensuing energy levels which were triplets for the $1/r_{12}$ operator are no longer degenerate. The definition of g_{12}^{diag} in terms of antisymmetrized products of spin orbitals mixes the $S = 1 m_s = 0$ state with the $S = 0 m_s = 0$ state. Our purpose in defining W_{12} as in Eq. II-16 was to include in a tractable form as much of the dynamics as possible. The destruction of symmetry is a very disturbing consequence of this choice and a compelling reason for modifying it. There are various modifications of g_{12}^{diag} which could be posed for keeping the symmetry. If g_{12}^{diag} were defined

$$g_{12}^{\text{diag}} = \sum_I |I\rangle \langle I | g_{12} | I\rangle \langle I |$$

	(cc)	(cv)	(vv)	(ce)	(ve)	(ee)
(cc)		○	○	○	○	○
(cv)	○		○	○	○	○
(vv)	○	○		○	○	○
(ce)	○	○	○			
(ve)	○	○	○			
(ee)	○	○	○			

Figure 7. Structure of W_{12} on the Two-Particle Space

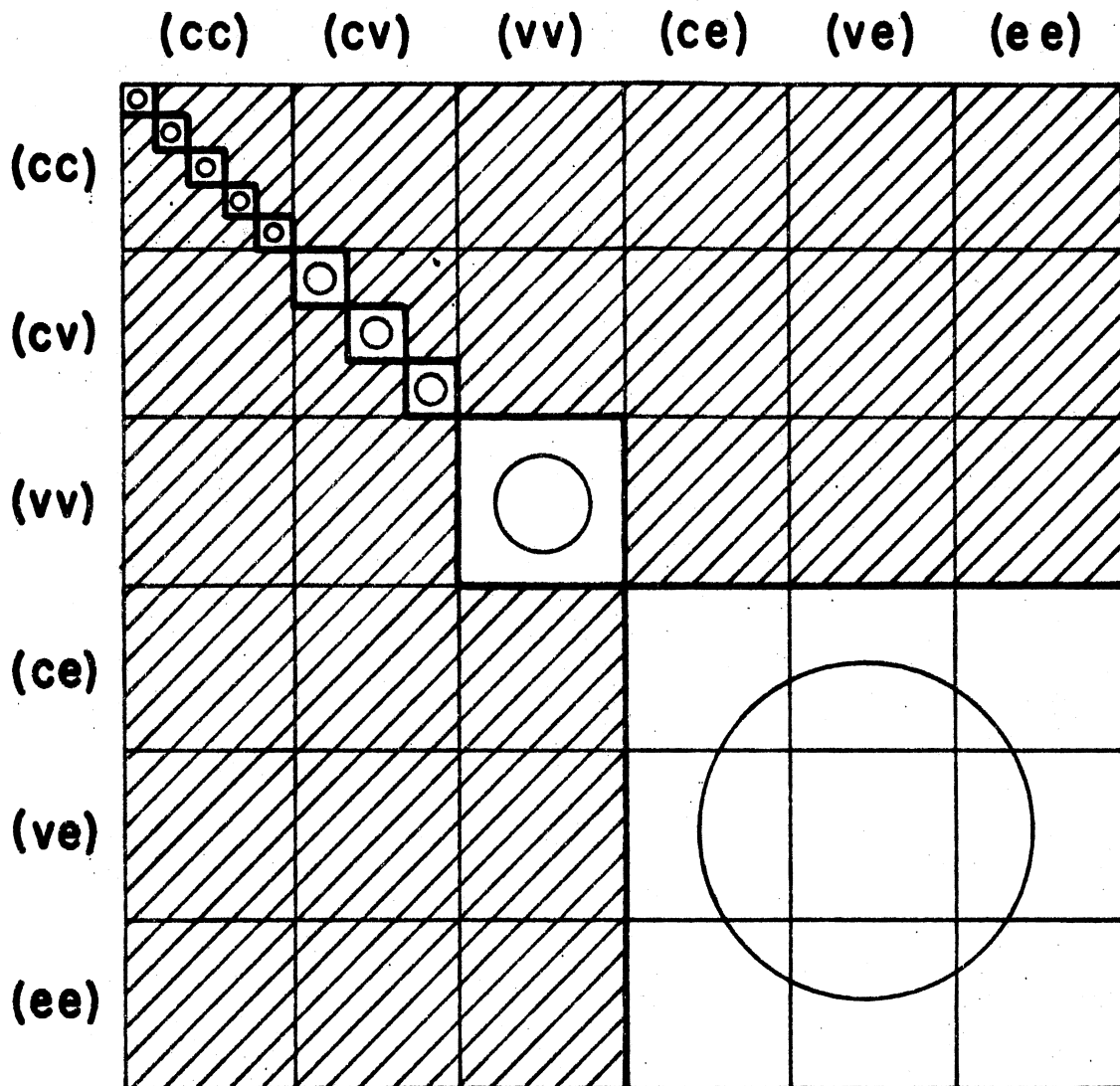


Figure 8. Structure of S_{12} on the Two-Particle Space

where the $|I\rangle$ are antisymmetrized two particle singlet and triplet bases, then the problem would not occur.

We might be tempted to quit after the two-body cluster terms. As a matter of fact, even if we consider only the two-body generators S_{12} , linked single commutators also occur in the three-body clusters. A detailed comparison of Harris' work and our three-body clusters indicate these three-body terms play a crucial role in defining the pi-electron effective interaction. In principle we should choose S_{123} so as to insure the linked three-body operators have the form shown in Figure 6. However, for the time being, we shall set $S_{123} = 0$ and use the S_{12} determined above to evaluate the three-body clusters.

In considering the three-body terms we again keep the double commutators; however, because of the definition of W_{12} , they can be re-expressed in the following form:

$$\begin{aligned}
 [S_{12}, [S_{13}, h_1 + h_3 + g_{13}]] &= [S_{12}, [S_{13}, h_1 + h_3 + g_{13}^{\text{diag}}]] \\
 &\quad + [S_{12}, [S_{13}, g_{13}^{\text{off-diag}}]] \\
 &= [S_{12}, i\{W_{13} - g_{13}^{\text{diag}} - g_{13}^{\text{off-diag}}\}] + [S_{12}, [S_{13}, g_{13}^{\text{off-diag}}]] \\
 &= -i[S_{12}, g_{13}^{\text{off-diag}}] + i[S_{12}, \{W_{13} - g_{13}^{\text{diag}}\}] \\
 &\quad + [S_{12}, [S_{13}, g_{13}^{\text{off-diag}}]]
 \end{aligned}$$

We find the three-body terms can be expressed as:

$$\begin{aligned}
\mathcal{A}(123) &= e^{-i[S_{12}+S_{13}+S_{23}]} [h_1+h_2+h_3+g_{12}+g_{13}+g_{23}] e^{i[S_{12}+S_{13}+S_{23}]} \\
&\quad - \left\{ e^{-iS_{12}} [h_1+h_2+g_{12}] e^{iS_{12}} + e^{-iS_{13}} [h_1+h_3+g_{13}] e^{iS_{13}} \right. \\
&\quad \left. + e^{-iS_{23}} [h_2+h_3+g_{23}] e^{iS_{23}} \right\} + h_1 + h_2 + h_3 \\
&= -i \left\{ [S_{12}, g_{13}] + [S_{12}, g_{23}] + [S_{13}, g_{12}] + [S_{13}, g_{23}] + [S_{23}, g_{12}] \right. \\
&\quad \left. + [S_{23}, g_{13}] \right\} + \frac{(-i)^2}{2!} \left\{ [S_{12}, [S_{12}, g_{13}+g_{23}]] + [S_{12}, [S_{13}, g_{12}+g_{23}]] \right. \\
&\quad \left. + [S_{12}, [S_{23}, g_{12}+g_{13}]] + [S_{12}, [S_{13}, h_1+h_3+g_{13}]] + [S_{12}, [S_{23}, h_2+h_3+g_{23}]] \right. \\
&\quad \left. + [S_{13}, [S_{13}, g_{12}+g_{23}]] + [S_{13}, [S_{12}, g_{13}+g_{23}]] + [S_{13}, [S_{23}, g_{12}+g_{13}]] \right. \\
&\quad \left. + [S_{13}, [S_{12}, h_1+h_2+g_{12}]] + [S_{13}, [S_{23}, h_2+h_3+g_{23}]] \right. \\
&\quad \left. + [S_{23}, [S_{23}, g_{12}+g_{13}]] + [S_{23}, [S_{13}, g_{12}+g_{23}]] + [S_{23}, [S_{12}, g_{13}+g_{23}]] \right. \\
&\quad \left. + [S_{23}, [S_{12}, h_1+h_2+g_{12}]] + [S_{23}, [S_{13}, h_1+h_3+g_{13}]] \right\}
\end{aligned}$$

Combining the previous two equations we get (disregarding terms with two or more commutators):

$$\begin{aligned}
 \mathcal{H}(123) = & \frac{-i}{2} \left\{ [S_{12}, g_{13}^{\text{off-diag}}] + [S_{12}, g_{23}^{\text{off-diag}}] + [S_{13}, g_{12}^{\text{off-diag}}] \right. \\
 & + [S_{13}, g_{23}^{\text{off-diag}}] + [S_{23}, g_{12}^{\text{off-diag}}] + [S_{23}, g_{13}^{\text{off-diag}}] \\
 & + [S_{12}, \{g_{13}^{\text{diag}} + W_{13}\}] + [S_{12}, \{g_{23}^{\text{diag}} + W_{23}\}] + [S_{13}, \{g_{12}^{\text{diag}} + W_{12}\}] \\
 & \left. + [S_{13}, \{g_{23}^{\text{diag}} + W_{23}\}] + [S_{23}, \{g_{12}^{\text{diag}} + W_{12}\}] + [S_{23}, \{g_{13}^{\text{diag}} + W_{13}\}] \right\} \quad (\text{II-19})
 \end{aligned}$$

Valence Shell Hamiltonian

We are now ready to construct the valence hamiltonian. That is, we evaluate the matrix elements which appear in equations II-4a and II-4b subject to the approximations stated above in equations II-17. From equations II-4a and II-4b we see that the matrix elements needed to construct the valence hamiltonian are the following:

$$\langle v | \mathcal{H}(1) | v' \rangle, \quad \langle cv | \mathcal{H}(12) | cv' \rangle, \quad \text{and} \quad \langle cc'v | \mathcal{H}(123) | cc'v' \rangle$$

for $H_{vv'}^{v1}$; and

$$\langle vv' | \mathcal{H}(12) | v''v''' \rangle \quad \text{and} \quad \langle cvv' | \mathcal{H}(123) | cv''v''' \rangle$$

for $H_{vv'v''v'''}^{v2}$. To facilitate the discussion of equation II-17, we

note

$$\langle cv | W_{12} | cv' \rangle = \langle cv | g_{12} | cv' \rangle$$

and

$$\langle vv' | W_{12} | v''v''' \rangle = \langle vv' | g_{12} | v''v''' \rangle$$

We further see that

$$\langle cv | [S_{12}, W_{12}] | cv' \rangle = 0$$

$$\langle cv | [S_{12}, g_{12}^{\text{diag}}] | cv' \rangle = 0$$

$$\langle vv' | [S_{12}, W_{12}] | v''v''' \rangle = 0$$

and

$$\langle vv' | [S_{12}, g_{12}^{\text{diag}}] | v''v''' \rangle = 0$$

These results follow from the structure of S_{12} and W_{12} as shown in Figures 7 and 8. Thus, by inserting a complete set of anti-symmetrized two-body states

$$1 = \sum_{p_1 < p_2} |p_1 p_2\rangle \langle p_1 p_2|$$

in $[S_{12}, g_{12}^{\text{off-diag}}]$ we find that

$$\begin{aligned} \langle cv | \mathcal{H}(12) | cv' \rangle &= \langle cv | g_{12} | cv' \rangle \\ &- \frac{i}{2} \sum_{p_1 < p_2} \left\{ \langle cv | S_{12} | p_1 p_2 \rangle \langle p_1 p_2 | g_{12}^{\text{off-diag}} | cv' \rangle \right. \\ &\quad \left. - \langle cv | g_{12}^{\text{off-diag}} | p_1 p_2 \rangle \langle p_1 p_2 | S_{12} | cv' \rangle \right\} \end{aligned}$$

For convenience, we now define the symbol

$$\begin{aligned} M_{\substack{\lambda_1, \lambda_2 & \lambda_3, \lambda_4 \\ \mu_1, \mu_2 & \mu_3, \mu_4}} &= i \left\{ \langle \lambda_1, \lambda_2 | S_{12} | \lambda_3, \lambda_4 \rangle \langle \mu_1, \mu_2 | g_{12}^{\text{off-diag}} | \mu_3, \mu_4 \rangle \right. \\ &\quad \left. - \langle \lambda_1, \lambda_2 | g_{12}^{\text{off-diag}} | \lambda_3, \lambda_4 \rangle \langle \mu_1, \mu_2 | S_{12} | \mu_3, \mu_4 \rangle \right\} \\ &= - \langle \lambda_1, \lambda_2 | g_{12}^{\text{off-diag}} | \lambda_3, \lambda_4 \rangle \langle \mu_1, \mu_2 | g_{12}^{\text{off-diag}} | \mu_3, \mu_4 \rangle \\ &\quad \left\{ \frac{1}{\epsilon_{\lambda_1} + \epsilon_{\lambda_2} + \langle \lambda_1, \lambda_2 | g_{12} | \lambda_1, \lambda_2 \rangle - \epsilon_{\lambda_3} - \epsilon_{\lambda_4} - \langle \lambda_3, \lambda_4 | g_{12} | \lambda_3, \lambda_4 \rangle} \right. \\ &\quad \left. - \frac{1}{\epsilon_{\mu_1} + \epsilon_{\mu_2} + \langle \mu_1, \mu_2 | g_{12} | \mu_1, \mu_2 \rangle - \epsilon_{\mu_3} - \epsilon_{\mu_4} - \langle \mu_3, \mu_4 | g_{12} | \mu_3, \mu_4 \rangle} \right\} \end{aligned}$$

where the second equation follows from our choice of the matrix elements of S_{12} . Examination of these matrix elements reveals that

$$M_{\mu_1 \mu_2 \mu_3 \mu_4}^{\lambda_1 \lambda_2 \lambda_3 \lambda_4} = \left(M_{\lambda_3 \lambda_4 \lambda_1 \lambda_2}^{\mu_3 \mu_4 \mu_1 \mu_2} \right)^*$$

and

$$M_{\mu_1 \mu_2 \mu_3 \mu_4}^{\lambda_1 \lambda_2 \lambda_3 \lambda_4} = -M_{\lambda_1 \lambda_2 \lambda_3 \lambda_4}^{\mu_1 \mu_2 \mu_3 \mu_4}$$

