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NRCC NATIONAL RESOURCE FOR COMPUTATION IN CHEMISTRY

POST HARTREE-FOCK: CONFIGURATION INTERACTION

REPORT
on the Workshop
August 14 - 16, 1978

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA

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NATIONAL RESOURCE FOR COMPUTATION IN CHEMISTRY

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MASTER

FOREWORD

The National Resource for Computation in Chemistry (NRCC) was established as a Division of Lawrence Berkeley Laboratory (LBL) in October, 1977. The functions of the NRCC may be broadly categorized as follows: (1) to make information on existing and developing computational methodologies available to all segments of the chemistry community, (2) to make state-of-the-art computation facilities (both hardware and software) accessible to the chemistry community, and (3) to foster research and development of new computational methods for application to chemical problems.

Workshops are one facet of the NRCC's program for both obtaining and making available information on new developments in computationally oriented subdisciplines of chemistry. The goal of this workshop was to bring together some of the principal developers of new methods that go beyond the Hartree-Fock formalism in the description of the electronic structure of molecules. In the Hartree-Fock model the motion of each electron is governed only by the average field of the other electrons. "Post Hartree-Fock" refers to methods that aim at describing the instantaneous motion of each electron. This electron correlation effect plays an important role in determining the structure of molecules in their ground and excited states. Quantum chemists must be able to reliably account for this correlation energy if they are to accurately predict molecular properties and interpret experimental data.

The first part of the workshop concerned the more familiar configuration interaction (CI) method in which the electronic wavefunction is expanded in a basis set of configurations, i.e., a linear combination of Slater determinants in which each of the electrons of the system is assigned to a different spin orbital. The wavefunction is determined by applying the variational principle. Except for a few very small molecular systems, a "full CI" calculation is not generally possible so that considerable care must be taken in choosing the molecular orbital expansion functions and in selecting configurations for inclusion in the CI expansion. The first session addressed the determination of the molecular orbitals for the construction of the configurations, and the second session examined the selection of configurations for the CI expansion.

The computation of the Hamiltonian matrix elements between configurations, although straightforward, is time consuming. The third session considered advances in the past year on this problem. One alternative presented is the simultaneous construction of the Hamiltonian matrix as one proceeds through the calculation of matrix elements. Another possibility is to create a list of the formal expressions for all matrix elements and to substitute the electron repulsion integrals into these expressions to obtain the values of the matrix elements. This latter technique is referred to as the "formula tape" method. The fourth session was devoted to discussing the relative merits of the two methods.

An earlier NRCC workshop held during the summer of 1978, "Numerical Algorithms in Chemistry: Algebraic Methods" (LBL-8158), discussed in detail the tools available for finding the lowest roots of large, diagonally dominant matrices. Such root searches are one step of the CI

technique, and a short summary of the problem with suggested solutions was presented at the current workshop.

The Direct CI method solves the secular equations directly from the electron repulsion integrals without explicitly constructing a Hamiltonian matrix. The most recent developments in the field of Direct CI were the subject of a session at the current workshop.

Methods different from the CI Method are also used to obtain a correlated wavefunction. Several sessions were devoted to a presentation of these algorithms, such as Coupled Electron Pair Approximation (CEPA), Pseudo Natural Orbital (PNO)-CI/CEPA, Self Consistent Electron Pair (SCEP), along with the many-body Perturbation Theory and the Coupled Cluster Theory.

Logistics and program design were the subject of the last and one of the more important sessions. The computational efficiency and flexibility of the FORTRAN CI programs are a prime concern to both the NRCC and those in the chemistry community who wish to perform CI calculations.

The present volume is an attempt to present a timely digest of each session, and therefore closely follows the style of presentation of the speakers. Annotated bibliographies are included as a guide to the literature of the various areas.

The NRCC is indebted to Dr. Charles Bender, Lawrence Livermore Laboratory, and Professor John Pople, Carnegie-Mellon University, for organizing this workshop. We also thank Dr. Bender, and Drs. Michel Dupuis and John Wendoloski of the NRCC for their efforts in organizing this volume.

The NRCC is jointly funded by the Department of Energy and the National Science Foundation.

William A. Lester, Jr.
Director NRCC

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NRCC Workshop on
Post Hartree-Fock: Configuration Interaction

August 14-16, 1978

Lawrence Berkeley Laboratory
Bldg. 50B, Room 4205

C. Bender and J. Pople, Co-organizers

Monday, August 14

9:00 a.m.	Opening Remarks - W. Lester / J. Pople / C. Bender
9:30 a.m.	Molecular Orbitals - T. Dunning, E. Davidson, K. Ruedenberg
10:45 a.m.	Coffee
11:00 a.m.	Configurations - B. Liu, J. Hay, K. Ruedenberg
12:30 p.m.	Lunch
1:30 p.m.	Matrix Elements - I. Shavitt, J. Paldus, W. Goddard, G. Diercksen
2:45 p.m.	Coffee
3:00 p.m.	Formula Tape or Not? - E. Davidson, M. Yoshimine, G. Diercksen
4:30 p.m.	Diagonalization Techniques - I. Shavitt

Tuesday, August 15

8:30 a.m.	Direct Methods - B. Roos, C. Bender
9:45 a.m.	Coffee
10:00 a.m.	Non-Standard Variational Methods - W. Meyer, C. Dykstra
11:30 a.m.	Lunch
1:00 p.m.	Perturbation Theory - R. Bartlett, E. Davidson, J. Pople, B. Kirtman
2:45 p.m.	Coffee
3:00 p.m.	Coupled Cluster Techniques - J. Pople, J. Paldus, R. Bartlett

Wednesday, August 16

8:30 a.m.	Logistics and Program Design - G. Diercksen, M. Yoshimine, J. Hay, C. Bender, S. Peyerimhoff, S. Langhoff
10:45 a.m.	Coffee
11:00 a.m.	Open Discussion
12:30 p.m.	Lunch
2:00 p.m.	Summary Manuscript Outline/Preparation
4:30 p.m.	Wine Tasting - LBL Directors Office
7:00 p.m.	Working Dinner - Inn Season

Evenings reserved for document preparation, as needed.
Underlined are section chairmen; other persons are invited participants.

Attendees

Post Hartree-Fock: Configuration Interaction

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WORKSHOP RECOMMENDATIONS TO NRCC

Recommendations from the session on matrix elements:

The recommendations for this session cannot be separated from those of the other sessions. Essentially they involve the acquisition of several existing CI program packages and their adaptation to the NRCC environment, including the design and implementation of a common Standard Data Interface to be incorporated into these programs, along the lines pioneered in the Munich System.

The actual programs to be acquired have been discussed in other sessions. The principal candidates are open-eneded programs, such as the University of Washington (Davidson) programs (or their NASA-Ames version), but others, such as the Caltech/LASL (F. Bobrowicz) programs, should also be considered.

The design of the Standard Data Interface should be assigned to a small working group or committee.

Recommendations from the session on diagonalization techniques:

These are the same as the recommendations from the workshop on Numerical Algorithms. The programs to be set up at NRCC should include standard (in core) diagonalization packages, such as EISPACK, and special CI-oriented large-matrix programs. In this last category, the principal candidates are the simultaneous multiroot versions of Davidson's method (by B. Liu) and of the coordinate relaxation method (by R. C. Raffenetti and/or by I. Shavitt). Also, a collection of typical CI matrices of various sizes should be assembled, in order to facilitate testing, development, and comparison of new methods.

Recommendations from the session on direct CI methods:

NRCC should keep a close eye on the coming work on the unitary group approach to direct CI.

NRCC should set up a few of the existing direct CI programs, e.g.

CICS	**(Roos, Lund)**	**(CDC, IBM)**
CIDU	**(Bucskay, Sidney)**	**(CD 7600)**
CITRI	**(Schaefer, Berkeley)**	**(Harrish/y, CDC^2)**
CIMC	**(Roos, Lund)**	**(CDC, IBM)**
CIS	**(Siegbahn, Stockholm)**	**(CDC, IBM)**
SVM	(Bender, Livermore)	

Recommendations from the session on program logic and design:

C. Bender, G.H.F. Diercksen (Chairman), J. Hoy,
S. Langhoff, M. Yoshimine

1. It is recommended to NRCC to study the suitability of the concept of standardized data lists as general means to link different programs to flexible and open-ended general purpose molecular program systems serving equally well as a black box to experimental chemists, and as a working tool for further research in theoretical chemistry, and, if apt, to define Standard Data Interfaces. Special emphasis should be given to data transportability and data reduction (a study group may be set up for this purpose).

2. It is recommended to NRCC to study the creation of a Data Base, accessible by a network system, containing quantum mechanically calculated wavefunctions and expectation values of atomic and molecular systems

INTRODUCTORY REMARKS

J.A. Pople

The following are desirable features for a theoretical model chemistry incorporating electron correlation;

MODEL CHEMISTRY FEATURES

1. Unique, continuous energy surface.
2. Efficient for large systems.
3. Size consistent.
   $E(X+Y) = E(X)+E(Y)$ for isolated systems.
4. Variational.
   $E\ (\text{model}) \geqslant E\ (\text{exact})$
5. Transformation invariance within degenerate sets.

The various methods described in this workshop should be examined with these in mind. All the five criteria are satisfied at the Hartree-Fock level. Beyond Hartree-Fock, it is difficult to satisfy them all short of full configuration interaction within the basis set employed.

I. DETERMINATION OF ORBITALS FOR USE IN CONFIGURATION INTERACTION CALCULATIONS

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DETERMINATION OF ORBITALS FOR USE IN CONFIGURATION INTERACTION CALCULATIONS

by

Thom. H. Dunning, Jr.

Before beginning our discussion of the determination of the orbitals for use in configuration interaction (CI) calculations, we should take note of the intimate relationship between the specification of the orbital set and the classes of configurations included in the calculations. To take an extreme case, note that for a full CI calculation the choice of orbitals is completely irrelevant, i.e., the calculated wavefunction is unaffected by an arbitrary unitary transformation of the orbitals; it depends only on the space spanned by the original basis set. Of course, for most chemical systems it is not possible to realistically carry out a full CI calculation, so that specification of the orbital set is important. Even for less-than-full CI calculations, it can be shown, however, that for certain types of calculations the wavefunction is unaffected by restricted transformations among the orbital set. For example, for CI calculations based on a single configuration plus a complete set of excitations of a given type (single, double, etc.), the calculated wavefunction is independent of transformations among the set of "occupied" orbitals and among the set of "virtual" orbitals. The wavefunction does, however, depend on transformations which mix the occupied and virtual orbitals.

While in the above we were primarily concerned with the dependence of the calculated wavefunction on the orbitals used in the calculations, a particular orbital set may be preferable for other reasons. For example, in interpreting the results of a CI calculation, it is important that the orbitals be determined in a physically reasonable manner so as to simplify insofar as is possible the assignation of specific correlation effects to the configurations included in the calculations. Also, the cost of calculating a wavefunction *of given accuracy* depends on the orbital set used. For CI calculations the cost is related to the number of configurations included in the expansion. Thus, a given orbital set may be preferred because it leads to a more compact representation of the wavefunction.

ORBITALS FOR USE IN CI CALCULATIONS

CLASSIFICATION OF ORBITALS

PRIMARY ORBITAL SET

— ORBITAL SET NECESSARY FOR PROPER ZERO-ORDER DESCRIPTION

SECONDARY ORBITAL SET

— ORBITAL SET NEEDED FOR CORRECTIONS TO ZERO-ORDER DESCRIPTION

METHODS OF DETERMINING THE ORBITALS FOR USE IN CONFIGURATION INTERACTION CALCULATIONS

— HARTREE-FOCK METHOD

— GENERALIZED VALENCE BOND METHOD

— MULTICONFIGURATION SELF-CONSISTENT FIELD METHODS

— NATURAL ORBITAL METHODS

Figure 1.

To begin let us divide the orbitals to be used in the CI calculations into two sets:

(1) the primary orbital set which is the minimum set of orbitals necessary to provide a proper zero-order description of the chemical system of interest, and

(2) the secondary orbital set which consists of those orbitals needed to provide minor corrections to the zero-order wavefunction.

In selected cases the primary orbital set may consist of just the Hartree-Fock orbitals. In general, however, the primary orbital set will be larger than the Hartree-Fock orbital set.

This division of the orbitals into a primary and a secondary set is more than just a bookkeeping convenience for different techniques can be used to determine the orbitals in the two sets. Thus, the energy of a system is critically dependent on the orbitals in the primary set. As a result, variational techniques such as

(1) the Hartree-Fock (HF) method,

(2) the generalized valence bond (GVB) method,

(3) the multiconfiguration self-consistent field (MCSCF) method, and

(4) iterative natural orbital (NO) techniques

are required. Although the NO methods are not strictly variational methods, they are *near*-variational and in practice have been found to yield satisfactory results.

The energy of the system is far less dependent on the orbitals in the secondary set. For example, one common method of obtaining a secondary orbital set is just to make use of the "virtual" orbitals from a HF calculation. These orbitals are not at all defined in a physically reasonable manner; nonetheless, satisfactory results can be obtained if the orbitals and resulting configurations are not truncated unreasonably. Except in selected cases, this method is not, however, recommended. Rather, it is advisable to obtain the secondary orbital set using energy related techniques, e.g., as the NOs obtained from perturbation theory or as the weakly occupied orbitals obtained with the methods mentioned above. Because of the weak dependence of the energy on the secondary orbital set, however, these latter methods undoubtedly contain a certain amount of "overkill". One of the challenges before us in advancing the CI method is the development of fast, efficient methods for determining a secondary orbital set which takes full advantage of the weak dependence of the system energy on these orbitals.

THE HARTREE-FOCK METHOD

OVERVIEW OF RESTRICTED HARTREE-FOCK METHODS

CLOSED SHELL CONFIGURATIONS

OPEN SHELL CONFIGURATIONS

FULL VARIATION METHODS

PARTIAL VARIATIONAL METHODS

— EXTENDED HARTREE-FOCK METHOD

— IMPROVED VIRTUAL ORBITAL METHOD

Figure 2.

THE HARTREE-FOCK METHOD

ADVANTAGES AND DISADVANTAGES OF RESTRICTED HARTREE-FOCK METHODS

ADVANTAGES

- WELL DEFINED (USUALLY)
- ECONOMICAL
- SIMPLE ORBITAL MODEL

DISADVANTAGES

- SINGLE REFERENCE CONFIGURATION
- SECONDARY ORBITAL SET UNSATISFACTORY

Figure 3.

For a closed shell configuration the Hartree-Fock wave-function takes a particularly simple form, namely,

$$\Psi_{HF} = \mathscr{A}\phi_1\phi_1\cdots\phi_n\phi_n\alpha\beta\cdots\alpha\beta \tag{1}$$

The orbitals in (1) are solutions of the pseudo-eigenvalue equations

$$\begin{aligned} \mathscr{H}_{HF}\phi_i &= \varepsilon_i\phi_i \\ \mathscr{H}_{HF} &= h + \sum_i (2J_i - K_i) \end{aligned} \tag{2}$$

For a derivation of (2) and a discussion of its solution using basis set expansion techniques the reader is referred to C. C. J. Roothaan, "New Developments in Molecular Orbital Theory," Rev. Mod. Phys. 23, 69 (1951). If (2) is solved in a basis of N functions then the first n eigenfunctions of (2) correspond to the orbitals occupied in (1) and the remaining (N-n) eigenfunctions are referred to as the "virtual" orbitals.

It can easily be shown that the virtual orbitals are those appropriate for a (2n+1)-electron system *if no changes are allowed in the 2n-electron core represented by (1).* For most, but not all, chemical systems these orbitals have positive energies (ε_i)

and in the limit of a complete solution of (2) would not be bound, i.e., ε_i would approach zero and the virtual orbitals would become continuum functions. Such functions would be of little use in CI calculations. Fortunately, for general molecular systems basis set expansion techniques are used to solve (2) so that the virtual orbitals are constrained to lie within the space spanned by the original basis set. Only for basis sets containing very diffuse functions does the continuum nature of the virtual orbitals cause difficulties.

For open shell configurations, while the wavefunction is still of a simple form, e.g., for doublet states

$$\Psi_{HF} = \mathcal{A}\phi_1\phi_1\cdots\phi_n\phi_n\phi_{n+1}\alpha\beta\cdots\alpha\beta\alpha \ , \tag{3}$$

determination of the optimum set of orthonormal orbitals is not quite so straightforward. In general, more than one pseudo-eigenvalue equation must be solved, although in some cases it is possible to combine the different equations into one master equation using coupling operator techniques, see, e.g., C. C. J. Roothaan, "Self-Consistent Field Theory for Open Shells of Electronic Systems," Rev. Mod. Phys. 32, 179 (1960). With multiple equations to be solved, special procedures are required to insure that

(1) the orbitals so determined are indeed the optimum orbitals with respect to variations in both the occupied and virtual spaces

(2) the occupied orbitals from all of the pseudo-eigenvalue equations form an orthogonal set.

Within the last few years techniques have been developed for the full variational computation of the orbitals in general open shell configurations. For a discussion of these techniques the reader is referred to W. J. Hunt, W. A. Goddard, III and T. H. Dunning, Jr., "The Incorporation of Quadratic Convergence into Open-Shell Self-Consistent-Field Equations," Chem. Phys. Lett. 6, 147 (1970) [For a review of these and related techniques see F. W. Bobrowicz and W. A. Goddard, III, "The Self-Consistent Field Equations for Generalized Valence Bond and Open-Shell Hartree-Fock Wavefunctions" in *Methods of Electronic Structure Theory*, ed. by H. F. Schaefer, III, (Plenum Publishing Corporation, New York, 1977)] and E. R. Davidson, "Spin-Restricted Open-Shell Self-Consistent Field Theory," Chem. Phys. Lett. 21, 565 (1973).

Partial variational methods, which restrict the variations allowed in the orbitals of open shell configurations such as (3), have also been developed. While these methods of necessity do not yield as low an energy as the full variational methods, they are more economical and describe the ground and excited state(s) in terms of a single set of orthonormal orbitals, a beneficial feature if CI calculations are also to be carried out. In addition, when the resulting orbitals are used in CI calculations which include single excitations into the virtual space, the results usually closely approximate those obtained with the full variational orbital set.

Two partial variational methods will be mentioned here: the extended Hartree-Fock (EHF) method and the improved virtual orbital (IVO) method. Both of these methods assume that the orbitals of the closed shell HF ground state have been predetermined. Let us denote the orbitals occupied in the ground state by $\{\phi_o\}$ and the corresponding virtual orbitals by $\{\phi_v\}$. Relative to the closed shell configuration a singly excited state may be represented by an excitation from one of the occupied orbitals to one of the virtual orbitals, $\phi_{io} \rightarrow \phi_{jv}$. In the EHF method, K. Morokuma and S. Iwata, "Extended Hartree-Fock Theory for Excited States," Chem. Phys. Lett. 16, 192 (1972), the variations in the set $\{\phi_o\}$, including ϕ_{io}, are limited to transformations among the ground state occupied orbital space $\{\phi_o\}$, while the variations in ϕ_{jv} are limited to transformations among the ground state virtual orbital space $\{\phi_v\}$. In the IVO method, W. J. Hunt and W. A. Goddard, III, "Excited States of H_2O Using Improved Virtual Orbitals," Chem. Phys. Lett. 3, 414 (1969), only the orbital ϕ_{jv} is variationally determined. As in the EHF method, the variations in this orbital are restricted to transformations among the ground state virtual orbital set.

The advantages of determining the primary orbital set with the HF method are numerous, e.g.,

(1) the HF configuration for a system is well defined, although exceptions do exist in situations in which a single configuration is not adequate.

(2) the HF method is economical, and

(3) the HF model provides a simple orbital description of ionization, excitation, etc. Such models are useful in developing a qualitative understanding of the phenomena being studied, thus allowing the results to be extended to systems for which computations are not feasible.

On the disadvantage side, the HF model provides only a single reference configuration and corresponding set of orbitals while the theoretical description of many chemical processes of interest, e.g., dissociation, reaction, excitation and ionization, often require more than this minimal set. Also, for the reasons noted earlier, the virtual orbitals from a HF calculation are not a particularly appropriate set of secondary orbitals for use in CI calculations. Their use in such calculations is recommended only in selected cases, e.g., if the entire virtual space is to be included in the calculation or if sophisticated selection techniques are used.

THE GENERALIZED VALENCE BOND METHOD

Overview of the Generalized Valence Bond Method

Unrestricted GVB Method

- AN ORBITAL PER ELECTRON
- GENERAL SPIN COUPLING
- NO ORTHOGONALITY CONSTRAINTS

Restricted GVB Method

- PERFECT PAIRING RESTRICTION
- STRONG ORTHOGONALITY CONSTRAINT
- DISSOCIATION TO "HF ATOMS"

Figure 4.

THE GENERALIZED VALENCE BOND METHOD

ADVANTAGES AND DISADVANTAGES OF THE (RESTRICTED) GENERALIZED VALENCE BOND METHOD

ADVANTAGES

- WELL DEFINED
- ECONOMICAL
- MULTICONFIGURATION REFERENCE WAVEFUNCTION
- FULL VALENCE ORBITAL SET
- SIMPLE, BUT ACCURATE, ORBITAL MODEL

DISADVANTAGES

- PROBLEMS WITH PERFECT-PAIRING RESTRICTION
- SECONDARY ORBITAL SET UNDEFINED

Figure 5.

In the generalized valence bond (GVB) method, a valence bond form is taken for the wavefunction and the orbitals and associated spin-coupling are optimized using variational methods. At infinite nuclear separations the orbitals so determined are just the atomic orbitals of the constituent atoms. As the molecule is formed the GVB orbitals hybridize, delocalize, etc. in response to the perturbing environment of the surrounding atoms. In the unrestricted form of the method there is an orbital for each electron and the spin function is a combination of all linearly independent spin functions associated with N electrons. In general, the unrestricted GVB orbitals are non-orthogonal. Unfortunately, determination of the GVB orbitals for a system involving more than just a few electrons is prohibitively expensive. In addition, because the orbitals are not orthogonal, they do not form a convenient basis for CI calculations.

To overcome these difficulties two approximation have been invoked

(1) that the spin function be restricted to a single perfect pairing function (perfect pairing restriction), and

(2) that the orbitals be constrained to be orthogonal if they are not singlet coupled (strong orthogonality restriction).

Unrestricted GVB calculations provide justification for both of these approximations. For most molecular systems near their equilibrium geometries, the perfect pairing function has been found to be the dominant spin function. Even when the perfect pairing function does not dominate, e.g., upon dissociation, the orbitals obtained with the perfect pairing restriction are a good approximation to the unrestricted orbitals so that the changes in the spin coupling can be described by a very limited CI calculation. It has also been found that the total wavefunction, and hence the system energy, is not sensitive to the overlap of orbitals which are not singlet coupled. Again, to a large extent any adverse effects associated with the strong orthogonality restriction can be corrected for with a very small CI calculation. In addition to the above restrictions, the GVB wavefunction for a molecule is usually taken to be that which describes dissociation to Hartree-Fock wavefunctions of the atoms. The one major exception occurs for those atoms (and states of atoms) with ns-np near-degeneracy corrections; for these atoms a two configuration wave-function, containing both the ns^2np^m and np^{m+2} configurations, is adopted for the separated atom limit.

Although the GVB orbitals determined in this way are pair-wise non-orthogonal, the resulting GVB wavefunction can be recast into a natural orbital form which is identically a (type of) separated pair wavefunction and which involves an orthogonal set of orbitals, the GVB natural orbitals. The equations for the GVB natural orbitals take a particularly convenient form; see

W. J. Hunt, P. J. Hay and W. A. Goddard, III, "Self-Consistent Procedures for Generalized Valence Bond Wavefunctions. Applications to H_3, BH, H_2O, C_2H_6 and O_2," J. Chem. Phys. 57, 738 (1972) and F. W. Bobrowicz and W. A. Goddard, III, "The Self-Consistent Field Equations for Generalized Valence Bond and Open-Shell Hartree-Fock Wavefunctions" in *Methods of Electronic Structure Theory*, ed. H. F. Schaefer, III, (Plenum Publishing Corporation, New York, 1977). This method, with the approximations given above, is referred to as the restricted GVB, or GVB(pp,so), method.

The GVB orbitals of a system are usually localized into inner shell orbitals, bonding and anti-bonding orbitals, lone pair orbitals, etc. For use in CI calculations these orbitals are often transformed to symmetry adapted orbitals, formally reducing the length of the CI expansion but complicating the form of the CI wavefunction itself.

In many modern CI methods the full set of molecular orbitals which correlate with the atomic orbitals of the constituent atoms are of special importance; see, e.g., the following discussion of configuration selection for CI calculations. This set of orbitals is often referred to as the valence orbital set (the core orbitals, being fixed to be doubly occupied in the calculations, are ignored) and for most systems is the primary orbital set. Such an expanded orbital set and the associated configurations are necessary to describe processes such as dissociation, reactions, etc. The HF method does not provide a complete valence orbital set, e.g., it contains the bonding and non-bonding combinations of the atomic

orbitals, but it does not contain all of the needed anti-bonding combinations. For most systems the GVB orbitals, on the other hand, do form a complete set of valence orbitals and, as such, provide a proper zero-order description of most chemical systems and processes of interest.

The advantages of determining the orbitals for a CI calculation using the restricted GVB method include:

(1) the GVB wavefunction for a system is well defined,

(2) the GVB method, with perfect-pairing and strong orthogonality restrictions, is economical,

(3) the GVB method provides a multiconfiguration reference function and a complete set of valence, or primary, orbitals,

(4) the GVB wavefunction provides for a simple orbital description of chemical processes, more accurate and chemically oriented than that provided for by the HF method.

The disadvantages of determining the orbitals using the restricted GVB method include:

(1) difficulties arising from the use of the perfect-pairing restriction, e.g., some molecules such as benzene are not well described by a single perfect-pairing configuration, and

(2) as in the HF method, the secondary orbital set is essentially undefined.

Before concluding our discussion of the GVB method, it should be noted that techniques have recently been developed which relax the perfect-pairing restriction while retaining the strong

orthogonality restriction. This method is particularly suitable for studying chemical reactions which often involve changes in the spin coupling in the transition state region. To date applications of this method have been limited; see, e.g., B. J. Moss, F. W. Bobrowicz and W. A. Goddard, III, "The Generalized Valence Bond Description of O_2," J. Chem. Phys. 63, 4632 (1975). For a more complete discussion of the strongly orthogonal GVB (SO-GVB) method, see F. W. Bobrowicz, Ph.D. Thesis (California Institute of Technology, 1974).

THE MULTICONFIGURATION SELF-CONSISTENT-FIELD METHOD

OVERVIEW OF MULTICONFIGURATION SELF-CONSISTENT-FIELD METHODS

TECHNIQUES FOR SOLVING MCSCF EQUATIONS

- HAMILTONIAN METHOD
- "2x2" ROTATION METHOD
- GENERALIZED BRILLOUIN THEOREM METHOD

MCSCF METHODS

- HARTREE-FOCK WITH PROPER DISSOCIATION METHOD
- OPTIMIZED VALENCE CONFIGURATIONS METHOD
- "FULL CONFIGURATIONAL REACTION SPACE" METHOD
- SEPARATED PAIRS METHOD

Figure 6.

THE MULTICONFIGURATION SELF-CONSISTENT-FIELD METHOD

ADVANTAGES AND DISADVANTAGES OF MULTICONFIGURATION SELF-CONSISTENT-FIELD METHODS

ADVANTAGES

- REASONABLY ECONOMICAL
- FLEXIBLE MULTICONFIGURATION REFERENCE WAVEFUNCTION
- FULL PRIMARY ORBITAL SET
- PARTIAL SECONDARY ORBITAL SET

DISADVANTAGES

- NOT WELL DEFINED
- MAJORITY OF SECONDARY ORBITAL SET NOT EASILY DETERMINED

Figure 7.

Rather than determining the primary orbital set from simple orbital-type (HF or GVB) wavefunctions, it is, of course, possible to determine the orbitals from a general multiconfiguration wavefunction

$$\Psi_{MCHF} = \sum_k C_k \Phi_k$$

with both the CI coefficients, {C}, and the orbitals, {ϕ} in {Φ}, being optimally determined — this is the multiconfiguration self-consistent-field (MCSCF) method. Despite numerous difficulties in solving the more complicated equations associated with a multiconfiguration wavefunction, a number of general techniques have been developed, including

(1) a Hamiltonian method similar to that used in single configuration calculations, A. C. Wahl and G. Das, "The Multiconfiguration Self-Consistent Field Method" in *Methods of Electronic Structure Theory*, ed. H. F. Schaefer, III, (Plenum Press, New York, 1977).

(2) a "2x2" rotation method, J. Hinze, "MC-SCF. I. The Multi-Configuration Self-Consistent Field Method," J. Chem. Phys. 59, 6424 (1973) and

(3) a generalized Brillouin theorem method, L. M. Cheung, S. T. Elbert and K. Ruedenberg, "MCSCF Optimization through Combined Use of Natural Orbitals and the Brillouin-Levy-Berthier Theorem," Intern. J. Quantum Chem. (in press).

Each of these techniques has been applied to many chemical problems and, while each has its advantages and disadvantages (in regard to speed, convergence, generality, etc.), all have been generally successful.

To be efficient the number of orbitals and configurations involved in the MCSCF wavefunction must be limited insofar as is possible. This is the case because (1) the time involved in determining the MCSCF wavefunction strongly depends on the number of orbitals and configurations included in the multiconfiguration expansion (the former far more than the latter) and (2) convergence can be troublesome if an orbital contributes only weakly to the MCSCF wavefunction. On the other hand, the energetic results can depend critically on the orbitals and configurations included in the wavefunction. Thus, it is clear that an MCSCF procedure by itself is incomplete; additional prescriptions indicating how to choose configurations are required to make it a well defined method. With such rules, which can be deduced from physical reasoning and/or from quantitative experience, one obtains a specific *MCSCF model*.

One possible choice is represented by the restrictions imposed on the wavefunction by the GVB model. Other models that have been found useful are the following ones.

(1) The "Hartree-Fock with proper dissociation" method, G. C. Lie and E. Clementi, "Study of the Electronic Structure of Molecules. XXI. Correlation Energy Corrections as a Functional

of the Hartree-Fock Density and Its Application to Hydrides of the Second Row Atoms," J. Chem. Phys. 60, 1275 (1974) and G. C. Lie and E. Clementi, "Study of the Electronic Structure of Molecules. XXII. Correlation Energy Corrections as a Functional of the Hartree-Fock Density and Its Application to the Homonuclear Diatomic Molecules of the Second Row Atoms," J. Chem. Phys. 60, 1288 (1974), which is just the GVB method recast into a MCSCF form,

(2) The OVC method, A. C. Wahl and G. Das, "The Method of Optimized Valence Configurations: A Reasonable Application of the Multiconfiguration Self-Consistent-Field Technique to the Quantitative Description of Chemical Bonding," Adv. Quantum Chem. 5, 261 (1970), which attempts to include only those types of correlation effects which change upon molecular formation and

(3) The "Full Optimized Reaction Space" (FORS) method of K. Ruedenberg, K. R. Sundberg, and M. G. Dombek, which is described in a separate article in this report. In the FORS method, the orbitals are divided into two sets: those basically unaffected in a chemical reaction and those affected (or replaced); within the second set all possible configurations are constructed and included in the MCSCF wavefunction.

Before concluding our discussion of the various MCSCF methods we should take note of the separated pair method; see, e.g., D. M. Silver, E. L. Mehler and K. Ruedenberg, "Electron Correlation and Separated Pair Approximation in Diatomic Molecules. I. Theory," J. Chem. Phys. 52, 1174 (1970) and subsequent papers in this series. Although not as general as the MCSCF wavefunctions discussed above, the separated pair wavefunction nonetheless is

able to account for many important molecular correlation effects. For example, as has been noted earlier, the GVB wavefunction with perfect pairing and strong orthogonality restrictions is a limited form of a separated pair wavefunction, and K. R. Sundberg and K. Ruedenberg have, in fact, presented it from this point of view under the name "Separated Pair Independent Particle Model" (K. R. Sundberg, Ph.D. Thesis, Iowa State University, 1975, to be published). The use of the orbitals obtained from separated pair calculations in CI calculations was first practiced by K. J. Miller and K. Ruedenberg for small atomic systems, "Electron Correlation and Augmented Separated-Pair Expansion," J. Chem. Phys. 48, 3444 (1968) and "Electron Correlation and Augmented Separated-Pair Expansion in Berylliumlike Atomic Systems," J. Chem. Phys. 48, 3450 (1968). For molecular systems it is discussed in L. B. Harding and W. A. Goddard, III, "Intermediates in the Chemiluminescent Reaction of Singlet Oxygen with Ethylene. Ab Initio Studies," J. Amer. Chem. Soc. 99, 4520 (1977).