Furthermore, interchanging two indices within any of the four pairs $(\lambda_1 \lambda_2)$, $(\lambda_3 \lambda_4)$, $(\mu_1 \mu_2)$, $(\mu_3 \mu_4)$ also changes the sign of M . These observations simplify the summations in constructing the valence hamiltonian. In this notation we find

$$\langle cv | \mathcal{H}(12) | cv' \rangle = \langle cv | g_{12} | cv' \rangle - \frac{1}{2} \sum_{\substack{p_1 < p_2 \\ p_1 p_2 < v}} M_{p_1 p_2 < v}^{cv} p_1 p_2 \quad (\text{II-21a})$$

Similarly, we obtain

$$\langle vv' | \mathcal{H}(12) | v'' v''' \rangle = \langle vv' | g_{12} | v'' v''' \rangle - \frac{1}{2} \sum_{p_1 < p_2} M_{p_1 p_2 v'' v'''}^{vv'} p_1 p_2 \quad (\text{II-21b})$$

We now evaluate the matrix elements of the three-body terms found in equation II-19. The general considerations found in the appendix are used. Only the first six commutators in equation II-19 yield non-vanishing contributions to $\langle cc'v | \mathcal{H}(123) | cc'v' \rangle$ and $\langle cvv' | \mathcal{H}(123) |$

$cv''v'''$. That the contributions of the last six commutators vanish can be seen by using equation A-4 with $Y = W_{12} + \xi_{12}^{\text{diag}}$ and noting the explicit structures of $W_{12} + \xi_{12}^{\text{diag}}$ and noting the explicit structures of W_{12} and S_{12} as indicated in Figures 7 and 8. Hence, in equation A-4 with $Y = \xi_{12}^{\text{off-diag}}$ and identifying $\lambda_1 = \mu_1 = c$, $\lambda_2 = \mu_2 = c'$, and $\lambda_3 = v$, $\mu_3 = v'$, we obtain

$$\begin{aligned}
 \langle cc'v | \mathcal{H}(123) | cc'v' \rangle = & -\frac{1}{2} \sum_{\rho} \left\{ M_{\rho c' cv'}^{cv c' \rho} \right. \\
 & + M_{c \rho c' v'}^{c' v \rho c} + M_{c' \rho c' v'}^{cv c \rho} + M_{\rho c cv'}^{c' v \rho c'} \\
 & + M_{\rho v cv'}^{cc' \rho c'} + M_{v \rho c' v'}^{cc' \rho c} + M_{c' \rho cc'}^{cv v' \rho} \quad (\text{II-22}) \\
 & \left. + M_{c \rho cc'}^{c' v \rho v'} + M_{v \rho cc'}^{cc' \rho v'} \right\}
 \end{aligned}$$

Again, the general result of equation A-4 can be used with $\lambda_1 = \mu_1 = c$, $\lambda_2 = v$, $\mu_2 = v''$, and $\lambda_3 = v'$, $\mu_3 = v'''$ in order to find

$$\begin{aligned}
\langle cvv' | \mathcal{X}(123) | cv''v''' \rangle &= -\frac{1}{2} \sum_p \left\{ M_{cp}^{vv' pc} \right. \\
&+ M_{v'p}^{cv pc} + M_{vp}^{cv' cp} + M_{cp}^{vv' pv''} + M_{pc}^{vv' pv''} \quad (\text{II-23}) \\
&\left. + M_{pv'}^{cv pv''} + M_{v'p}^{cv pv''} + M_{pv}^{cv' v'' p} + M_{vp}^{cv' v''' p} \right\}
\end{aligned}$$

These results for the two- and three-body matrix elements are summed over the core orbitals as indicated in equations II-4a and II-4b. Certain two- and three-body cluster terms can be combined. Furthermore, summing over the core orbitals and taking into account the symmetry of the M 's results in restricted sums. The resulting one- and two-body matrix elements for the valence hamiltonian can now be written.

$$\begin{aligned}
\langle v | H^{v1} | v' \rangle &= \epsilon_v \delta_{vv'} + \sum_c \langle cv | g_{12} | cv' \rangle \\
&- \frac{1}{4} \left\{ - \sum_c \sum_{c'} \sum_{c''} M_{c'c''cv'}^{cv c'c''} + \sum_c \sum_{p_1 \notin [c]} \sum_{p_2 \notin [c]} M_{p_1 p_2 cv'}^{cv p_1 p_2} \right\}
\end{aligned}$$

$$\begin{aligned}
& +2 \sum_c \sum_{c'} \sum_{p \notin [v]} M_{c'p cv'}^{cv cp} + 2 \sum_c \sum_{c'} \sum_{p \notin [c]} \left(M_{pv cv'}^{cc' pc'} + M_{pc' cc'}^{cv pv'} \right) \\
& \quad + \left. \sum_c \sum_{c'} \sum_p M_{vp cc'}^{cc' pv'} \right\} \quad (\text{II-24})
\end{aligned}$$

$$\langle vv' | \mathbb{H}^{v2} | v'' v''' \rangle = \langle vv' | g_{12} | v'' v''' \rangle$$

$$-\frac{1}{4} \left\{ - \sum_c \sum_{c'} M_{c'c v''v'''}^{vv' c'c} + \sum_{p_1 \notin [c]} \sum_{p_2 \notin [c]} M_{p_1 p_2 v''v'''}^{vv' p_1 p_2} \right.$$

$$\left. + 2 \sum_c \sum_{p \notin [v]} \left(M_{v'p v''v'''}^{cv pc} + M_{vp v''v'''}^{cv' cp} + M_{cp cv''}^{vv' pv''} + M_{pc cv''}^{vv' pv''} \right) \right.$$

$$\left. + 2 \sum_c \sum_{p \notin [c]} \left(M_{pv' cv''}^{cv pv''} + M_{vp cv''}^{cv pv''} + M_{pv cv''}^{cv' v''p} + M_{vp cv''}^{cv' v''p} \right) \right.$$

(II-25)

We now have explicit formulae for the valence hamiltonian. Depending on how we choose the core and valence orbitals, we can construct the various model hamiltonians of semi-empirical quantum chemistry from first principles. In practice, this requires the approximation of truncating the set of excited orbitals. The valence shell hamiltonian depends on our choice of [c] and [v] which define the model space, \mathcal{T}_N . Furthermore, given a specific choice of [c] and [v] the accuracy of any particular calculation depends on how we choose the truncated set of excited orbitals. In the next section we construct the pi-electron hamiltonian.

CHAPTER III

PI ELECTRON HAMILTONIAN

We now address the sigma-pi problem. From the formulae developed in Chapter II, we can construct a pi-electron hamiltonian. We started out with an N-electron problem on the full N-electron space. We then transformed the full N-electron hamiltonian to an effective N-electron hamiltonian operating on a truncated space. We further reduced the problem by defining our concept of a valence shell hamiltonian H^v and the conditions which it must satisfy. We now want to consider a planar molecule with a pi electron system and let N_v equal the number of pi electrons. Our model consists of a core of sigma orbitals--designated σ_c --a set of valence pi orbitals--labeled π_v --and an excited set of orbitals consisting of both symmetries--labeled σ_e and π_e . With this idea in mind, we then can construct a pi electron hamiltonian which will in principle yield the exact low-lying excitation potentials. Such a hamiltonian has been the essential starting point of semi-empirical calculations of large organic molecules. To the extent we succeed, we would have a non-empirical basis for applying quantum mechanics to the mobile pi-electron subsystem of such molecules.

First, however, we note a traditional ab initio pi electron calculation corresponds essentially to choosing the generator of the canonical transformation $S_{12} = \hat{0}$, in Eq. II-24 and II-25, whence we

have

$$H_{\pi_i \pi_j}^{v1} = \epsilon_{\pi_i} \delta_{\pi_i \pi_j} + \sum_{\sigma_c} \langle \sigma_c \pi_i | g_{12} | \sigma_c \pi_j \rangle \quad (\text{III-1})$$

and

$$H_{\pi_i \pi_j \pi_k \pi_l}^{v2} = \langle \pi_i \pi_j | g_{12} | \pi_k \pi_l \rangle \quad (\text{III-2})$$

Here $\delta_{\pi_i \pi_j}$ is the Kronecker delta symbol. Thus, the presence of the core is introduced only into the one-body terms by summing over the core orbitals. The effects of the excited orbitals as well as the remaining effects of the core orbitals are ignored. We use these operators to perform a pi electron approximation calculation.

The canonically transformed one-particle matrix elements $\langle \pi_i | H^{v1} | \pi_j \rangle$ are given by Eq. II-24 by identifying $v \rightarrow \pi_j$ and $v' \rightarrow \pi_j$. In fact, simplifications are obtained due to the sigma-pi symmetry which implies the vanishing of two-body matrix elements such as $\langle \pi \pi' | g_{12} | \pi'' \sigma \rangle$ and $\langle \sigma \sigma' | g_{12} | \sigma'' \pi \rangle$. Thus, for example, examination of the structure of the M's given by Eq. II-20 implies that

$$M_{\substack{\sigma_c \pi_v \sigma_c' \sigma_c'' \\ \sigma_c' \sigma_c'' \sigma_c \pi_v}} = 0$$

and so no terms arise from the three-fold sum over core orbitals,

($\sum_{\sigma_c} \sum_{\sigma_c'} \sum_{\sigma_c''}$) in Eq. II-24. Similar restrictions in the sums over ρ in the other terms also occur with the final result that

$$\begin{aligned}
\langle \pi_i | H^{V1} | \pi_j \rangle &= \epsilon_{\pi_i} \delta_{\pi_i, \pi_j} + \sum_{\sigma_c} \langle \sigma_c \pi_i | g_{12} | \sigma_c \pi_j \rangle \\
&- \frac{1}{2} \sum_{\sigma_c} \sum_{\pi_v} \sum_{\sigma_e} M_{\pi_v \sigma_e \sigma_c \pi_j}^{\sigma_c \pi_i \pi_v \sigma_e} - \frac{1}{2} \sum_{\sigma_c} \sum_{\pi_e} \sum_{\sigma_e} M_{\pi_e \sigma_e \sigma_c \pi_j}^{\sigma_c \pi_i \pi_e \sigma_e} \\
&- \frac{1}{2} \sum_{\sigma_c} \sum_{\sigma'_e} \sum_{\pi_e} M_{\sigma'_e \pi_e \sigma_c \pi_j}^{\sigma_c \pi_i \sigma_c \pi_e} - \frac{1}{2} \sum_{\sigma_c} \sum_{\sigma'_e} \sum_{\sigma_e} \left(M_{\sigma_e \pi_i \sigma_c \pi_j}^{\sigma_c \sigma'_e \sigma_e \sigma'_e} + M_{\sigma_e \sigma'_e \sigma_c \pi_j}^{\sigma_c \pi_i \sigma_e \pi_j} \right) \\
&- \frac{1}{4} \sum_{\sigma_c} \sum_{\sigma'_c} \sum_{\pi_v} M_{\pi_i \pi_v \sigma_c \sigma'_c}^{\sigma_c \sigma'_c \pi_v \pi_j} - \frac{1}{4} \sum_{\sigma_c} \sum_{\sigma'_c} \sum_{\pi_e} M_{\pi_i \pi_e \sigma_c \sigma'_c}^{\sigma_c \sigma'_c \pi_e \pi_j}
\end{aligned}$$

(III-3)

Here we have labeled the core summation index c as σ_c to emphasize it is in fact a sigma orbital. The restrictions on the ρ summations are indicated explicitly by specifying the sets over which the

summations extend as \sum_{σ_e} , \sum_{σ_c} , \sum_{π_v} , and \sum_{π_e} .

Turning now to the effective two-body interactions, we identify $v \rightarrow \pi_i$, $v' \rightarrow \pi_j$, $v'' \rightarrow \pi_k$, and $v''' \rightarrow \pi_l$. The summation index over core orbitals c is again rewritten σ_c . Sigma-pi symmetry is invoked to restrict the general sums over ρ to specific subsets of orbitals. This time we obtain

$$\begin{aligned}
 \langle \pi_i \pi_j | H^{v^2} | \pi_k \pi_l \rangle &= \langle \pi_i \pi_j | g_{12} | \pi_k \pi_l \rangle \\
 &+ \frac{1}{4} \sum_{\sigma_c} \sum_{\sigma_c'} M_{\sigma_c \sigma_c' \pi_k \pi_l}^{\pi_i \pi_j \sigma_c \sigma_c'} - \frac{1}{4} \sum_{\sigma_e} \sum_{\sigma_e'} M_{\sigma_e \sigma_e' \pi_k \pi_l}^{\pi_i \pi_j \sigma_e \sigma_e'} \\
 &- \frac{1}{4} \sum_{\pi_e} \sum_{\pi_e'} M_{\pi_e \pi_e' \pi_k \pi_l}^{\pi_i \pi_j \pi_e \pi_e'} - \frac{1}{2} \sum_{\pi_v} \sum_{\pi_e} M_{\pi_v \pi_e \pi_k \pi_l}^{\pi_i \pi_j \pi_v \pi_e} \\
 &- \frac{1}{2} \sum_{\sigma_c} \sum_{\pi_e} \left\{ M_{\pi_j \pi_e \pi_k \pi_l}^{\sigma_c \pi_i \pi_e \sigma_c} + M_{\pi_i \pi_e \pi_k \pi_l}^{\sigma_c \pi_j \sigma_c \pi_e} \right. \\
 &\quad \left. + M_{\sigma_e \pi_e \sigma_c \pi_k}^{\pi_i \pi_j \pi_e \pi_l} + M_{\pi_e \sigma_c \sigma_c \pi_l}^{\pi_i \pi_j \pi_e \pi_k} \right\} \\
 &- \frac{1}{2} \sum_{\sigma_c} \sum_{\sigma_e} \left\{ M_{\sigma_e \pi_j \sigma_c \pi_l}^{\sigma_c \pi_i \sigma_e \pi_k} + M_{\pi_j \sigma_e \sigma_c \pi_k}^{\sigma_c \pi_i \sigma_e \pi_l} \right. \\
 &\quad \left. + M_{\sigma_e \pi_i \sigma_c \pi_l}^{\sigma_c \pi_j \pi_k \sigma_e} + M_{\pi_i \sigma_e \sigma_c \pi_k}^{\sigma_c \pi_j \pi_l \sigma_e} \right\}
 \end{aligned}$$

We now wish to make a specific division of the π space. We envision all pi-orbitals are in the valence space and consequently have no pi-orbitals in the excited set; thus, the summations containing π_e 's simply do not occur. However, in theory, this leads to a valence space defined by an infinite number of orbitals and consequently, we would have to perform an infinite CI calculation to arrive at the exact energies. In practice, we must perform a limited configuration interaction calculation within the N_v pi-electron space, and thus we compute only approximate excitation energies. With this choice in mind, we eliminate three summations in the calculations of each matrix element of H^{v1} and H^{v2} . Of the remaining terms in H^{v2} , the $\sum_{\sigma_c} \sum_{\sigma_e}$ sums are the "particle conserving" terms so called by Harris. These terms arise exclusively from the three body terms in the cluster expansion. The relevant matrix elements which enter these sums have one valence orbital in each of the initial, final, and intermediate states. The two remaining sums, $\sum_{\sigma_c} \sum_{\sigma_c'}$ and $\sum_{\sigma_e} \sum_{\sigma_e'}$ result from both two- and three-body cluster contributions and correspond to the scattering of electrons in two pi orbitals to two pi orbitals through two intermediate sigma orbitals.

We note in each particle conserving term of $\sum_{\sigma_c} \sum_{\sigma_e}$ only one excited orbital appears; this limits the number of two-body matrix elements $\langle \lambda_1 \lambda_2 | g_{12} | \lambda_3 \lambda_4 \rangle$ that need be evaluated for use in this particular summation. We envision the set of excited orbitals, which is infinite in principle, to be approximated by a finite but large orbital set, $[e]$. We then find that if we neglect the terms $\sum_{\sigma_e < \sigma_e'}$ the number of two body matrix elements required in the calculation is a linear function of the number of excited orbitals. Thus,

larger basis sets $[e]$ can be used. In the calculations reported here, terms involving two external orbitals ee' are kept in both H^{v1} and H^{v2} .

In neglecting the π_e summations, we have envisioned the number of valence pi orbitals to be infinite. In practice, of course, only a finite set of M_v valence pi orbitals can be introduced. Hence, the effective valence shell hamiltonian is truncated and acts in the resulting finite dimensional vector space. According to the formalism the remaining π orbitals should appear in the excited set making themselves felt through the canonical transformation.

We now have the formulae for the coefficients (matrix elements) in the second quantized expansion of the valence shell hamiltonian (Eq. II-3). These coefficients will be used to calculate the representative of the valence shell hamiltonian in N_v -particle space. The basis which defines this representation consists of antisymmetrized products of N_v spin orbitals from $[v]$. There are

$$Q = \frac{M_v!}{(N_v! (M_v - N_v)!)}$$

members in this basis. This number could prove to be astronomical so even this basis might be truncated. (In the case of ethylene the number was small enough for both basis sets to use all Q configurations)

Once the representative of the valence shell hamiltonian is constructed, it is diagonalized. The eigenvalues and eigenvectors are then our source for solutions.

CHAPTER IV

PROGRAMMING CONSIDERATIONS

During the last three years we have written, debugged and checked the programs necessary for the computations in this thesis. As anyone familiar with large scale programming knows, the frustrations are many and persistent. However, in the end we feel the struggle was worthwhile and rewarding. Our programming must:

1. obtain a basis set of orbitals. We do a self-consistent-field calculation (SCF) using contracted gaussian orbitals;
2. generate the one- and two-body matrix elements in the (orthonormal) molecular orbital basis. This involves transforming the atomic orbital matrix elements with the transformation matrix arising from the SCF procedure.
3. evaluate the matrix elements of H^V according to the canonical transformation and core averaging formulae developed in previous chapters.
4. perform a configuration interaction calculation on the valence shell hamiltonian to determine the excitation energies of the molecule.

The self-consistent-field calculation is performed by a QCPE program GAUSSIAN-70. GAUSSIAN-70 requires as input the molecular geometry and a basis set. Alternatively, one can specify that GAUSSIAN-70 use one of its own internally stored basis sets. In either case the basis sets consist of groups of contracted gaussian functions. These functions usually approximate Slater-type atomic orbitals centered on each nucleus. Thus,

$$\phi_j \approx \sum_{i=1}^N C_{ij} \chi_i$$

where ϕ_j is a Slater type function and is defined as:

$$\begin{aligned} \phi_j &= \phi_{n_s, l m_l} \\ &= \left[\frac{(2 \zeta_j)^{2n_s+1}}{(2n_s)!} \right]^{\frac{1}{2}} r^{n_s-1} e^{-\zeta_j r} Y_{l m_l}(\theta, \varphi) \end{aligned}$$

and $Y_{l m}(\theta, \varphi)$ is the spherical harmonic. The χ_i are gaussian functions:

$$\begin{aligned} \chi_i &= \chi_{n_g, l m_l} \\ &= \left[\frac{\left(\frac{2}{\pi}\right)^{\frac{1}{2}} 2^{n_g+1}}{(2n_g-1)!!} \right]^{\frac{1}{2}} r^{n_g-1} \alpha_i^{\frac{2n_g+1}{4}} e^{-\alpha_i r^2} Y_{l m_l}(\theta, \varphi) \end{aligned}$$

Stewart¹ did calculations on gaussian function expansions of Slater type orbitals and published the results of one, two, . . . six function expansions of various Slater type orbitals. Stewart's expansion coefficients and exponents are used in this work.

The first part of GAUSSIAN-70 calculates all of the one-body integrals

$$\int \chi_i^*(\vec{r}) \left\{ \frac{\hbar^2}{2m} \nabla^2 + \sum_{\alpha=1}^A \frac{-Z_\alpha e^2}{|\vec{r} - \vec{R}_\alpha|} \right\} \chi_j(\vec{r}) d\vec{r}$$

and all of the two-body integrals

$$(\chi_i \chi_j | \chi_k \chi_l) = \iint \chi_i^*(\vec{r}_1) \chi_j^*(\vec{r}_2) \frac{1}{r_{12}} \chi_k(\vec{r}_1) \chi_l(\vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

The second part of GAUSSIAN-70 performs a self-consistent-field calculation. That is, the program finds the eigenvalues and eigenvectors self-consistently of the closed shell Fock operator

$$F(1) = -\frac{\hbar^2}{2m} \nabla_1^2 + \sum_{\alpha=1}^A \frac{-Z_\alpha e^2}{|\vec{r}_1 - \vec{R}_\alpha|} + \sum_{\mu = \text{occupied}} \left(J_\mu(\vec{r}_1) - K_\mu(1) \right)$$

where

$$J_\mu(\vec{r}_1) f(\vec{r}_1) = \int d\vec{r}_2 \phi_\mu^*(\vec{r}_2) \frac{1}{r_{12}} \phi_\mu(\vec{r}_2) f(\vec{r}_1)$$

$$K_\mu(1) f(\vec{r}_1) = \int d\vec{r}_2 \phi_\mu^*(\vec{r}_2) \frac{1}{r_{12}} f(\vec{r}_2) \phi_\mu(\vec{r}_1)$$

GAUSSIAN-70 first diagonalizes the atomic orbital representation of

$$-\frac{\hbar^2}{2m} \nabla^2 + \sum_{\alpha=1}^A \frac{-Z_\alpha e^2}{|\vec{r}_1 - \vec{R}_\alpha|}$$

and constructs the eigenvectors of this one-body operator. These eigenvectors are then used as an initial guess for the ϕ 's in the self-consistent-field procedure. The solutions are iterated until a desired convergence tolerance is reached. The end result is a set of eigenvalues ϵ_i belonging to the set of eigenfunctions ϕ_i . The ϕ_i are linear combinations of the input atomic orbitals.

The resulting output data are one-body matrix elements, two-body matrix elements, overlap matrix elements (all in the atomic orbital representation), the eigenvalues ϵ_i and the coefficient matrix which transforms the atomic orbital (AO) basis into the (SCF) molecular orbital (MO) basis.

The second part of our programs uses the coefficient matrix to transform the one- and two-body matrix elements into the MO basis. The transformation of the two-body matrix elements involves the four-fold summations.

$$(\phi_i \phi_j | \phi_k \phi_l) = \sum_a \sum_b \sum_c \sum_d C_{ai} C_{bj} C_{ck} C_{dl} (\chi_a \chi_b | \chi_c \chi_d)$$

where i, j, k, l refer to the molecular orbitals and a, b, c, d refer to atomic orbitals. The problem as stated involves a computation time proportional to M^8 where M is the number of spatial orbitals. Using Horner's rule² however, the time for the four-fold summation for each of the M^4 molecular orbital integrals can be reduced to a time proportional to M^5 . The transformation is broken up and the indices are transformed one at a time as follows:

$$(ab|cl) = \sum_d C_{dl} (ab|cd)$$

$$(ab|kl) = \sum_c C_{ck} (ab|cl)$$

$$(aj|kl) = \sum_b C_{bj} (ab|kl)$$

$$(ij|kl) = \sum_a C_{ai} (aj|kl)$$

Because we are working on pi-electron systems, we found that the more efficient procedure for transforming the two-body matrix elements was to take advantage of the sigma-pi symmetry. Whence, four separate subroutines were written, one for each of the following types of MO matrix element:

$$(\sigma\sigma|\sigma\sigma)$$

$$(\sigma\pi|\sigma\pi)$$

$$(\sigma\sigma|\pi\pi)$$

$$(\pi\pi|\pi\pi)$$

where

$$(\sigma_i \sigma_j | \sigma_k \sigma_l) = \iint d\vec{r}_1 d\vec{r}_2 \phi_{\sigma_i}^*(\vec{r}_1) \phi_{\sigma_j}^*(\vec{r}_2) \frac{1}{r_{12}} \phi_{\sigma_k}(\vec{r}_1) \phi_{\sigma_l}(\vec{r}_2)$$

Following the MO transformation we construct the Hartree-Fock potential U_{ij} :

$$U_{ij} = (\phi_i | U | \phi_j) = \epsilon_i \delta_{ij} - \left(\phi_i \left| -\frac{\hbar^2}{2m} \nabla^2 + \sum_{\alpha=1}^A \frac{-Z_\alpha e^2}{|\vec{r} - \vec{R}_\alpha|} \right| \phi_j \right)$$

The pair potential matrix elements, $(ij | g_{12} | kl)$ are then constructed from the two-body matrix elements and the Hartree-Fock potential:

$$(ij | g_{12} | kl) = (ij | \frac{1}{r_{12}} | kl) - \frac{U_{ik} \delta_{jl} + U_{jl} \delta_{ik}}{N-1}$$

All these data are then sorted and arranged on various direct access files for ease of later manipulations. We found that the greatest amount of computer time was spent on these two steps (vis. SCF and MO transformation), approximately 80-90%. If the canonical transformations could be carried out in a non-orthogonal basis, both of these steps could be eliminated.

The third part of our series of programs uses the $(ij | g_{12} | kl)$'s and the ϵ_i 's to construct the matrix elements of the effective hamiltonian. That is, we construct according to Eqs. III-3 and III-4

$$\langle \pi_i | \mathbb{H}^{v1} | \pi_j \rangle \quad \text{and} \quad \langle \pi_i \pi_j | \mathbb{H}^{v2} | \pi_k \pi_l \rangle.$$

Here, the angular brackets refer to antisymmetrized products of spin orbitals. The output of this series of programs serves as input to the configuration interaction programs.

The fourth and final part of our programs performs a configuration interaction calculation on the valence space, or in this case the pi electron space.

The first subroutine in this series sets up the pi space basis functions. We have chosen to represent this N_v -particle basis in the occupation number representation and found that the binary bit positions in the IBM single precision word do this job admirably. For both basis sets the number of possible determinants was sufficiently small so that a complete configuration interaction calculation on the pi electron space was possible.

The next subroutine inserts the effective operator matrix elements into the correct locations of the CI matrix. We chose to construct the CI matrix elements in this manner rather than do the sums explicitly because the number of two-body matrix elements in future calculations could become too large for the computer storage at hand.