The MCSCF method has many advantages as a method for determining the orbitals for use in CI calculations. For example,

(1) the MCSCF method is reasonably economical if the number of orbitals and configurations included in the MCSCF expansion is wisely limited,

(2) the MCSCF method provides a general multiconfiguration reference wavefunction,

(3) the MCSCF method can provide

(a) a full set of primary orbitals and

(b) (at least) a partial set of secondary orbitals.

On the disadvantage side, there may exist ambiguities and uncertainties in regard to the optimal MCSCF model for a specific system, particularly if configurations involving the secondary orbitals are included.

THE NATURAL ORBITAL METHOD

OVERVIEW OF NATURAL ORBITAL METHODS

METHODS FOR DETERMINATION OF NATURAL ORBITALS

- ITERATIVE NATURAL ORBITAL METHOD
- LIMITED-CI NATURAL ORBITAL METHOD
- PERTURBATION METHODS
  - FIRST-ORDER PERTURBATION THEORY
  - B_K METHOD

Figure 8.

THE NATURAL ORBITAL METHOD

ADVANTAGES AND DISADVANTAGES OF NATURAL ORBITAL METHODS

ADVANTAGES

- FLEXIBLE MULTICONFIGURATION REFERENCE WAVEFUNCTION
- FULL PRIMARY ORBITAL SET
- FULL SECONDARY ORBITAL SET

DISADVANTAGES

- NOT ECONOMICAL (EXCEPT FOR PERTURBATION METHODS)
- NON-VARIATIONAL

Figure 9.

The natural orbitals (NOs) of a system are those orbitals which lead to a diagonal representation of the first-order density matrix. Natural orbitals were first introduced by P.-O. Löwdin, "Quantum Theory of Many Particle Systems. I. Physical Interpretaion by Means of Density Matrices, Natural Spin Orbitals, and Convergence Problems in the Method of Configuration Interaction," Phys. Rev. 97, 1479 (1955). For a two-electron system it was shown, P.-O. Löwdin and H. Shull, "Natural Orbitals in the Quantum Theory of Two-Electron Systems," Phys. Rev. 101, 1730 (1956), that, for a given number of configurations, expansion of the wavefunction in NOs leads to *maximum overlap* with the exact wavefunction, with the magnitude of the orbital occupation numbers being directly related to the importance of the resulting configuration in the configuration expansion. This maximum overlap principle, rather than a minimum energy principle, is the reason that we refer to NO methods as *near*-variational methods for determining the orbitals for use in CI expansions. Unfortunately, for many electron systems the importance of a configuration in the CI expansion is not determined solely from the occupation numbers of the orbitals involved. Nonetheless, by minimizing the importance of configurations which involve orbitals with small occupation numbers, the use of NOs in CI calculations substantially improves the "compactness" of the resulting wavefunction.

The NOs of a system can usually be divided into a "strongly occupied" set with occupation numbers $n \gtrsim 0.5$ and a "weakly occupied" set with occupation numbers $n < 0.1$. This, in fact, was the motivation for our categorization of the orbitals for use in CI calculations into primary (strongly occupied) and secondary (weakly occupied) sets. For systems dominated by a single configuration the strongly occupied orbitals are closely related to the HF orbitals, e.g., it has been found that the two sets of orbitals span nearly the same space, i.e., they are related by a near-unitary transformation. While in this case the weakly occupied orbitals are likewise a near-unitary transformation of the HF virtual orbitals, the spatial characteristics of the orbitals with the largest occupation numbers differ substantially from those of the low-lying virtual orbitals. Similar relationships hold when multiconfiguration reference wavefunctions are used. The properties of NOs have been discussed in detail in E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry*, (Academic Press, New York, 1976).

The difficulty with the use of NOs in CI calculations is that the first-order density matrix, and hence the CI wavefunction, is required to calculate the NOs. Fortunately, it has been found that the convergence of the CI expansion is not strongly dependent on having the exact NOs, only a reasonable approximation thereto. Taking advantage of this, a number of methods have been developed to calculate an approximate set of

NOs. The more important of these methods include:

(1) the iterative natural orbital (INO) method, C. F. Bender and E. R. Davidson, "Studies in Configuration Interaction: The First-Row Diatomic Hydrides," Phys. Rev. 183, 23 (1969) in which an initial set of configurations, based on, say, the HF occupied and virtual orbitals, is energy selected, the corresponding CI wavefunction and NOs determined, and then the whole process is repeated until the NOs and/or the energy has converged; it should be noted that the convergence of neither the NOs nor the energy is guaranteed and, in fact, in many cases these quantities may start to diverge after a few iterations [see, e.g., K. H. Thunemann, J. Romelt, S. D. Peyerimhoff and R. J. Buenker, "A Study of the Convergence in Iterative Natural Orbital Procedures," Int. J. Quantum Chem. 11, 743 (1977)],

(2) limited-CI natural orbital (CI-NO) methods, see, e.g., R. J. Buenker and S. D. Peyerimhoff, "Individual Configuration Selection in CI Calculations with Subsequent Energy Extrapolation," Theoret. Chim. Acta 35, 33 (1974), which calculate the NOs from truncated CI wavefunctions, e.g., by selecting configurations with a "loose" energy criterion, by limiting the types of configurations generated, etc.; using this technique it is important that all of the orbitals be involved in the truncated configuration list,

(3) perturbation methods, see, e.g., G. C. Lie, J. Hinze and B. Liu, "Valence Excited States of CH. I. Potential Curves," J. Chem. Phys. 59, 1872 (1973), P. J. Hay, "On the Calculation of Natural Orbitals by Perturbation Theory," J. Chem. Phys. 59,

2468 (1973) and A. K. Q. Siu and E. F. Hayes, "Configuration Interaction Procedure Based on the Calculation of Perturbation Theory Natural Orbitals: Applications to H_2 and LiH," J. Chem. Phys. 61, 37 (1974). These methods use either first-order perturbation theory or the B_k method to determine the NOs; this can, of course, be done with considerable savings in computer time over the first two methods.

It should be noted that, unlike the INO method, the latter two methods require an appropriate reference wavefunction be determined *before* the calculation of the NOs.

The advantages of natural orbital methods for determining the orbitals for use in CI calculations include:

(1) the NO methods provide a completely general, multiconfiguration reference wavefunction, although, as noted above, the limited CI-NO and the perturbation methods require this function to be predetermined (by, e.g., GVB or MCSCF techniques) and

(2) the NO methods can provide complete primary *and* secondary orbital sets; of course, for use in the final CI calculations the secondary orbital set may be truncated based on a minimum occupation number restriction.

On the other hand,

(1) the NO methods are not economical, e.g., the INO method requires repeated transformations of the integrals and construction and diagonalization of the Hamiltonian matrix; however, use of the perturbation methods may largely negate this objection and

(2) the NO methods are non-variational; although formally this is a problem, in practice, except for a few isolated cases, this has not been found to be the case.

DETERMINATION OF ORBITALS AND SELECTION OF CONFIGURATIONS THROUGH THE METHOD OF THE FULL OPTIMIZED REACTION SPACE (FORS)

Comments by Klaus Ruedenberg

1. MCSCF Approximations along Reaction Paths

The strongest impact of Quantum chemistry can be expected to occur in the field of chemical reactions because theoretical calculations of reaction paths and transition states are in principle no different in nature than those of stable molecules, whereas the experimental elucidation of reaction intermediates is subject to many uncertainties due to their fleeting appearance and disappearance.

Even for the theoretical approach however, there exists a difference in the degree of difficulty between the calculation of stable species and that of intermediate structures. This is because the standard self-consistent-field method, while being a very serviceable "dominant approximation" for many stable molecules, is rarely adequate for systems in the flux of reactive changes, where orbitals not only deform but, in addition, change occupation numbers due to changes in configurational mixing. In fact, on the basis of currently available experience it is not possible to anticipate which configurations will dominate a wave function at various points on a reaction path. Consider for example the case that products and reactants are well described by HF-SCF functions and that many, but not all of the occupied reactant orbitals continuously deform into certain occupied product orbitals. Some of the doubly occupied reactant orbitals deform however into virtual reactant orbitals and, correspondingly, some of the virtual reactant orbitals deform into doubly occupied product orbitals. In such a case, there is a temptation to calculate the reaction using a two-determinant wavefunction. More often than not it will be found, however, that in the intermediate region where the "reaction orbitals" have occupation numbers close to unity, there exist numerous other configurations which turn out to have similar

weighting factors. Their inclusion in the dominant part of the wave-function proves to be essential, in particular for the calculation of reaction barriers.

Conversely, it is also important to know which parts of the exact wave-function can be completely neglected for the calculations along a specific reaction path. Since full recovery of correlation is out of the question, even with present-day computers, the practical goal is always the calculation of energy curves which are reliably parallel to the exact curve by including all those correlation terms which change significantly (i.e. more than kT, which is 10^{-3} Hartree at room temperature) and omitting all those terms which do not and, hence, would cancel when energy differences are taken. When applied to reactants and products of a dissociation, this requirement encompasses the postulate of size-consistency. However, the required parallelism is equally important for the intermediate portions of an energy curve, in particular for the determination of energy barriers.

From the preceding discussion it can be inferred that it is essential to avoid unjustified restrictions in the construction of wave functions and orbitals, so that all pertinent changes can be reflected without bias in the calculations, if reliable results are to be obtained for transition states. At the same time the calculations have to remain practical of course. It is with this goal in mind that the method of the "Full Optimized Reaction Space" has been developed. Experience gained so far indicates that it goes a considerable way towards the desired objective.

The reported work was accomplished with the help of several coworkers whose names are mentioned in the Acknowledgement. The first working versions of the MCSCF program were operative in 1972[1] and informally reported at the 1972 Boulder Conference on Theoretical Chemistry. Formal presentations were given at the 1975 Midwest Theoretical Chemistry Conference at the University of Wisconsin. The method is described in a 1975 Iowa State University thesis[2] and in a paper currently in press in the International Journal of Quantum Chemistry.[3] The concept as well as applications of the Full Optimized Reaction Space were first discussed in another 1975 Iowa State University thesis[4], in a 1977 paper in "Quantum Science,"[5] and in another paper currently in press in the "International Journal of Quantum Chemistry."[6]

Further developments and applications were given in a 1977 Iowa State University thesis.[7] They were presented at the 1977 Midwest Theoretical Chemistry Conference at Argonne National Laboratory, at the 1977 Canadian Symposium on Theoretical Chemistry at the University of New Brunswick, at the 1978 Peter Leermakers Symposium at Wesleyan University and they are in preparation for publication.

2. Spin-Adapted Antisymmetrized Products (SAAP's)

In the FORS method, as presently implemented, the antisymmetric N-electron wavefunctions are assumed to be eigenstates of S^2 and S_z and expressed as expansions of the form

$$\Psi(\text{spin, space}) = \sum_{K,s} C_{Ks}\Psi_{Ks}^{SM}(\text{spin, space}),$$

$$\Psi_{Ks}^{SM}(\text{spin, space}) = N_K A\{\Theta_s^{SM}(\text{spin})U_K(\text{space})\}$$

where $A = (N!)^{-1/2}\Sigma_P(-1)^P$ is the antisymmetrizer over N electrons and N_K is a normalization constant. The functions $\Theta_s^{SM}(\text{spin})$ form a complete basis of $f_S = N!(2S + 1)/(\frac{1}{2}N + S + 1)!(\frac{1}{2}N - S)!$ pure spin functions that are eigenfunctions of S^2 and S_z. The $U_K(\text{space})$ form a complete basis of N-electron space functions and are assumed to consist of all possible products of the members of a complete set of orthonormal, real, symmetry adapted orbitals $f_1(r)$, $f_2(r)$, $f_3(r)$,... . Any one f_ν cannot occur more than twice as a factor in any one U_K. The spin functions Θ_s^{SM} are chosen to form an <u>orthonormal</u> basis for an irreducible representation of the symmetric group of N elements, so that the relations

$$\Theta_t^{SM} = \sum_{s=1}^{f_S} \Theta_s^{SM} \langle \Theta_s^{SM}|P|\Theta_t^{SM}\rangle$$

hold for any permutation P, where the matrices $\langle \Theta_s^{SM}|P|\Theta_t^{SM}\rangle$ are independent of M. Consequently the set of N-electron basis functions $A\{\Theta_s^{SM}U\}$, $s = 1,2,\ldots,f_S$, spans the same function space as the set $A\{\Theta_s^{SM}PU\}$, $s = 1,2,\ldots,f_S$, where P is an arbitrary permutation. Hence, for any one choice of N orbitals $f_{\nu_1}, f_{\nu_2}, f_{\nu_3}, \ldots, f_{\nu_N}$,

there exists exactly one set of functions Ψ_{Ks}, $s = 1,2,\ldots,f_S$ and a unique order can be arbitrarily chosen for the arrangement of the orbitals in the product U_K. We call the Ψ_{Ks}^{SM} "spin-adapted antisymmetrized orbital products" and abbreviate them as SAAP's.[8]

The expectation value of Ψ requires the calculation of the matrix elements $\langle Us|H|Ut\rangle$ where $|Us\rangle = A\{U\Theta_s^{SM}\}$ with $U = u_1u_2\ldots u_N$, and $|Vt\rangle = A\{V\Theta_t^{S'M'}\}$ with $V = v_1v_2\ldots v_N$ are two representative SAAP's. The expressions of the $\langle Us|H|Vt\rangle$'s in terms of one- and two-electron integrals between orbitals are very similar in structure to the familiar Slater Condon rules for Slater determinants.[8] For example, when $H = 1/r_{12}$ and U and V differ in two orbitals, u_α, u_β and v_α, v_β say, then

$$\langle Us|r_{12}^{-1}|Vt\rangle = [L]_{st}\langle u_\alpha u_\beta|r_{12}^{-1}|v_\alpha v_\beta\rangle + [T_{\alpha\beta}L]_{st}\langle u_\beta u_\alpha|r_{12}^{-1}|v_\alpha v_\beta\rangle$$

multiplied by a simple function of the occupation numbers. The difference to the Slater-Condon rules lies in the appearance of the matrix elements $[L]_{st} = (-1)^P\langle\Theta_s^{SM}|P|\Theta_t^{SM}\rangle$ for the permutation $P = L$, where L is the "line-up permutation" which brings V in maximal orbital coincidence with U, and for the permutation $P = T_{\alpha\beta}L$, where $T_{\alpha\beta}$ is the transposition between the electrons that occupy the orbitals u_α and u_β in U. These spin matrix elements are readily calculated independently of the orbital integrals.[8,9]

The SAAP formalism is convenient for generating and dealing with orbital excitations under preservation of spin-symmetry, as is required in our MCSCF procedure. We use "Serber SAAP's", i.e. SAAP's based on Serber-type spin functions all of which are either symmetric or antisymmetric with respect to the geminal transpositions (12), (34), (56), etc. This specific choice leads to a large number of zero matrix elements. It is however not essential for the SAAP formalism as outlined above.

3. Full Reaction Space

The orbital variation space is spanned by the quantitative basis orbitals (QBO's). These latter are chosen to be contracted even-tempered Gaussian AO's.[10] The principal QBO's are chosen to be the atomic SCF AO's. The secondary QBO's are chosen to be one or several of the most diffuse even-tempered primitives in the expansions of the principal QBO's,[11] as well as polarization functions.

This type of QBO basis requires integral programs able to handle general (i.e., unsegmented) contracted AO's. The only program able to do this at present is Raffenetti's BIGGMOLI program[11], whose initial version originated when its author was with this research group.

The orbital reaction space[4,5] is spanned by the configuration generating orbitals (CGO's). They are linear combinations of the QBO's and their expansion coefficients are eventually determined through molecular MCSCF optimizations. A choice has to be made only with respect to the number of CGO's, i.e., the dimension of the orbital reaction space. Ideally this number is equal to the total number of valence AO's in a formal minimal basis set on all atoms that participate in a reaction. Under appropriate conditions one may exclude certain bonds or lone pairs which remain unaffected. These latter and the inner shells are the closed shell orbitals.

The full configurational reaction space[4,5] is spanned by all possible SAAP's (see Section 2) that can be constructed using all reaction orbitals with all possible spin couplings, but keeping all closed shell orbitals doubly occupied in all SAAP's. Depending upon the CGO's the dimension of this space may vary from about ten to over a thousand. This space is of course size-consistent in the sense of given correct dissociation products.

If the dimension of the orbital reaction space equals the total number of all valence AO's in the formal minimal basis set, then the full configurational reaction space becomes the full configurational valence space.

The full configurational reaction space is invariant against all non-singular transformations among the configuration generating reaction orbitals. It is therefore possible to construct especially adapted "reaction orbitals" and the following types have been found useful.

Natural reaction orbitals (NRO's) which diagonalize the first order density and, because of their good convergence properties, characterize the molecule most succinctly during a reaction.[4,5]

Localized reaction orbitals (LRO's), obtained by appropriate localization procedures, are found to localize near the atoms. The number on each atom equals the number of minimal basis set AO's on that atom. Hence they represent "molecule adapted minimal basis set AO's."[5,7]

Directed localized reaction orbitals (DLRO's)[7] which, in addition to being localized on atoms are either lone pairs or directed into various bonds. They characterize the participation of various atoms in a specific reaction.

4. Optimization in the Full Reaction Space

The Full Optimized Reaction Space (FORS) wavefunction is defined as the optimal wavefunction in the full reaction space where, furthermore, the reaction orbitals as well as the closed shell orbital have been optimized so that $\langle\psi|H|\psi\rangle$ is an extremum. This then is an MCSCF problem, whose dimension may be quite large. The optimization procedure currently used by this group[7] depends upon the dimension of the full configurational reaction space and also upon the dimension of the virtual space spanned by the singly excited SAAPs generated during the MCSCF step (see Section 5).

If the dimension of the configurational reaction space is ≤ 20 then it is nearly always possible to optimize MC coefficients and CGO's in the full space directly by the MCSCF procedure described below.

The MCSCF calculation proceeds in three steps:

(1) Preliminary (closed or open-shell) SCF calculation yields <u>occupied</u> SCF MO's which are the first approximations for all closed shells and <u>part</u> of the CGO's.

(2) A preliminary MCSCF calculation, using about 5-12 reasonably selected configurations containing <u>all</u> CGO's is carried out with the occupied SCF orbitals frozen. This yields first approximations to those CGO's that lie in the virtual SCF space.

(3) With these first approximations a full MCSCF calculation is made.

If the dimension of the configurational reaction space lies between 20 and 40, then it is often possible to apply the MCSCF procedure directly to the full space, if certain orbitals are frozen. Full optimization is achieved by several MCSCF passes, iteratively freezing different orbitals.

If the dimension of the configurational reaction space is larger than 40, then the space of the virtual SAAP's may become too large. In this case, the following iterative procedure is effective.

(1) Preliminary SCF calculation as described above.

(2) Preliminary MCSCF calculation as described above.

(3) (a) CI calculation in the <u>full</u> configurational reaction space of the orbitals determined in (2).

(b) Determination of natural reaction orbitals.

(c) CI wavefunction is expressed in terms of configurations made from natural reaction orbitals ("NRO-based configurations").

(4) (a) MCSCF calculation on the about 10 most important configurations from the NRO-based expansion of step 3(c) yields new CGO's.

(b) CI calculation in full reaction space generated by new CGO's.

(c) Determination of new natural reaction orbitals.

(d) CI wavefunction is expressed in terms of new NRO-based configurations.

(5) Step 4 can be repeated with a larger number of configurations, if this proves necessary.

(6) Total self-consistency-test on: a) Total CI energy; b) Natural reaction orbitals; c) Order of configurations in NRO-based expansion.

It is felt, however, that with the help of further refinements and more powerful computers (this group has been limited to an IBM 360/158 type computer), direct full MCSCF optimization on larger-dimensional configurational spaces will be possible.

5. MCSCF Procedure

The described wavefunction optimizations require a completely general fast MCSCF procedure. The method developed at Iowa State University in recent years[2,3] determines the MC coefficients and the orbitals $\varphi_1 \ldots \varphi_N$ in a MC function $\Psi = \Sigma_K C_K \Phi_K(\varphi_1 \ldots \varphi_N)$, which is a completely arbitrary superposition of SAAP's with entirely arbitrary spin-couplings and multiplicities. The orbitals lie in a M(>N) dimensional space of QBO's. The optimization is accomplished through combined use of natural orbitals and the Brillouin-Levy-Berthier theorem and typically converges to chemical accuracy within five iterations.

"MC-single-excitations" (MCSX's) are defined by the combination of single substitutions

$$\Psi_{ij} \simeq \Psi(\varphi_i \rightarrow \varphi_j) - \varepsilon_j \Psi(\varphi_j \rightarrow \varphi_i) ,$$

where φ_i is an occupied orbital and $\varepsilon_j = 1$ or 0 for φ_j being occupied or virtual respectively. These functions are orthogonalized and if necessary reduced to a linearly independent set. The Brillouin-Levy-Berthier Theorem states that the following two statements are equivalent:

(i) Ψ cannot be improved by changing the occupied orbitals;

(ii) Ψ cannot be improved by admixture of Single Excitations Ψ_{ij}.

The optimization procedure is based on the following iterative cycle

(1) Given a set of approximate MO's, determine the MC coefficient C_K by a "MC-CI" calculation;

(2) Using these coefficients, form single excitations Ψ_{ij}. Then find the CI wavefunction in the enlarged configuration space spanned by Ψ and the Ψ_{ij}'s.

(3) From this wavefunction find improved MO's by substituting its dominant natural orbitals in place of the natural orbitals of the MC wavefunction. Special care is taken that "corresponding" natural orbitals are matched.

It is noteworthy that the dimension of the "single excitation space" spanned by the Ψ_{ij}'s cannot be larger than the number of orbital substitutions $i \rightarrow j$ (with $i < j$) <u>independently</u> of the size of the full configurational reaction space.

6. Illustrative Example

An illustration of the workings of the procedure is given by the following calculation of the dissociation energy of N_2 at the experimental equilibrium distance recently carried out by M. Schmidt at his laboratory.[12] The full reaction space consists of 176 SAAP's (not symmetry adapted to $C_{\infty v}$) and the basis set is a (14s, 7p, 2d) even-tempered primitive set contracted to a (5s, 3p, 2d) QBO set. The sequence of calculations and the corresponding dissociation energies (with respect to the 2N SCF energy) are as follows:

	D(ev)
SCF	5.01
Full CI with SCF orbitals (occupied MO's + 3 lowest virtuals)	7.73
8 configuration preliminary MCSCF (4 MO's frozen, 6 variable), 4 iterations,	7.54
Full CI with these MO's	8.63
13 configuration MCSCF, 7 iterations	8.75
Full CI with these MO's	9.05
19 configuration MCSCF, 3 iterations	8.91
Full CI with these MO's	9.06
23 configurations MCSCF: no change in orbitals and CI energy	

In order to illustrate the timing in a machine independent manner (the calculation were done on an Itel AS/5 computer), we choose as unit of time the total amount of time needed to carry out the restricted Hartree Fock SCF calculation on N_2. In this unit the various steps consumed the following amounts of CPU times

Preparation of SCF calculation including integral evaluations	0.84
HF-SCF iterations	0.16
Subtotal	1.00
Integral transformation preparatory to MCSCF and CI	0.68
First MCSCF (8 SAAP's, 4 iterations)	0.48
Full CI and natural orbital rearrangement	0.27
Second MCSCF (13 SAAP's, 7 iterations)	1.49
Full CI and natural orbital rearrangement	0.27
Third MCSCF (19 SAAP's, 3 iterations)	0.94
Full CI and natural orbital rearrangement	0.27
TOTAL	5.38

The total time could possibly be reduced, if it should prove possible to carry out the MCSCF calculation directly on all 176 SAAP's. Even then it would be advisable to carry out first the (8 SAAP/4 Frozen MO) preliminary MCSCF to obtain good starting orbitals.

To put the quality of the calculation in perspective, we note that the experimental dissociation energy is 9.9 eV, and that a recent CI calculation based on SCF orbitals and claiming to include the effect of 10^5 configurations yielded a dissociation energy of 9.33 eV.[13] By contrast, only about 40 SAAP's in the Full Optimized Reaction Space contribute to yield the quoted value of 9.06 eV to within one milli-Hartree. A recent GVB + CI calculation of Dunning et al. yielded 8.93 eV.[14]

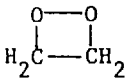
Thus the FORS approach recovers 83% of the valence correlation energy changes during the N_2 dissociation which is known to be a difficult case. Under investigation are appropriate ways to go outside the FORS to recover the remaining correlation energy changes.

7. Applications to Reactions

The MCSCF approach is essential for systems for which there exists no one dominant SCF configuration. This is particularly important for the calculation

of the intermediate portions of energy surfaces for chemical reactions because, here, the order of importance of the dominant configurations cannot be anticipated. In such cases the FORS method yields an unbiased description. The subsequent figures exhibit some of the results that were obtained in this manner for the following reactions

$H_2C = CH_2 \rightleftharpoons 2CH_2$ (FORS dimension = 8) See ref. 2 and 6,



$\rightleftharpoons 2CH_2O$ (FORS dimension = 12) See ref. 4 and 5,

$HNO \rightleftharpoons NOH$ (FORS dimension = about 1500) See ref. 7 and 15.

Figure 3 in particular illustrates the necessity for an unbiased MCSCF approach in as much as many SAAP's contribute in the central portion, whereas only one is dominant for reactants and products.

Conclusions

It appears that the FORS approach is a substantive first step towards the recovery of correlation energy changes during chemical reactions. In addition we infer from the results obtained that, in general, the choice of the configuration generating orbitals (CGO's) has a marked effect on CI calculations because, in fact, the number of CGO's is necessarily limited. Optimal are those CGO's which minimize the dominant part of the final full CI expansion. What this dominant part is, will vary from case to case so that some bootstrapping seems unavoidable at this time. In many cases, the standard HF-SCF wave function is an inadequate representation of the dominant part, so that an MCSCF procedure is called for.

Acknowledgements

I wish to acknowledge the able and stimulating cooperation of my coworkers, R. D. Bardo, L. M. Cheung, S. T. Elbert, D. F. Feller, M. G. Dombek, R. C. Raffenetti, W. I. Salmon, M. Schmidt and K. R. Sundberg. The work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

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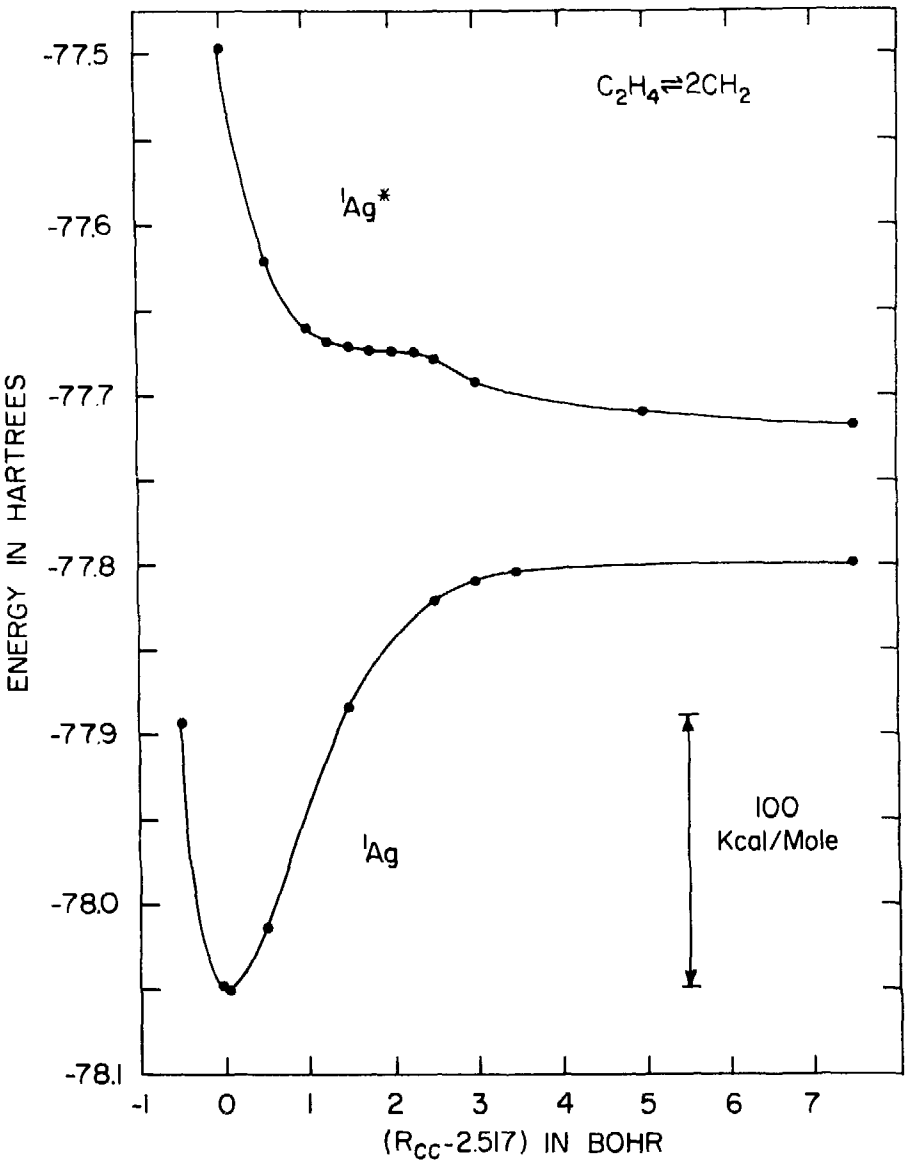

Figure 1. Variation of energies of the two lowest ^1A_g states during the dissociation of ethylene into two methylenes.

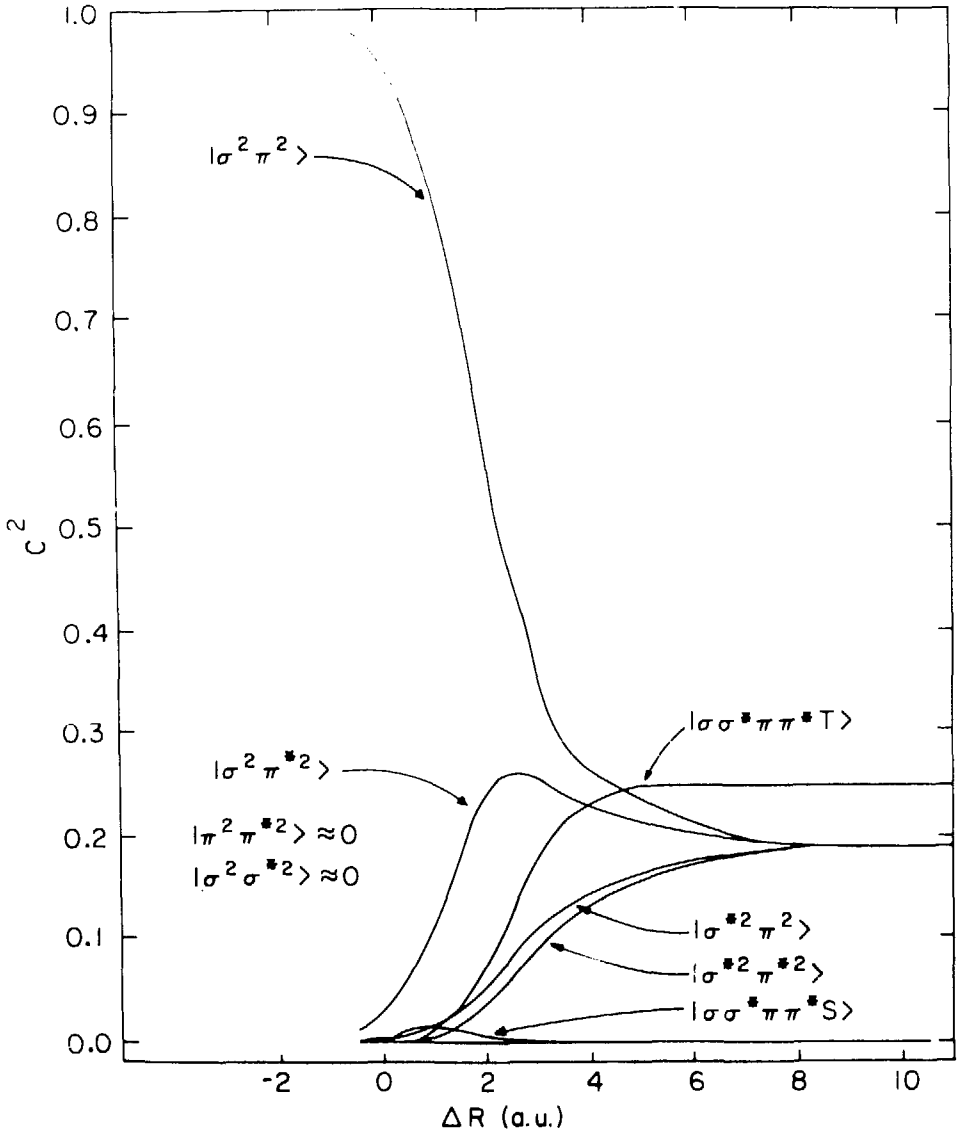

Figure 2. Variation of weights of configurations in the Full Optimized Reaction Space during the dissociation of the ethylene groundstate.

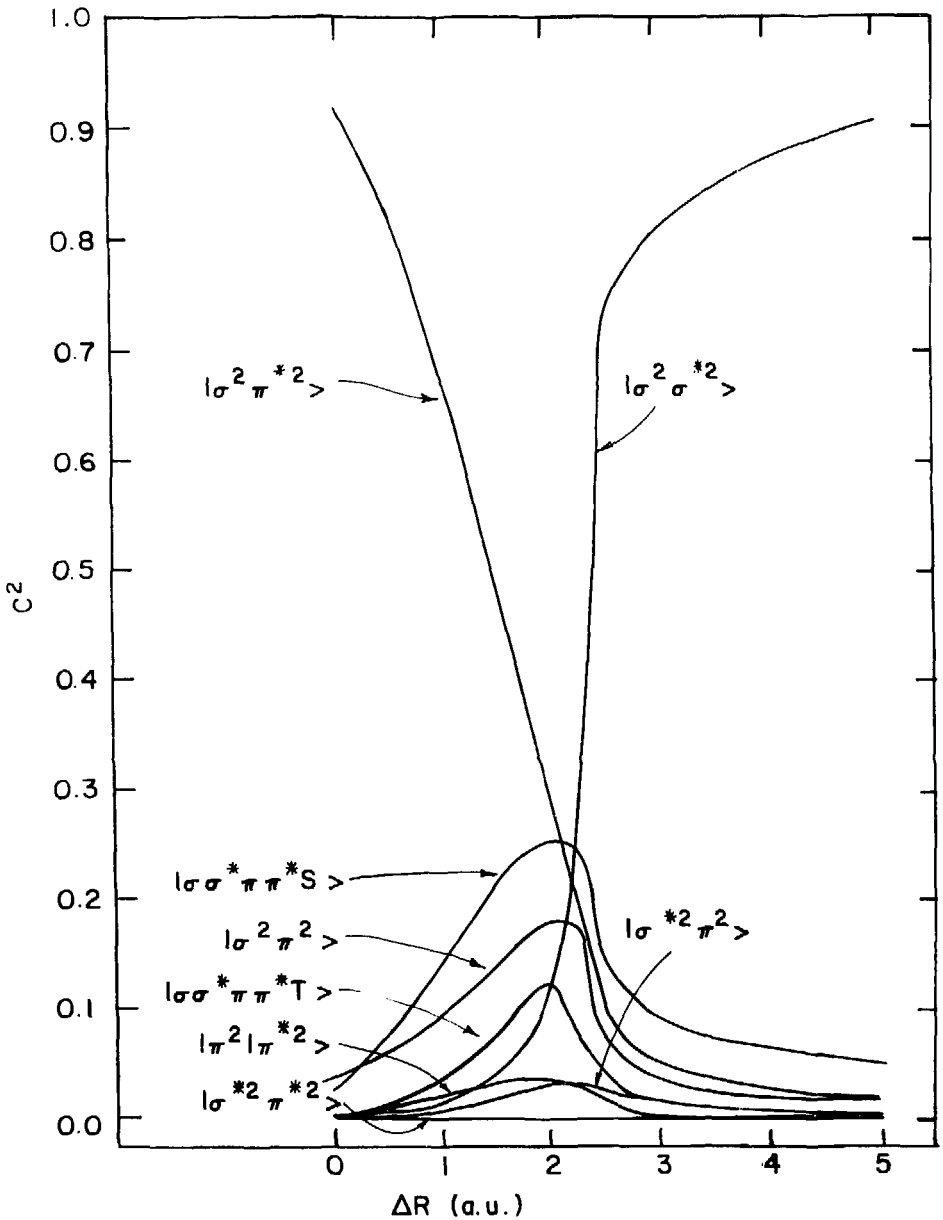

Figure 3. Variations of weights of configurations in the Full Optimized Reaction Space during dissociation of first $^1A_g^*$ ethylene excited state.

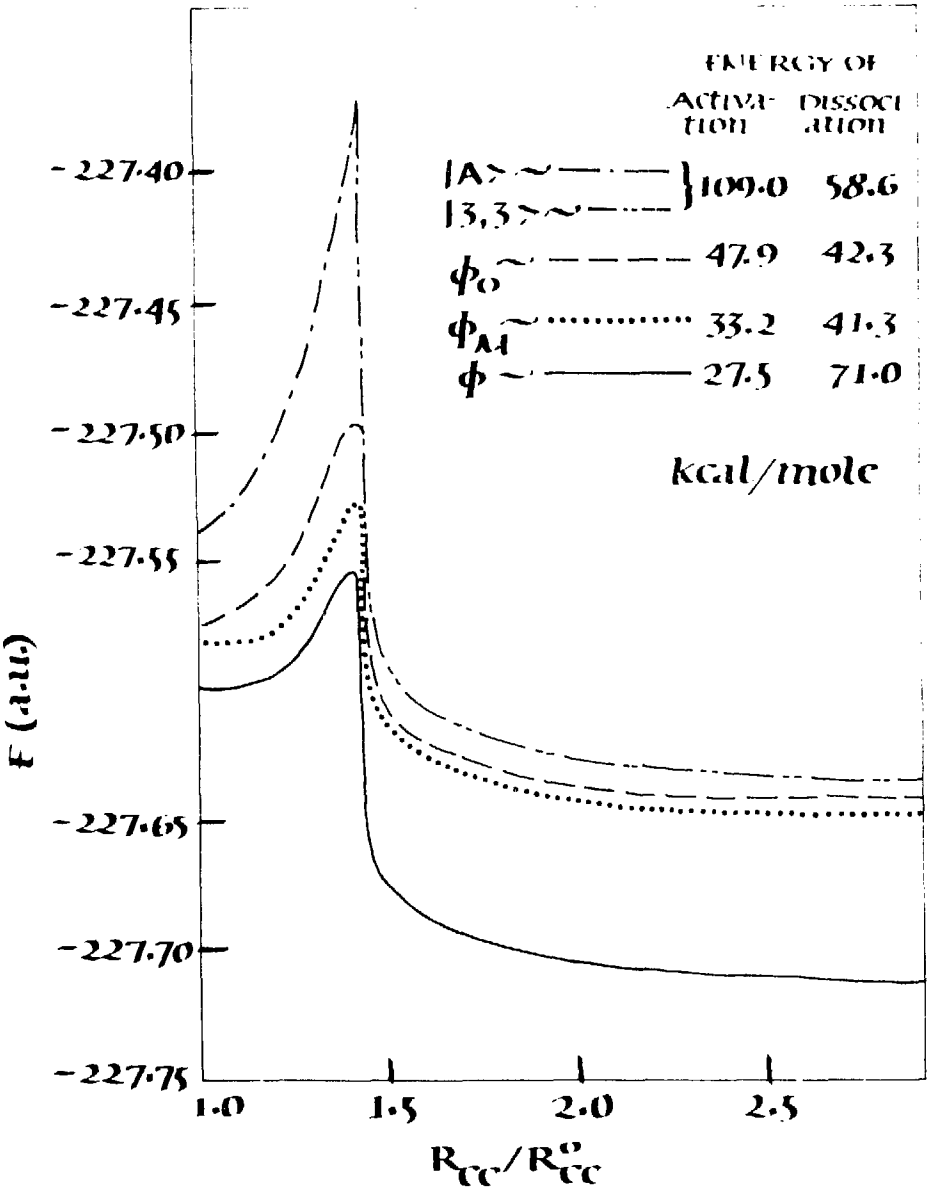

Figure 4. Groundstate energy variation for dissociation $H_2\overset{O-O}{C-CH_2} \rightarrow 2CH_2O$.

$|A\rangle$ = Reactant HF-SCF, $|3,3\rangle$ = Product HF-SCF, Φ = FORS MCSCF,

Φ_0 = Two-term MCSCF (Superposition of $|A\rangle$ and $|3,3\rangle$),

Φ_M = Separated-Pair-Independent-Particle model (= strongly-orthogonal GVB-pp).

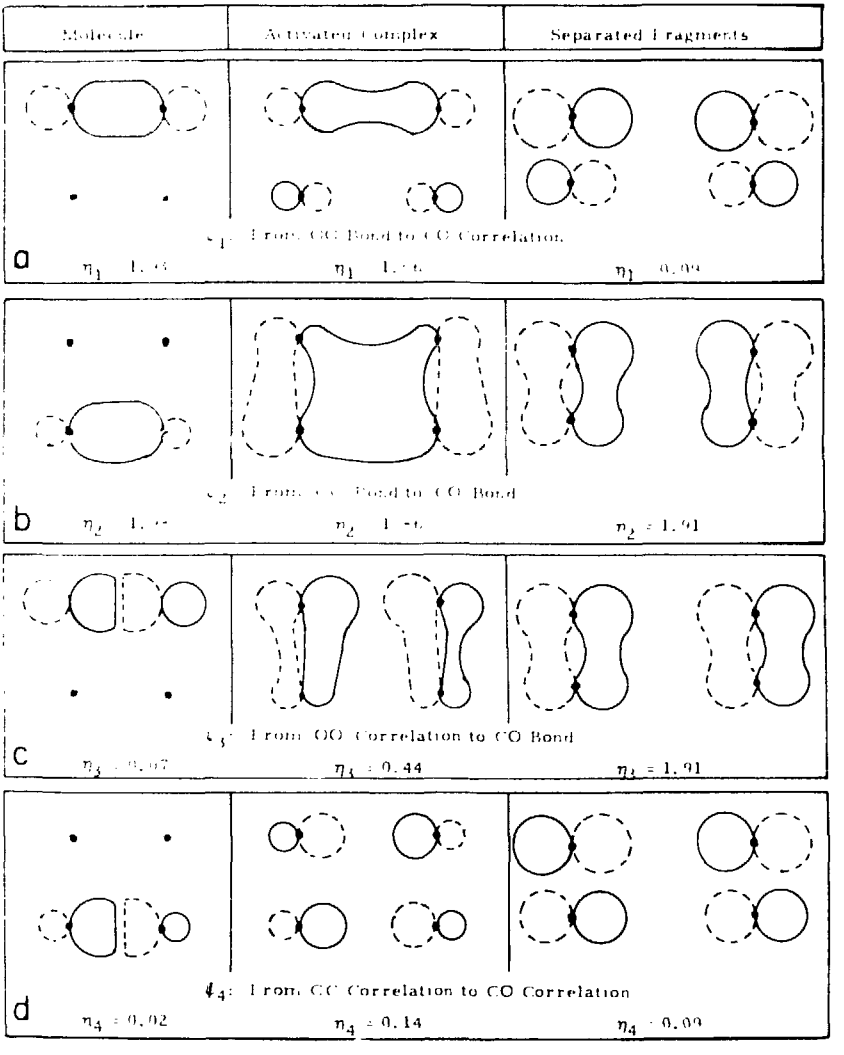

Figure 5. Schematic plots of actual Natural Reaction Orbital deformations during groundstate dissociation $H_2\overset{O-O}{C-CH_2} \rightarrow 2CH_2O$.

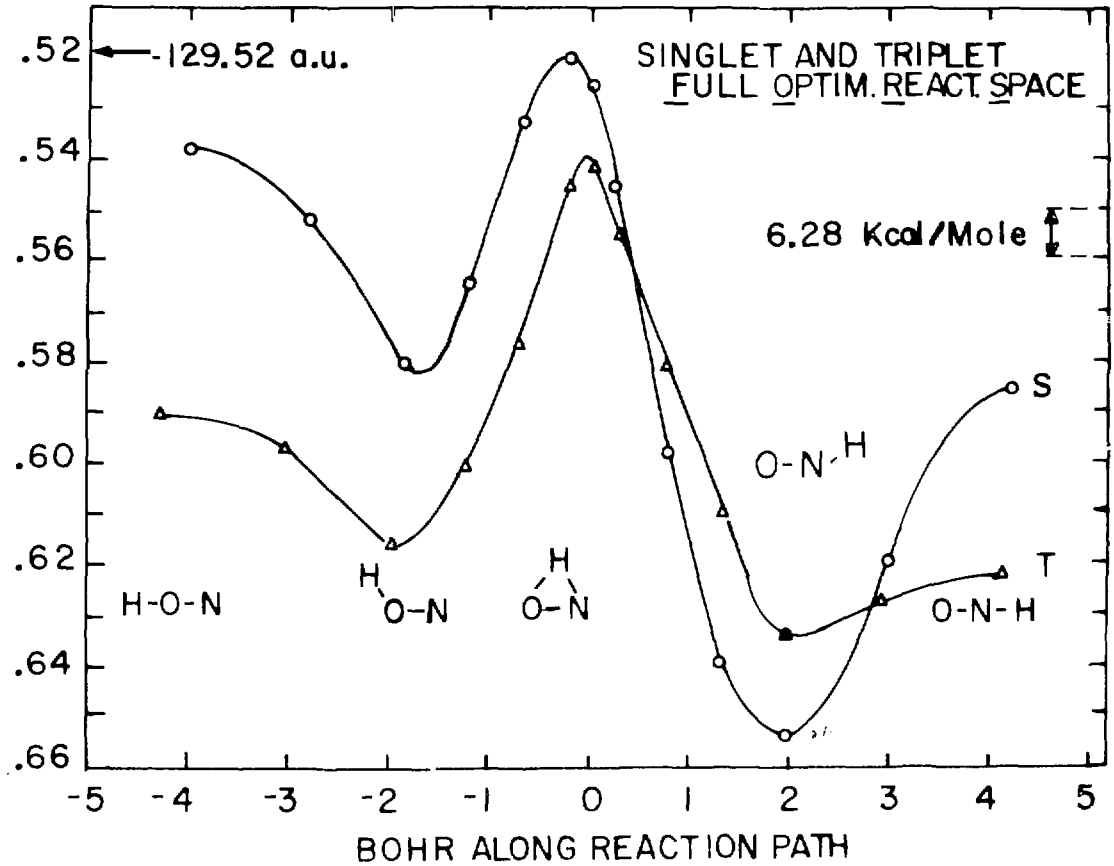

Figure 6. Energy variations of lowest two states during HON→HNO isomerization.

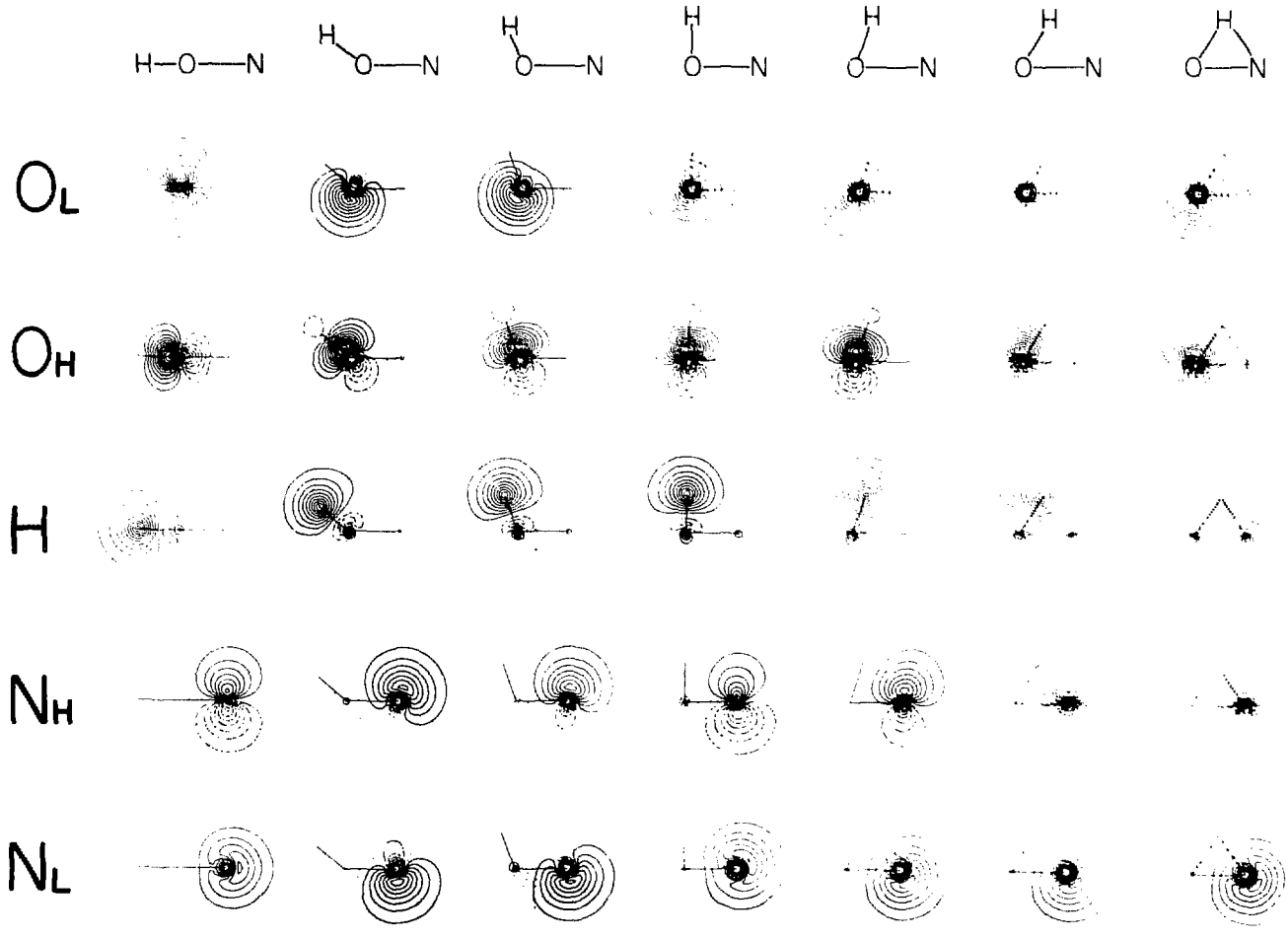

Figure 7. Variations of Directed Localized Reaction Orbitals during HON→HNO isomerization.

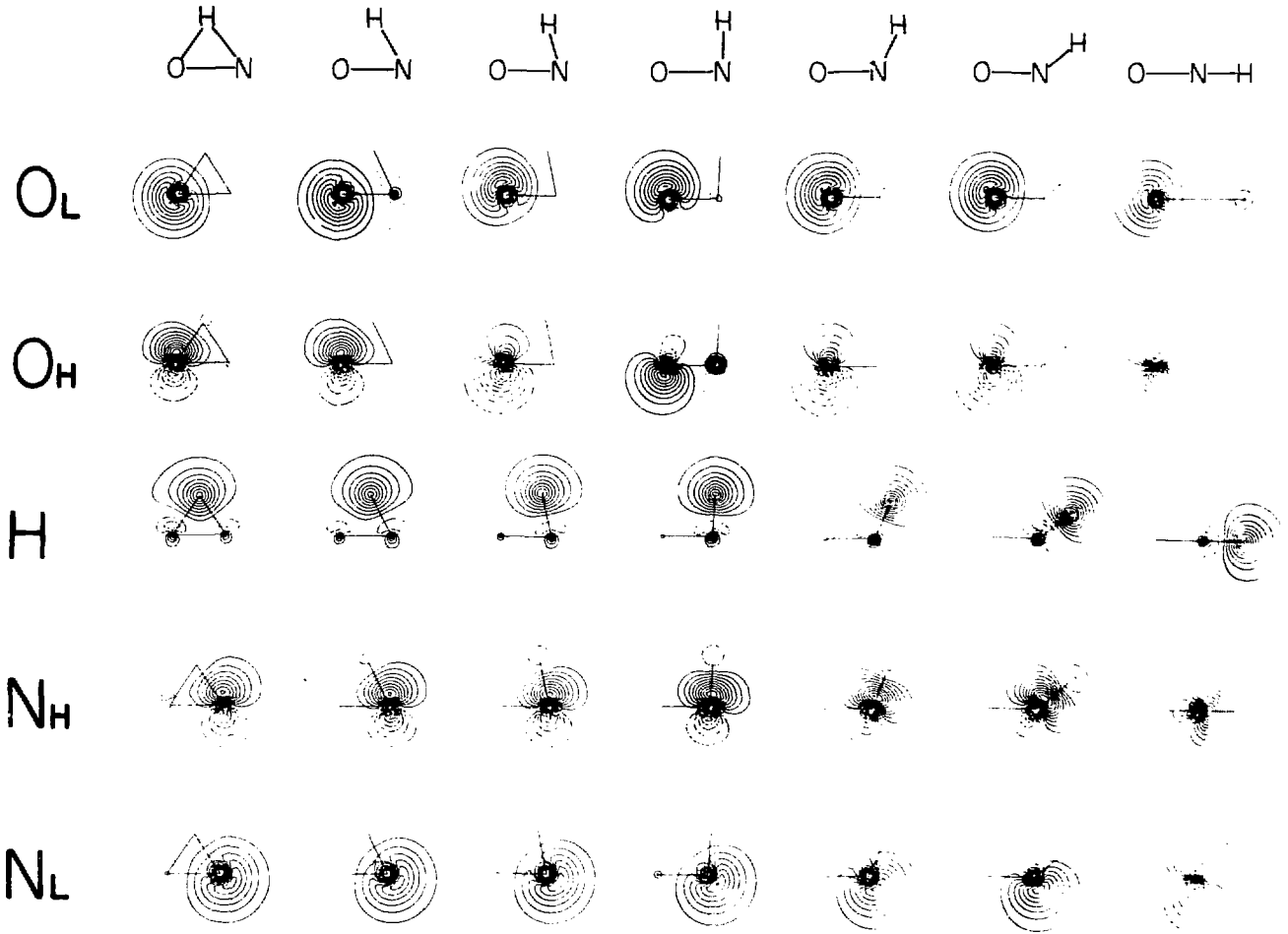

Figure 8. Variations of Directed Localized Reaction Orbitals during HON→HNO isomerization, ctd.

TYPES OF ORBITALS IN CURRENT USE
BELIEVED 'BEST' FOR GIVEN APPLICATIONS

Comments by E. R. Davidson

SCF: Canonical Ground State Orbitals

IVO or ICSCF Orbitals

Parent Configuration Orbitals

MCSCF Orbitals

GVB Orbitals

RHF or UHF Orbitals

Delocalized vs Localized Orbitals

Symmetry Constrained/Unconstrained Orbitals

NO: INOs

Pair NOs

Perturbation NOs

Average NOs

Others: Exchange

'BEST' ORBITAL DEPENDS ON PROPERTY WANTED AND TYPE OF STATE

Types:

1. Sparse energy level region (low valence states), good SCF description, "regular" state.
2. Broken symmetry states (localized hole, Jahn-Teller, etc.).
3. Dense energy spectrum with valence/Rydberg mixing.
4. Non-variational states (deep holes, resonances, etc.).
5. Non-SCF states or irregular only for some $\vec{R}$.

Properties:

1. One state
   - A. Energy surface
   - B. First order charge and spin values
     $\delta(r_A)$, $P_\ell(\Omega_A)/r_A{}^{\ell+1}$, $\vec{r}^{\,\ell}$ ..., spin-spin, ...
   - C. Second order polarizability, spin-orbit.
2. Two states
   - A. ΔE
   - B. Transition probability

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MCSCF ORBITAL DETERMINATION

Comments by J. Hinze

I. *Extended Brillouin Theorem CI*

The MCSCF reference function is

$$\Psi = \sum_I \Phi_I C_I$$

The Hamiltonian is (spin free)

$$\mathcal{H} = \sum_{ij} h_{ij}\{a_i^+ a_j\} + \frac{1}{2}\sum_{ijkl} g_{ij,kl}\{a_i^+ a_k^+ a_l a_j\}$$

with

$$\{a_i^+ a_j\} = a_i^+ a_j + \bar{a}_i^+ \bar{a}_j$$

$$\{a_i^+ a_k^+ a_l a_j\} = a_i^+ a_k^+ a_l a_j + \bar{a}_i^+ a_k^+ a_l \bar{a}_j + a_i^+ \bar{a}_k^+ \bar{a}_l a_j + \bar{a}_i^+ \bar{a}_k^+ \bar{a}_l \bar{a}_j$$

and $a_i a_j + a_j a_i = 0$; $a_i^+ a_j + a_j a_i^+ = \delta_{ij}$

The energy of the system is then given by

$$\bar{E} = \langle\Psi|\mathcal{H}|\Psi\rangle = \sum_{ij} h_{ij}\Gamma_{ij} + \frac{1}{2}\sum_{ijkl} g_{ijkl}\Gamma_{ijkl}$$

with the density matrix elements

$$\Gamma_{ij} = \langle\Psi|\{a_i^+ a_j\}|\Psi\rangle$$

$$\Gamma_{ijkl} = \langle\Psi|\{a_i^+ a_k^+ a_l a_j\}|\Psi\rangle$$

$$\Gamma_{ijklmn} = \langle\Psi|\{a_i^+ a_k^+ a_m^+ a_n a_l a_j\}|\Psi\rangle \quad \text{etc.}$$

A single (Brillouin type) excitation is

$$\Psi_{p\to q} = \{a_q^+ a_p\}\Psi = (a_q^+ a_p + \bar{a}_q^+ \bar{a}_p)\Psi$$

The Brillouin conditions are

$$\langle\Psi_{p\to q}|\mathcal{H}|\Psi\rangle - \langle\Psi_{q\to p}|\mathcal{H}|\Psi\rangle = 0$$

For the Brillouin CI we need

$$\langle\Psi_{p\to q}|\Psi\rangle = \Gamma_{pq} = \langle\Psi|\{a_p^+ a_q\}|\Psi\rangle$$

$$\langle\Psi_{p\to q}|\Psi_{r\to s}\rangle = \langle\Psi|\{a_p^+ a_q\}\{a_s^+ a_r\}|\Psi\rangle$$

$$\langle\Psi_{p\to q}|\mathcal{H}|\Psi\rangle \text{ and } \langle\Psi_{p\to q}|\mathcal{H}|\Psi_{r\to s}\rangle$$

with $q > p$ and $s > r$; $(qp) \geq (sr)$

We get four types of formulae

1. $q > s$; $p \neq r$
2. $q > s$; $p = r$
3. $q = s$; $p > r$
4. $q = s$; $p = r$

giving the matrix elements in terms of the 1-, 2-, 3- and 4-order reduced density matrix of the reference.

The formulae are done once and for all!

II. *Double Excitations from General Reference*

Using

$$\Psi_{pq\to rs} = \{a_r^+ a_s^+ a_p a_q\}\Psi$$

and

$$[a_r^+ a_s^+ a_p a_q]\Psi \quad \text{(other spin coupling)}$$

There will be 16 types of formulae done once and for all!

The 5- and 6- order reduced density matrices of the reference will be required also.

III. *Orthogonal Gradient Method to Obtain MCSCF Orbitals*

(with A. Golebiewski and E. Yurtsever)

The MCSCF equations are

$$\sum_m F_{im}|\phi_m\rangle = \sum_j |\phi_j\rangle\varepsilon_{ji}$$

$$F_{im} = h\Gamma_{im} + \sum_{kl}\langle k|\frac{1}{r_{12}}|l\rangle\Gamma_{im,kl}$$

$$\varepsilon_{ji} = \langle\phi_j|\sum_m F_{im}|\phi_m\rangle = \sum_m \mathbb{C}_j^+ F_{im}\mathbb{C}_m$$

$$= \sum_m\{h_{jm}\Gamma_{im} + \sum_{kl}{}' g_{jmkl}\Gamma_{imkl}\}$$

These equations are solved if and only if

$$\varepsilon_{ij}^* = \varepsilon_{ji}$$

i.e. $\varepsilon = \left(\begin{array}{c|c} \diagup & 0 \\ \diagup & \\ \diagup & \end{array}\right)$ should be made Hermitian

Or,

$$\mathbb{U}^+\varepsilon = \varepsilon^+\mathbb{U}$$

and find $\mathbb{U}$ which makes ε Hermitian.

This is obtained as

$$\mathbb{U} = \varepsilon(\varepsilon^+\varepsilon)^{-1/2}$$

For a more complete discussion of this method, see A. Golebiewski, J. Hinze and E. Yurtsever, "The Orthogonal Gradient Method. A Simple Method to Solve the Closed, Open and Multiconfiguration SCF Equations," J. Chem. Phys. (to be published).

II. CONFIGURATION SELECTION METHODS

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A PARTIAL REVIEW OF CONFIGURATION SELECTION METHODS

Presentation by

B. Liu

- is not a complete review
- is not impartial
- emphasizes methods rather than history

Why do quantum chemistry calculations?

- To understand chemical phenomena
- To obtain chemical data
- To develop and test new quantum chemical methods

What is a good calculation?

- One that gives the correct answer to our questions
- ∴ The <u>best</u> calculation is the one that gives the <u>most accurate answer to our question</u>. This is <u>not</u> <u>necessarily</u> the one that gives the lowest total energy

How do we know our answer is correct?

- Convergence with respect to improved calculations.

The configuration Interaction Method

$$H_{op}\Psi = E\Psi$$

$$\Psi = \sum_I C_I \Phi_I, \qquad \langle \Phi_I | \Phi_J \rangle = \delta_{IJ}$$

$$\Phi_I : \text{l.c. of } A|\psi_1(1), \ldots \psi_n(n)|$$

$$\psi_i = \sum_p C_p^i \chi_p$$

Variational principle →

$$\underline{\underline{H}}\underline{C} = E\underline{C}, \qquad H_{IJ} = \langle \Phi_I | H_{op} | \Phi_J \rangle$$

Three steps of a CI calculation

- selection of basis functions χ_p
- construction of orbital basis ϕ_i
- selection of configurations Φ_I

Why do we need configuration selection?

- Complete CI is usually too large
- For a limited basis set, a restricted CI often produces better results than a complete CI.

Two types of configuration selection methods

- Energy oriented methods select configurations to achieve the lowest possible total energy
- Chemistry oriented methods use criteria other than the lowest total energy

Energy oriented selection: Classification of configurations by perturbation theory

- Rayleigh-Schrödinger perturbation theory

$$H = H_o + \lambda V$$

$$\Psi = \sum_n \lambda^n \psi^n$$

$$E = \sum_n \lambda^n E^n$$

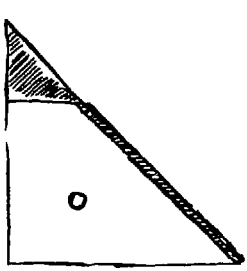
$$H_o \psi^o = E^o \psi^o$$

$$H_o \psi^1 + V\psi^o = 0$$

$$H_o \psi^n + V\psi^{n-1} = \sum_{k=2}^{n} E^k \psi^{n-k} \qquad n \geqslant 2$$

- In the CI context choose $\left\{\Phi_I^o\right\}$, and define the H_o matrix from the H matrix as shown on the diagram

$$H_o = \left\{\Phi_I^o\right\} \qquad \left\{\right.$$



Classify configurations by the order of perturbation wavefunction in which they first appear.

Energy oriented selection: The Interacting Subspaces

- zeroth order subspace $\{\Phi_I^0\}$ chosen on either energy or chemistry basis.
- 1st order subspace $\{\Phi_I^1\}$ $(\Phi_I^1|H|\Phi_J^0) \neq 0$ for some I
- 2nd order subspace $\{\Phi_K^2\}$ $(\Phi_K^2|H|\Phi_J^1) \neq 0$ for some J

Further selection in the 1st order interacting subspace.