After the CI matrix is constructed, all that remains is the matrix diagonalization and construction of the eigenvectors. This was done by an IBM scientific subroutine package (SSP) program EIGEN.

With this series of programs the calculations were performed in double precision. Also because of the extensive use of peripheral equipment these programs are localized to the IBM 360-370 series of computers. However, it is anticipated that only minor modifications would be necessary for use on another brand of computer.

REFERENCES

1. R. F. Stewart, J. Chem., 52, 431 (1970).
2. Numerical Methods and Fortran Programming, D. D. McCracken and W. S. Dorn, John Wiley and Sons, New York (1964).

CHAPTER V

THE ETHYLENE MOLECULE

The main objective of this thesis was to write and execute programs which do the canonical transformation on pi-electron systems in molecules. The first molecule of interest is the ethylene molecule which is the smallest pi-electron system. This chapter is concerned with the particulars of the ethylene molecule.

Calculations on the ethylene molecule date back to the 1930's and 1940's when semi-empirical methods were used to determine vibrational force constants and twisting frequency. Parr and Crawford¹ calculated the out-of-plane vibrational force constants using the method of antisymmetrized molecular orbitals. They considered ethylene as a two electron problem and claimed no semi-empirical data other than molecular geometry. However, in allowing for the interaction of the two electrons with the core they ignored altogether the hydrogen atoms. Further, they described the interaction of the electrons with the carbon atoms as

$$H_o(1) = H_{c_1}(1) + H_{c_2}(1)$$

where $H_o(1)$ is "mutual potential energy of electron 1 and the single-bonded H_2C-CH_2 framework"; $H_{c_1}(1)$ is the "potential representing attraction of electron (1) by carbon atom C_1 plus repulsion of

electron 1 by the other 5 electrons." Thus, each pi-electron is in a field of C^+ ions. Obviously some dynamics have been left out of this picture. However, this was "a step towards the ideal 'first principle' treatment."

In 1965 Moskowitz and Harrison² did the first full SCF calculation on ethylene including all the sigma and pi electrons. Their results showed that gaussian functions could be used in such a calculation and accuracy attained. Theirs also was one of the first molecular electronic structure calculations to make large scale use of the computer. They concluded that the idea of sigma-pi separation is a valid one. The calculation of excitation energies achieved only fair agreement with experiment, however. Also to be noted is the single configuration used. No attempt was made to include configuration mixing.

About two years later, Schullman, et al³ published results of an SCF calculation using contracted gaussian basis sets. They used virtual orbitals to construct the excited states and thence the excitation energies. Some of their findings are listed in the following table (Table I). Again these numbers are the results of single configurations studies.

TABLE I

ENERGIES OF EXCITED STATES RELATIVE TO GROUND STATE
(Schullman, Moskowitz, and Hollister)³

$^1B_{1u}$	$(\pi \rightarrow \pi^*)$	9.3eV	(V)
$^3B_{1u}$	$(\pi \rightarrow \pi^*)$	4.19eV	(T)
$^1B_{3u}$	$(\pi \rightarrow \sigma^*)$	9.82eV	
$^3B_{3u}$	$(\pi \rightarrow \sigma^*)$	9.46eV	
$^1B_{1g}$	$(\sigma \rightarrow \pi^*)$	9.79eV	
$^3B_{1g}$	$(\sigma \rightarrow \pi^*)$	9.27eV	

McKoy and Dunning⁴ used the equations of motion method for the excitation operator to study the excited states of ethylene. They performed SCF calculations with a minimum basis set then used the random-phase approximation to calculate the excitation energies. Their result on the lowest lying singlet state was 9.44eV above the ground state. For reasons of convergence they did not report the triplet energy of interest. However, they did report other low-lying excited states.

In 1971 Buenker, Peyerimhoff, and Kammer⁵ published the first combined SCF and limited CI calculations on ethylene. They performed separate SCF calculations on the ground states and each of several excited states. From each SCF calculation came the molecular orbitals and corresponding orbital energies. For the calculation of the CI ground state the MO's from the SCF calculation of the ground state were used to construct the 16-particle determinants. For the calculation of the first excited triplet state ($1b_{3u} \rightarrow 1b_{2g}$; ${}^3B_{1u}$ state) the MO's from the SCF open-shell calculation of the ${}^3B_{1u}$ state were used.

The CI calculations were limited calculations on each state of interest. All configurations which differed from the ground state by less than four electronic excitations were included in each CI calculation. The point of using different MO's for different states was the following: If all the CI states were considered, the need to use different orbitals for different states would not arise, since the space would then be as complete as the finite number of orbitals would allow. However, since there would be a truncation of the number of CI states allowed, it was hoped that by using orbitals that were constructed with a particular state in mind improved accuracy would result. This proved not entirely true, however, when a lower ground state was achieved during a calculation aimed at the first excited triplet state.

The calculation of the excited singlet and triplet states ($\pi \rightarrow \pi^*$) yielded the following results:

TABLE II
 ETHYLENE EXCITATION ENERGIES BY BUENKER, ET AL⁵
 (Energies in eV)

State		Excitation	Energy	Experiment
$1B_{1u}$	(V)	$1b_{3u} \rightarrow 1b_{2g}$	8.323	7.66 ^a
$3B_{1u}$	(T)	$1b_{3u} \rightarrow 1b_{2g}$	4.255	4.6 ^b

^aP. G. Wilkinson and R. S. Mulliken, J. Chem. Phys., 23, 1895 (1955).

^bD. F. Evans, J. Chem. Soc., 1960, 1735.

The results of the calculations of Buenker et al are encouraging to theoreticians because the numbers were closer to experimental values than any previous ab initio calculation.

In a later calculation which also appeared in 1971 Del Bene, Ditchfield and Pople⁸ studied the results of an extended basis set and limited CI on the calculations of excited states of ethylene (among other molecules). They chose two different basis sets STO-46 (which is close to minimal) and 4-31G (extended basis set) and calculated excitation energies with and without CI. The CI calculations were limited in the following manner: select M highest occupied orbitals and M lowest unoccupied orbitals and form from these all singly excited configurations. M was allowed to vary from 1 to 8.

M = 1 refers to a single configuration (i.e., no configuration interaction). Their results follow:

TABLE III
ETHYLENE EXCITATION ENERGIES BY DEL BENE, ET AL⁸
(Energies in eV)

State	STO-4G		4-31G		Experiment
	No CI	With CI	No CI	With CI	
$^1B_{1u}$	12.83	10.97	10.31	9.16	7.65 ^a
$^3B_{1u}$	3.46	3.29	3.85	3.80	4.59 ^a

^aG. Herzberg, Molecular Spectra and Molecular Structure (Van Nostrand, Princeton, N.J. 1966) Vol. 3.

In August 1972, Bender, Dunning, Schaefer, Goddard, and Hunt¹⁰ published work on ethylene using multiconfiguration wave functions. They carried out calculations on the T($^3B_{1u}$) and V($^1B_{1u}$) states only, using previous ground state calculations of Dunning.¹¹ Their calculated singlet-triplet splitting was ~3.9eV. When this is added to Dunning's previous calculation of the N→T transition energy of 4.22eV we find

$^3B_{1u}$	N → T	4.22eV
$^1B_{1u}$	N → V	8.1eV

This calculation again involved configuration interaction and studied the effects of different "classes of configurations included." The largest CI performed included the ground state SCF configuration plus all singly- and doubly-excited configurations.

We have discussed some of the ab initio calculations on ethylene. The recurring themes in these calculations follow: 1) The T state is better defined both theoretically and experimentally than the V state. The experimental value for the N → T excitation energy most often quoted is 4.6eV and most large ab initio calculations fall in the range 3.6-4.2eV for this excitation. Also, in the calculations the triplet state is easy to identify with the spectroscopic T state.

Experimental discussion of the T state is found in Mullikin's¹² paper. Much of his discussion of this state is based on the work of Evans.¹³ The paper of Evans reports observations of ethylene spectra in the range 3500-2600Å⁰ (3.54-4.77eV). The light absorption curve of ethylene starts at 3500Å⁰ and increases with humps (showing vibrational states) until it reaches a maximum at about 2700Å⁰ (4.59eV). Evans concludes that this particular electronic transition is the $^1A_g \rightarrow ^3B_{1u}$ (N → T) transition of ethylene. Mulliken points out that although the curve should reach a maximum at 2700Å⁰ it actually is swamped by the beginning of an N → V transition.

2) The singlet V state is not well defined, either theoretically or experimentally. Ab initio calculations have found it to be

anywhere from 6.5eV to 10eV above the ground state. The interpretations of the calculations are clouded by the appearance of a diffuse singlet very near the V state. This state shows up when diffuse orbitals are added to the basis. Theoretically the V state has been assigned the ($\pi\pi^*$) configuration which in a simple valence-bond model yields the first excited singlet state. However, with the addition of diffuse orbitals to the basis, not only is the energy of the V state lowered but also there appears additional singlet states (Rydberg states) very close to the V state. Experimentally, the question is whether the first excited state is the V state or a Rydberg state. Mulliken¹² states with some assurance that the absorption curve for the $N \rightarrow V$ transition starts at 2150Å and continues increasing with an irregular progression of bands until it disappears under the intense bands of the first Rydberg transition. However, if the curve were continued, it would have a maximum ab about 1620Å⁰ (7.65eV). Mulliken's extensive discussions about the excited states of ethylene conclude that the first excited singlet state is a Rydberg state occurring at 1744Å⁰ (7.11eV). The V state occurs at 1620Å⁰ (7.65eV). These conclusions were based on analysis of spectrographs and theoretical assignments of states.

From the above discussion we found the most often quoted experimental excitation energies for the T state and the V state are 4.6eV and 7.6eV, respectively. Further, we feel the best ab initio calculation is that of Buenker, et al. We will relate our calculations to these numbers.

Ab initio calculations involving all N electrons (N = 16 in ethylene) are difficult and time consuming. Since the number of

configurations necessary to span the N particle space is generally very large, severe truncations of the N particle basis are necessary. The first serious attempts to reformulate this problem in terms of a true valence shell hamiltonian for ethylene was based upon Freed's¹⁴ ab initio derivation of the pi-electron hamiltonian from many-electron theory. Using two different basis sets (one small, the second containing the first plus 1 diffuse 2s orbital and 1 diffuse 2p shell), Iwata and Freed¹⁴ calculated the singlet and triplet excitation energies. For the V state they got 9.44eV and 9.73eV for the small and large basis sets, respectively. For the T state they got 4.79 eV and 4.84eV.

This brings us to our calculations on ethylene and comparison with other work.

SCF Calculations

We begin by doing an SCF calculation on ethylene using GAUSSIAN-70. We chose three atomic orbital basis sets. The atomic functions are linear combinations of gaussian functions which approximated best atom value Slater functions. The first basis set contained 1s, 1s', 1s'', 2s, 2s', 3s, 3s', 4s, 4s', and 2p functions on each carbon atom and 1s and 2 s functions on each hydrogen atom. The second contained 1s, 2s, 3s, 2p, and 3p functions on each carbon atom and 1s and 2s functions on each hydrogen atom. The third basis set contained the second plus a diffuse 2s and 2p function on each carbon atom. The second and third basis sets were chosen to be very similar to Freed's choice for comparison purposes. The diffuse orbitals were added in Freed's work to try to lower the excitation energy of

the V state. Table IV describes more fully the basis sets. Table V and Figure 9 show the SCF results.

After the SCF calculation the one- and two-body matrix elements were transformed to the MO basis, sorted, and arranged for easy access on disk storage.

The Canonical Transformation

The canonical transformation was performed using the molecular orbital matrix elements generated by GAUSSIAN-70. The equations which were summed follow:

$$\begin{aligned} \langle \pi_i | H^V | \pi_j \rangle &= \epsilon_{\pi_i} \delta_{ij} + \sum_{\sigma_c} \langle \sigma_c \pi_i | g_{12} | \sigma_c \pi_j \rangle \\ &- \frac{1}{2} \sum_{\sigma_c} \sum_{\pi_v} \sum_{\sigma_c} M_{\pi_v \sigma_e}^{\sigma_c \pi_i \pi_v \sigma_e} \sigma_c \pi_j \\ &- \frac{1}{2} \sum_{\sigma_c} \sum_{\sigma_c'} \sum_{\sigma_e} \left(M_{\sigma_e \pi_i \sigma_c \pi_j}^{\sigma_c \sigma_c' \sigma_e \sigma_c'} + M_{\sigma_e \sigma_c' \sigma_c \sigma_c'}^{\sigma_c \pi_i \sigma_e \pi_j} \right) \\ &- \frac{1}{4} \sum_{\sigma_c} \sum_{\sigma_c'} \sum_{\pi_v} M_{\pi_i \pi_v \sigma_c \sigma_c'}^{\sigma_c \sigma_c' \pi_v \pi_j} \end{aligned}$$

(V-1)

TABLE IV
 TABLE OF THREE BASIS SETS USED
 IN THIS THESIS

Atom	Type	Zeta (ζ)	Number of Gaussian Functions	
I				
Carbon	1s	32.0	3	
	1s'	16.0	3	
	1s''	8.0	3	
	2s	4.0	3	
	2s'	2.0	3	
	3s	0.8	3	
	3s'	0.2	3	
	4s	0.08	3	
	4s'	0.02	3	
	2p	1.59	3	
Hydrogen	1s	1.24	3	
	2s	1.24	3	

II				
Carbon	1s	5.67266	4	
	2s	1.60833	3	
	3s	1.60833	2	
	2p	1.56789	4	
	3p	1.56789	4	
Hydrogen	1s	1.24000	3	
	2s	1.24000	3	

III				
Carbon	1s	5.67266	4	
	2s	1.60833	3	
	2s'	0.20000	3	diffuse
	3s	1.60833	2	
	2p	1.56789	4	
	2p'	0.20000	4	diffuse
	3p	1.56789	4	
Hydrogen	1s	1.24000	3	
	2s	1.24000	3	

TABLE V
 SCF RESULTS
 (1Au = 27.2116eV)

Orbital	Symmetry	Energy (Au)	Orbital	Symmetry	Energy (Au)
BASIS SET I: $M_c = 7$ $M_v = 2$ $M_e = 23$					
1	b_{1u}	-11.1307	17	π b_{2g}	0.2614
2	a_g	-11.1205	18	b_{2u}	0.3737
3	a_g	- 1.0219	19	a_g	0.5092
4	b_{1u}	- 0.7750	20	b_{1u}	0.5398
5	b_{2u}	- 0.6200	21	b_{3g}	0.5669
6	a_g	- 0.5478	22	b_{1u}	0.8928
7	b_{3g}	- 0.4797	23	b_{2u}	1.1888
8	π b_{3u}	- 0.3575	24	a_g	1.5529
9	b_{1u}	- 0.0000213	25	b_{1u}	1.6518
10	a_g	0.0000267	26	b_{3g}	1.6572
11	a_g	0.000414	27	a_g	7.2611
12	b_{1u}	0.00133	28	b_{1u}	8.1619
13	a_g	0.00514	29	a_g	104.18
14	b_{1u}	0.00865	30	b_{1u}	106.58
15	b_{1u}	0.1238	31	a_g	919.07
16	a_g	0.1325	32	b_{1u}	926.27

Total Energy = -77.035802 Au.