1. Energy selection: discard all configurations whose estimated energy contribution is below some threshold.

   (i) perturbation theory

   $$\Delta E_K = (\Phi_K|H|\Phi^0)^2/(H_{KK} - H^0)$$

   (ii) $$\Phi^K = (1 - C_K^2)^{-1/2} \sum_{I \neq K} C_I \Phi_I$$

   $$\Delta E_K = (E - H_{KK})\ C_K^2/(1 - C_K^2)$$

   E and C_K estimated by perturbation theory

2. Natural orbital truncation: discard all configurations constructed from natural orbitals with occupation numbers below some threshold

   - not efficient for total energy
   - very useful for treating higher order subspaces

Extrapolation based on energy selection

- Calculate energy for different values of the threshold
- extrapolate to the zero threshold limit
- Can give close estimate of the complete 1st order interacting space limit by a series of relatively small calculations

---

Chemistry oriented methods: Complete valence CI

- All configurations generated by distributing valence electrons in valence orbitals
- Includes near-degeneracy effects
- Correct asymptotic behavior
- Size consistent

Chemistry oriented methods: First order CI, POL-CI, OVC, charge wavefunction

- VCI + all single excitations
- essentially correct asymptotic behavior
- include polarization and semi-internal correlation energy
- based on the qualitative idea of the separation of atomic and molecular correlation energies

---

What is the best configuration selection method? There is no simple answer. It depends on:

- the nature of the problem at hand
- the accuracy needed
- the orbital basis
- characteristics of the computer program

What are the most important ingredients of a good calculation?

- Understanding of the nature of the problem at hand
- A great deal of care
- A chemistry oriented approach

Energy difference at Re between CH $a^4\Sigma^-$ and $A^2\Delta$
Natural orbital truncation, all singles and doubles from HF

σ	π	$E(^4\Sigma^-)$	error	$E(^2\Delta)-E(^4\Sigma^-)$	error
4	1	-38.304755	.014373	.107820	.000948
6		.314663	.004448	.107936	.000832
8		.317609	.001511	.108720	.000048
23		.319111		.108768	
23	3	.356300	.007666	.099552	.002149
	6	.362760	.001206	.097735	.000364
	8	.363515	.000451	.097574	.000203
	13	.363966		.097371	

- Convergence on energy difference much better than convergence on total energy

---

Vibrational quanta of $CO(X^1\Sigma^+)$ in cm^{-1}

Method	$\Delta G_{1/2}$	error	$\Delta G_{3/2}$	error
VCI	2128.3	-15.6	2102.4	-14.4
FOCI	2140.3	-3.0	2114.7	-2.1
SDHF	2235.9	92.6	2213.9	96.1
Observed	2143.3		2116.8	

- VCI and FOCI give much better vibrational quanta in spite of higher total energies
- needs six-fold excitations to describe the stretch of a triple bond.

Force constants of HCN in mdyne/Å

	K_1	K_2	K_{12}
Experiment	3.12(0.10)	9.39(0.09)	-0.21(0.08)
Δ(VCI)	-0.07	-0.15	0
Δ(SDHF)	+0.15	+0.94	+0.06

K_1 - CH stretch

K_2 - CN stretch

K_{12} - coupling between CH and CN stretches

- VCI gives much better force constants
- Need six-fold excitation to describe the vibration

THE METHOD OF INTERACTING CORRELATED FRAGMENTS FOR VAN DER WAALS INTERACTION:

GROUND STATE OF He_2

- Interacting HF, neglect atomic correlation
  $1s_a^2 1s_b^2 + 1s_a^2 1s_b i\psi + 1sa1s_b^2 i\psi + 1s_a 1s_b i\psi j\psi$
  D_e = 12.1°K too large by ~1.5°K

- Interacting correlated atoms, limited atomic correlation
  $(1s_a^2 + 2s_a^2 + 2p_a^2)\ (1s_b^2 + 2s_b^2 + 2p_b^2)$
  + all singles and doubles that vanish at $R = \infty$
  D_e = 10.7°K within 0.3°K

GROUND STATE OF Mg_2

- Neglect K- and L-shell correlation
- Interacting HF
- Interacting $3s^2 \div 3p^2$ atoms
- Singles + Doubles from HF

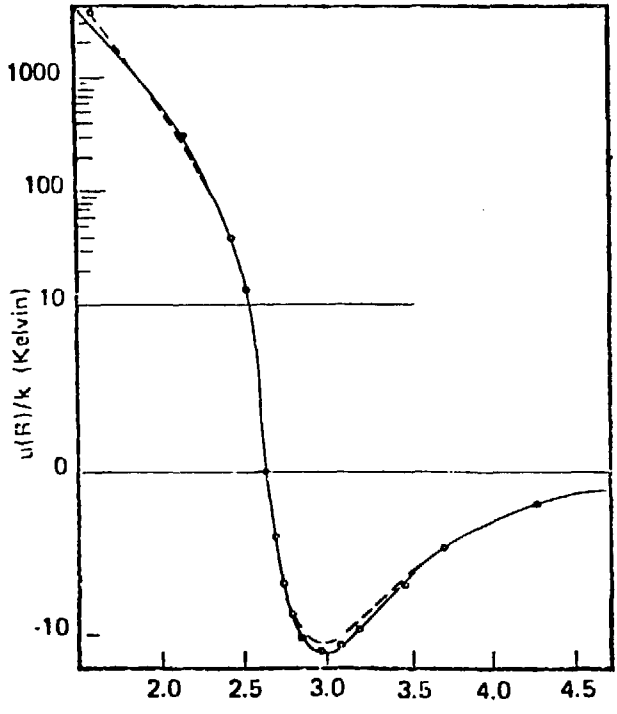


Figure 1. Potential curve of He_2 $^1\Sigma_g^+$.

● theoretical curve

---- empirical curves

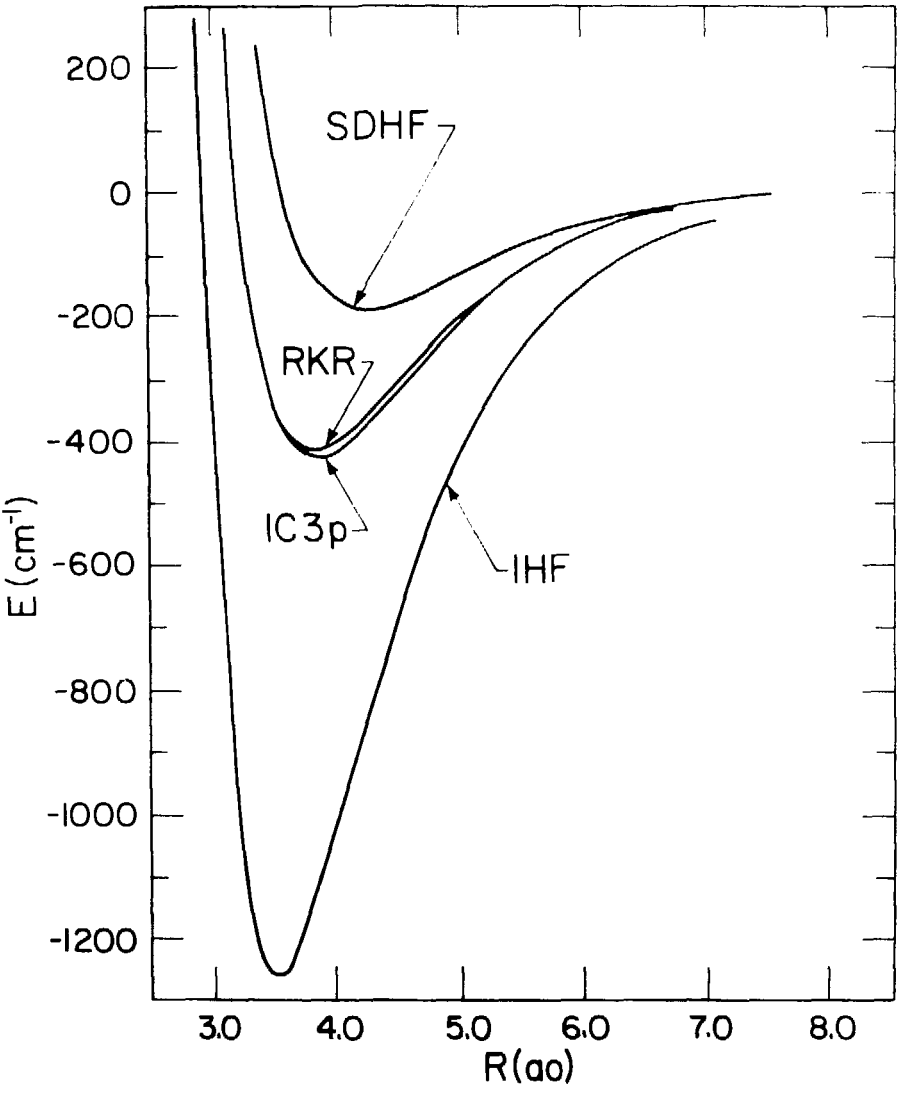


Figure 2. Potential curve of Mg_2 $X^1\Sigma_g^+$.

- RKR denotes the empirical curve
- IHF denotes the Interacting HF curve
- IC3p denotes the Interacting Correlated Fragments curve
- SDHF denotes the Single + Doubles from HF curve

Conclusion

NRCC should support a general purpose CI program

- Capability to deal with a wide variety of chemical problems
- Useful for testing new methods

Strategies for Handling Configurations in CI Calculations

COMMENTS BY P. JEFFREY HAY

- Typically reference set of configurations $\{\Psi_0\}$ defined and (1+2) excitations relative to the set are generated

- Restrictions can be placed on configuration list by partitioning the orbital space
  - --(Valence/virtual) or (valence/Rydberg/virtual)
    - First-order wavefn (Schaefer, Bender[1])
    - POL CI wavefn (Hay, Dunning[2])
  - --(Valence / secondary NO / virtual)
    - OVC wavefn (Das, Wahl[3])
    - GVB CI wavefn (Harding, Goddard[4])

  where valence orbitals determined by MC-SCF, GVB INO or related methods.

- Procedure can be effective for "semi-quantitative" calculation of potential energy curves of many electronic states

O_3 Calculations[2]

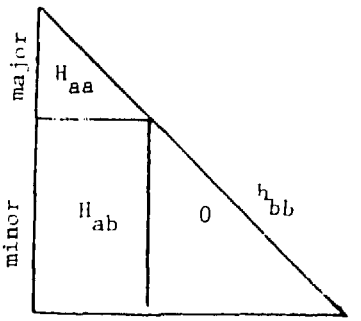
	n_{virt}	N	E_{corr}	Ring form - open form
Hartree-Fock	0	1	---	0.36 eV
Valence CI	0	198	-0.2254	0.52
POL CI	1	1394*	-0.3602	1.20
(1+2) CI	2	5381*	-0.4793	1.22

*SELECTED CONFIGURATIONS ONLY

- ACCURACY IMPROVES AS THE RESTRICTION ON ORBITAL PARTITIONING DECREASES

Partitioning of Configurations

- Alternatively H_{CI} can be partitioned into major and minor configurations according to energy contributions or classes of orbitals



- Handling of partitioned matrix
  - --Obtain roots directly (B_k method)[5]
  - --Retain minor configs. with $|\Delta\varepsilon_i| > \varepsilon_c$ and form resulting full matrix
  - --As above for $\varepsilon_c^{(1)} > \varepsilon_c^{(2)} > \varepsilon_c^{(3)}$ and extrapolate results to zero threshold[6]
  - --Reject minor configs. with $\Sigma\, \Delta\varepsilon_i \leqslant$ const. and form resulting full matrix[7]
  - --Obtain approx. CI coefficients

$$\tilde{\phi} = \sum_i \tilde{c}_i\, \phi_i$$

and evaluate variational energy for full H_{CI}

$$E = \langle \tilde{\phi} | H | \tilde{\phi} \rangle$$

- Flexible generation and selection techniques should be implemented at NRCC

References

1. H. F. Schaefer, J. Chem. Phys. 54, 2207 (1971)
2. P. J. Hay and T. H. Dunning Jr., J. Chem Phys. 67, 2290 (1977).
3. G. Das and A. C. Wahl, J. Chem. Phys. 56, 1769 (1972).
4. L. B. Harding and W. A. Goddard III, Chem. Phys. Lett. 55, 217 (1978).
5. Z. Gershgorn and I. Shavitt, Int. J. Quantum Chem. 2, 751 (1968).
6. R. J. Buenker, S. D. Peyerimhoff and W. Butscher, Mol. Phys. 35, 771 (1978).
7. R. C. Raffenetti, unpublished.

[illegible] MULTI-REFERENCE CONFIGURATION LIST

[illegible]

A. [illegible] Multi-reference Configuration Interaction

1. [illegible] of a given symmetry equivalently over a set of [illegible] geometries.
2. To account for the important contributions through quadruple excitations as simultaneous single and double excitations from members of the reference list.

B. Basic Method

1. Determine zeroth order wavefunctions for the first k states of a given symmetry.

$$\Psi_k^o = \sum_i C_{ik} \Phi_i$$

where the C_{ik} are determined in a small CI calculation involving only the reference configuration functions (CF's). The small set of important CF's are determined from small CI calculations at representative points on the potential surface.

2. Generate all single and double excitations from each CF in the reference list.

3. Select a subset of configurations generated in step 2 to be included in the final wavefunction by some procedure such as perturbation theory. The energy contribution of configuration Φ_ℓ to the kth state can be estimated as

$$\Delta E_\ell^k = \frac{\left| \langle \sum_{i=1}^{N} C_{ik} \Phi_i | H | \Phi_\ell \rangle \right|^2}{\langle \Phi_\ell | H | \Phi_\ell \rangle - E_o}$$

where E_o is the expectation value of $\langle \Psi_k^o | H | \Psi_k^o \rangle$. If ΔE_ℓ^k for any of the k state exceeds some designated threshold value T, it is included in the final wavefunction. Alternately, one can determine the energy lowering of the ℓth configuration to each of the k state (Buenker and Peyerimhoff).

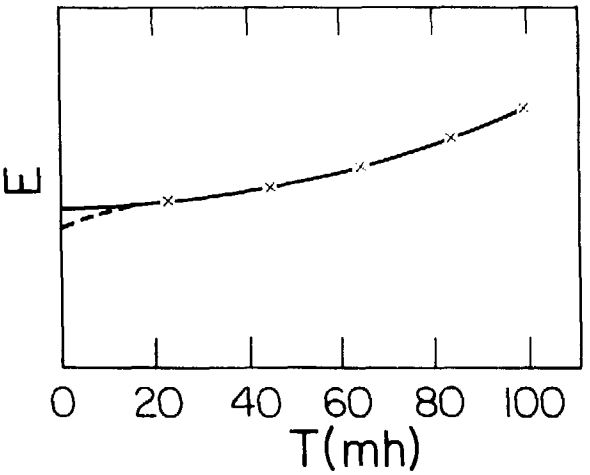
4. Determine the energies E_k as a function of T. This requires little more work than solving the problem for the smallest threshold since it requires obtaining k roots of different subsets of the full matrix given a good initial guess to the eigenvectors.
5. Once the energy is known as a function of threshold one can extrapolate to T=0. (See Buenker and Peyerimhoff in Theoret Chim Acta).

C. Shortcomings of the Method

1. There exists some impression in the determined energies due to the CF selection process and particularly to the extrapolation procedure. This can introduce difficulties where high precision is required such

as computing vibrational energies or in computing polarizabilities by the finite field method.

2. It has recently been suggested (see forthcoming paper by C. Jackels and I. Shavitt) that for multi-reference lists the extrapolated energy may underestimate the energy obtained if all CF's were retained (see accompanying figure). That is, the relationship between E and T may become substantially different (dotted line) at very small threshold (1 μm or less). This point was subsequently discussed at the meeting by I. Shavitt.



Energy extrapolation diagram.

III. HAMILTONIAN MATRIX CALCULATION

Isaiah Shavitt, Chairman
Battelle Memorial Institute, and
The Ohio State University
Columbus, Ohio

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TYPICAL PROBLEMS IN H-MATRIX CALCULATION

Presentation by Danah Shavitt

- Determination of formulas

$$\langle \Phi_s | \hat{H} | \Phi_s \rangle = \sum_{ij} a_{ij}^{ss} h_{ij} + \sum_{ijkl} b_{ijkl}^{ss} g_{ijkl}$$

where

$$h_{ij} \equiv \langle \varphi_i(\mathbf{r}_1) | \hat{h}_1 | \varphi_j(\mathbf{r}_1) \rangle$$

$$g_{ijkl} \equiv \langle \varphi_i(\mathbf{r}_1) \varphi_k(\mathbf{r}_2) | g_{12} | \varphi_j(\mathbf{r}_1) \varphi_l(\mathbf{r}_2) \rangle$$

- Data access problem

  (because both **H** and g are very large, and access patterns are irregular for at least one of them)

DETERMINATION OF FORMULAS

- Strongly dependent on type of CF's (configuration functions) used.
- Involves extensive "nonproductive" work (in the general case).
- Can be done as a single-stage or a two-stage (formula tape) process.
- Can be done from $\underset{\sim}{H}$ elements to integrals or (in some cases) vice versa (i.e., for given H_{st}, find all integrals and coefficients, or, for a given integral, find all its contributions to $\underset{\sim}{H}$).
- Can be done relative to true vacuum, or in a particle-hole formalism (relative to a closed-shell reference configuration).

REMOVAL OF "CORE" ORBITALS FROM H-MATRIX CALCULATION

("Core" orbitals are those which are kept fully occupied in all configuration functions)

Replace the combined $(\hat{h} = \hat{T} + \hat{V}_{ne})$ one-electron integrals matrix by

$$\tilde{h}_{ij} = h_{ij} + \sum_{k \in \text{core}} (2[ij;kk] - [ik;kj]) \quad (i,j \notin \text{core})$$

and omit the core orbitals and electrons from the rest of the calculation.

(See, e.g., R.-P. Hosteny, T. H. Dunning Jr., R. R. Gilman, A. Pipano, and I. Shavitt, J. Chem. Phys. 62, 4764 (1975))

USE OF A PARTICLE-HOLE FORMALISM

is advantageous when

$$N_v \gg p_{max}$$

where:

N_v = number of electrons in variable occupancy orbitals,

p_{max} = maximum level of excitation included (relative to the reference configuration)

FORMULAS FOR SLATER DETERMINANTS

- Relatively simple formulas (Slater-Condon rules) but excessively long expansions. But even in this case detailed matching of Φ_i and Φ_f is required, including finding a <u>maximum coincidence permutation</u> and its parity.

- Simplified treatment is possible for special cases (e.g., single and double excitations only).

- All nonzero coefficients a_{ij}^{μ} and b_{ijkl}^{μ} are ± 1.

COMPARISON OF SLATER DETERMINANTS AND SPIN-ADAPTED CF's

for all single and double excitations from a closed-shell reference CF

N = No. of electrons

n = No. of (spatial) orbitals

$h = \frac{1}{2}N$ = No. of orbitals occupied in ref. CF

$p = n-h$ = No. of orbitals vacant in ref. CF

Assume $p \gg h \gg 1$

Type of CF	No. of CF's	No. of SD's[a]
$i \to a$	hp	$2hp$
$i^2 \to a^2$	hp	hp
$ij \to a^2$	$\frac{1}{2}h^2p$	h^2p
$i^2 \to ab$	$\frac{1}{2}hp^2$	hp^2
$ij \to ab$ ($\times 2$)	$\frac{1}{2}h^2p^2$	$\frac{3}{2}h^2p^2$

[a] Summed over allowed spin assignments.

- No. of SD's $\approx 3 \times$ No. of spin-adapted CF's

NO. OF NONZERO MATRIX ELEMENTS

for above example

Type[a]	Spin-adapted[b]	SD's
$\langle ij \to ab \mid H \mid ij \to cd \rangle$	$\frac{1}{4}h^2p^4$ $(\frac{1}{8}h^2p^4)$	$\frac{5}{8}h^2p^4$
$\langle ij \to ab \mid H \mid ik \to ac \rangle$	$2\,h^3p^3$	$3\,h^3p^3$

[a] Most prevalent types only; each represents a 2×2 block.

[b] The number in parentheses is for a choice of spin couplings which diagonalizes these blocks, i.e., $((ij)^1(ab)^1)^1$ and $((ij)^3(ab)^3)^1$.

- Typically, the ratio of the numbers of nonzero elements for the two cases is about $1:2$.

INTERMEDIATE PROCEDURE

- Compute a "spin block" of H elements in terms of SD's, then transform to CF's.
- Can use projection operator property to reduce the size of the SD block required (Nesbet, Davidson).
- For double excitations from a closed shell, the typical SD spin block is 6×2, containing 2 - 6 nonzero elements, and is transformed to 2×2.
- Can also be used for spatial symmetry.

References:

R. K. Nesbet, Ann. Phys. (N.Y.) 3, 397 (1958);
J. Math. Phys. 2, 701 (1961).

E. R. Davidson, Int. J. Quantum Chem. 8, 83 (1974).

D. Munch and E. R. Davidson, J. Chem. Phys. 63, 980 (1975).

METHOD BASED ON "BONDED FUNCTIONS"

(Boys, Reeves, Sutcliffe, Shavitt)

Form of functions:

$$(aa)(bb)\ldots(pq)(rs)\ldots(u(v\ldots$$

where

$$(aa) = a\bar{a}$$

$$(pq) = \frac{1}{\sqrt{2}}(p\bar{q} + q\bar{p})$$

$$(u = u$$

(the antisymmetrizer is implied).

Example:

$$(aa)(bc)(dc)(f \qquad (\pi = 3)$$

$$(aa)(bc)(d(ef) \qquad (\pi = 2)$$

$$(aa)(b(cd)e)(f \qquad (\pi = 1)$$

$$(aa)(b(cd)(ef) \qquad (\pi = 1)$$

$$(aa)(b(c(de)f) \qquad (\pi = 1)$$

References:

C. M. Reeves, Ph.D. Thesis, Cambridge University (1957); Commun. ACM 9, 276 (1966).

B. Sutcliffe, J. Chem. Phys. 45, 235 (1966).

G.H.F. Diercksen and B. Sutcliffe, Theor. Chim. Acta 34, 105 (1974).

G.H.F. Diercksen, Theor. Chim. Acta 40, 283 (1975).

I. Shavitt, The Method of Configuration Interaction, in "Modern Theoretical Chemistry, Vol. 3, Methods of Electronic Structure Theory", Ed. H. F. Schaefer III (Plenum, New York, 1977), p. 189.

The set of bonded functions for a given orbital product is linearly independent, but not orthogonal.

A single Schmidt orthonormalization matrix can be used for all "spin blocks", taking appropriate upper-left sub-matrices, as required (Pipano, Shavitt).

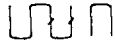
Spatial symmetry for axial point groups can easily be superimposed (Gershgorn, Shavitt)

References:

Z. Gershgorn and I. Shavitt, Int. J. Quantum Chem. Symp. 1, 403 (1967).

A. Pipano and I. Shavitt, The Use of Complex Orbitals in Large Scale Molecular Configuration Interaction Calculations (preprint).

"CYCLES" AND "CHAINS" PATTERNS

Bonded Functions	Max Coincidence Rearrangement	Patterns	Parameters
	i = 1 2 3 4 5 6 7	1 2 3 4 5 6 7	
(ab)(cd) (ad)(bc)	(a b)(c d) (a (b c) d)		$\sigma = \sigma' = 0,\ c = 1,\ J = 0,\ \Gamma = -\frac{1}{2}$ $Q_i = Q_{ij} = 1$ for all i, j $q_{12} = q_{14} = q_{23} = q_{34} = 1,\ q_{13} = q_{24} = -2$
(ab)(c(d (ad)(e(f	(d (a b)(c (d a)(e (f		$\sigma = 1,\ \sigma' = 0,\ c = 0,\ J = 0,\ \Gamma = \frac{1}{2}$ $Q_{34} = 1,\ q_{34} = -1$
(aa)(bc)(d (ab)(cd)(e	(a a)(b c)(d (e (a b)(c d)		$\sigma = \sigma' = 0,\ c = 0,\ J = 1,\ \Gamma = \frac{1}{4}\sqrt{2}$ $Q_1 = Q_{1j} = 1$ for all j $q_{12} = 0,\ q_{14} = 1,\ q_{13} = q_{15} = -2$
(ab)(cd)(e(f (af)(gh)(c(d	(f (a b)(e (c d) (f a)(g h)(c (d		$\sigma = 1,\ \sigma' = 0,\ c = 0,\ J = 0,\ \Gamma = -\frac{1}{4}$ $R = 0,\ Q_{34} = 1,\ q_{34} = 0$
(aa)(bc)(de)(f (ab)(cc)(df)(g	(a a)(c b)(e d)(f (a (c c) b)(g (d f)		$\sigma = \sigma' = 0,\ c = 1,\ J = 2,\ \Gamma = \frac{1}{2}$ $Q_{25} = 1,\ c = -\frac{1}{2}$

MATRIX ELEMENT FORMULA FOR BONDED FUNCTIONS

$$\langle B|\hat{H}|B'\rangle = \Gamma\{RQV_{nn} + R\sum_i Q_i\langle b_i|\hat{h}|b_i'\rangle$$
$$+ \sum_{i<j} Q_{ij}[R\langle b_ib_j|g|b_i'b_j'\rangle + q_{ij}\langle b_ib_j|g|b_j'b_i\rangle]\}$$

$$R = \begin{cases} 1 & \text{if there are no even chains} \\ 0 & \text{otherwise} \end{cases}$$

$$Q_{ij\ldots} = \begin{cases} 1 & \text{if } b_k = b_k' \text{ for all } k \neq i, j, \ldots \\ 0 & \text{otherwise} \end{cases}$$

$$\Gamma = (-1)^{\sigma+\sigma'}(-\tfrac{1}{2})^{(N/2)-S-c}2^{J/2}$$

See Shavitt, in "Modern Theoretical Chemistry, Vol. 3, Methods of Electronic Structure Theory" for definitions of other symbols, etc.

UNITARY GROUP APPROACH

- The entire spin-adapted orthonormal basis of N-electron configuration functions is defined globally, not individually for each orbital product.
- As a result, matrix element formulas can be derived without reference to permutations.
- A "lexical" ordering of the configuration functions leads to certain regularities in the contributions of each integral to the H matrix.

A detailed review, with many references, has been given by:

J. Paldus, Many-Electron Correlation Problem. A Group Theoretical Approach, in "Theoretical Chemistry: Advances and Perspectives", Volume 2, Ed. H. Eyring and D. J. Henderson (Academic Press, New York, 1976), p. 131.

See also:

W. G. Harter and C. W. Patterson, "A Unitary Calculus for Electronic Orbitals" (Lecture Notes in Physics 49) (Springer-Verlag, Berlin, 1976).

F. A. Matsen, Adv. Quantum Chem. 11 (in press).

UNITARY GROUP METHODS FOR MATRIX ELEMENTS

Some recent work:

J.-F. Gouyet, R. Schranner, and T. H. Seligman, J. Phys. A 8, 285 (1975).

G.W.F. Drake and M. Schlesinger, Phys. Rev. A 15, 1990 (1977).

C. R. Sarma and S. Rettrup, Theor. Chim. Acta 46, 63 (1977); S. Rettrup and C. R. Sarma, Theor. Chim Acta 46, 73 (1977).

M. J. Downward and M. A. Robb, Theor. Chim. Acta 46, 129 (1977).

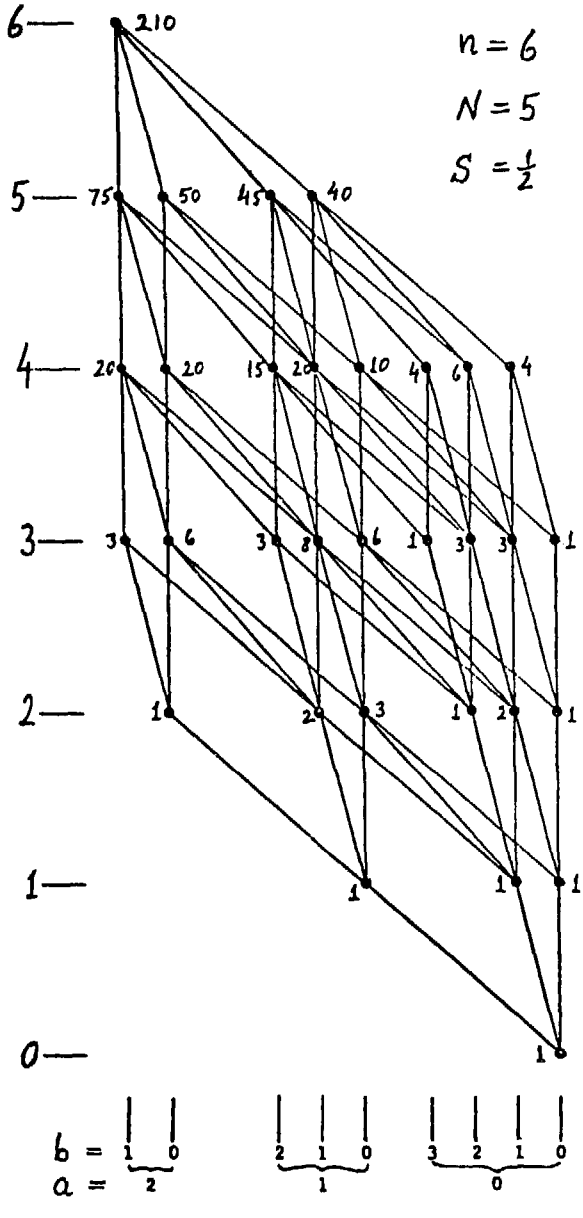
I. Shavitt, Int. J. Quantum Chem. Symp. 11, 131 (1977); Int. J. Quantum Chem. Symp. 12 (in press).

METHOD BASED ON THE GRAPHICAL UNITARY GROUP APPROACH

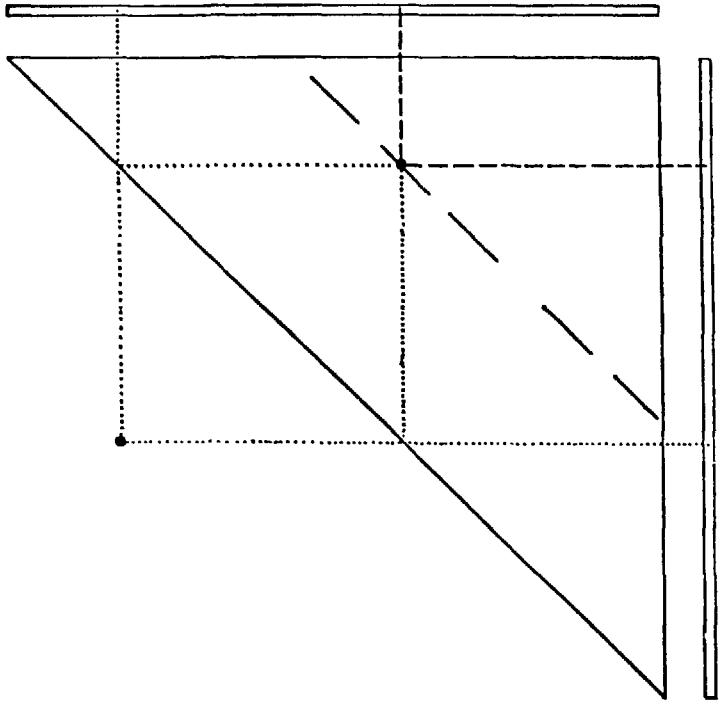
- Global definition of an orthonormal CF set (does not allow individual selection, but allows selection of classes of orbital subset occupancies).
- Systematic numbering scheme, easily determined from CF specification.
- Compact representation (in terms of the "distinct row table" and corresponding graph).
- Easy direct generation of "inverted" formula tape (i.e., ordered by integrals).
- Equal contributions of each integral to systematic sequences of matrix elements.

References:

I. Shavitt, Int. J. Quantum Chem. Symp. 11, 131 (1977);
Int. J. Quantum Chem. Symp. 12 (in press).



Example of the distinct row graph for 6 orbitals, 5 electrons, doublet state (full CI). Each configuration function is represented by one path from tail to head.



The pattern of equal contributions of one integral to elements of the H matrix, and their use in the direct CI iterative eigenvector determination.

METHOD BASED ON ONE-ELECTRON INTEGRAL CONTRIBUTIONS

(Wetmore and Segal)

$$\hat{E}_{ij} = \sum_{\mu} |i(\mu)\rangle\langle j(\mu)| = \sum_{\sigma=\alpha,\beta} \hat{X}^{\dagger}_{i\sigma}\hat{X}_{j\sigma}$$

$$\hat{H} = \sum_{j} h_{ij}\hat{E}_{ij} + \tfrac{1}{2}\sum_{ijk\ell} g_{ijk\ell}(\hat{E}_{ij}\hat{E}_{k\ell} - \delta_{jk}\hat{E}_{i\ell})$$

Then:

$$a^{st}_{ij} = \langle\Phi_s|\hat{E}_{ij}|\Phi_t\rangle$$

$$b^{st}_{ijk\ell} = \langle\Phi_s|\hat{E}_{ij}\hat{E}_{k\ell} - \delta_{jk}\hat{E}_{i\ell}|\Phi_t\rangle$$

$$= \sum_{u} \langle\Phi_s|\hat{E}_{ij}|\Phi_u\rangle\langle\Phi_u|\hat{E}_{k\ell}|\Phi_t\rangle - \delta_{jk}\langle\Phi_s|\hat{E}_{i\ell}|\Phi_t\rangle$$

$$= \sum_{u} a^{su}_{ij}\, a^{ut}_{k\ell} - \delta_{jk}\, a^{st}_{i\ell}$$

(The summation over u may include CF's which are not in the original list.)

References:

R. W. Wetmore and G. A. Segal, Chem. Phys. Lett. 36, 478 (1975).

G. A. Segal, R. W. Wetmore, and K. Wolf, Chem. Phys. 30, 478 (1978).

USE OF "PATTERNS"

Classify noncoincidence pattern between the two configuration functions into several types, and provide special treatment for each type.

Examples:

- F. E. Harris, J. Chem. Phys. 46, 2769 (1967) (using the Sanibel Coefficient approach, 20 types).
- J. Karwowski, Theor. Chim. Acta 29, 151 (1973) (using the symmetric group approach, 15 types, but representation matrices of S_N for the "line up" permutation are still required).
- R. W. Wetmore and G. A. Segal, Chem. Phys. Lett. 36, 478 (1975); G. A. Segal, R. W. Wetmore, and K. Wolf, Chem. Phys. 30, 478 (1978) (in conjunction with their method for the determination of 2-electron integral coefficients from those of 1-electron integrals).
- C. R. Sarma and S. Rettrup, Theor. Chim Acta 46, 63 (1977) (using the unitary group approach).

SHORT SURVEY OF OTHER METHODS

- Projection operator approach (Löwdin, etc.)
  Sanibel coefficients. Projections are not orthogonal. Line-up permutations required.

- Methods based on the symmetric group S_N
  Related to the unitary group method, but less systematic. Most forms require representation matrices of S_N.

- Serber spin functions (Salmon and Ruedenberg)
  Related to the S_N methods, but a particular choice of spin functions simplifies the representations required.

Some general survey references:

R. Pauncz, "Alternant Molecular Orbitals" (Saunders, Philadelphia, 1967).

F. E. Harris, Adv. Quantum Chem. 3, 61 (1967); in "Energy, Structure, and Reactivity", Ed. D. W. Smith and W. B. McRae (Wiley, New York, 1973), p. 112.

I. Shavitt, in "Modern Theoretical Chemistry, Vol. 3, Methods of Electronic Structure Theory", Ed. H. F. Schaefer III (Plenum, New York, 1977), p. 189.

W. I. Salmon, Adv. Quantum Chem. 8, 37 (1974).

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W. I. Salmon, Adv. Quantum Chem. 8, 37 (1974).

SOME REFERENCES ON OTHER METHODS

- Projection operators and Sanibel coefficients:

P. O. Löwdin, Phys. Rev. 97, 1509 (1955).

F. E. Harris, J. Chem. Phys. 46, 2769 (1967); 47, 1047 (1967).

V. H. Smith and F. E. Harris, J. Math. Phys. 10, 771 (1969).

J. E. Harriman, J. Chem. Phys. 40, 2827 (1964).

R. Manne, Theor. Chim. Acta 6, 116 (1966).

K. Mano, J. Math. Phys. 12, 2361 (1971).

- Symmetric group methods:

F. A. Matsen, Adv. Quantum Chem. 1, 59 (1964); J. Am. Chem. Soc. 92, 3525 (1970).

J. Gerratt and W. N. Lipscomb, Proc. Nat. Acad. Sci. USA 59, 332 (1968).

D. J. Klein and B. R. Junker, J. Chem. Phys. 54, 4290 (1971).

G. A. Gallup, Adv. Quantum Chem. 7, 113 (1973).

- Serber functions:

K. Ruedenberg, Phys. Rev. Lett. 27, 1105 (1971).

W. I. Salmon and K. Ruedenberg, J. Chem. Phys. 57, 2776 (1972).

W. I. Salmon, K. Ruedenberg, and L. M. Cheung, J. Chem. Phys. 57, 2787 (1972).

K. Ruedenberg and R. D. Poshusta, Adv. Quantum Chem. 6, 267 (1972).

DATA ACCESS PROBLEM IN H-MATRIX CALCULATION

If H is accessed sequentially, then elements of g are needed at random, and vice versa.

Possible strategies:

- Multipass (work proportional to number of passes)
- Sorted formula tape (more efficient form of multipass, but needs explicit formula tape)
- Direct CI (inverted formula tape, or programmed for special cases)
- Special ordering of CF's and integrals

Some references:

Y. Yoshimine, J. Comp. Phys. 11, 333 (1973).

G. H. F. Diercksen and B. Suttcliffe, Theor. Chim. Acta 34, 105 (1974).

SPECIAL ORDERING APPROACH

(based on the assumption that $p >> h$)

The CF list is arranged so that all CF's which involve the same set of "particles" with all possible "holes", e.g.,

$$\Phi_{ij}^{ab}, \Phi_{ik}^{ab}, \ldots, \Phi_{k\ell}^{ab}, \ldots,$$

appear contiguously. Matrix element blocks involving two such sets, e.g.,

$$\langle \Phi_{xx}^{ab} | \hat{H} | \Phi_{xx}^{ac} \rangle$$

(where the x's stand for any hole combination), require integrals involving only certain particles (a, b, c above) plus holes. If the integrals are suitably arranged according to particle indices, then a whole block of $\underset{\sim}{H}$ can be computed with a limited (core-contained) set of integrals.

MATRIX ELEMENTS

Comments by J. Paldus

Graphical methods of spin-algebras[1-6] can be conveniently exploited in obtaining spin-free form of various theories exploiting the spin-independent Hamiltonian, particularly in conjunction with the graphical techniques based on the second quantization and Wick's theorem (see, for example, Refs. 7-14). In connection with the unitary group approach (see, for example, Refs. 15-21) they were exploited by Gouyet et al.[11] and via symmetric group approach by Drake and Schlesinger [12]. With this approach formulas analogous to those obtained earlier for elementary generators[17-19] can be obtained, as well as their generalization to the non elementary generators by Shavitt[21]. Moreover, following Drake and Schlesinger's approach[12], simpler formulas for the matrix elements of the generator products may be obtained as schematically indicated in Fig. 1. This Figure shows schematically the spin graphs (Jucys-Bandzaitis type[2]) for a general electronic Gelfand state[17,18], overlap, one and two generator matrix elements, and a schematic evaluation of the two-electron matrix elements using Shavitt[21] and Drake and Schlesinger[12] approaches. Note that dashed lines carry zero angular momentum and thin lines in Jucys-Bandzaitis diagrams carry ½ angular momentum.

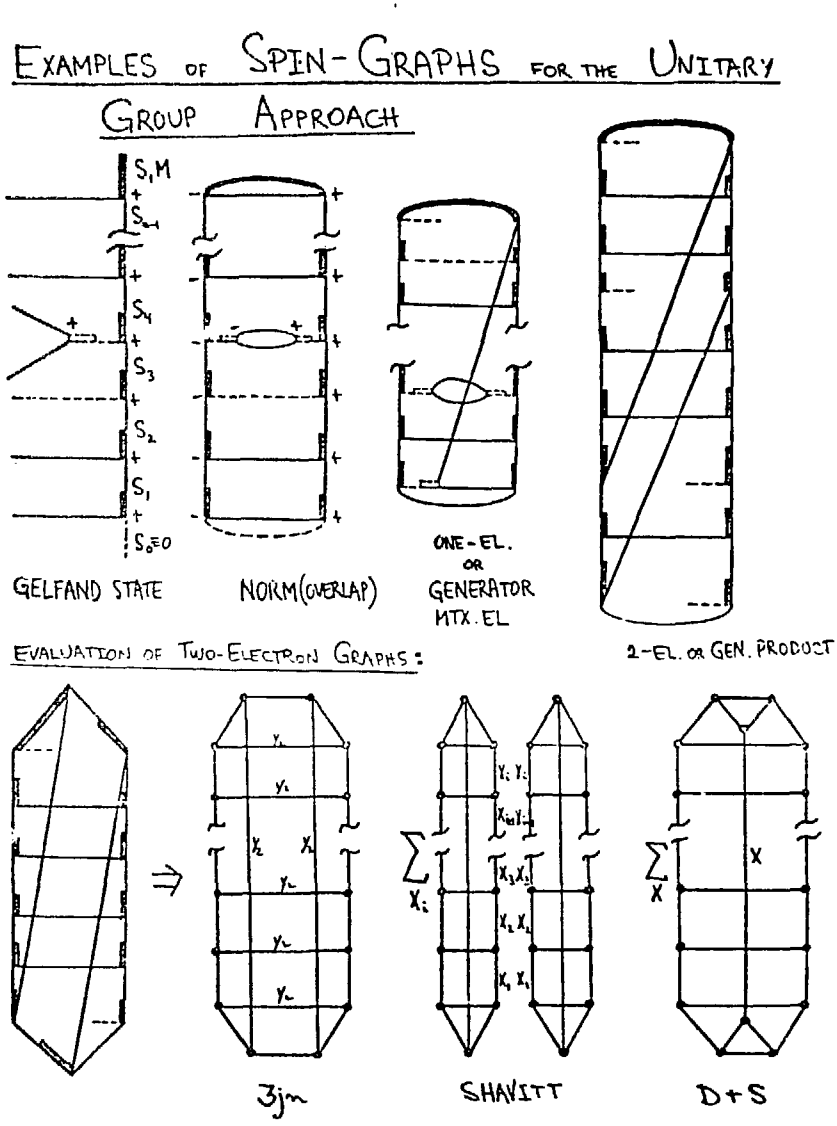
EXAMPLES OF SPIN-GRAPHS FOR THE UNITARY GROUP APPROACH
S,M
S_{n-1}
S_4
S_3
S_2
S_1
S_0=0
GELFAND STATE
NORM(OVERLAP)
ONE-EL.
OR
GENERATOR
MTX. EL
2-EL. OR GEN. PRODUCT
EVALUATION OF TWO-ELECTRON GRAPHS:
3jm
SHAVITT
D+S

Figure 1

Following Drake and Schlesinger[12] in the unitary group approach[7-14] one can avoid the summations in Shavitt's expressions[21] for the generator products, so that only two terms (corresponding to $x = 0$ and $x = 1$ in the Figure) have to be evaluated by multiplying contribution for each pertinent level in Gelfand tableau. The contributions for the "overlapping" part of the generator product are of two basic types as shown in the Table. For non-overlapping part the expressions given by Shavitt[21] apply (with $g(b) = 1$ and $f(b) = (-1)^b$ in the chosen phase factor convention). For the end-levels of the overlapping region formulas similar to those for elementary or single generator matrix elements result[22]. Using the same approach, similar results were also obtained for the particle-hole formalism[23].

INTERMEDIATE FACTORS FOR THE "OVERLAPPING" REGION OF THE TWO-ELECTRON MATRIX ELEMENTS IN THE UNITARY GROUP APPROACH

TYPE	X=0			X = 1		
	b b	b+2 b	b-2 b	b b	b+2 b	b-2 b
11	1	0	0	$-\rho(b-1)$	1	$\rho(b-2)$
22	1	0	0	$\rho(b)$	$\rho(b+1)$	1
12	0	0	—	$-\tau(b+1)$	$\tau(b+2)$	—
21	0	—	0	$-\tau(b)$	—	$\tau(b-1)$
00	1	0	0	$1-\delta_{b0}$	1	1
33	1	0	0	$1-\delta_{b0}$	1	1

WHERE $\rho(k) = \sqrt{\dfrac{k(k+3)}{(k+1)(k+2)}}$, $\tau(k) = (-)^k \sqrt{\dfrac{2}{k(k+1)}}$

PHASE CONVENTION USED CORRESPONDS TO THE FOLLOWING CHOICE OF SHAVITT'S $f(b)$ and $g(b)$ FUNCTIONS:

$$f(b) = (-)^b \ , \ g(b) = 1$$

Figure 2

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23. M. Boyle and J. Paldus, unpublished results.

A NOTE ON THE EXPRESSION OF FORMULAE FOR THE H-MATRIX

Comments by Kiyoshi Tanaka

Use of Second Quantization

(A) $\psi = \sum_i \psi_i C_i$

$$H = V_N + \Sigma h_{ij} C_i^+ C_j + \frac{1}{2} \Sigma (ij|kl)\ C_i^+ C_k^+ C_l C_j \qquad \text{(i)}$$

$\{\psi_i\} \rightarrow \{\{\psi_r\},\{\psi_k\}\}$

vacuum $|0\rangle = A \prod_r^n \phi_{r\alpha}\phi_{r\beta}$

$b_k = C_k$ particle

$a_r^+ = C_r$ hole

$E_o = \langle 0|H|0\rangle$

$\varepsilon_{ij} = h_{ij} + \sum_r^n \{2(ij|rr) - (ir|rj)\}$

(B) $\Psi = \sum_r \psi_r a_r^+ + \sum_k \phi_k b_k$

$$\begin{aligned} H = {} & E_o + \Sigma\, \varepsilon_{k\ell} b_k^+ b_\ell - \sum_{rs} \varepsilon_{rs} a_r^+ a_s \\ & + \Sigma\{(kr|s\ell) - (k\ell|sr)\} b_k^+ b_\ell a_r^+ a_s \\ & + \frac{1}{2} \Sigma\ (kn|\ell m) b_k^+ b_\ell^+ b_m b_n + \frac{1}{2} \Sigma (ur|ts)\ a_r^+ a_s^+ a_t a_u \\ & + \Sigma\ (\varepsilon_{kr} b_k^+ a_r^+ + h.c.) \\ & + \frac{1}{2} \Sigma\ [\{(kr|\ell m) - (km|\ell r)\} b_k^+ a_r^+ b_\ell b_m + h.c.] \\ & - \frac{1}{2} \Sigma\ \{(kr|st) - (kt|sr)\}\ b_k^+ a_r^+ a_t a_s + h.c.] \\ & + \frac{1}{2} \Sigma\ \{(kr|\ell s)\ b_k^+ b_\ell^+ a_s^+ a_r^+ + h.c.\} \end{aligned} \qquad \text{(II)}$$

where h.c. $\equiv$ hermitian conjugate.

(C) CSF's are expressed by b^+'s and a^+'s <u>for any spin multiplicity</u>

(D) Number of terms in Expression Formulae

example

$|0\rangle : \pi_1^2(\sigma\text{-core})$

(i) diagonal of $\pi_2\pi_1$(σ-core)

- $\varepsilon_{\pi_2\pi_2}, \varepsilon_{\pi_1\pi_1}, (\pi_2\pi_2|\pi_1\pi_1), (\pi_2\pi_1|\pi_1\pi_2)$ by (II)
- $h_{\pi_2\pi_2}, h_{\pi_1\pi_1}, (\pi_2\pi_2|\pi_1\pi_1), (\pi_2\pi_1|\pi_1\pi_2)$

  $h\sigma_i\sigma_i, (\pi_2\pi_2|\sigma_i\sigma_i), (\pi_1\pi_1|\sigma_i\sigma_i), (\pi_2\sigma_i|\sigma_i\pi_2), (\pi_1\sigma_i|\sigma_i\pi_1)$

  $(\sigma_i\sigma_i|\sigma_j\sigma_j), (\sigma_i\sigma_j|\sigma_j\sigma_i)$ (for all 's) by (I)

(ii) off diagonal $\pi_2\pi_1$(σ-core) & $\pi_3\pi_1$(σ-core)

- $\varepsilon_{\pi_3\pi_2}, (\pi_3\pi_2|\pi_1\pi_1), (\pi_3\pi_1|\pi_1\pi_2)$ by (II)
- $h_{\pi_3\pi_2}, (\pi_3\pi_2|\pi_1\pi_1), (\pi_3\pi_1|\pi_1\pi_2)$

  $(\pi_3\pi_2|\sigma_i\sigma_i), (\pi_3\sigma_i|\sigma_i\pi_2)$ (for all σ's) by (I)

in general

	Formulae (I)	Formulae (II)
diagonal	$\sim Ne^2$	$\sim(N_p+N_h)^2$
one orbital difference	$\sim Ne$	$\sim(N_p+N_h)$
two orbital difference	several	several

(E) <u>Effectiveness</u>

(i) system of large number of electrons
(ii) the first order CI & MCGBT in which number of elements due to one orbital difference is considerable

<u>Key</u>!

Use of closed shell function as a vacuum and ε's with hole-particle description

1. Use of the second quantized particle - hole description in order to reduce the number of terms of Expression Formulae
2. Comparison of the number of terms by (II) with those by (I)

n_e ; number of electrons

n_p ; number of particles

n_h ; number of holes

IV. FORMULA TAPE OR NOT

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FORMULA TAPE OR NOT

Presentation by E. R. Davidson

Depends on:

- Computer Hardware
- Physical Problem
- Acceptable Approximations

Nature of Problem:

$$\sum_{\mu\nu}^{\xi} \sum_{J}^{K} \sum_{ijkl}^{M^4} \Gamma_{ijkl}^{IJ\mu\nu} \quad W_{\mu I} W_{\nu J} [ij \| kl] C_J = E C_I$$

$[ij \| kl]$ Integral over MO's

$W_{\mu I}$ Symmetry/Spin Coupling Coefficients

$\Gamma_{ijkl}^{IJ\mu\nu}$ "Formula" for matrix element between elementary pieces of wavefunction

M = # of MO's 10 - 200

K = # of Config 1 - 10^5

ξ = # of elementary pieces/config 1 - 10^3

"Simple" special case CI

$$\tilde{\Gamma}^{IJ}_{ijkl} = \sum_{\mu\nu} \Gamma^{IJ\mu\nu}_{ijkl} \; W_{\mu I} \; W_{\nu J}$$

Tabulate by "Classes" of configurations based on excitations from one generating form.

Roos & Siegbahn

All SD excitations from one closed shell SCF configuration

$\tilde{\Gamma}$ held in core for each pattern

Schaefer extension to one SCF determinant open shell

Munch & Davidson V_a Atom $\tilde{\Gamma}$ on formula file (random), interacting subspace

Direct CI

$$\sum_{J\in B} \sum_{ijkl} \tilde{\Gamma}^{A,B}_{ijkl} [ij \parallel kl] \quad C_J = E \; C_I \qquad I\in A$$

Indirect CI

$$H_{IJ} = \sum_{ijkl} [ij \parallel kl] \; \tilde{\Gamma}^{AB}_{ijkl} \qquad I\in A,\ J\in B$$

Advantage: Speed

Disadvantage: Inflexible, range of problems limited

GENERAL CI

SHAVITT: Tabulate $\Gamma^{IJ\mu\nu}_{ijkl}$ on tape

Form $\sum_{\mu\nu} W_{\mu I} \; W_{\nu J} \left(\sum_{ijkl} \Gamma^{IJ\mu\nu}_{ijkl} \; [ij \parallel kl] \right) = H_{IJ}$

IBM: Tabulate $\tilde{\Gamma}^{IJ}_{ijkl}$, Sort on ijkl ,

Form $\tilde{\Gamma}^{IJ}_{ijkl} \; [ij \parallel kl]$, sort on IJ $\rightarrow H_{IJ}$

BENDER: Tabulate $\tilde{\Gamma}^{IJ}_{ijkl}$ on tape

Direct CI

$$\sum_{ijkl} [ij \parallel kl] \sum_{J} \tilde{\Gamma}^{IJ}_{ijkl} \; C_J = E \; C_I$$

Or Indirect $H_{IJ} = \sum_{ijkl} \tilde{\Gamma}^{IJ}_{ijkl} \; [ij \parallel kl]$

DAVIDSON: Tabulate ijkl for each IJ , in core ,

Replace Label ijkl in Table by $[ij \parallel kl]$

Form $H_{IJ} = \sum_{\mu\nu} \left(\sum_{ijkl} [ij \parallel kl] \; \Gamma^{IJ\,\mu\nu}_{ijkl} \right) W_{\mu I} \; W_{\nu J}$

Generating $\Gamma^{IJ\,\mu\nu}_{ijkl}$ as needed

FORMULA TAPE

ADVANTAGE

- SAVES TIME IF SAME SET OF CONFIGURATIONS IS USED FOR SEVERAL CALCULATIONS

DISADVANTAGE

- SLOW IF CONFIG. LIST IS USED ONLY ONCE
- LARGE STORAGE REQUIREMENTS
- OFTEN CAUSES CHOICE OF CONFIGS. TO BE ADAPTED TO USE OF FORMULA TAPE. CONFIGS. USED REPEATEDLY EVEN IN INO GENERALLY SLOWER THAN CLASS FORMULA HELD IN CORE

NO FORMULA TAPE

ADVANTAGE

- LOW STORAGE REQUIREMENTS
- ENCOURAGES BETTER CHOICE OF CONFIGURATIONS AT EACH GEOMETRY OR INO

DISADVANTAGE

- REPEATS MUCH LOGIC IF SAME SET OF CONFIGURATIONS IS USED
- CLASS FORMULA IS FASTER FOR "SIMPLE" CI
- REQUIRES MULTI-READ OR RANDOM ACCESS TO INTEGRALS

Comments by M. Yoshimine

- Formula tape is needed for:

  1) Potential surface calculations,
  2) Very long integral list.

- Construction of H_I by blocks.

  Integral list $\chi \Rightarrow \chi_1 + \chi_2 + \dots \chi_N$.

  $$H_I = \Sigma\, C_{I,P}\chi_P \Rightarrow H_I = \sum_n H_{I,n} ,$$

  $$H_{I,n} = \sum_{P_n} C_{I,P_n}\, \chi_{P_n} .$$

Three step process:

1. Reorder $C_{I,P}$ to C_{I,P_n};
2. Carry out $H_{I,n} = \sum_{P_n} C_{I,P_n}\chi_{P_n}$;
3. Carry out $H_I = \sum_n H_{I,n}$.

- Packing of the formula tape (ALCHEMY program - IBM computer).

$C^I_{P_n}$:

I	P	C
4	4	8 bytes

Packed $C^I_{P_n}$

I'	P'	C'
1	2	1

Table of C

I' = chained I index
P' $1 \leqslant P' < N_e$ 30,000
c' = index of C in the table.

MUNICH MOLECULAR PROGRAM SYSTEM

Comments by G. H. F. Diercksen

CI Program:

includes subprograms for

- Configuration Generation
- Symbolic Matrix Element Generation
- Symbolic Matrix Element "Inversion"
- Numerical Matrix Element
- Diagonalization

All subprograms are logically independent and use the Standard Data Interface philosophy. The CI program is based on the work of Boys, Reeves, and Yoshimine.

Characteristics

- Dynamic main and external storage allocation, thus no fixed dimension is necessary. The maximum size of soluble problem is defined by main storage, and computer time available at the time.
- The formula tape may be generated explicitly or implicitly; in the second case it is not saved.
- The program may be run stepwise, extensive interrupt/restart/checkpoint procedures are available.

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V. DIAGONALIZATION TECHNIQUES

(Report from the Numerical Algorithms Workshop)

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Presentation by I. Shavitt

LANCZOS METHOD

In effect, the desired eigenvectors are expended in the Schmidt-orthogonalized version of the Krylov sequence,

$$\underset{\sim}{v},\ \underset{\sim}{A}\underset{\sim}{v},\ \underset{\sim}{A}^2\underset{\sim}{v},\ \ldots$$

In exact arithmetic, the orthogonal sequence obeys a 3-term recurrence relation, but numerical errors lead to loss of orthogonality, and eventually loss of linear independence. However, this loss is a symptom of convergence (e.g., if $\underset{\sim}{v}$ is an eigenvector, then $\underset{\sim}{A}\underset{\sim}{v}$ is linearly dependent upon it). Selective orthogonalization (parlett and Scott) can be used to remove the converged vectors.

The Lanczos method is not competitive with quantum-chemical methods for diagonally dominant matrices.

References:

C. C. Paige, J. Inst. Math. Applies 10, 373 (1972); 18, 341 (1976).

B. N. Parlett and D. S. Scott, "The Lanczos Algorithm with Implicit Deflation," Memorandum No. UCB/ERL M77/70, Electronics Research Laboratory, UC Berkeley (2 Dec. 1977).

R. Underwood, "An Iterative Block Lanczos Method for the Solution of Large Sparse Eigenproblems," Report STAN-CS-75-496 (Stanford, Comp. Sci. Dept. 1975).

DAVIDSON'S METHOD

This is similar, in some ways, to the Lanczos method, except that the Krylov sequence is replaced, in effect, by the sequence

$$\underset{\sim}{v},\ (\underset{\sim}{D}-\rho)^{-1}\ \underset{\sim}{A}\underset{\sim}{v},\ \ [(\underset{\sim}{D}-\rho)^{-1}\underset{\sim}{A}]^2\ \underset{\sim}{v},\ \ldots$$

where $\underset{\sim}{D} = \mathrm{diag}(\underset{\sim}{A})$, and ρ is the Rayleigh quotient of the current approximation. This is not strictly correct, since ρ and $\underset{\sim}{v}$ vary as the iterations proceed.

This is much more effective than the Lanczos method for diagonally dominant matrices, but produces one eigenvector at a time. It is closely related to perturbation theory.

References:

R. E. Davidson, J. Comput. Phys. 17, 87 (1975).

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PERTURBATION-VARIATION METHODS
(Roos & Siegbahn; Seeger, Krishnan & Pople)

These are closely related to Davidson's method. The expansion is in a sequence of the type

$$\underset{\sim}{v}_o,\ (H_o-\rho)^{-1}\ \underset{\sim}{H}\underset{\sim}{v}_o,\ [(\underset{\sim}{H}_o-\rho)^{-1}\ \underset{\sim}{H}]^2\ \underset{\sim}{v}_o,\ \ldots$$

where

$$\underset{\sim}{H}_o = \sum_s |s\rangle\ \alpha_s\ \langle s|$$

$\alpha_s = H_{ss}$ (Davidson)

$\alpha_s = \sum_{i \in s} \eta_i \varepsilon_i$ (Roos, Pople)

$\rho, \underset{\sim}{v}_o$ from best current approximation (Davidson, Pople - actually sequence of 1st-order calculations)

$\rho = E_o$, $\underset{\sim}{v}_o$ fixed (Roos).

References:

B. J. Roos and P. E. M. Siegbahn, in "Methods of Electronic Structure Theory," Ed. H. F. Schaefer III (Plenum, New York, 1977) p. 277.

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SIMULTANEOUS ITERATIONS FOR SEVERAL ROOTS

For Davidson's method: B. Liu
For Coordinate relaxation: R. C. Raffenetti, I. Shavitt

Advantages:

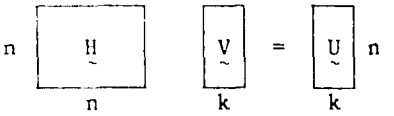
- Reduced I/O costs (one read through the matrix per iteration for all roots combined).
- For relaxation method, overcomes slow convergence for closely-spaced roots.

Disadvantages:

- More central storage required (2 vectors per root sought).
- For Davidson's method, higher-dimensional "small" eigenvalue problems.

SIMULTANEOUS COORDINATE RELAXATION

For k roots,



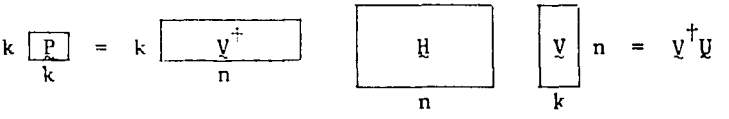
$\underset{\sim}{V}$ is the current set of trial vectors. The i-th row of $\underset{\sim}{V}$ is relaxed simultaneously, using coordinate relaxation with root shifting, for i=1,2,...,n. Then we solve a small generalized eigenvalue problem (k×k)

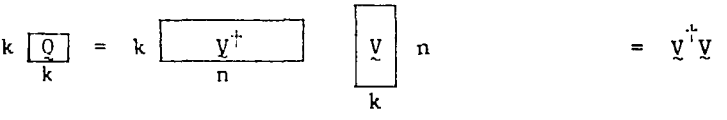
$$\underset{\sim}{P}\underset{\sim}{Y} = \underset{\sim}{Q}\underset{\sim}{Y}\underset{\sim}{R} \quad \text{(diagonal)}$$

subject to

$$\underset{\sim}{Y}^{+}\underset{\sim}{Q}\underset{\sim}{Y} = 1 \ ,$$

where





and then transform to new $\underset{\sim}{V}' = \underset{\sim}{V}\underset{\sim}{Y}$.

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R. C. Raffenetti (to be published)

I. Shavitt (unpublished)

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L. E. Nitsche & R. E. Davidson, J. Chem. Phys. 68, 3103 (1978); J. Am. Chem. Soc. (in press).

VI. THE DIRECT CI METHOD

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THE DIRECT CI METHOD

Presentation by B.Roos

A CI-METHOD IS CALLED DIRECT IF THE CORRESPONDING SECULAR PROBLEM IS SOLVED DIRECTLY FROM THE INTEGRAL REFERENCES WITHOUT THE EXPLICIT CONSTRUCTION OF A HAMILTONIAN MATRIX.

VARIANT A: NO USE OF A FORMULA TAPE

THE STOCKHOLM DIRECT CI PROGRAMS.

THE APPROACH OF THE TORUN GROUP?(3)

VARIANT B: WITH FORMULA TAPE

THE VECTOR METHOD BY BENDER ET AL.(4)

METHODS BASED ON GELFAND STATES AND THE UNITARY GROUP (PALDUS, ROBB AND SHAVITT(2)).

Figure 1

Comments to Figure 1

There have recently been some arguments regarding when a CI method is direct. I therefore found it appropriate to start this overview with a definition of what I mean by a direct CI method. The original formulation of the method[1] included some important features apart from those given in the definition. No formula tape was used. Instead, for each two-electron integral (the one-electron integrals are trivial to handle) a loop structure could be defined and the coupling coefficients could be programmed explicitly into these loops. In this way the program became almost completely core-bound, which made it possible to work with very large CI-expansions (a current study of the H_2O energy surface includes around 76,000 configuration state functions).

In the extension of the original program (closed shell plus all single-double replacements) to treat more general cases, we have tried to follow the original philosophy since it has been our feeling that the use of a formula tape would lower the effectiveness of the method too much and would not make it more efficient than conventional CI methods. With the new unitary group approach, especially that developed along the lines advocated by Shavitt,[2] this may no longer be true. A similar extension of the direct scheme to treat the case of an arbitrary open-shell reference configuration has recently been proposed by Duch and Karwowski.[3] It is based on so-called SAAP's instead of Gelfand states, and the coupling coefficients are also given here in forms of irreducible representations of the unitary group. It remains to be seen whether this method can be effectively programmed.

The vector method of Bender and co-workers[4] represents a direct scheme where a formula tape is utilized. The efficiency of this method compared to conventional CI techniques is, however, at present not apparent to me.