TABLE V (Continued)

Orbital	Symmetry	Energy (Au)	Orbital	Symmetry	Energy (Au)
BASIS SET II: $M_c = 7$ $M_v = 4$ $M_e = 15$					
1	a_g	-11.2020	14	b_{1u}	0.7150
2	b_{1u}	-11.2008	15	π b_{3u}	0.8552
3	a_g	- 1.0163	16	a_g	0.8571
4	b_{1u}	- 0.7759	17	b_{2u}	0.9027
5	b_{2u}	- 0.6250	18	a_g	0.9928
6	a_g	- 0.5641	19	b_{1u}	1.0342
7	b_{3g}	- 0.4879	20	π b_{2g}	1.0860
8	π b_{3u}	- 0.3516	21	a_g	1.5310
9	π b_{2g}	0.2330	22	b_{2u}	1.5835
10	a_g	0.3219	23	b_{3g}	1.6014
11	b_{2u}	0.3480	24	b_{1u}	1.6080
12	b_{1u}	0.3673	25	b_{3g}	1.9790
13	b_{3g}	0.5369	26	b_{1u}	2.2126

Total Energy = -77.668159 Au

TABLE V (Continued)

Orbital	Symmetry	Energy (Au)	Orbital	Symmetry	Energy (Au)
BASIS SET III: $M_c = 7$ $M_v = 6$ $M_e = 21$					
1	a_g	-11.2052	18	a_g	0.3486
2	b_{1u}	-11.2040	19	b_{2u}	0.3560
3	a_g	- 1.0196	20	b_{1u}	0.4261
4	b_{1u}	- 0.7788	21	b_{3g}	0.5530
5	b_{2u}	- 0.6280	22	b_{1u}	0.7799
6	a_g	- 0.5674	23	π b_{3u}	0.8724
7	b_{3g}	- 0.4906	24	a_g	0.8888
8	π b_{3u}	- 0.3541	25	b_{2u}	0.9131
9	a_g	0.00887	26	a_g	1.0056
10	b_{1u}	0.0130	27	π b_{2g}	1.1049
11	b_{2u}	0.0199	28	b_{1u}	1.1594
12	π b_{3u}	0.0234	29	a_g	1.5674
13	π b_{2g}	0.0384	30	b_{2u}	1.6099
14	b_{3g}	0.0387	31	b_{3g}	1.6370
15	a_g	0.0504	32	b_{1u}	1.7217
16	b_{1u}	0.0981	33	b_{3g}	1.9762
17	π b_{2g}	0.2374	34	b_{1u}	2.2250

Total Energy = -77.670498 Au

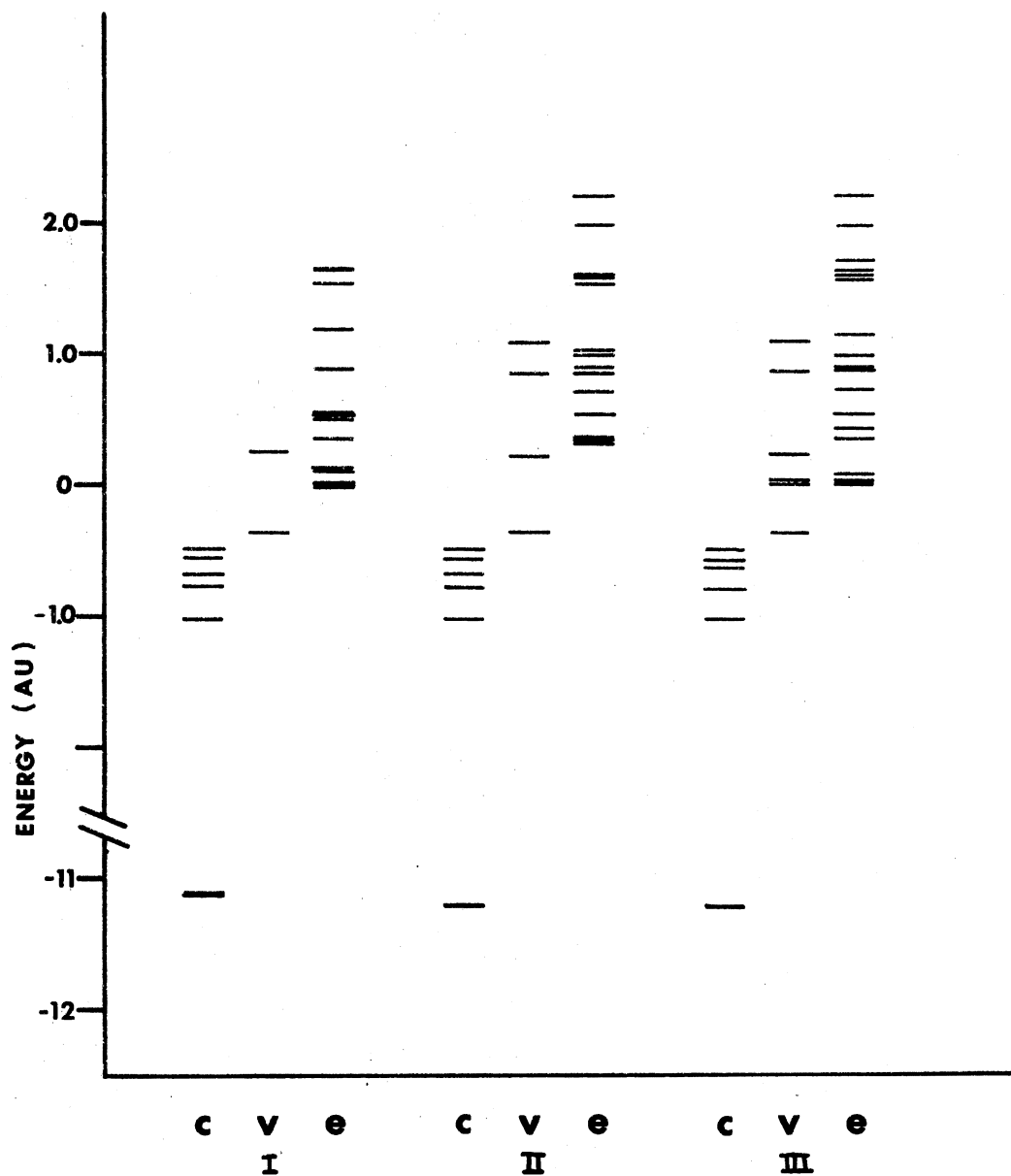


Figure 9. Energy Levels of SCF Orbitals.

This is a one-body effective hamiltonian matrix element. Since we included no excited pi orbitals, the sums over these orbitals do not occur. The effective two-body matrix elements are given by

$$\begin{aligned}
 \langle \pi_i \pi_j | \mathbb{H}^v | \pi_k \pi_l \rangle &= \langle \pi_i \pi_j | g_{12} | \pi_k \pi_l \rangle \\
 - \frac{1}{4} \sum_{\sigma_c} \sum_{\sigma_c'} M_{\sigma_c' \sigma_c \pi_k \pi_l}^{\pi_i \pi_j \sigma_c \sigma_c'} &- \frac{1}{4} \sum_{\sigma_e} \sum_{\sigma_e'} M_{\sigma_e \sigma_e' \pi_k \pi_l}^{\pi_i \pi_j \sigma_e \sigma_e'} \\
 - \frac{1}{2} \sum_{\sigma_c} \sum_{\sigma_e} &\left[M_{\sigma_e \pi_j \sigma_c \pi_l}^{\sigma_c \pi_i \sigma_e \pi_k} + M_{\pi_j \sigma_e \sigma_c \pi_k}^{\sigma_c \pi_i \sigma_e \pi_l} \right. \\
 &\left. + M_{\sigma_e \pi_i \sigma_c \pi_l}^{\sigma_c \pi_j \pi_k \sigma_e} + M_{\pi_i \sigma_e \sigma_c \pi_k}^{\sigma_c \pi_j \pi_l \sigma_e} \right] \quad (V-2)
 \end{aligned}$$

We chose two definitions for W_{12} Eq. II-16. The first

$$W_{12} = g_{12} - i \left[S_{12}, \left\{ h_1 + h_2 + g_{12}^{\text{diag}} \right\} \right] \quad (V-3a)$$

is the definition used to develop the formalism. However, the resulting effective interaction does not possess the symmetry of the original hamiltonian as discussed in Chapter II. To overcome this problem, we have chosen an alternate definition for W_{12} :

$$W_{12} = g_{12} - i [S_{12}, h_1 + h_2] \quad (V-3b)$$

This definition avoids the symmetry problem by simply dropping g_{12}^{diag} . Our calculations were done using both definitions.

Configuration Interaction

After constructing the one- and two-body terms in the valence shell hamiltonian, we next perform configuration interaction studies to diagonalize this valence shell hamiltonian on the N_v particle valence space. In the ethylene problem there are two valence electrons (pi electrons), $N_v = 2$. The number of configurations is given by

$$Q = \frac{M_v!}{(M_v - N_v)! N_v!}$$

and for basis sets I, II, and III, Q equals 6, 28, and 66, respectively. In all three instances the number of configurations was small enough to perform complete CI calculations. For each basis set the same determinantal basis was used in i) the pi electron calculation, ii) the effective operator calculation without two-body matrix elements in the denominator and iii) the effective operator calculation with two-body matrix elements in the denominator.

Prior to CI studies with the canonically transformed effective operators, we did CI studies in the pi-electron approximation with

matrix elements defined in Eq.'s III-1 and III-2.

The third part of our programs generated the necessary matrix elements for use in the configuration interaction programs. The CI calculations were run with both definitions for W_{12} and for all three basis sets. The results of the CI calculations in the pi electron approximation and using the canonically transformed operators are in Table VI. The calculations without two-body terms in the denominator (Eq. V-3b) are denoted IDENOM = 0; calculations with two-body terms in the denominator (Eq. V-3a) are denoted IDENOM = 1.

TABLE VI
 EXCITATION ENERGIES WITH PI ELECTRON APPROXIMATION,
 WITHOUT TWO-BODY TERMS IN DENOMINATORS, AND
 WITH TWO-BODY TERMS IN DENOMINATORS
 (Energies in eV)

		Basis Set		
		I	II	III
Pi Electron Approximation				
N	T	4.780	4.6616	4.6066
	V	13.072	11.730	11.993
	Z	18.277	16.570	17.797

Canonical Transformation IDENOM = 0				
	T	3.1527	3.4044	3.9288
	V	10.5909	10.1057	10.6148
	Z	15.8824	15.3077	15.2340

Canonical Transformation IDENOM = 1				
	T	3.1526(3.1437) ^a	3.8241(3.8258) ^a	3.3088(3.2894) ^a
	V	10.5724	10.0278	9.9812
	Z	15.8899	15.6918	14.7017

^aBecause the spin symmetry is broken when IDENOM = 1, the triplet states split and we get one energy for $m_s = \pm 1$ and another energy for $m_s = 0$ (inside parenthesis).

REFERENCES

1. Robert G. Parr and Bryce L. Crawford, J. Chem. Phys. 16, 526 (1948).
2. J. W. Moskowitz and M. C. Harrison, J. Chem. Phys. 42, 1726 (1965).
3. J. M. Schullman, J. W. Moskowitz, and C. Hollister, J. Chem. Phys. 46, 2759 (1967).
4. T. H. Dunning and V. McKoy, J. Chem. Phys. 47, 1735 (1967).
5. R. J. Buenker, S. D. Peyerimhoff, and E. Kammer, J. Chem. Phys. 55, 814 (1971).
6. P. G. Wilkinson and R. S. Mulliken, J. Chem. Phys. 23, 1895 (1955).
7. C. Reid, J. Chem. Phys. 18, 1299 (1950); D. F. Evans, J. Chem. Soc. 1960, 1735.
8. J. E. Del Bene, R. Ditchfield, J. A. Pople; J. Chem. Phys. 55, 2236 (1971).
9. G. Herzberg, Molecular Spectra and Molecular Structure (Van Nostrand, Princeton, N. J., 1966) Vol. 3.
10. C. F. Bender, T. H. Dunning, H. F. Schaefer, W. A. Goddard, and W. J. Hunt, Chem. Phys. Letters, 15, 171 (1972).
11. T. H. Dunning, W. J. Hunt, and W. A. Goddard, Chem. Phys. Letters 4, 147 (1969).
12. A. J. Mere and R. S. Mulliken, Chem. Rev. 69, 639 (1969).
13. D. F. Evans, J. Chem. Soc. 1735 (1960).
14. K. F. Freed, Chem. Phys. Lett. 13, 181 (1972); S. Iwata and K. F. Freed, J. Chem. Phys. 61, 1500 (1974).