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OUTLINE OF THE DIRECT CI-METHOD

SECULAR PROBLEM

$$(\underline{H}-E\underline{S})\underline{c}=0 \qquad (1)$$

ANY METHOD OF SOLUTION BASED ON THE CONSTRUCTION OF THE VECTOR $\underline{\sigma}$ IS PERMITTED IN THE DIRECT CI SCHEME

$$\underline{\sigma}=\underline{H}\underline{c} \qquad (2)$$

$\underline{\sigma}$ IS RESOLVED INTO INTEGRAL REFERENCES:

$$\sigma_K = \sum_{PQ} H_{PQ} \sum_L A_1(KL:PQ)c_L + \sum_{PQRS}(PQ/RS) \sum_L A_2(KL:PQRS)c_L \qquad (3)$$

THE PROBLEM IN A DIRECT CI SCHEME IS

A. TO REDUCE THE DOUBLE LOOP KL OVER CONFIGURATIONS

B. TO FIND EASY-TO-USE ALGORITHMS TO DETERMINE A_1 AND A_2.

Figure 2

Comments to Figure 2

The direct CI scheme is based on the direct construction of the $\underline{\sigma}$-vector, Eq. (2), from the integral list according to Eq. (3). This means that the secular problem has to be solved by an iterative or perturbative method where the essential step is the construction of $\underline{\sigma}$ from the $\underline{c}$-vector obtained in the preceding iteration. Methods based on Krylov sequences are thus suitable here, as are methods based upon perturbation theory, where $\underline{\sigma}$ is used to construct the perturbation vector $\underline{c}^{(n)}$ from $\underline{c}^{(n-1)}$. In practice we use a variation-perturbation method[5] suggested by Brändas and Goscinski[6] where the perturbation expansion is followed by a variational calculation using the perturbations as basis functions. This procedure normally converges very fast; more than 6 to 8 iterations are seldom needed.

The crucial step in the direct scheme is the calculation of the $\underline{\sigma}$-vector according to Eq. (3). For each integral there is in principle a double loop over all configurations. For the method to be useful this loop has to be reduced. In the case of a closed shell reference configuration, comprising in the CI expansion all single and double replacements, this is done by dividing the integrals into different classes.

References

5. B.Roos and P.Siegbahn, in Chemical and Biochemical Reactivity, The Jerusalem Symposia on Quantum Chemistry and Biochemistry, The Israel Academy of Sciences and Humanities, Jersalem, 1974.

6. E.Brändas and O.Goscinski, Phys. Rev. A1, 552 (1970).

Classes of Integrals contributing to Q, from the interaction between doubly excited configurations (μ = ij → ab, ν = kl → cd)

i, j, k, l = occupied orbitals ; a, b, c, d = virtual orbitals

1	(ik ‖ jl) ,	(il ‖ kj)	4 occ.	0 virt.
2	(ai ‖ ck) ,	(aj ‖ ck)	2 occ.	2 virt.
	(bi ‖ ck) ,	(bj ‖ ck)		
3	(ac ‖ ki) ,	(ac ‖ kj)	2 occ.	2 virt.
	(bc ‖ ki) ,	(bc ‖ kj)		
4	(ac ‖ bd) ,	(ad ‖ bc)	0 occ.	4 virt.

Figure 3

Comments to Figure 3

These classes are illustrated in Fig. 3 for the case of interactions between doubles in the closed shell case. As you can see there are only four different classes of integrals in this case [the addition of single replacements also introduces the classes (ai/jk) and (ab/ci)]. Each class corresponds to a double loop over orbital indices. Thus the loop over configurations occurring in (3) is reduced to an n^2, nm or m^2 loop (n and m being the number of occupied and virtual orbitals, respectively). The second class of integrals is most time-consuming and since they are of the order of n^2m^2 the whole calculation becomes approximately an n^3m^3 procedure (notice that n is much smaller than m).

LOOP STRUCUTRE FOR THE CALCULATION OF THE $\underline{\sigma}$-VECTOR.

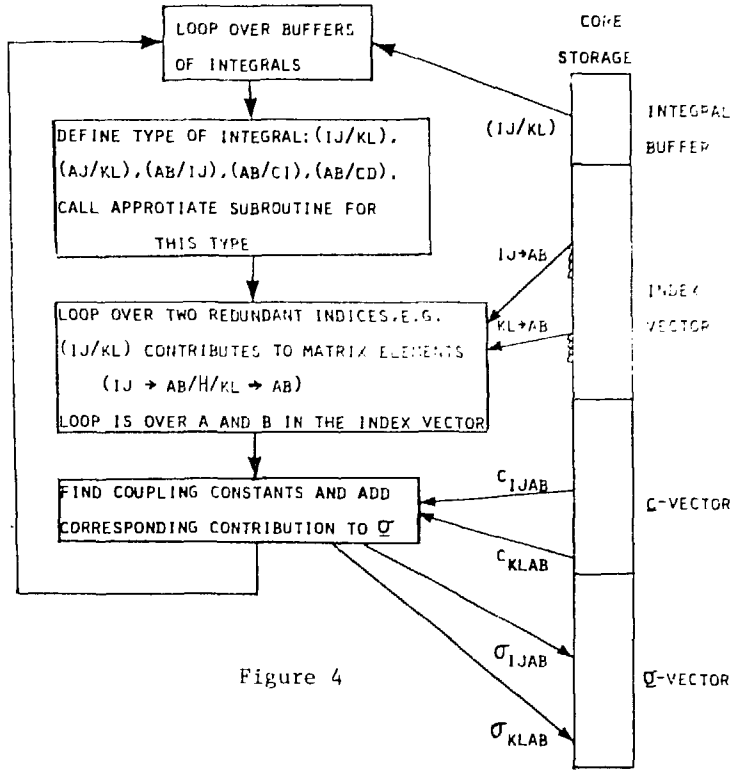


Figure 4

Comments to Figure 4

The figure shows the detailed structure of the calculation of the $\underline{\sigma}$-vector in the closed shell case. There is an outer loop over two-electron integrals. Each integral is classified and the appropriate subroutine corresponding to the loop structure of that class is called. Addresses of the CI coefficients are given by an index vector which stores them canonically by the indices i,j and a,b. Indirect addressing can also be used for this if the length of the index vector becomes too large. The double loop over redundant indices now defines the pair of interacting configurations. The corresponding coupling coefficients are explicitly programmed into these subroutines. The contribution to the appropriate components of the $\underline{\sigma}$-vector can therefore be immediately obtained. I shall show later that this loop structure can actually be used also in the general case (arbitrary open-shell reference configuration).

TIMING DATA FOR THE CISD PROGRAM ON AN IBM 360/91 COMPUTER

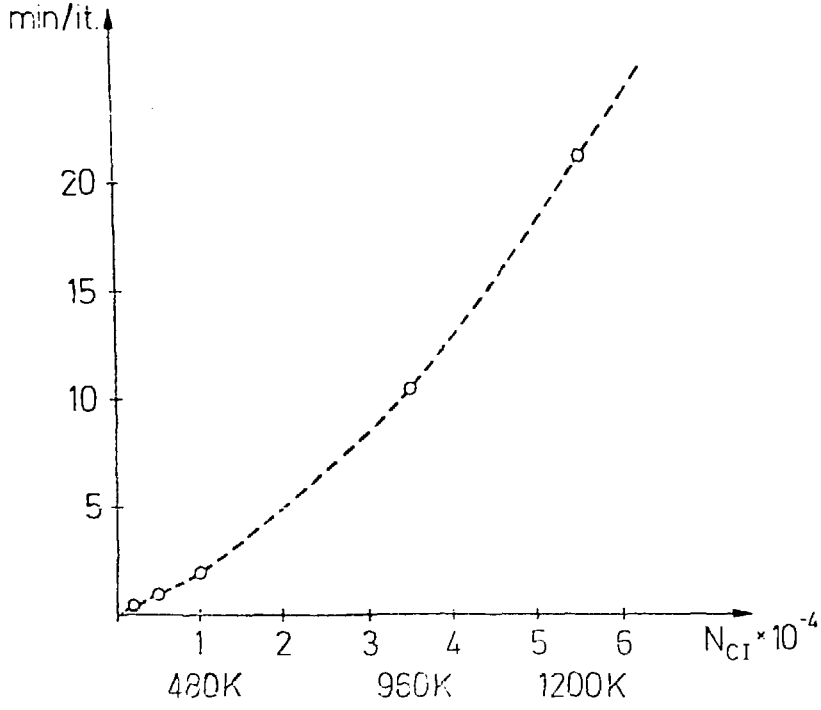


Figure 5

Comments to Figure 5

This figure shows some timing data obtained in calculations on the IBM 360/91 computer at the Max-Planck institute at München, using the CISD program. The curve shows a dependence on N_{CI} which is smaller than $N_{CI}^{1.5}$ for N_{CI} less than around 30,000 configurations, but approaches this dependence for larger expansions. Limit of present day programs lies around 10^5 configuration.

Actually the core-space requirements can be reduced considerably by a two-level addressing system for the index vector. In a first vector each configuration is given as present (1) or not present (0). This information can be stored bit-wise. A second small vector counts the number of one's in each full word and thus gives the address. A small assembler routine is used to perform this addressing. The whole procedure leads to an increase in CPU time of around 20%, but the core memory requirements can be reduced by one-third.

OUTLINE OF THE DIRECT CI-METHOD WITH AN MC REFERENCE STATE

CI-EXPANSION $$\Psi = \sum_{i=1}^{N} \left\{ C_{i0}\Phi_{i0} + \sum_{\nu} C_{i\nu}\Phi_{i\nu} \right\} = \sum_{i} \mathbb{C}_i \Phi_i$$

WHERE $$\Psi_0 = \sum_{i=1}^{N} C'_{i0}\Phi_{i0}$$

IS AN MC-SCF WAVE FUNCTION

AND $\Phi_{i\nu}$ REPRESENT SINGLE AND DOUBLE REPLACEMENT STATES WITH RESPECT TO THE MC CONFIGURATION Φ_{i0}.

THE SCHRÖDINGER EQUATION TAKES THE FORM

$$\begin{bmatrix} \langle\Phi_1|\hat{H}|\Phi_1\rangle & \langle\Phi_1|\hat{H}|\Phi_2\rangle & \cdots\cdots \\ \langle\Phi_2|\hat{H}|\Phi_1\rangle & \langle\Phi_2|\hat{H}|\Phi_2\rangle & \cdots\cdots \\ \cdots & \cdots & \cdots \\ & & \\ & & \end{bmatrix} \begin{bmatrix} \mathbb{C}_1 \\ \mathbb{C}_2 \\ \vdots \\ \\ \\ \end{bmatrix} = E \begin{bmatrix} \mathbb{C}_1 \\ \mathbb{C}_2 \\ \vdots \\ \\ \\ \end{bmatrix}$$

THE PRESENT VERSION ASSUMES Φ_{i0} TO BE CLOSED SHELL DETERMINANTS.

SOLUTION IS OBTAINED BY MEANS OF VARIATION-PERTURBATION THEORY AS IN THE CASE OF A SINGLE REFERENCE CONFIGURATION.

Figure 6

Comments to Figure 6

The direct CI method in variant A has recently been extended to include a multiconfigurational reference state. The wave function is expanded in a small set of reference configurations, and all single and double replacements out of these configurations. The reference configurations have in the first version of the program been restricted to be closed shell determinants. Redundant configurations occurring in the CI expansion are eliminated via the index vector introduced earlier. The orbitals and a zeroth order wave function are obtained by an MC-SCF calculation which precedes the CI step. The CI secular problem is then solved by the same variation-perturbation treatment as was used in the single reference configuration case. This method is easily extended to the case of an MC zeroth order wave function. Included in the CI expansion are also the other roots of the MC problem. The coefficients C_{io} and C'_{io} in the first equations of this figure are therefore in general different.

The secular problem can be blocked into subspaces corresponding to the replacements in the different reference configurations. This greatly simplifies the calculation of the $\underline{\sigma}$-vector, since the diagonal blocks can be treated in the same way as was done in existing programs. The only additions needed to the loop structure given in Fig. 4 is a loop over reference configurations and a relabelling of integral indices. The timing in this part is therefore proportional to the number of reference configurations. New subroutines had to be written for the off-diagonal blocks of matrix elements. Only those blocks where the reference configurations differ in two, four or six spin-orbitals will give a non-zero contribution to $\underline{\sigma}$. The case of two is handled the direct way, while the other blocks are obtained by calculating the actual matrix elements, since there are very few of them.

AN EXAMPLE OF AN CIMC CALCULATION

ENERGY SURFACE FOR THE H_2O MOLECULE, ESPECIALLY THE CHANNELS

$$H_2O - H_2(^1\Sigma_G^+) + O(^1D)$$

AND $$H_2O - H(^2S) + OH(^2\Pi)$$

NUMBER OF BASIS FUNCTIONS: 44
NUMBER OF REFERENCE CONFIGURATIONS: 10
NUMBER OF CSF'S: 76471

CPU-TIME PER ITERATION: 21 MINUTES (ALMDAHL 470)

Figure 7

Comments to Figure 7

As an example of a calculation with this new direct CI, we give some data from a study of the energy surface for the water molecule.

Notice that the timing here (ALMDAHL is only slightly faster than IBM 360/91) is much more favorable than in the single reference configuration case (Fig. 5). The reason is that most of the time is spent in the diagonal blocks, and the iteration time is therefore proportional to

$$N_{ref} \times N_{sub}^{1.5}$$

where N_{ref} is the number of reference configurations and N_{sub} is the number of excitations out of a given reference configuration. This is much smaller than

$$N_{CI}^{1.5} = (N_{ref} \times N_{sub})^{1.5} .$$

In the water case, $N_{ref} = 10$ and $N_{sub} = 8000$ (approx.), which fits very nicely to the curve given on Fig. 5.

THE CASE OF A GENERAL REFERENCE CONFIGURATION (DUCH AND KARWOWSKI(3)).

A. REFERENCE CONFIGURATION OF GENERAL SPIN-MULTIPLICITY

B. NO LIMITATION TO EXCITATION LEVEL

C. CSF'S ARE CONSTRUCTED AS SAAP'S:

$$\Phi_{SM}(\underline{r},\sigma) = \frac{1}{\sqrt{f_S^N}} \sum_{k=1}^{f_S^N} \chi_{S,k}(\underline{r})\, \Theta_{SM,k}(\sigma)$$

D. EXAMPLE OF A MATRIX ELEMENT

$$H_{KL} = \langle \Phi_K | H | \Phi_L \rangle$$ WHERE

$N_K(P)=N_K(R)=1$ AND $N_K(Q)=N_K(S)=0$ $\qquad$ $P=Q=R=S$

$N_L(P)=N_L(R)=0$ AND $N_L(Q)=N_L(S)=1$

$$H_{KL} = \left[(PQ/RS) + U_S^N((QS))(RQ/PS)\right] U_S^N(P_0)$$

WHERE U_S^N ARE THE IRREDUCIBLE REPRESENTATION MATRICES OF THE PERMUTATION GROUP CORRESPONDING TO THE N OPEN SHELLS OF CONFIGURATION K, P_0 IS THE SO CALLED LINE UP PERMUTATION IN THE OPEN SHELL PART AND (QS) IS A TRANSPOSITION

Figure 8

Comments to Figure 8

The theoretical chemistry group in Torun, Poland has recently come out with a method for calculating the coupling constants needed in a direct CI scheme, for a general spin-adapted reference configuration and any level of excitation from it. The configurations are in this method given as spin-adapted antisymmetrized products of orbital and spin functions (SAAP's), where the spin-functions are chosen to transform according to the irreducible representations of the permutation group. The space-functions will then transform according to the dual representations. I will not go through the theory presented by them in any detail, especially since it is rather new to me also. The example of a matrix element expression given in Fig. 8 will probably suffice to give an idea of the method.

The problem is probably to be able to store all the information imbedded in the irreducible representation matrices in such a way that the corresponding coupling constants can be easily retrieved, when needed. This problem has not yet been sufficiently analyzed.

OCCUPATION NUMBERS FOR THE INTEGRAL (PQ/RS) WITH ALL INDICES DIFFERENT IN DK'S METHOD.

No	$N_K(P)$	$N_K(Q)$	$N_K(R)$	$N_K(S)$	$N_L(P)$	$N_L(Q)$	$N_L(R)$	$N_L(S)$	CASE*
1	1	0	1	0	0	1	0	1	1
2	1	0	1	1	0	1	0	2	7
3	1	1	1	1	0	2	0	2	11
4	1	0	2	1	0	1	1	2	3
5	1	1	2	1	0	2	1	2	9
6	2	1	2	1	1	2	1	2	6

*J. KARWOWSKI, THEORET CHIM ACTA 29,151 (1973).

LOOP STRUCUTRE FOR K AND L FOR CASE No 1
(DOUBLY EXCITED CONFIGURATIONS)

G.S. OCCUPATION					
$N_0(P)$	$N_0(Q)$	$N_0(R)$	$N_0(S)$	K	L
1	1	1	1	QS - CD	PR - CD
1	0	0	1	IS - CR	IP - CQ
0	1	1	0	QI - PC	RI - CS

LOOP INDICES (REDUNDANT INDICES) ARE UNDERLINED. IF THE INTEGRAL IS ALSO CLASSIFIED ACCORDING TO THE OCCUPATION NUMBERS OF CORRESPONDING ORBITALS IN THE REFERENCE CONFIGURATION, THE LOOP STRUCUTRE IS DEFINED.

Figure 9

Comments to Figure 9

Duch and Karwowski (DK) also give for each type of integral the occupation numbers of the configurations interacting via this integral. Their tables can actually be used to obtain a loop structure corresponding to a given class of integrals. The integral classes will be defined by: 1) the number of equal indices, and 2) occupation numbers of the corresponding orbitals in the reference state. An example is given on this figure. The table shows possible occupation numbers in configurations interacting via an integral (pq/rs) with all indices being different. The case numbers given in the last column of the table give the form of the matrix element as reported by Karwowski in an earlier paper.

The lower part of the figure shows the three possible loop structures corresponding to different occupations of p, q, r, and s in the reference configuration. The example shows the interaction between doubly excited configurations and corresponds to the first line in the table. Obviously these loop structures are identical to those obtained in the closed shell case (Fig. 4). It should thus (if the coupling constants can easily be obtained) be possible to write a parallel direct CI program for the general spin-state, using the same philosophy as was used in the closed shell case.

DIRECT CI PROGRAMS IN WORK TODAY

1. CISD (CS REFERENCE CONFIGURATION+ ALL SINGLES AND DOUBLES)[1a]

2. CIUHF (UHF REFERENCE DETERMINANT + ALL SINGLES AND DOUBLES)[1b]

3. CI3 (COMPLETE CI FOR THREE ELECTRONS)[7]

4. CITRI (TRIPLET REFERENCE CONF. + ALL SINGLES AND DOUBLES)[8]

5. CIMC (MC REF.STATE +ALL SINGLES AND DOUBLES OUT OF ALL REFERENCE CONFIGURATIONS)[9]

Figure 10

References

7. P.Siegbahn, Quantum Chemistry: The State of the Art, edited by V.R.Saunders and J.Brown (Science Research Council, London, 1975).

8. R.R.Lucchese and H.F.Schaefer III, J. Chem. Phys. 68, 769 (1978).

9. B.Roos and P.Siegbahn, J. Amer. Chem. Soc. 99, 7716 (1977).

Comments to Figure 10

This figure lists some of the direct CI programs presently in work.

1. CISD is the original closed shell CI program which has now been rewritten so that pp-hh coupling can be used instead of ph-ph coupling, which was the original form.
2. CIUHF works with determinants and can use UHF orbitals as the one-electron basis. It has mainly been used for studies of radical systems. Comparison with other programs shows that almost identical results are obtained with UHF-CI and RHF-CI (if the CI is complete in the interacting space) in spite of the fact that UHF-CI wavefunction is not a proper spin function.
3. This program (CI3) works with a complete CI expansion for three electrons.
4. The direct CI program for triplet states was written by Lucchese. It is interesting since it was written for a Harris/4 minicomputer, showing that the direct CI method is practical on such computers. Due to core limitations it was found preferable to work with a formula tape, in spite of the fact that the program was originally written in variant A. A double-level addressing in the index vector would probably have made it possible to treat much larger expansions in core, without the necessity to go on tape.
5. The CIMC program has been described above. So far it has been used in a number of studies of energy surfaces, such as H_2O, CH_2, O_3, C_4H_4, and a number of diatomics.
6. One program is missing in this figure -- a direct CI program for doublet states written by Taylor and Bacskay in Sidney.[10] Except for the variational single and double CI, it includes a number of CEPA-like procedures also, for including corrections from higher order excitations.

Reference

10. P.Taylor, G.Bacskay, A.C.Hurley, and N.S.Hush, J. Chem. Phys., (submitted for publication).

Comments by C. F. Bender

VECTOR METHOD SYNOPSIS

+ Near linear relationship between number of determinants and computer times

+ Faster than standard CI diagonalization techniques

+ Handles multiroot, multiconfiguration states

- Configurations can be easily generated

- Formula tape technique further reduces computer time

– Slater determinant rather than spin eigenfunctions

EARLY VECTOR METHOD CODES

NSM

- 60 spin orbitals
- 30 K Slater determinants
- Lanczos and Davidson diagonalization
- Vectorized sort/merge techniques

VM

- 60 spin orbitals
- 10 K Slater determinants
- Davidson diagonalization
- Hermiticity of H_{op} incorporated
- Formula tape generation for increased speed

BASIC VECTOR METHOD (VM)

$$H_{op}\, \underset{\sim}{d}_E^+ \underset{\sim}{\varphi} = E \underset{\sim}{d}_E^+ \underset{\sim}{\varphi}$$

$$H_{op} = \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta \,|\, H \,|\, \gamma\delta \rangle\, a_\alpha^+ a_\beta^+ a_\delta\, a_\gamma$$

$$\langle \alpha\beta \,|\, H \,|\, \gamma\delta \rangle = \frac{1}{N-1} \langle \alpha \,|\, H_1 \,|\, \delta \rangle \langle \beta \,|\, \gamma \rangle + \frac{1}{2} \langle \alpha\beta \,|\, H_2 \,|\, \gamma\delta \rangle$$

φ_p is a Slater determinant

Closure

$$\underset{\sim}{H}_{op}\, \underset{\sim}{d}_E^+ \underset{\sim}{\varphi} = \underset{\sim}{e}^+ \underset{\sim}{\varphi} + \underset{\sim}{R}$$

$$E = \langle \underset{\sim}{d}_E^+ \underset{\sim}{\varphi} \,|\, \underset{\sim}{e}^+ \underset{\sim}{\varphi} + \underset{\sim}{R} \rangle / \langle \underset{\sim}{d}^+ \underset{\sim}{\varphi} \,|\, \underset{\sim}{d}^+ \underset{\sim}{\varphi} \rangle$$

$$= \langle \underset{\sim}{d}_E^+ \underset{\sim}{\varphi} \,|\, \underset{\sim}{e}^+ \underset{\sim}{\varphi} \rangle / \langle \underset{\sim}{d}^+ \underset{\sim}{\varphi} \,|\, \underset{\sim}{d}^+ \underset{\sim}{\varphi} \rangle$$

SPIN ADAPTED VECTOR METHOD (SVM)

$$H_{op} \underset{\sim}{\Psi} = E \underset{\sim}{\Psi}$$

Ψ_p are spin eigenfunctions

$$\Psi_p = \sum_k C_{pk} S_{pk}$$

where S_{pk}'s are Slater determinants. Because of closure for Slater determinants

$$H_{op} \underset{\sim}{\Psi} = \underset{\sim}{e}^{+} \underset{\sim}{\Psi} + \underset{\sim}{R}$$

$$E \equiv \langle \underset{\sim}{\Psi} H_{op} \underset{\sim}{\Psi} \rangle / \langle \underset{\sim}{\Psi} \mid \underset{\sim}{\Psi} \rangle$$

$$= \langle \underset{\sim}{\Psi} \underset{\sim}{e}^{+} \underset{\sim}{\Psi} \rangle / \langle \underset{\sim}{\Psi} \mid \underset{\sim}{\Psi} \rangle$$

thus spin eigenfunctions (linear combinations) of Slater determinants can be used.

SPIN-ADAPTED VECTOR METHOD FORMULA TAPE

For all unique orbital indices

$$Q_{ijkl}\underset{\sim}{\Phi} \rightarrow \underset{\sim}{V}_{ijkl}\underset{\sim}{\Phi}$$

For $ij \neq kl$ $\underset{\sim}{V}_{ijkl}$ is very sparse and can be stored compactly

$$Q_{ijij}\underset{\sim}{\Phi} = \underset{\sim}{B}\,\underset{\sim}{\Phi}$$

where

$$\underset{\sim}{B}_k = \langle \underset{\sim}{\Phi}_k | H_{op} | \underset{\sim}{\Phi}_k \rangle$$

Formula tape steps

1. Construct and save $\underset{\sim}{V}_{ijkl}$
2. At diagonalization time
   a. construct $\underset{\sim}{B}$
   b. broadcast $\tilde{A}_{ijkl} * \underset{\sim}{V}_{ijkl}$
   c. diagonalize by repeated steps

$$H\underset{\sim}{\Psi} = E\underset{\sim}{\Psi}$$

ALTERNATIVE FORM OF HAMILTONIAN OPERATOR

$$H_{op} = \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | H | \gamma\delta \rangle \, a^+_\alpha a^+_\beta a_\delta a_\gamma$$

$\alpha, \beta, \gamma, \delta$ are spin orbitals

$$= \sum_{\substack{i \geq j \\ l \geq k \\ (ij) \geq (kl)}} A_{ijkl} \left[Q_{ijkl} + (1 - \delta(ij, kl)) Q_{lkji} \right]$$

i, j, k, l are orbitals

$$Q_{ijkl} = \sum_{p,q} a^+_{ip} a^+_{jq} a_{lq} a_{kp}$$

$$A_{ijkl} = \langle ij | H | kl \rangle + (1 - \delta_{ij})(1 - \delta_{kl}) \langle ji | H | lk \rangle - (1 - \delta_{ij}) \langle ji | H | kl \rangle - (1 - \delta_{lk}) \langle ij | H | lk \rangle$$

This form of the Hamiltonian preserves hermiticity features and reduces the number of two-body matrix elements by approximately 16

MAJOR SECTIONS OF SVM

CONFIG	– generates configurations
FORM	– constructs formula tape for H-matrix
FORR	– constructs formula tape for ρ-matrix
PREP	– replaces symbolic integrals with values
FORH	– forms numerical H-matrix (from PREP)
HPQ	– forms numerical H-matrix directly
EIGEN	– Davidson multiroot diagonalization
ALLE	– Jacobi diagonalization for all roots
SOME	– Givens diagonalization
RHOF	– forms density matrix
TRANS	– compute $Tr(\underset{\sim}{\rho}\ \underset{\sim}{o})$
SAVF GETF	– for saving & retrieving formula tapes

THE GRAPHICAL UNITARY GROUP APPROACH TO ELECTRONIC WAVEFUNCTION CALCULATION

Comments by Isaiah Shavitt

FEATURES

- Efficient procedure for "direct" CI
- Spin adapted (also spatial symmetry for Abelian point groups)
- General (any state)
- Can use multireference zero-order function
- Can take integrals in any order
- May also be applicable to perturbation theory calculations

CONFIGURATION FUNCTIONS

(for the expansion of the wave function)

are

- Spin eigenfunctions
- Orthonormal
- Specified compactly

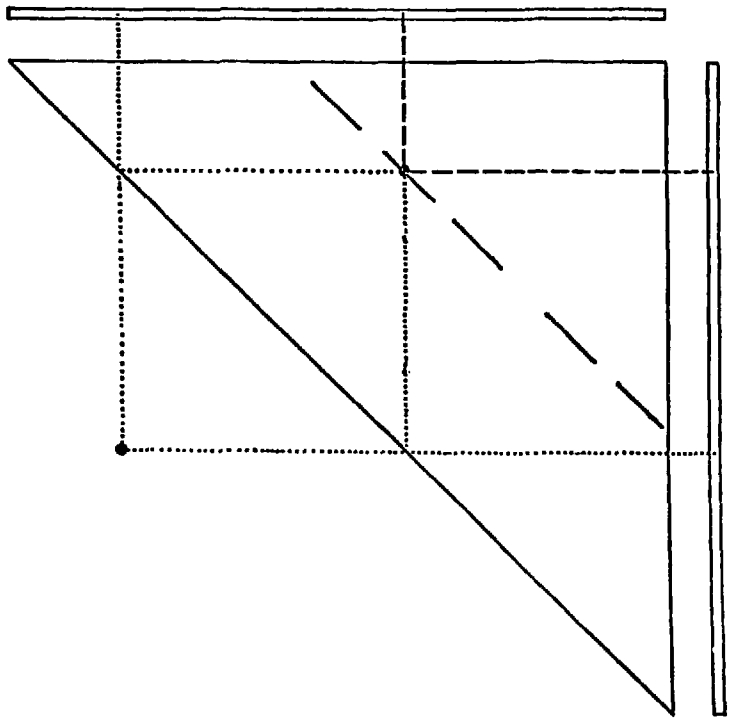
There is a unique "lexical" ordering of the configuration functions. Contiguous lexical indices are assigned to the set of functions actually used (whether full or limited CI, including the utilization of Abelian point group symmetry) in such a way that the index of a function is easily obtained from its specification.

COMPACT FORMULA TAPE

Lists sets of equal contributions of an integral to sequences of diagonally contiguous H matrix elements. Hence:

- Fast formula tape generation
- Fast eigenvector iterations

Diagram shows an example of H matrix elements sequences.



THE UNITARY GROUP APPROACH PROVIDES:

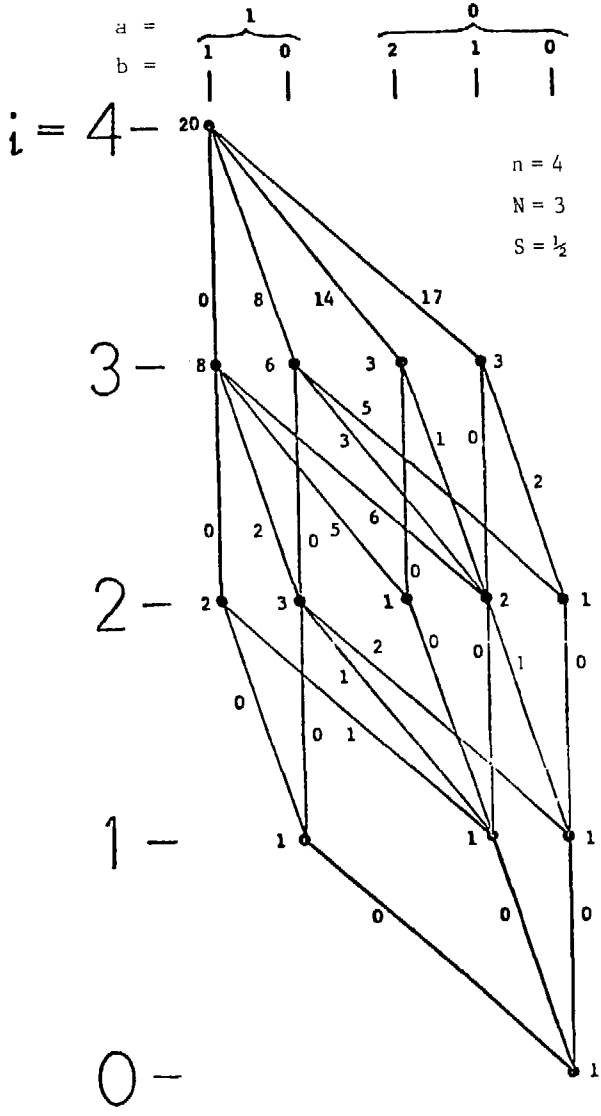
- a method for constructing an orthonormal spin-adapted complete set of configuration functions from a given set of orthonormal orbitals,

- a formalism for the efficient computation of matrix elements of quantum mechanical operators between these configuration functions.

The resulting configuration functions are called <u>Gelfand states</u>, and the complete set of these is the <u>Gelfand-Zetlin basis</u> (or the canonical basis).

i	[m]	[p]	[s]	[W]
6	2 2 1 1 0 0	2 2 2	1	1 3
5	2 2 1 0 0	2 1 2	2	2 5
4	2 1 1 0	1 2 1	0	3
3	2 1 1	1 2 0	3	6
2	1 1	0 2 0	1	
1	1	0 1 0	1	
		0 0 0		

$$\Phi = \frac{1}{\sqrt{6}}\left(|\bar{1}23\bar{3}56| + |1\bar{2}3\bar{3}56| - 2\cdot|123\bar{3}\bar{5}6|\right)$$



Example of the distinct row graph for 4 orbitals.

Each co-oriented walk from the tail to the head of the graph (visiting one vertex at each level) represents one Gelfand state. The lexical index ot that state is equal to the weight of that walk, plus one (the weight of a walk is the sum of the weights of the arcs it traverses).

An upper (lower) walk of a vertex (i,j) is a walk connecting it to the head (tail) of the graph. The set of Gelfand states represented by all the walks which share a particular upper walk of (i,j), and have all possible lower walks of that vertex, have contiguous lexical indices,

$$m = m_h + k, \quad k = 1, 2, \ldots, x_{ij}$$

where m_h is the weight of the shared upper walk.

LIMITED CI

Occupancy and spin coupling limitations can be imposed on subsets of orbitals

$$\{1, 2, \ldots, i_1\},$$

$$\{1, 2, \ldots, i_2\},$$

etc., by leaving out some distinct rows. For example, to include all single and double excitations from a closed shell reference configuration, include only those distinct rows which satisfy

$$N_i = 2i,\ 2i-1,\ 2i-2 \qquad (1 \le i \le \tfrac{1}{2}N)$$

$$N_i = N,\ N-1,\ N-2 \qquad (\tfrac{1}{2}N \le i \le n-1)$$

The matrix element

$$\langle m' | E_{ij} | m \rangle \qquad (i < j)$$

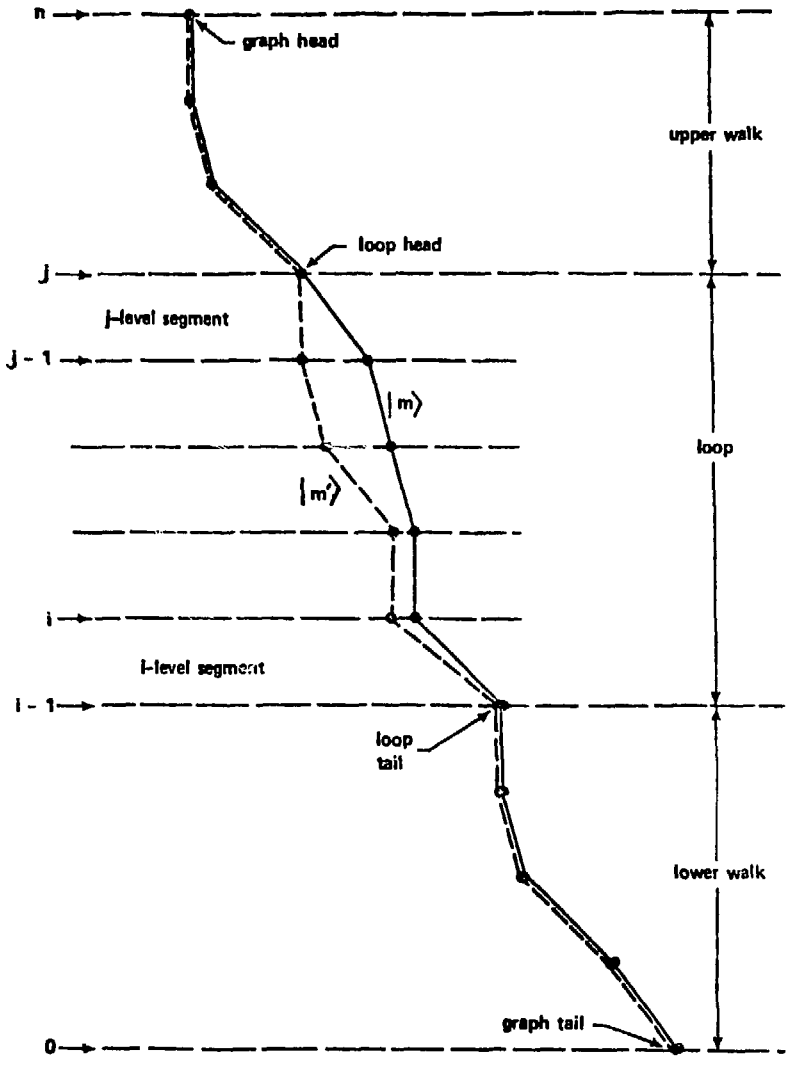
vanishes unless the distinct rows $\underset{\sim}{p}_k$ and $\underset{\sim}{p}'_k$ of the Paldus arrays for $|m\rangle$ and $|m'\rangle$, respectively, satisfy

$$\underset{\sim}{p}'_k = \underset{\sim}{p}_k \qquad (k < i \quad \text{or} \quad k \geq j)$$

$$N'_k = N_k + 1 \qquad (i \leq k < j)$$

$$b'_k = b_k \pm 1 \qquad (i \leq k < j)$$

The graphical representation of two Gelfand states which satisfy these conditions forms a <u>loop</u> between levels i-1 and j. The value of the matrix element depends only on the loop (on its shape and on the b-value of the loop head).



Graphical representation of 2 Gelfand states.

The set of all matrix elements

$$\langle m' | E_{ij} | m \rangle$$

which share a common loop provide the same coefficient value for the integral $\langle i | \hat{h} | j \rangle$ in the expansion of all the Hamiltonian matrix elements $\langle m' | \hat{H} | m \rangle$,

$$m = m_h + m_\ell + m_t + 1$$

$$m' = m_h + m'_\ell + m_t + 1$$

where m_ℓ and m'_ℓ are the weights of the two branches of the loop, and m_h and m_t range over the weights of all the upper walks of the loop head and all the lower walks of the loop tail, respectively. Furthermore, the range of values of m_t is given by

$$m_t + 1 = 1, 2, \ldots, x_t$$

where x_t is the weight of the loop tail.

FACTORIZATION OF GENERATOR MATRIX ELEMENTS

$$\langle m' | E_{ij} | m \rangle = \prod_{k=i}^{j} W(T_k, b_k)$$

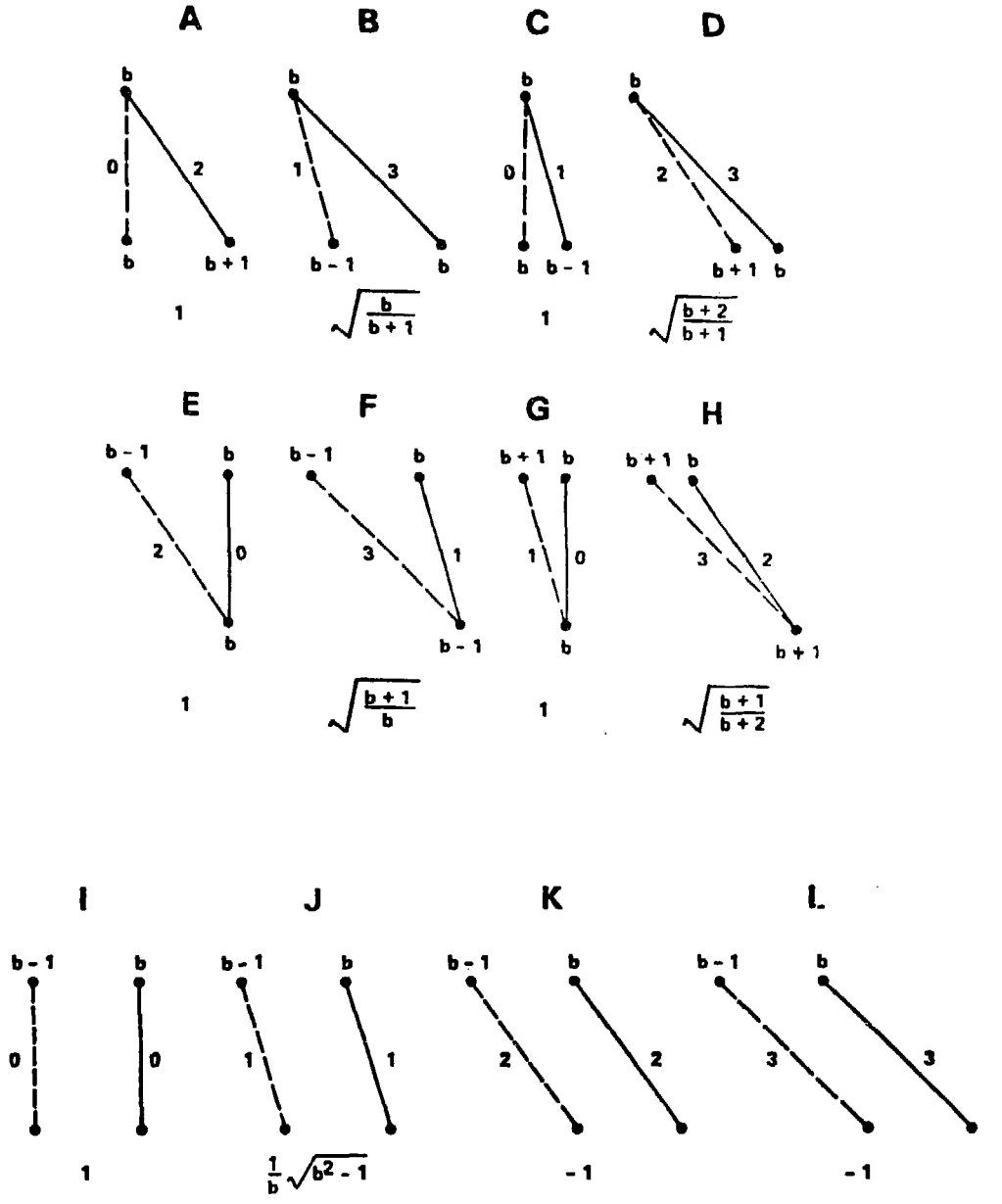
where the summation is over the segments of the loop.

T_k identifies the <u>shape</u> of the k-level segment.

b_k is the b-value of the k-level vertex on the $|m\rangle$ branch.

For the derivation of the <u>segment values</u> $W(T_k, b_k)$ we use

$$E_{ij} = E_{ik}E_{kj} - E_{kj}E_{ik} \quad (i < k < j)$$


A
B
C
D
E
F
G
H
I
J
K
L
M
N
O
P
Q
R
1
$\sqrt{\frac{b}{b+1}}$
1
$\sqrt{\frac{b+2}{b+1}}$
1
$\sqrt{\frac{b+1}{b}}$
1
$\sqrt{\frac{b+1}{b+2}}$
1
$\frac{1}{b}\sqrt{b^2-1}$
-1
-1
1
-1
$\frac{1}{b+2}\sqrt{(b+2)^2-1}$
-1
$\frac{1}{b}$
$-\frac{1}{b+2}$

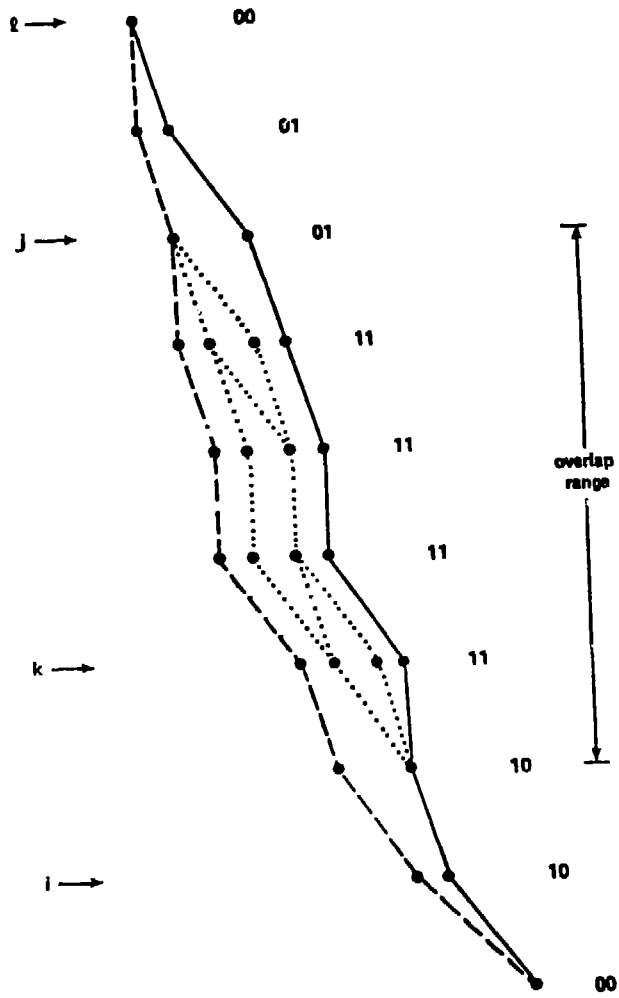
TWO-ELECTRON MATRIX ELEMENTS

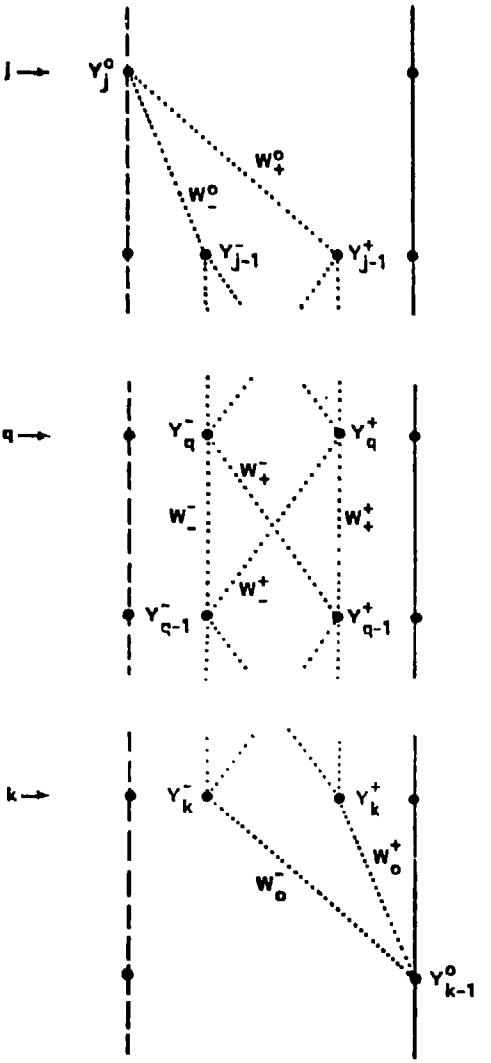
$$\langle m' | E_{ij} E_{k\ell} | m \rangle = \sum_{m''} \langle m' | E_{ij} | m'' \rangle \langle m'' | E_{k\ell} | m \rangle$$

$$Y^{\pm}_{j-1} = W^{0}(T_j, b_j)\, Y^{0}_{j}$$

$$Y^{\pm}_{q-1} = W^{-}_{\pm}(T_q, b_q)\, Y^{-}_{q} + W^{+}_{\pm}(T_q, b_q)\, Y^{+}_{q} \qquad (q = j-1,\ j-2,\ \ldots,$$

$$Y^{0}_{k-1} = W^{-}_{0}(T_k, b_k)\, Y^{-}_{k} + W^{+}_{0}(T_k, b_k)\, Y^{+}_{k}$$




j →
Y_j^o
W_+^o
W_-^o
Y_{j-1}^-
Y_{j-1}^+
q →
Y_q^-
Y_q^+
W_+^-
W_-^-
W_+^+
W_-^+
Y_{q-1}^-
Y_{q-1}^+
k →
Y_k^-
Y_k^+
W_o^+
W_o^-
Y_{k-1}^o

VII. NON-STANDARD VARIATIONAL METHODS

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NON-STANDARD VARIATIONAL METHODS

Presentation by W. Meyer

Variational Methods:

a) $E_{var} \geq E_{true}$, e.g. $E = \langle \psi | \hat{H} | \psi \rangle / \langle \psi | \psi \rangle$ may not involve any variation.

b) $\delta E = 0$, variation of orbital/configuration coefficient

$$E^{CI} = E_o + \langle \psi_o + \psi_D | \hat{H} - E_o | \psi_o + \psi_D \rangle / \langle \psi_o + \psi_D | \psi_o + \psi_D \rangle$$

$$\langle \psi_o | \hat{H} - E | \psi_o + \psi_D \rangle = 0 \qquad \text{obeys a)}$$

$$\langle \psi_{ij}^{ab} | \hat{H} - E | \psi_o + \psi_D \rangle = 0 \qquad \text{not size consistent}$$

$$E^{PT3} = E_o + \langle \psi_o + \psi_D | \hat{H} - E_o | \psi_o + \psi_D \rangle$$

$$\langle \psi_o | \hat{H} - E_o | \psi_o + \psi_D \rangle = 0 \qquad \text{not a)}$$

$$\langle \psi_{ij}^{ab} | \hat{H} - E_o | \psi_o + \psi_D \rangle = 0 \qquad \text{but size consistent}$$

$\delta E = 0 \rightarrow$ quadratic errors in E only, gradient calculation possible.

c) CPMET

$$\langle \psi_o | \hat{H} - E | \psi_o + \psi_D \rangle = 0$$

$$\langle \psi_{ij}^{ab} | \hat{H} - E | \psi_o + \psi_D + \psi_Q \rangle = 0; \quad \psi_D \Rightarrow \psi_Q$$

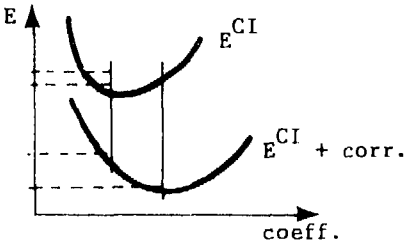
CEPA

$$\langle \psi_o | \hat{H} - E | \psi_o + \psi_D \rangle = 0$$

$$\langle \psi_{ij}^{ab} | \hat{H} - E_{ij} | \psi_o + \psi_D \rangle = 0 \quad ; \quad E_{ij} = \langle \psi_o | \hat{H} | \psi_{ij}^{ab} \rangle$$

Non-linear equations $\rightarrow$ self-consistency procedures.

Linear errors in E, no gradients(?)



Some kind of self-consistency desirable for smoothness of energy and property surfaces.

CI, PT3, CPA consider same configuration space explicitly [ref. + doubles (+singles)] → same configuration interaction technique.

Standard techniques

a) Orthogonal configurations

b) Orthogonal orbitals

Disadvantages:

Long configuration expansion, four-index integrals transf.

"Non-Standard"

PNO-CI/CEPA, pair natural orbitals, partially nonorthogonal

Advantages:

Configuration expansion reduced from N^2k^2 to $N^2k\begin{pmatrix} N & \text{occ} & \\ & & \text{orbit} \\ k & \text{virt.} & \end{pmatrix}$

e.g., transition probabilities: $k^4 \rightarrow k^2$ matrix element)

Small subset of orbital integrals → no complete transformation.

Disadvantages:

PNO's from perturbation theory → some loss of variational degree of freedom

Self-Consistent Electron Pairs Technique (SCEP)

a) Complete interacting space: ψ_o + doubles + singles (expansion coefficients may refer to non-orthogonal configurations)

b) Direct (CI) technique

c) No four-index transformation, instead, limited two-index transformation Coulomb and exchange operators, e.g., $K_{ij} \equiv [\rho i|\sigma j]$.

d) Strictly structured according to spin-adapted hole pairs.

Advantages:

1) "Formula" logic at level of configuration classes (particle pairs).

2) Pair expansion coefficients (=symmetric/antisymmetric matrices) can be updated independently, i.e. iteration may focus on pairs of largest variance.
3) External orbitals may be adapted to each pair optimizing the perturbation iteration.
4) Core usage can be restricted to the equivalent of 4-6 Fock matrices (1/2 matrices).
5) Complete variation of wavefunction — including orbitals of ψ_o — possible with reasonable extra effort → gradients efficiently.

Disadvantages:

1) As yet implemented for single configuration reference only.
2) Repeated calculation of operators may be costly in case of slow convergence.
3) Not sufficiently "general"?

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.

6) Relatively simple implementation of symmetry, e.g. "equivalent pairs".

Sketch of Formalism

Overlap matrix $S^{\rho\sigma} = \langle \xi_\rho | \xi_\sigma \rangle$

Bare Hamiltonian $H^{o\,\rho\sigma} = \langle \xi_\rho | \hat{H}^o | \xi_\sigma \rangle$

Coulomb operator $J(C)^{\rho\sigma} = \sum_{\mu\nu} C^{\mu\nu} [\mu\nu|\rho\sigma]$

Exchange operator $K(C)^{\rho\sigma} = \sum_{\mu\nu} C^{\mu\nu} [\mu\rho|\nu\sigma]$

(e.g., $K(|i\rangle\langle j|) \equiv K_{ij} = \sum C_i^\mu C_j^\nu [\mu\rho|\nu\sigma] = [\rho i|j\sigma]$)

Fock operator $F(D) = H^o + J(D) - K(D)/2$

Note: trace $(A^+ J(B)) \equiv \langle A^+ J(B) \rangle = \langle B^+ J(A) \rangle$

Hartree-Fock:

$$E_o = \langle D_o \{H^o + \tfrac{1}{2}J(D_o) - \tfrac{1}{4}K(D_o)\}\rangle$$

$$\delta E_o = \langle \delta D_o \, F(D_o)\rangle$$

$$\delta D_o = RD_o + D_o R^+$$

$$R = \sum_{i,a} dC_{ia}(|a\rangle\langle i| - |i\rangle\langle a|)S \quad , \quad i\text{:occ}, \quad a\text{:virt.}$$

$$\frac{\partial E}{\partial C_{ia}} = 4\,\langle a|F(D_o)|i\rangle$$

$$\frac{\partial^2 E}{\partial C_{ia}\partial C_{jb}} \approx 4\,\delta_{ij}\delta_{ab}(\langle a|F|a\rangle - \langle i|F|i\rangle)$$

<u>2-Electron System</u>

$$\psi_p = \sum_{\rho\sigma} C_p^{\rho\sigma}\,|\xi_\rho\bar{\xi}_\sigma| \;; \qquad C_p^+ = pC_p \quad , \qquad p = \pm 1$$

$$\langle |\xi_\rho\bar{\xi}_\sigma| \,\big|\, |\xi_\mu\bar{\xi}_\nu| \rangle = S^{\rho\mu}\,S^{\sigma\nu}$$

$$\langle |\xi_\rho\bar{\xi}_\sigma| \,\big|\, r_{12}^{-1} \,\big|\, |\xi_\mu\bar{\xi}_\nu| \rangle = [\rho\mu|\sigma\nu]$$

$$\langle \psi_p|\psi_p\rangle = \langle C_p^+ S C_p S\rangle$$

$$E = \langle C_p^+ \{2H^o C_p S + K(C_p)\}\rangle$$

$$\delta E = 2\,\langle \delta C_p^+ \{2H^o C_p S + K(C_p) - ESC_pS\}\rangle = 2\,\langle \delta C_p^+ G_p\rangle$$

$$\delta C_p = \sum_{a\geq b} dC_p^{ab}\,(|a\rangle\langle b| + p|b\rangle\langle a|)\,n_{ab}$$

$$\frac{\partial E}{\partial C_p^{ab}} = 2n_{ab}\,\langle a|G_p + pG_p^+|b\rangle \equiv T_p^{ab} \Rightarrow 0$$

$$\frac{\partial E}{\partial C_p^{ab}\partial C_p^{cd}} \approx 2\delta_{ac}\delta_{bd}\langle a|F(D) - \tfrac{1}{2}J(D)|b\rangle$$

$\rightarrow$ ϕ_a eigenvectors of $F(D) - 1/2\ J(D) \cong V_{N-1}$ potentials

$$C_p^{(n+1)} = C_p^{(n)} - T_p^{ab}/E_p^{ab}\cdot n_{ab}(|a\rangle\langle b| + p|b\rangle\langle a|)$$

<u>N-Electron System</u>

ψ_o, in general, multi-configurational,

Internal orbitals $\phi_i \equiv |i\rangle$

External orbitals $\phi_a \equiv |a\rangle$

Internal pairs $n_{ij}(\phi_i\phi_j + p\phi_j\phi_i)\begin{matrix}\alpha\alpha\\ (\alpha\beta-p\beta\alpha)/r_2\\ \beta\beta\end{matrix}$ $\begin{matrix} p=-1,\ m=1\\ p=\pm1,\ m=0\\ p=-1,\ m=-1\end{matrix}$

Spin-adapted creation/annihilation operators

$$(\eta_i\eta_j|pm) \quad ; \quad (\eta_a^+\eta_b^+|pm)$$

Consider two-electron-part of Hamiltonian

$$\sum_{p=\pm1}\sum_{a>b}\sum_{i>j}([ai|jb] + p[aj|ib])\sum_m(\eta_a^+\eta_b^+|pm)(\eta_i\eta_j|pm)$$

$\rightarrow$ "interacting space" spanned by

$$\phi_{ijp}^{ab} = \sum_m(\eta_a^+\eta_b^+|pm)\underbrace{(\eta_i\eta_j|pm)\psi_o\ (1\ldots N)}$$

$$\psi_{p\equiv ijp} = \sum_{a>b}C_p^{ab}\sum_m(\eta_a^+\eta_b^+|pm)\ \phi_{p_m}\ (3\ldots N)$$

ϕ_{p_m}'s may turn out non-orthogonal for MC-ψ_o $\rightarrow$ then orthogonalize:

P $\equiv$ linear combination of internal pairs.

Note: All "formula" information contained in reduced transition density matrices for ϕ_{p_m}'s.

Expansion coefficients for ψ_o may be relaxed during iterations by including other linear combinations of the configurations of ψ_o.

Energy for Closed-Shell Case

$$C_p = \sum_{k\ell} X_p^{k\ell} |k\rangle\langle\ell| \quad ; \qquad X_{ijp}^k = (\delta_{ik}\delta_{j\ell} + \delta_{i\ell}\delta_{jk}) n_{ij}$$

$$\underline{C}_p = \sum_{a>b} C_p^{ab} \left(|a\rangle\langle b| + p|b\rangle\langle a|\right) n_{ab}$$

$$D_{PQ} = C_p S C_Q^+ \ , \qquad \underline{D}_{PQ} = \underline{C}_p S \underline{C}_Q$$

$$fE = f\langle D_o(H^o + F(D_o))\rangle/2 + \sum_p 2\sqrt{2-p}\ \langle \underline{C}_p^+ K(C_p)\rangle + \langle \underline{C}_p^+ K(\underline{C}_p)\rangle + \langle \underline{D}_{pp}\ F(D_o)\rangle$$

$$+ \tfrac{1}{2}\sum_{p,q} \underline{D}_{pq} S\left[\langle C_q^+ K(C_p)\rangle - \langle D_{qp}\ F(D_o)\rangle\right] + \sum_{p,q} \langle \underline{D}_{pq}\Big[\sqrt{(2-p)(2-q)}^{\,\frac{1}{2}}\ K(D_{qp})$$

$$- \delta_{qp}\ J(D_{qp})\Big]\rangle$$

$$f = 1 + \vartheta\ \Sigma_p \langle \underline{D}_{pp}\rangle/2 \qquad \vartheta = 1 \rightarrow CI$$
$$\vartheta = 0 \rightarrow PT3$$

$$D = D_o + f^{-1}\Sigma_p\ [\underline{D}_{pp} - \Sigma_q \langle \underline{D}_{pq} S\rangle/2]$$

$$\delta E = 2f^{-1}\sum_{ij} \langle \delta i|G_{ij}|j\rangle + 2f^{-1}\ \Sigma_p \langle \delta \underline{C}_p^+\ G_p\rangle$$

$$G_p = \sqrt{2-p}\ K(C_p) + K(\underline{C}_p) + (2F(D_o) - \vartheta ES)\underline{C}_p S$$

$$+ \ \Sigma_q\left\{\sqrt{(2-p)(2-q)}\ K(D_{pq}) - \delta_{pq}\ J(D_{pq}) + S\langle C_q^+\ K(C_p)\rangle - S\langle F(D_o)D_{pq}\rangle\right\}\ \underline{C}_q S$$

$$G_{ij} = \delta_{ij}\ 2f\ F(D) + \sum_p \left\{2\sqrt{2-p}\ K(\underline{C}_p) + \sum_q K(C_q)\langle \underline{D}_{pq} S\rangle\right\} X_p^{ij}$$

$$+ \ K(\underline{D}_{ij}^k) - J(\underline{D}_{ij}^J) - F(D_o)\langle \underline{D}_{ij}^J S\rangle/2$$

$$\underline{D}_{ij}^K = \sum \underline{D}_{pq}\sqrt{(2-p)(2-q)}\ \sum_\ell X_q^{j\ell}\ X_p^{i\ell}$$

$$\underline{D}_{ij}^J = \sum \underline{D}_{pq}\ \delta_{pq}\ 2\sum_\ell X_q^{j\ell}\ X_p^{i\ell}$$

$$\delta \underline{C}_p = \sum_{a\ b} d\underline{C}_p^{ab}\, n_{as}\left(|a\rangle\langle b| + p|b\rangle\langle a|\right) - \sum_{ia} d\lambda_{ia}\left(|i\rangle\langle a|\ S\underline{C}_p + \underline{C}_p S|a\rangle\langle i|\right)$$

$$|\delta i\rangle = \sum_a d\lambda_{ia}\ |a\rangle$$

dC_p^{ab} : variation of external expansion coefficients

$d\lambda_{ia}$: rotations between internal/external space

To be calculated from integrals tape:

a) <u>For optimizing $\underline{C}_p$</u>

(1) All operators $J_{ij} \equiv [p\sigma|ij]$ once

$K_{ij} \equiv [pi|j\sigma]$

(→ limited 2-index transformation, about $N \times k^4$ multiplications).

(2) Operators $K(\underline{C}_p)$ per iteration on $\underline{C}_p$

(~ about same expense as above, $N^2 \times k^4$).

b) <u>For optimizing $|i\rangle$</u>

(1) $K(\underline{D}_{ij}^K)$, $J(\underline{D}_{ij}^J)$ $(N^2 \times k^4)$

(2) a (1) again if new cycle on $\underline{C}_p$.

c) <u>To get G_p, G_{ij}</u>

Little logic, random access to K_{ij}, J_{ij}, $K(C_p)$, C_p, plus lots of matrix multiplications (N^3K^3)

Explicit inclusion of singles:

Representation: $\underline{C}_s = \sum_{ai} C_i^a\ |a\rangle\langle i|$

$$G_p \rightarrow G_p + K(\underline{C}_s\, S\, C_p^+) + S\underline{C}_s(SC_p\, F_o - K(C_p^+)) \quad ,$$

i.e., instead of $K(\underline{C}_p)$, now calculate

$$K(\underline{C}_p + \tfrac{1}{2}\underline{C}_s S\, C_p^+ + \tfrac{1}{2} C_p\, S\underline{C}_s^+)$$

→ no more work than before.

Open-Shell States

Due to semi-internal configurations, pairs are represented by

$$\underline{C}_p^{ext} + \sum_i |a_i\rangle\langle i|$$

→ In G_p, write $K(\underline{C}_p^{ext} + \frac{1}{2}\sum_i |a_i\rangle\langle i| + p|i\rangle\langle a_i|)$

→ Symmetry of K-operators preserved, remaining terms involve only K_{ij}, J_{ij}.

RHF with same efficiency as closed-shell HF (UHF: twice as many operators + coefficient matrices)

Coupled Clusters - Spin Adapted

Terms like

$$\sum_{P,Q,R} \langle \delta\underline{C}_P \; S\underline{C}_Q\rangle \langle \underline{C}_R \; K_{ij}\rangle \gamma_{PQR}^{ij}$$

References

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OTHER DEVELOPMENTS AND APPLICATIONS OF THE SCEP METHOD

Comments by C. E. Dykstra

The flexibility of the SCEP method is shown by the ease of direct extension of the basic method to special open-shell cases[1] and to quadruple substitutions.[2] Important in showing the power of the method are applications to real molecular problems as shown below. Among these applications are problems involving large configuration expansions (over 63,000 for H_2C_2O isomers[3]), large basis sets (53 functions[4] for CH_3^- and 63 functions[5] for H_3^+), and SCEP/CEPA calculations[6] in Be_4.

Studies of Molecular Systems Using the SCEP Method:

- Be_4 cluster energy
- D_{2h} and D_{2d} energy differences in allene
- Vinylidene → acetylene rearrangement
- Inversion potential of CH_3^-
- H_3^+ potential surface
- Ground state energies of H_2C_2O isomers
- Formation and rearrangement of the vinyl anion
- Basis set and correlation effects in the H_2C_2 and H_2N_2 systems

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Comments by G. P. Das

1. The method is specialized to study energetics of chemical reactions of the type: $AB + C \rightleftharpoons A + BC$

2. Procedure

a. First, the atomic and diatomic wavefunctions for A, C, AB and BC are obtained, the diatoms at various 'R'.

b. A CI consisting of the configurations that represent incoming channel is constructed and MCSCF performed. The same is also done for the outgoing channel.

c. The wavefunctions for the two channels are then combined in the form:

$$\Psi = A_I \Psi_I + B_0 \Psi_0$$

and the corresponding secular equation solved. Only the off-diagonal element deals with non-orthogonal set of orbitals.