CHAPTER VI

DISCUSSION AND CONCLUSIONS

We will discuss our configuration interaction results in the context of the ground state $|N\rangle$, and excited triplet $|T\rangle$ and singlet $|V\rangle$ states associated with the single excitation configuration $\pi\pi^*$. For the purpose of this preliminary discussion we will assume the configuration interaction effects can be neglected. The two-electron independent particle states are written:

$$|N\rangle = |\pi_u \alpha \pi_u \beta\rangle$$

$$|T\rangle = \frac{1}{\sqrt{2}} \left\{ |\pi_u \alpha \pi_g^* \beta\rangle - |\pi_u \beta \pi_g^* \alpha\rangle \right\}$$

and

$$|V\rangle = \frac{1}{\sqrt{2}} \left\{ |\pi_u \alpha \pi_g^* \beta\rangle - |\pi_u \beta \pi_g^* \alpha\rangle \right\}$$

Here π_u is the lowest energy ungerade pi molecular orbital. It can be expressed as (neglecting the overlap $\langle p_a | p_b \rangle$)

$$\pi_u = \frac{1}{\sqrt{2}} \left\{ p_a + p_b \right\}$$

where p_a (p_b) is an atomic pi orbital on center a(b). π_g^* is the first

excited π orbital. Its inversion symmetry is gerade and it is expressed as:

$$\pi_g^* = \frac{1}{\sqrt{2}} \left\{ p_a - p_b \right\}$$

Our discussion involves only two pi atomic orbitals. If we choose to include more, we may consider that they are part of the excited set. To include them in this discussion would obscure the conclusions with tedious algebra and arguments about overlap.

The single configuration two-particle ground state can be represented in terms of p_a and p_b :

$$\begin{aligned} |N\rangle &= |\pi_u \alpha \pi_u \beta\rangle \\ &= \frac{1}{2} \left\{ p_a(1) p_a(2) + p_a(1) p_b(2) \right. \\ &\quad \left. + p_b(1) p_a(2) + p_b(1) p_b(2) \right\} \frac{\alpha_1 \beta_2 - \beta_1 \alpha_2}{\sqrt{2}} \end{aligned}$$

The triplet and singlet states are represented:

$$\begin{aligned} |T\rangle &= \frac{1}{\sqrt{2}} \left\{ |\pi_u \alpha \pi_g^* \beta\rangle + |\pi_u \beta \pi_g^* \alpha\rangle \right\} \\ &= \left\{ p_b(1) p_a(2) - p_a(1) p_b(2) \right\} \frac{\alpha_1 \beta_2 + \beta_1 \alpha_2}{\sqrt{2}} \end{aligned}$$

and

$$\begin{aligned}
 |V\rangle &= \frac{1}{\sqrt{2}} \left\{ |\pi_{u\alpha} \pi_{g\beta}^* \rangle - |\pi_{u\beta} \pi_{g\alpha}^* \rangle \right\} \\
 &= \left\{ p_a(1) p_a(2) - p_b(1) p_b(2) \right\} \frac{\alpha_1 \beta_2 - \beta_1 \alpha_2}{\sqrt{2}}
 \end{aligned}$$

Note the triplet state is purely covalent (electrons 1 and 2 are always on two different centers) and the singlet state is purely ionic (the electrons are either both on center "a" or both on center "b").

If we now examine the expectation value of the effective hamiltonian in the N, T, and V states, we find the following:

$$\begin{aligned}
 E_N &= \langle N | \tilde{H}^V | N \rangle = 2 \left\{ \frac{1}{2} (p_a + p_b | \tilde{H}^{V1} | p_a + p_b) \right\} \\
 &+ \frac{1}{2} \left\{ (p_a p_b | \tilde{H}^{V2} | p_a p_a) + (p_a p_a | \tilde{H}^{V2} | p_b p_b) \right. \\
 &\quad + (p_a p_b | \tilde{H}^{V2} | p_a p_a) + (p_a p_a | \tilde{H}^{V2} | p_a p_b) \\
 &\quad + (p_a p_b | \tilde{H}^{V2} | p_b p_a) + (p_a p_a | \tilde{H}^{V2} | p_b p_a) \\
 &\quad \left. + (p_a p_b | \tilde{H}^{V2} | p_b p_b) + (p_a p_b | \tilde{H}^{V2} | p_a p_a) \right\}
 \end{aligned}$$

$$E_T = \langle T | H^V | T \rangle = \frac{1}{2} (\rho_a + \rho_b | \tilde{H}^{V1} | \rho_a + \rho_b) \\ + \frac{1}{2} (\rho_a - \rho_b | \tilde{H}^{V1} | \rho_a - \rho_b) \\ + \left\{ (\rho_a \rho_b | \tilde{H}^{V2} | \rho_a \rho_b) - (\rho_a \rho_b | \tilde{H}^{V2} | \rho_b \rho_a) \right\}$$

and

$$E_V = \langle V | H^V | V \rangle = \frac{1}{2} (\rho_a + \rho_b | H^V | \rho_a + \rho_b) \\ + \frac{1}{2} (\rho_a - \rho_b | \tilde{H}^{V1} | \rho_a - \rho_b) \\ + \left\{ (\rho_a \rho_b | \tilde{H}^{V2} | \rho_a \rho_a) - (\rho_a \rho_a | \tilde{H}^{V2} | \rho_b \rho_b) \right\}$$

Here

$$(\rho_a | \tilde{H}^{V1} | \rho_b) = \langle \rho_a \xi_1 | H^{V1} | \rho_b \xi_1 \rangle$$

and

$$(\rho_a \rho_b | \tilde{H}^{V2} | \rho_c \rho_d) = \langle \rho_a \xi_1, \rho_b \xi_2 | H^{V2} | \rho_c \xi_1, \rho_d \xi_2 \rangle$$

are matrix elements of the effective two-body operators. Now since H^{V2} is invariant under particle exchange and inversion operations we have the following identity:

$$(\rho_a \rho_b | \tilde{H}^{V2} | \rho_a \rho_a) = (\rho_b \rho_a | \tilde{H}^{V2} | \rho_a \rho_a) = (\rho_a \rho_b | \tilde{H}^{V2} | \rho_b \rho_b)$$

The transition energies are given by

$$\begin{aligned} E_T - E_N &= -(\rho_b | \rho_a) - (\rho_a | \rho_b) \\ &\quad - \frac{1}{2} \left\{ (\rho_a \rho_a | \rho_a \rho_a) - (\rho_a \rho_b | \rho_a \rho_b) \right\} \\ &\quad - \left[(\rho_a \rho_a | \rho_b \rho_b) + (\rho_a \rho_a | \rho_a \rho_b) + (\rho_a \rho_b | \rho_b \rho_b) \right. \\ &\quad \left. + (\rho_a \rho_b | \rho_a \rho_a) + (\rho_a \rho_a | \rho_b \rho_a) - (\rho_a \rho_b | \rho_b \rho_a) \right] \end{aligned}$$

where

$$(\rho_a | \rho_b) = (\rho_a | \tilde{H}^{V1} | \rho_b)$$

$$(\rho_a \rho_b | \rho_a \rho_b) = (\rho_a \rho_b | \tilde{H}^{V2} | \rho_a \rho_b)$$

and

$$E_V - E_N = -(\rho_b | \rho_a) - (\rho_a | \rho_b)$$

$$\begin{aligned}
& + \frac{1}{2} \left\{ (p_a p_a | p_a p_a) - (p_a p_b | p_a p_b) \right\} \\
& - \left[(p_a p_a | p_b p_b) + (p_a p_a | p_a p_b) + (p_a p_b | p_b p_b) \right. \\
& \left. + (p_a p_b | p_a p_a) + (p_a p_b | p_a p_a) + (p_a p_b | p_b p_a) \right]
\end{aligned}$$

We thus have expressions for the T and V state excitation energies. At this point we could discuss the triplet-singlet splitting with respect to these calculated single configuration energies. However, by invoking the zero differential overlap approximation, we will be better able to relate to the semiempiricists point of view. Further, we should see the largest contributions to the splitting. Therefore, in the ZDO scheme

$$E_T - E_N = -(p_a | p_b) - (p_b | p_a) - \frac{1}{2} \Delta$$

and

$$E_V - E_N = -(p_a | p_b) - (p_b | p_a) + \frac{1}{2} \Delta$$

where

$$\begin{aligned}
\Delta & = (p_a p_a | p_a p_a) - (p_a p_b | p_a p_b) \\
& = \gamma_{aa} - \gamma_{ab}
\end{aligned}$$

We are then led to

$$E_V - E_T = \Delta$$

Empirical values for Δ depend on the semiempirical parameters γ_{aa} and γ_{ab} . The success or failure in predicting the V-T splitting is partly reflected in how well γ_{aa} and γ_{ab} are modified from their bare coulomb values towards their semiempirical values.

From Eq.'s V-1 and V-2 we calculate corrections to the one-body and two-body operators in the molecular orbital basis. Since the γ_{aa} and γ_{ab} refer only to the two-body terms in the AO basis, we transform the corrections of the two-body terms back to the atomic orbital basis. These corrections can then be looked upon as corrections to the bare coulomb matrix elements as is shown in Appendix B. Our corrected values for γ_{aa} and γ_{ab} as well as the bare coulomb values and semi-empirical values are listed in the following table (Table VII).

Our γ_{aa} matrix elements are reduced by 0.8 to 1.6eV and γ_{ab} is raised about 0.2eV (depending on approximations and basis set). However, we are still 2.5-3.0eV from the empirical values derived from experimental results.

We have used four basic approximations in our work:

- i) truncating the cluster expansion and including only up through the three-body terms
- ii) keeping at most only part of the second order commutators
- iii) approximating the solutions to the equations for the generator S_{12} , as well as assuming $S_{123} = 0$
- iv) using a finite basis set for the excited orbital space to evaluate the formulae

We feel that of these four sources of error the basis set problem is the most serious. The extent of the basis set bears on two conceptually

TABLE VII
TWO BODY ONE AND TWO CENTER MATRIX ELEMENTS

			γ_{aa}	γ_{ab}	Δ
$\frac{1}{r_{12}}$	(using STO's)		16.93	9.31	7.62
Semiempirical			10.53 ^a	7.38 ^a	3.15
CT	Basis set I	ID = 0	15.47	8.96	6.51
		1	15.46	9.66	5.80
CT	Basis set II	0	15.76	9.50	6.26
		1	16.02	9.44	6.58
CT	Basis set III	0	16.09	9.38	6.70
		1	15.34	9.67	5.67

^aR. Pariser and R. G. Parr, J. Chem. Phys., 21, 767 (1953).

distinct questions. The first is the completeness of the pi orbital valence space. In principle, we have taken it to be infinite whence, the effective valence shell hamiltonian should be represented by an infinite matrix. Diagonalizing the effective hamiltonian--assuming we have somehow found its exact matrix elements--on a finite subspace yields at best approximate stationary states. The second question concerns the completeness of the sigma orbital space. Calculation of any one matrix element of the effective hamiltonian requires in principle a complete set of sigma orbitals (e.g., the sum over σ_e is infinite).

In practice these two questions influence each other because of the manner in which the core, valence, and excited orbitals are in fact found. A finite atomic orbital basis is introduced and a self consistent field calculation yields the sigma core orbitals, the occupied and virtual pi valence orbitals, and the virtual sigma orbitals which carry the burden of mimicing the space of excited sigma orbitals. Thus, the finite dimensional pi space will influence the division of the sigma orbital space into core and excited orbitals through the SCF procedure.

It is not surprising that the practical considerations associated with the extent and character of the finite atomic orbital basis set must be thoroughly understood before drawing any conclusions from the numerical application application of the formalism. Our intuitive feeling--coloured perhaps by the hope that the formalism will be a practical aid in performing semiempirical calculations--is that we should try to get accurate values for the effective hamiltonian on a somewhat restricted valence space, rather than trying to extend

the pi orbital space at the outset. Hence, we are led to introduce an extended set of sigma orbitals as the most direct way of computing the matrix elements of the effective hamiltonian on the limited valence space.

The results of our configuration interaction studies are shown in the following table (Table VIII). Energy diagrams of the V state and the T state using the data from Table VIII are shown in the following figures (Figures 10 and 11).

These results are rather coarse and are to be expected from examination of the transformed matrix elements. Our singlet-triplet splitting is too high for all three choices of basis. A discussion of the shortcomings of these calculations along with suggestions for future work follow.

Conclusions

Our studies were not aimed at making definite conclusions about the lowest singlet and triplet excitation energies of the ethylene molecule. Rather, they were to develop the canonical transformation approach to quantum chemical calculations. Large molecules of fifty or more electrons are inaccessible to rigorous quantum computations which include correlation effects. Our intent is to develop a rigorous albeit useful scheme for studying such molecules.

We chose, as a starting point, to calculate the pi-electron hamiltonian of ethylene. What now follows is a summary of the difficulties we encountered.

i) Our choice of ethylene as a prototype molecule of pi-electron systems seems to have been a poor one. Although the molecular

TABLE VIII
 CONFIGURATION INTERACTION RESULTS
 (Energies in eV)

	N → T	N → V	V → T
Experiment ^a	4.6	7.65	3.05
<u>Ab Initio</u> ^b	4.25	8.32	4.07
Freed (1) ^c	4.793	9.444	4.65
Freed (2) ^c	4.845	9.729	4.88
Basis Set I			
Pi Approx	4.780	13.072	8.29
IDENOM=0 ^d	3.153	10.591	7.44
IDENOM=1	3.153	10.572	7.42
Basis Set II			
Pi Approx	4.662	11.730	7.07
IDENOM=0	3.404	10.106	6.70
IDENOM=1	3.824	10.028	6.20
Basis Set III			
Pi Approx	4.607	11.993	7.39
IDENOM=0	3.929	10.615	6.69
IDENOM=1	3.309	9.981	6.67

^aExperimental values for N→T and N→V transitions are listed and discussed in paper by A. J. Merer and R. S. Mulliken, Chem. Rev., 69, 639 (1969).

^bR. J. Buenker, S. D. Peyerimhoff, and E. Kammer, J. Chem. Phys. 55, 814 (1971).

^cBasis sets 1 and 2 of S. Iwata and K. F. Freed, J. Chem. Phys. 61, 1500 (1974).

^dIDENOM = $\begin{Bmatrix} 0 \\ 1 \end{Bmatrix}$ refers to $\begin{Bmatrix} \text{exclusion} \\ \text{inclusion} \end{Bmatrix}$ of two body potential in denominators in the calculation of the effective Hamiltonian.

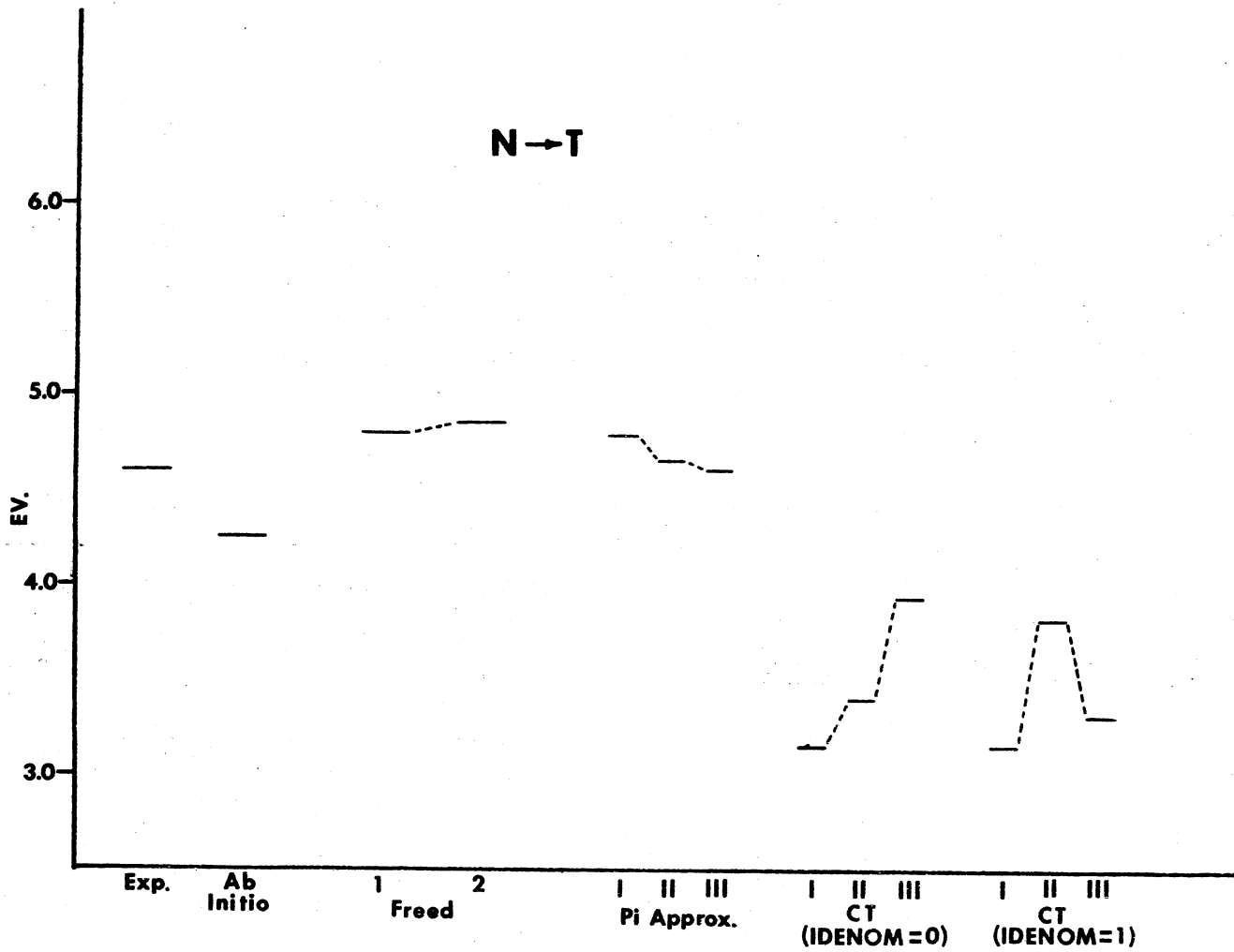


Figure 10. Diagram of the N → T Transition Energies Using the Various Approximations and Results of Other Workers

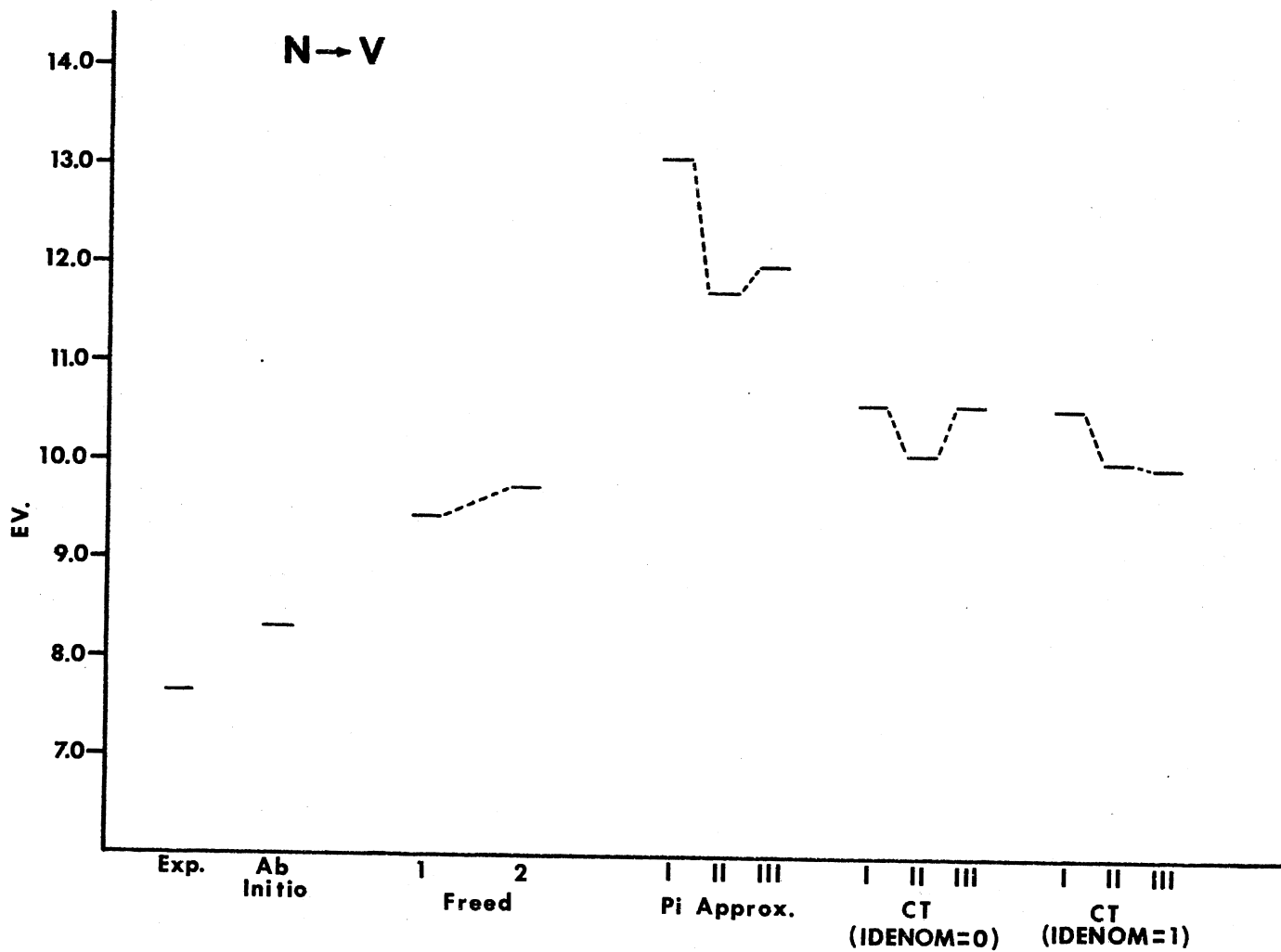


Figure 11. Diagram of the N → V Transition Energies Using the Various Approximations and Results of Other Workers.

orbital approach leads to the inclusion of a pi orbital on each carbon atom, the low lying excited states are strongly suspected to involve sigma orbitals. Furthermore, the actual interpretation of the experimental electronic excitation spectrum is disputed. The solution to this problem is to do the calculation in the valence electron approach. We need to generalize our programs to compute the valence hamiltonian. By choosing some of the highest occupied and lowest unoccupied sigma orbitals along with the pi orbitals to define the valence space, we feel more satisfying excitation energies would result. These changes and improvements are currently in progress.

ii) Because of the time consuming nature of transforming two body matrix elements from atomic orbitals to molecular orbitals, we were limited in the size of basis set. Our programming further limited us to transform basis sets of only thirty orbitals. (The symmetry of the sigma and pi orbitals allowed us to perform the calculation with basis set III.) Recent results of Westhaus and Bradford¹ suggest the importance of larger basis sets. They have performed canonical transformation calculations on first row atoms and have produced excitation energies in excellent agreement with experiment and relatively independent of the basis set chosen. Thus, the need for larger basis sets in molecular calculations is suggested. We have now generalized programs which can transform up to one hundred orbitals in approximately 150 kilobytes of core storage. The programming problem is now eliminated. Only the amount of computer time required remains as a burden.

iii) Our version of GAUSSIAN-70 has no provisions for orbitals with "d" symmetry. Recent results of P. C. Hariharan and

J. P. Pople² showed the total SCF energy of ethylene to be lowered by 0.8eV. We feel that to properly account for the delocalized nature of some of the excited states, inclusion of "d" orbitals is a necessity. We require a molecular integral program which can handle "d" orbitals. Efforts are in progress to obtain such a program.

Notwithstanding the above mentioned difficulties, we feel the results and progress thus far obtained merit further work. We anticipate molecular calculations having the same accuracy as the atomic calculations. The canonical transformation required less than 10 percent of the total computation time. If an ab initio N-electron CI calculation were desired, it could not be done due to the size of the N-electron basis. All other calculations depend on an arbitrary truncation of the N-electron basis and thus of the N-electron hamiltonian itself. Our method is an ab initio approach to the same problem which does not arbitrarily truncate the hamiltonian. It yields calculation times which are amenable to most computing systems and budgets and hopefully in the near future accurate results.

REFERENCES

1. P. Westhaus and E. G. Bradford, J. Chem. Phys., 63, 5416 (1975).
2. P. C. Hariharan and J. A. Pople, Chem. Phys. Lett., 16, 217 (1972).

APPENDIX A

REDUCTION OF THREE BODY MATRIX ELEMENTS

We consider the reduction of the three-body matrix elements to sums of products of two-body matrix elements. These three-body matrix elements arise in the three-body clusters discussed in Chapter IV, where the relevant operators are commutators like $[S_{12}, g_{13}^{\text{off-diag}}]$ and $[S_{12}, (W_{13} - g_{13}^{\text{diag}})]$. Thus, examining equation (IV-7) with the view of letting the two-body operator $Y_{13} = g_{13}^{\text{off-diag}}$ in one case and $Y_{13} = W_{13} - g_{13}^{\text{diag}}$ in another, we write

$$\begin{aligned} & \langle \lambda_1 \lambda_2 \lambda_3 | \left[\{S_{12} Y_{13} - Y_{13} S_{12}\} + \{S_{12} Y_{23} - Y_{23} S_{12}\} \right. \\ & + \{S_{13} Y_{12} - Y_{12} S_{13}\} + \{S_{13} Y_{23} - Y_{23} S_{12}\} + \{S_{23} Y_{12} - Y_{23} S_{12}\} \\ & \left. + \{S_{23} Y_{13} - Y_{13} S_{23}\} \right] | \mu_1 \mu_2 \mu_3 \rangle \quad (\text{A-1}) \end{aligned}$$

$$= 6 \langle \lambda_1 \lambda_2 \lambda_3 | \{S_{12} Y_{13} - Y_{12} S_{13}\} | \mu_1 \mu_2 \mu_3 \rangle$$

$$= \sum_{\rho_1} \sum_{\rho_2} \sum_{\rho_3} 6 \left[\langle \lambda_1 \lambda_2 \lambda_3 | S_{12} | \rho_1 \rho_2 \rho_3 \rangle (\rho_1 \rho_2 \rho_3 | Y_{13} | \mu_1 \mu_2 \mu_3 \rangle \right. \\ \left. - \langle \lambda_1 \lambda_2 \lambda_3 | Y_{12} | \rho_1 \rho_2 \rho_3 \rangle (\rho_1 \rho_2 \rho_3 | S_{13} | \mu_1 \mu_2 \mu_3 \rangle \right]$$

Recall that the normalized three-particle ket $|\mu_1\mu_2\mu_3\rangle$ is constructed as the antisymmetrized product of orbitals. On the other hand, $|\rho_1\rho_2\rho_3\rangle$ is simply the direct product of orbitals. The two types of three-particle kets and the corresponding bras are distinguished by the angular and rounded brackets, respectively. The last line of (A-1) follows upon using the identify operator

$$\mathbb{1} = \sum_{\rho_1} \sum_{\rho_2} \sum_{\rho_3} |\rho_1\rho_2\rho_3\rangle \langle \rho_1\rho_2\rho_3|$$

in the usual fashion. The three independent sums on ρ_1 , ρ_2 , ρ_3 are each over the complete set of orbitals.

It is necessary to use the identify on the entire three-particle Hilbert Space rather than just the antisymmetric subspace because the operator in line two of Equation (A-1) has no particle exchange symmetry. Now it follows that

$$\begin{aligned} \langle \lambda_1\lambda_2\lambda_3 | A_{12} | \rho_1\rho_2\rho_3 \rangle &= \frac{1}{\sqrt{3}} \left\{ \langle \lambda_1\lambda_2 | A | \rho_1\rho_2 \rangle \delta_{\lambda_3\rho_3} \right. \\ &+ \langle \lambda_3\lambda_1 | A | \rho_1\rho_2 \rangle \delta_{\lambda_2\rho_3} + \left. \langle \lambda_2\lambda_3 | A | \rho_1\rho_2 \rangle \delta_{\lambda_1\rho_3} \right\} \\ &= \frac{1}{\sqrt{6}} \left\{ \langle \lambda_1\lambda_2 | A | \rho_1\rho_2 \rangle \delta_{\lambda_3\rho_3} + \langle \lambda_3\lambda_1 | A | \rho_1\rho_2 \rangle \delta_{\lambda_2\rho_3} \right. \\ &\quad \left. + \langle \lambda_2\lambda_3 | A | \rho_1\rho_2 \rangle \delta_{\lambda_1\rho_3} \right\} \quad (A-2) \end{aligned}$$

where the angular brackets denote normalized antisymmetric products of two orbitals:

$$|\rho_1\rho_2\rangle = \frac{1}{\sqrt{2}} \left\{ |\rho_1\rangle_1 |\rho_2\rangle_2 - |\rho_2\rangle_1 |\rho_1\rangle_2 \right\}$$

Similarly, we find that

$$\begin{aligned} \langle \rho_1\rho_2\rho_3 | B_{13} | \mu_1\mu_2\mu_3 \rangle &= \frac{1}{\sqrt{6}} \left\{ \langle \rho_1\rho_3 | B | \mu_1\mu_3 \rangle \delta_{\rho_2\mu_2} \right. \\ &\left. + \langle \rho_1\rho_3 | B | \mu_3\mu_2 \rangle \delta_{\rho_2\mu_1} + \langle \rho_1\rho_3 | B | \mu_2\mu_1 \rangle \delta_{\rho_2\mu_3} \right\} \end{aligned} \quad (\text{A-3})$$

In the above equations A and B can be any two-body operators symmetric in their particle labels. Upon inserting the results (A-2) and (A-3) into (A-1) and performing the sums on ρ_2 and ρ_3 , we obtain

$$\begin{aligned} &\sum_{\rho} \left\{ \langle \lambda_1\lambda_2 | S_{12} | \rho\mu_3 \rangle \langle \rho\lambda_3 | Y_{12} | \mu_1\mu_3 \rangle - \langle \lambda_1\lambda_2 | Y_{12} | \rho\mu_2 \rangle \langle \rho\lambda_3 | S_{12} | \mu_1\mu_3 \rangle \right\} \\ &+ \sum_{\rho} \left\{ \langle \lambda_1\lambda_2 | S_{12} | \rho\mu_1 \rangle \langle \lambda_3\rho | Y_{12} | \mu_2\mu_3 \rangle - \langle \lambda_1\lambda_3 | Y_{12} | \rho\mu_1 \rangle \langle \lambda_3\rho | S_{12} | \mu_2\mu_3 \rangle \right\} \\ &+ \sum_{\rho} \left\{ \langle \lambda_1\lambda_2 | S_{12} | \rho\mu_3 \rangle \langle \lambda_3\rho | Y_{12} | \mu_1\mu_2 \rangle - \langle \lambda_1\lambda_2 | Y_{12} | \rho\mu_3 \rangle \langle \lambda_3\rho | S_{12} | \mu_1\mu_2 \rangle \right\} \\ &+ \sum_{\rho} \left\{ \langle \lambda_1\lambda_3 | S_{12} | \mu_2\rho \rangle \langle \rho\lambda_2 | Y_{12} | \mu_1\mu_3 \rangle - \langle \lambda_1\lambda_3 | Y_{12} | \mu_2\rho \rangle \langle \rho\lambda_2 | S_{12} | \mu_1\mu_3 \rangle \right\} \end{aligned}$$

$$\begin{aligned}
& + \sum_{\rho} \left\{ \langle \lambda_1 \lambda_3 | S_{12} | \mu_1 \rho \rangle \langle \lambda_2 \rho | Y_{12} | \mu_2 \mu_3 \rangle - \langle \lambda_1 \lambda_3 | Y_{12} | \mu_1 \rho \rangle \langle \lambda_2 \rho | S_{12} | \mu_2 \mu_3 \rangle \right\} \\
& + \sum_{\rho} \left\{ \langle \lambda_1 \lambda_3 | S_{12} | \mu_3 \rho \rangle \langle \lambda_2 \rho | Y_{12} | \mu_1 \mu_2 \rangle - \langle \lambda_1 \lambda_3 | Y_{12} | \mu_3 \rho \rangle \langle \lambda_2 \rho | S_{12} | \mu_1 \mu_2 \rangle \right\} \\
& + \sum_{\rho} \left\{ \langle \lambda_2 \lambda_3 | S_{12} | \rho \mu_2 \rangle \langle \rho \lambda_1 | Y_{12} | \mu_1 \mu_3 \rangle - \langle \lambda_2 \lambda_3 | Y_{12} | \rho \mu_2 \rangle \langle \rho \lambda_1 | S_{12} | \mu_1 \mu_3 \rangle \right\} \\
& + \sum_{\rho} \left\{ \langle \lambda_2 \lambda_3 | S_{12} | \rho \mu_1 \rangle \langle \lambda_1 \rho | Y_{12} | \mu_2 \mu_3 \rangle - \langle \lambda_2 \lambda_3 | Y_{12} | \rho \mu_1 \rangle \langle \lambda_1 \rho | S_{12} | \mu_2 \mu_3 \rangle \right\} \\
& + \sum_{\rho} \left\{ \langle \lambda_2 \lambda_3 | S_{12} | \rho \mu_3 \rangle \langle \lambda_1 \rho | Y_{12} | \mu_1 \mu_2 \rangle - \langle \lambda_2 \lambda_3 | Y_{12} | \rho \mu_3 \rangle \langle \lambda_1 \rho | S_{12} | \mu_1 \mu_2 \rangle \right\}
\end{aligned}$$

The summation over ρ is over all spin orbitals; core, valence, and excited orbitals.

In Chapter VI we can use the general result embodied in equation (A-4) by identifying Y with $g_{12}^{\text{off-diag}}$ in one set of terms and $W_{12} - g_{12}^{\text{diag}}$ in another, and by specifying $\lambda_1 \lambda_2 \lambda_3 \mu_1 \mu_2 \mu_3$ as the appropriate core and valence orbitals. As discussed in Chapter IV, these specific choices lead to further simplifications in the general result. For instance, with our choice of S_{12} and $(W_{12} - g_{12}^{\text{diag}})$ we find that

$$\langle cc'v | [S_{12}, (W_{13} - g_{13}^{\text{diag}})] | cc'v' \rangle \equiv 0$$

and

$$\langle cvv' | [S_{12}, (W_{13} - g_{13}^{\text{diag}})] | cv''v''' \rangle \equiv 0$$

This can be seen by equation (A-4) and noting that at least one factor in each term vanishes. Thus, only the matrix elements such as

$$\langle cc'v | [S_{12}, g_{13}^{\text{off-diag}}] | cc'v' \rangle$$

and

$$\langle cvv' | [S_{12}, g_{13}^{\text{off-diag}}] | cv''v''' \rangle$$

survive in the three-body cluster contributions to the effective interaction.

APPENDIX B

CORRECTIONS TO TWO BODY MATRIX ELEMENTS

In this Appendix we will show that from equations II-24 and II-25 we can derive

$$\begin{aligned} H^v = & \sum_{v v'} \left\{ \langle v | T + V | v' \rangle + \sum_c \langle c v' | \frac{1}{r_{12}} | c v' \rangle + G_{v v'}^1 \right\} a_v^\dagger a_{v'} \\ & + \sum_{v < v'} \sum_{v'' < v'''} \left\{ \langle v v' | \frac{1}{r_{12}} | v'' v''' \rangle + G_{v v' v'' v'''}^2 \right\} a_v^\dagger a_{v'}^\dagger a_{v''} a_{v'''} \end{aligned} \quad (\text{B-1})$$

where $G^1(G^2)$ is a canonical transformation correction to the one (two) body operator. We will show this by writing down the first three terms of the valence hamiltonian and showing that the Hartree-Fock potential U cancels explicitly.

The result of this cancelation is that we can consider G^2 to be a correction to the bare coulomb interaction matrix element, $(\pi_i \pi_j | \frac{1}{r_{12}} | \pi_k \pi_l)$. The N_V particle valence hamiltonian consists of (Eq. II-24 and II-25)

$$\begin{aligned} H^v = & \sum_{v v'} \left\{ \epsilon_v \delta_{v v'} + \sum_c \langle c v | g_{12} | c v' \rangle + G^1 \right\} a_v^\dagger a_{v'} \\ & + \sum_{v < v'} \sum_{v'' < v'''} \left\{ \langle v v' | g_{12} | v'' v''' \rangle + G^2 \right\} a_v^\dagger a_{v'}^\dagger a_{v''} a_{v'''} \end{aligned} \quad (\text{B-2})$$

Here

$$\begin{aligned} \sum_{vv'} \epsilon_v \delta_{vv'} a_v^\dagger a_v &= \sum_{vv'} \langle v | T+V+U | v' \rangle a_v^\dagger a_v \\ &= \sum_{vv'} \langle v | T+V | v' \rangle a_v^\dagger a_v + \sum_{vv'} \langle v | U | v' \rangle a_v^\dagger a_v. \end{aligned}$$

We want to show the U's cancel in the first two terms in the one-body operator and the first term in the two-body operator except for an additive constant. Thus, we will work with the following three sums:

$$\begin{aligned} \sum_{vv'} \langle v | U | v' \rangle a_v^\dagger a_v + \sum_v \sum_{v'} \sum_c \langle vc | \left\{ -\frac{U_1+U_2}{N-1} \right\} | v'c \rangle a_v^\dagger a_v \\ + \sum_{v < v'} \sum_{v'' < v'''} \langle vv' | \left\{ -\frac{U_1+U_2}{N-1} \right\} | v''v''' \rangle a_v^\dagger a_{v'}^\dagger a_{v''} a_{v'''} \end{aligned}$$

The second sum equals:

$$\begin{aligned} -\left(\frac{1}{N-1}\right) \sum_{vv'} \sum_c \left\{ U_{vv'} + U_{cc} \delta_{vv'} \right\} a_v^\dagger a_v \\ = -\left(\frac{1}{N-1}\right) N_{\text{core}} \sum_{vv'} U_{vv'} a_v^\dagger a_v - \left(\frac{1}{N-1}\right) \hat{N}_v \sum_c U_{cc} \end{aligned}$$

The third sum equals:

$$-\left(\frac{1}{N-1}\right) \frac{1}{4} \sum_{vv'} \sum_{v''v'''} \left\{ U_{vv''} \delta_{vv'''} - U_{vv'''} \delta_{v'v''} \right\}$$

$$+ U_{v'v''} \delta_{vv''} - U_{v'v''} \delta_{vv''} \} a_v^\dagger a_{v'}^\dagger a_{v''} a_{v''}$$

By relabeling the indices and summing over the delta functions, we get

$$-\left(\frac{1}{N-1}\right) \sum_{vv'v''} U_{vv'} a_v^\dagger a_{v'}^\dagger a_{v''} a_{v'} =$$

$$-\left(\frac{1}{N-1}\right) \sum_{vv'} U_{vv'} a_v^\dagger \left[\sum_{v''} a_{v''}^\dagger a_{v''} \right] a_{v'}$$

but

$$\sum_{v''} a_{v''}^\dagger a_{v''} = (N_v - 1) \hat{1}$$

when it operates to the left of a_v on an N_v particle ket. Hence, the third summation equals

$$-\left(\frac{1}{N-1}\right) (N_v - 1) \sum_{vv'} U_{vv'} a_v^\dagger a_{v'}$$

All three sums give

$$\sum_{vv'} U_{vv'} a_v^\dagger a_{v'} - \left(\frac{N_{\text{core}} + N_v - 1}{N-1}\right) \sum_{vv'} U_{vv'} a_v^\dagger a_{v'}$$

$$- \left(\frac{1}{N-1}\right) \hat{N}_v \sum_c U_{cc}$$

When this operator operates on any N_v -particle ket, the first two terms cancel, and we are left with the third term as an additive constant.

Hence, we may consider G_2 as a correction to the two-body-bare coulomb interaction.

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