3. Simplification and Approximations

a. In computing the matrix element $\langle \Psi_I | \mathcal{H} | \Psi_0 \rangle$, we write

$$\Psi_0 = \langle \Psi_I | \Psi_0 \rangle \Psi_I + \sum_k \langle \Psi_0 | \Psi_{Ik} \rangle \Psi_{Ik} + \sum a_j \Phi_{Ij}$$

where Ψ_{Ik}'s are other roots of the secular equation defining Ψ_I. Obviously Ψ_{Ik}'s don't contribute. Only the Φ_{Ij}'s, excitations not present in Ψ_I, of which only singles and doubles w.r.t Ψ_I need to be considered. Thus only the overlaps $\langle \Psi_I | \Psi_0 \rangle$ and $\langle \Phi_{Ij} | \Psi_0 \rangle$ are to be calculated. Note that Φ_{ij}'s are excitations involving transfer of electrons from the diatom to the atom.

b. With little loss of accuracy, the optimization in Step 2. can be carried out only in the basis function spaces for the individual atoms and diatoms. This implies that the Fock equations are modified to the form

$$\underset{\sim}{F}_i^{AB} \underset{\sim}{c}_i^{AB} = \sum \varepsilon_{ij}^{AB} \underset{\sim}{S}^{AB} \underset{\sim}{c}_j^{AB} \qquad (1)$$

and

$$\left(\underset{\sim}{F}_i^c - \sum_{j \subset AB} \underset{\sim}{F}_{ij}^c \, \underset{\sim}{f}_j^+\right) \underset{\sim}{C}_i^c = \sum_j \varepsilon_{ij}^C \left(\underset{\sim}{S}^c - \sum_{k \subset AB} \underset{\sim}{f}_K \underset{\sim}{f}_k^+\right) \underset{\sim}{C}_j^c \qquad (2)$$

where the orthogonality requirements in (1) are only amongst $\{C_i\}$, $i \subset AB$, while for C the orthogonality to the AB-orbitals introduces the additional terms in the Fock operator.

c. In the CI of step 2, one can omit configurations representing higher order correlations involving virtuals within the subsystems. The corresponding lost correlation energy as well as terms can be reinstated in the final energy and wavefunction coming out of Step 3. This is an important approximation and is explained as follows: Correct to second order, the contribution from these terms is of the form

$$\Delta E^{(2)} = - \frac{\langle \Psi_a | \mathcal{H} | \Psi_b \rangle}{\varepsilon_a' - \varepsilon_b'}$$

where ε_a' and ε_b' are the modified diagonal energies in the presence of the atom C. The numerator is more or less unchanged, while the change in the denominator is expected to be small, but in any case checked out and corrections introduced accordingly.

VIII. PERTURBATION THEORY

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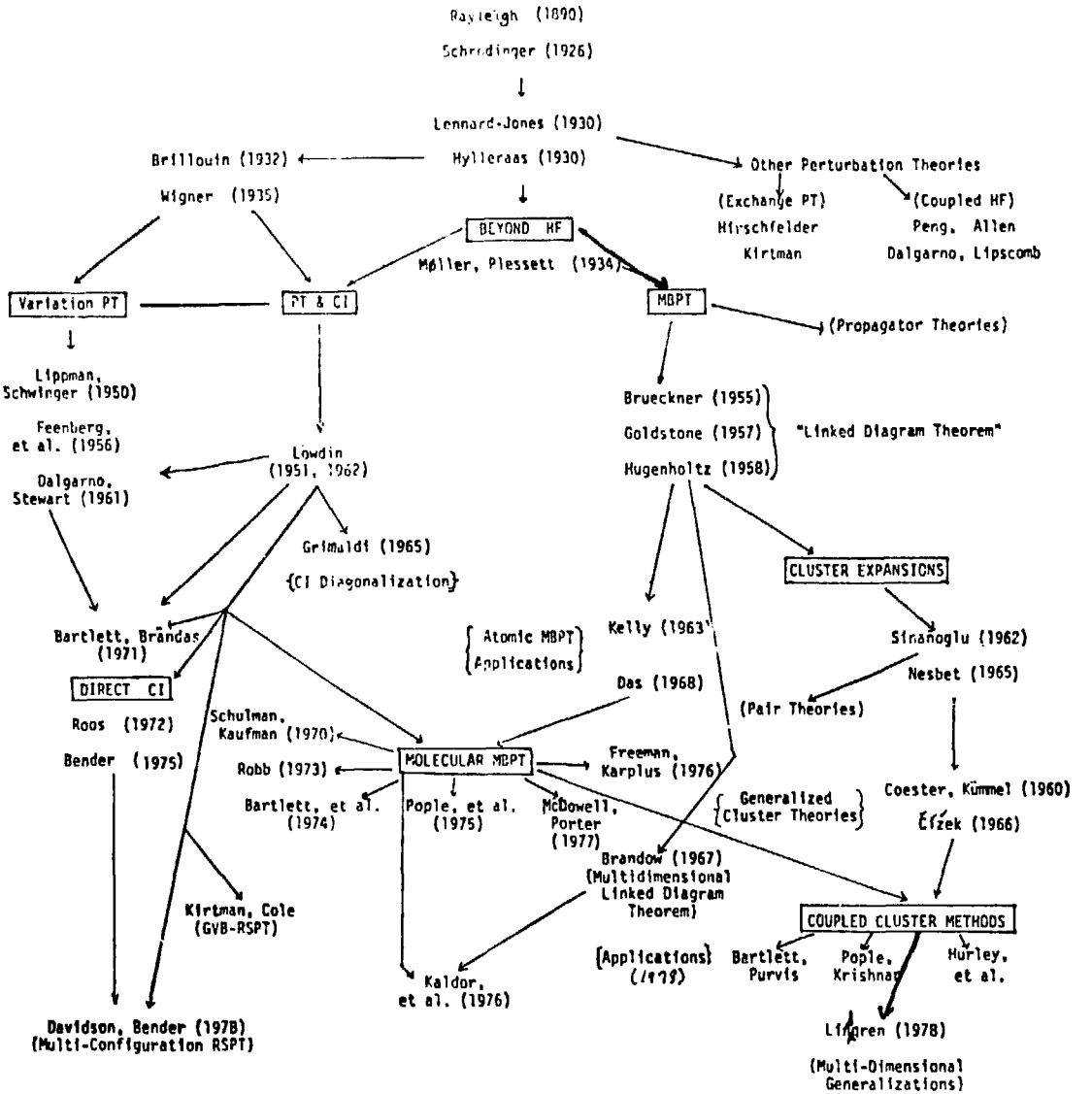
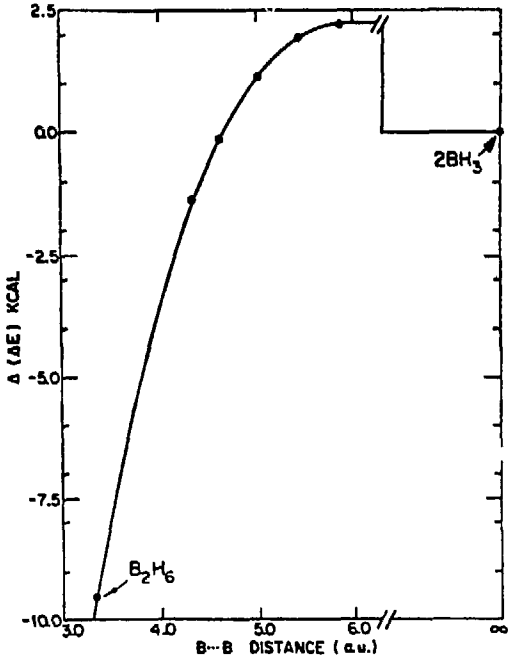


WHY PERTURBATION THEORY ?

- Organizes much of quantum chemistry into a single framework.
- Provides convenient, tractable formulae for a variety of computational problems.
- Small energy differences are computed directly.
- Facilitates maintenance of "size consistency" (separability conditions) for total energy, density matrix, excitation energies, etc.
- Perturbation theory formulations lead to vectorized computer code.
- Perturbation formulations suggest different approximations, including types of infinite order summations.
- Ideally suited for second-order properties.



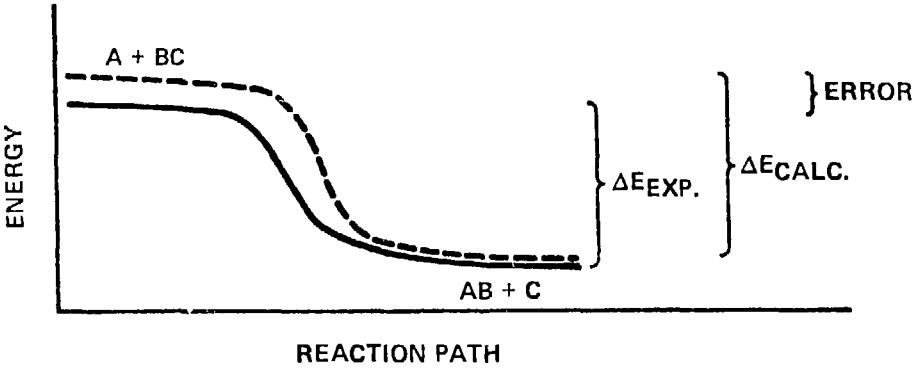
Dissociation of B_2H_6

Plot for configuration interaction changes as a function of B...B distance for the symmetric pathway. Values of E are E(SCF - CI) - E(SCF). From each ΔE we subtract 2ΔE for BH_2 to find Δ(ΔE). Units for the abscissa are in kilocalories per mole.

Ref.: Dixon, Pepperberg, and Lipscomb, J. Am. Chem. Soc.

ILLUSTRATION OF IMPORTANCE OF "SIZE-CONSISTENCY" FOR STUDIES OF POTENTIAL SURFACES

Exothermicities of Reactions and Predicted Barrier Heights



(a) If exothermicity is not correct have innate error in predicted barrier.

(b) In a "size-consistent" method $\Delta E = E(AB) + E(C) - E(BC) - E(A)$; and no supermolecules [ABC] need to be computed to obtain exothermicity.

(c) From a small number of calculations can predict exothermicities for many reactions at a given level of basis set or sophistication.

(d) Higher excitations are likely to be important in obtaining correct relative energies on a potential surface, and "size-consistent" methods, at a sufficient level of sophistication, include contributions from higher excitations.

MANY-BODY PERTURBATION THEORY

$$H = \sum_{i=1}^{N} h(i) + \sum_{i>j} r_{ij}^{-1}$$

$$H = H_0 + V$$

$$H_0 = \sum_{i=1}^{N} \left\{ h(i) + V^N(i) + p[(V(i) - V^N(i)]\ p \right\},$$

$$V = H - H_0 = \sum_{i<j} r_{ij}^{-1} - \sum_i \left\{ V^N(i) + p[V(i) - V^N(i)]\ p \right\}$$

$$[h(1) + V^N(1)]\ X_i(1) = \varepsilon_i X_i(1).$$

$$p\,[h(1) + p\,V(1)]\,p\,X_a(1) = \varepsilon_a X_a(1)$$

$$p = 1 - o \qquad o = \sum_{j=1}^{N} |X_j\rangle\langle X_j|$$

$$V^N(1) = \sum_{j=1}^{N} \int d\tau\ {}_2X_j^*(2)\, r_{12}^{-1}\,(1 - P_{12})X_j(2).$$

$$V(1) = V^{N-1}(1) = \sum_{j=1}^{N-1} \int d\tau\ {}_2X_j^*(2)\, r_{12}^{-1}\,(1 - P_{12})X_j(2)$$

MANY-BODY PERTURBATION THEORY (cont)

$$H_0 \Phi_0 = E_0 \Phi_0$$

$$\Phi_0 = A[X_1(1) \cdots X_N(N)]$$

$$E_0 = \sum_i \varepsilon_i$$

$$E = E_{SCF} + E_{CORR}$$

$$E_{SCF} = E_0 + \langle \Phi_0 | V | \Phi_0 \rangle$$

$$\text{RSPT}: \Delta E = E - E_0 = \sum_{K=0}^{\infty} \langle \Phi_0 | V [(E_0 - H_0)^{-1} P(V - \Delta E)]^K | \Phi_0 \rangle$$

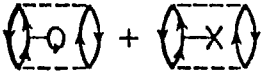
$$\text{MBPT}: \Delta E = \sum_{K=0}^{\infty} \langle \Phi_0 | V [(E_0 - H_0)^{-1} V]^K | \Phi_0 \rangle_L$$

$$= \sum_{i>j} \sum_{a>b} |\langle ij \| ab \rangle|^2 / D(ij\,ab)$$

$$= \sum_{i>j} \sum_{a>b} \sum_{c>d} \langle ij \| ab \rangle \langle ab \| cd \rangle \langle cd \| ij \rangle / D(ijab)\, D(ijcd)$$

$$= \sum_{i>j} \sum_{k>\ell} \sum_{a>b} \langle ab \| ij \rangle \langle ij \| k\ell \rangle \langle k\ell \| ab \rangle / D(ijab)\, D(k\ell ab)$$

$$= \sum_{ijk} \sum_{abc} \langle ab \| ij \rangle \langle ic \| ak \rangle \langle kj \| cb \rangle / D(ijab)\, D(kjcb)$$

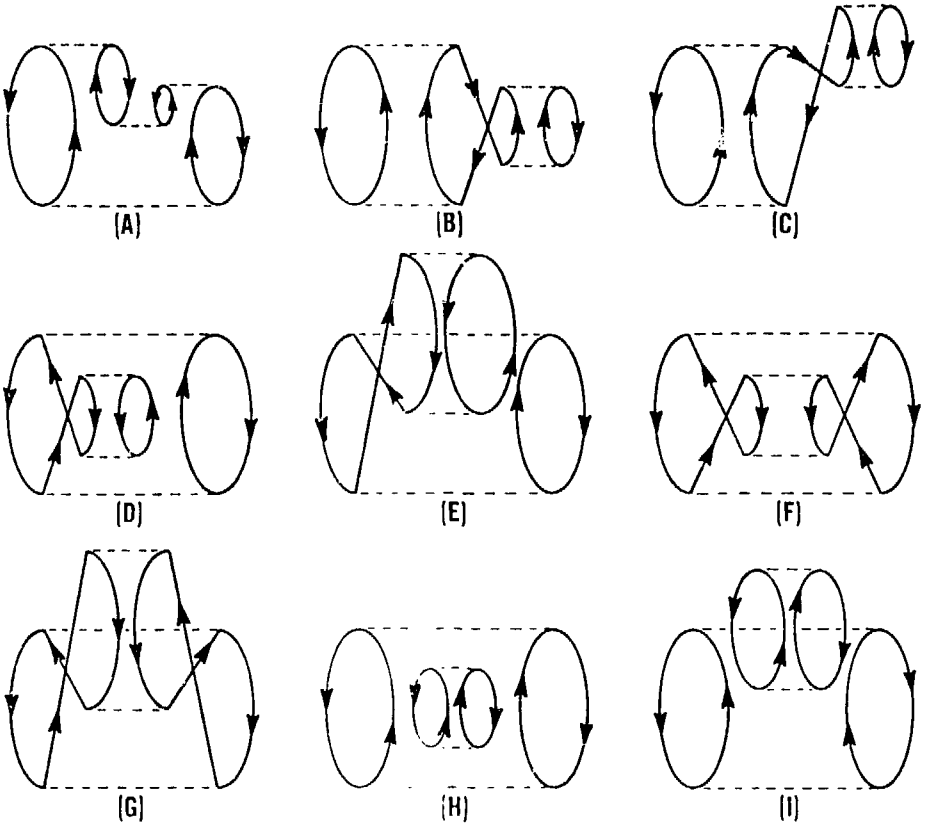


$$= \sum_{i>j} \sum_{abc} \langle ab \| ij \rangle \Big[\sum_n \langle cn \| an \rangle - \langle c | V | a \rangle\Big] \langle ij \| cb \rangle / D(ijab)\, D(ijcb)$$

$$D(ijab) = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b \; .$$

$$D^S(ijab) = D(ijab) + \Delta(ijab)$$

$$\Delta(ijab) = -\langle ab \| ab \rangle - \langle ij \| ij \rangle + \langle ai \| ai \rangle + \langle aj \| aj \rangle + \langle bi \| bi \rangle + \langle bj \| bj \rangle$$
$$- \Big[\sum_{n=1}^{N} \langle an \| an \rangle - \langle a | V | a \rangle \Big] - \Big[\sum_{n=1}^{N} \langle bn \| bn \rangle - \langle b | V | b \rangle \Big]$$


(A)
(B)
(C)
(D)
(E)
(F)
(G)
(H)
(I)

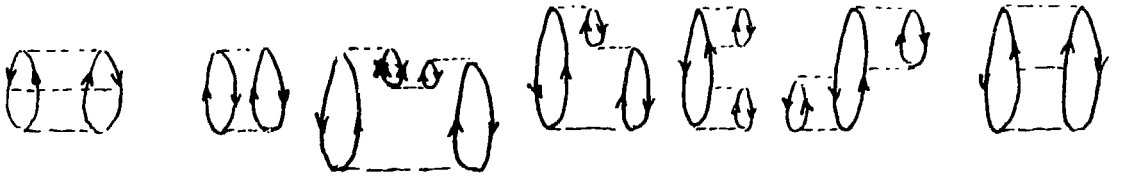
i, j, k, l occupied

a, b, c, d unoccupied

$\langle pq \| rs \rangle$

$\Downarrow$ main sort

$\langle ij \| kl \rangle$	$\langle ij \| ab \rangle$	$\langle ia \| jb \rangle$	$\langle ij \| ka \rangle$	$\langle ia \| bc \rangle$	$\langle ab \| cd \rangle$
hole-hole ladder	E_2, Quad	hole-particle	S.E.	T.E.	Particle ladder



$$E_2 \rightarrow \langle ij \| ab \rangle \langle ij \| ab \rangle / D = \langle ij \| ab \rangle \; C_{ij}^{ab}$$

$\left\{ C_{ij}^{ab} \right\}$ small sort

$$E_3 \text{ (HHL)} \rightarrow C_{ij}^{ab} \quad \langle ij \| kl \rangle \quad C_{kl}^{ab}$$

$$E_3 \text{ (PPL)} \rightarrow C_{ij}^{ab} \quad \langle ab \| cd \rangle \quad C_{ij}^{cd}$$

$$E_3 \text{ (HPL)} \rightarrow C_{ij}^{ab} \quad \langle ic \| ka \rangle \quad C_{jk}^{bc}$$

$$C_{ij}^{ab} \times X_{ij}^{ab}$$

linear loop

$$E_4 = \Sigma \; X_{ij}^{ab} \times X_{ij}^{ab} / D_{ijab} \rightarrow C_{ij}^{ab} \; (2)$$

$$D_{ijab} = E_i + E_j - E_a - E_b$$

NON-LINEAR PT SUMMATIONS

$$E = E_o + E_1 + E_2 = - - -$$

I Variation - Perturbation

$$\tilde{\psi} = \phi_o + \lambda_1\phi_1 + \lambda_2\phi_2 + - - -$$

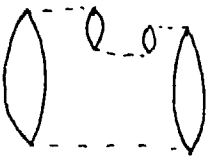
$$\tilde{E} = \langle \tilde{\psi} : H \mid \tilde{\psi} \rangle / \langle \tilde{\psi} \mid \tilde{\psi} \rangle = \underset{\sim}{H}\,\underset{\sim}{\lambda} = \underset{\sim}{\Delta}\,\underset{\sim}{\lambda}\,\underset{\sim}{E}$$

$$\underset{\sim}{H}\,,\ \underset{\sim}{\Delta} \rightarrow E_o,\ E_1,\ E_2,\ - - -\ \Delta_{12},\ \Delta_{22}$$

II Padé Approximants

$$E\left\{[N, N-1]\right\} = E_o + E_1 + [N, N-1]$$

$$[N, N-1] = [E_2\ E_3\ - - -] \begin{bmatrix} E_2 - E_3 & E_3 - E_4 & - - - \\ E_3 - E_4 & E_4 - E_5 & - - - \\ \vdots & & \end{bmatrix}^{-1} \begin{bmatrix} E_2 \\ E_3 \\ \vdots \end{bmatrix}$$



$$\Longrightarrow \sum_{\substack{k>\ell \\ c>d}} \langle k\ell \| cd \rangle \, C_{k\ell}^{ab} \, C_{ij}^{cd} + 6 \text{ more quadratic terms}$$

"Quadruple" Excitations Diagrams

Energy obtained from $\sum C_{ij}^{ab} \times \left(\sum_{\substack{k>\ell \\ c>d}} \langle k\ell \| cd \rangle \, C_{k\ell}^{ab} \, C_{ij}^{cd} + \ldots \right)$

Non-linear loop i

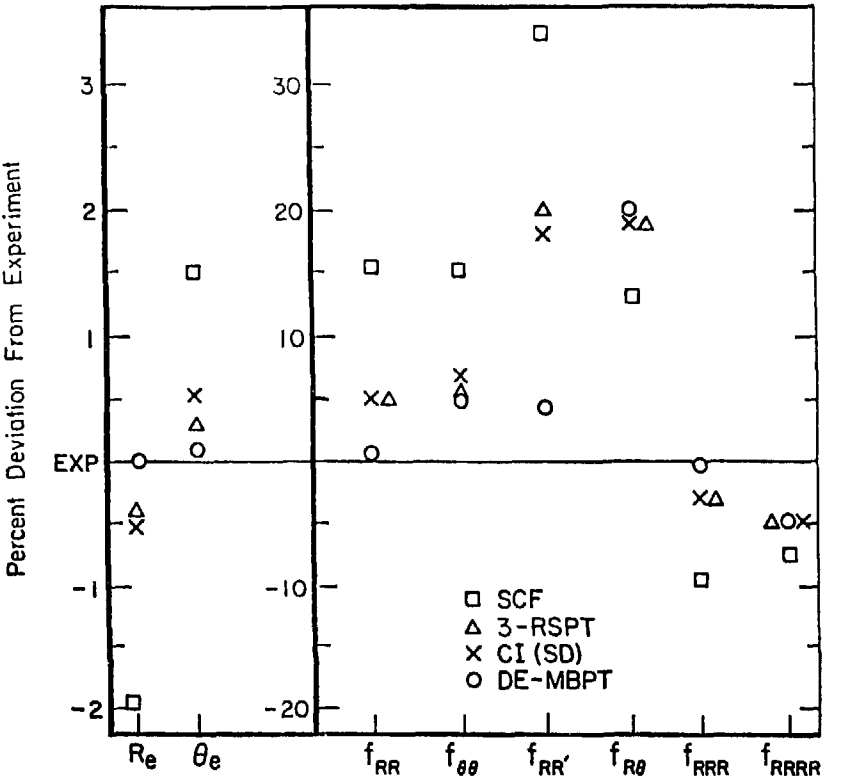
(Defines new part of coefficient)

$\downarrow$

Return to Linear Loop

QUARTIC FORCE FIELD FIT FOR GEOMETRY

OF H_2O (39 STO)



Reaction	#BFN	-ΔE (kcal/mole)	
		$\mathcal{D}$-MBPT (6)	EXP.
$2\ BH_3 \rightarrow B_2H_6$	68	35.6	38.4 ± 4[a]
$BH_3 + CO \rightarrow H_3BCO$	63	20.5	22.0 ± 2[a]
$BH_3 + NH_3 \rightarrow H_3BNH_3$	62	29.5[b]	—
$HNC \rightarrow HCN$	37	15.1	(10.3 ± 1)
$CH_3NC \rightarrow CH_3CN$	63	22.8	23.7 ± .14
$CH_3NC \rightarrow \left[CH_3 \begin{smallmatrix} N \\ C \end{smallmatrix}\right]$	63	−44.1 (−39)[a]	−38.4

[a]Adjusted for vibrational zero point energy and temperature.
[b]Including estimate for geometry relaxation.

FOURTH-ORDER PERTURBATION THEORY

$$E_4 = \langle \Phi_o | V\overset{D}{\downarrow}P(E_o - H_o)^{-1}\overset{D}{\downarrow}P(V - E_1)\overset{S,D,T,Q}{\downarrow}P(E_o - H_o)^{-1}\overset{S,D,T,Q}{\downarrow}P(V - E_1)\overset{D}{\downarrow}P(E_o - H_o)^{-1}\overset{D}{\downarrow}PV | \Phi_o \rangle - E_2\Delta$$

$$E_4 = \mathcal{E}_4 - E_2\Delta$$

$$\Delta = \langle \Phi_1 | \Phi_1 \rangle = \langle \Phi_o | VP(E_o - H_o)^{-1}P(E_o - H_o)^{-1}PV | \Phi_o \rangle$$

$$\Delta = 1/4 \sum_{k>l} [\langle kl || cd \rangle / \epsilon_k + \epsilon_l - \epsilon_c - \epsilon_d]^2$$

$$E_2 = \langle \Phi_o | VP(E_o - H_o)^{-1}PV | \Phi_o \rangle$$

$$E_2 = \sum_{\substack{i>j \\ a>b}} \langle ij || ab \rangle^2 / \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$$

$$P = |\underline{h}\rangle \langle \underline{h} | \underline{h} \rangle^{-1} \langle \underline{h} | \qquad \text{where} \quad \langle \Phi_o | h_k \rangle = 0$$

P may be separated into single, double, triple, and quadruple excitations

$$|\underline{h}\rangle = |\underline{h}_1, \underline{h}_2, \underline{h}_3, \underline{h}_4\rangle$$

$$\mathcal{E}_4 = \mathcal{E}_4^S + \mathcal{E}_4^D + \mathcal{E}_4^T + \mathcal{E}_4^Q$$

$E_2\Delta$ is solely determined by double excitations

FOURTH-ORDER PERTURBATION THEORY (Continued)

Inserting the quadruple excitation determinants, D^{abcd}_{ijkl}, into $\mathcal{E}_4$ in $E_4 = \mathcal{E}_4 - E_2\Delta$, it may be shown that

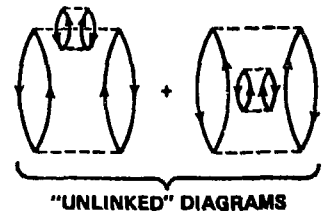
$$\mathcal{E}_4^Q = \sum_{\substack{i>j \\ a>b}} \frac{\langle ij||ab\rangle}{D_{ijab}} \left\{ \sum_{\substack{k>l \\ c>d}} \langle kl||cd\rangle \left[\overset{A}{\frac{\langle kl||cd\rangle}{D_{klcd}} \frac{\langle ij||ab\rangle}{D_{ijab}}} + \overset{B}{\frac{\langle kl||ab\rangle}{D_{klab}} \frac{\langle ij||cd\rangle}{D_{ijcd}}} \right.\right.$$

$$-2 \left(\overset{C}{\frac{\langle kl||bd\rangle}{D_{klbd}} \frac{\langle ij||ac\rangle}{D_{ijac}} + \frac{\langle kl||ac\rangle}{D_{klac}} \frac{\langle ij||bd\rangle}{D_{ijbd}}} \right) -2 \left(\overset{D}{\frac{\langle ik||ab\rangle}{D_{ikab}} \frac{\langle jl||cd\rangle}{D_{jlcd}} + \frac{\langle ik||cd\rangle}{D_{ikcd}} \frac{\langle jl||ab\rangle}{D_{jlab}}} \right)$$

$$\left.\left. +4 \left(\overset{E}{\frac{\langle ik||ac\rangle}{D_{ikac}} \frac{\langle jl||bd\rangle}{D_{jlbd}} + \frac{\langle ik||bd\rangle}{D_{ikbd}} \frac{\langle jl||ac\rangle}{D_{jlac}}} \right) \right] \right\}$$

But

$$\boxed{A = E_2\Delta = \sum_{\substack{i>j \\ a>b}} \sum_{\substack{k>l \\ c>d}} \left(\frac{\langle ij||ab\rangle}{D_{ijab}} \right)^2 \frac{\langle kl||cd\rangle^2}{D_{klcd}}} =$$



$$\boxed{E_4^Q = \mathcal{E}_4^Q - E_2\Delta = B + C + D + E}$$

FOURTH-ORDER PERTURBATION THEORY (Continued)

What happens if restrict space to just double excitations?

$$P = |\underline{h}_2\rangle \langle \underline{h}_2|\underline{h}_2\rangle^{-1} \langle \underline{h}_2|$$

Then, $E_4^D = \mathcal{E}_4^D - E_2\Delta$

But consider example of 2 separated He atoms, He_A and He_B.

$$E_2\Delta\ (He_2) = (E_2^A + E_2^B)\ (\Delta^A + \Delta^B)$$

$$= 4E_2^A\Delta^A \neq 2E_2^A\Delta^A$$

Thus, $E_2\Delta$ IS NOT SIZE-CONSISTENT

$\mathcal{E}_4^D$ IS SIZE-CONSISTENT

So, simplest size-consistent fourth-order PT approximation would just neglect RSPT renormalization terms.

TABLE 1.

Components of the correlation energy through fourth-order (millihartrees) (core electrons are frozen.)

Molecule[a]	E_2	E_3	E_4			E^4_{CORR}
			E^D_4	E^S_4	E^Q_4	
BH_3 (4s2pld/2slp)	-93.53	-19.3	-4.92	-3.65 -0.18	+1.45	-116.32
NH_3 (4s2pld/2slp)	-188.64	-12.8	-3.99	-2.16 -0.57	+2.48	-203.53
CO_2 (5s3pld)	-520.01	+20.53	-13.36	-16.27 -11.77	+8.86	-515.75
CO (5s3pld)	-309.82	+4.92	-9.98	-12.00 -6.92	+4.90	-316.89
HCN (4s2pld/2slp)	-284.52	-2.03	-9.04	-6.80 -3.70	+5.94	-293.36
N_2 (4s3pld;spd bond fxn.)	-340.58	+7.27	-11.58	-9.40 -5.12	+7.30	-342.70
N_2 (R=3.00 a_o); RHF	-555.34	+195.79	-148.60	+172.33 -35.91	+12.18	-531.88
N_2 (R=3.00 a_o); UHF	-227.03	-25.96	-7.30	-9.48 -7.16	+4.98	-262.47

(a) All molecules are at their equilibrium geometry unless otherwise specified.

TABLE 2.

Comparison of various correlation approximations with CPMET.[a)]

Molecule	D-CI [b)]	D-MBPT(4)	DQ-MBPT(4)	CPMET
BH_3	-113.40	-117.78	-116.32	-116.90
NH_3	-194.45	-205.44	-202.97	-203.30
CO	-289.66	-314.87	-309.97	-309.70
HCN	-265.94	-295.59	-289.66	-290.17
CO_2	-457.52	-512.84	-503.98	-504.01
$N_2(2.068\ a_o)$	-313.75	-347.04	-337.58	-337.22
$N_2(3.00\ a_o)$; RHF	-391.26	-508.15	-495.97	-447.80

a) All energies are in millihartrees.

b) D-CI is estimated from a variational upper bound obtained from $\Psi = \Phi_o + \lambda_1\Phi_1 + \lambda_2\Phi_2$ where Φ_1 and Φ_2 are the double-excitation parts of the perturbed wavefunction.

TABLE 3. $CH_3NC \rightarrow CH_3CN$; Basis set [4s2p1d]/[2s1p]; [a] Components of the correlation energy, energy of isomerization, and activation energy.

Order		CH_3NC	"Transition State" b)	CH_3CN	$-\Delta E$ c) Isomerization	E_A c)
SCF		-131.91865	-131.84204	-131.94918	19.16	48.07
2		-.41283	-.41839	-.42401	7.02	-3.49
3		-.01818	-.01772	-.01302	-3.24	0.29
4	S.E.	(-.00461)	(-.00531)	(-.00440)	(-0.13)	(-0.44)
	D.E.	(-.01265)	(-.01321)	(-.01292)	(+0.17)	(-0.35)
	Q.E.	(+.00814)	(+.01016)	(+.00863)	(-0.31)	(+1.27)
4	Total	-.00912	-.00836	-.00869	-0.27	0.48
E_{CORR}		-.44013	-.44448	-.44572	+3.51	-2.73
E_{TOTAL}		-132.35878	-132.28652	-132.39491	22.67	45.34
Corrected for zero point d)					22.7	~39-40
Experimental e)					23.7 ± 0.14	38.4

a) Basis set is Dunning's contraction[20] of Huzinaga's (9s5p)/(4s) primitive set[21] augmented with polarization functions on all atoms.

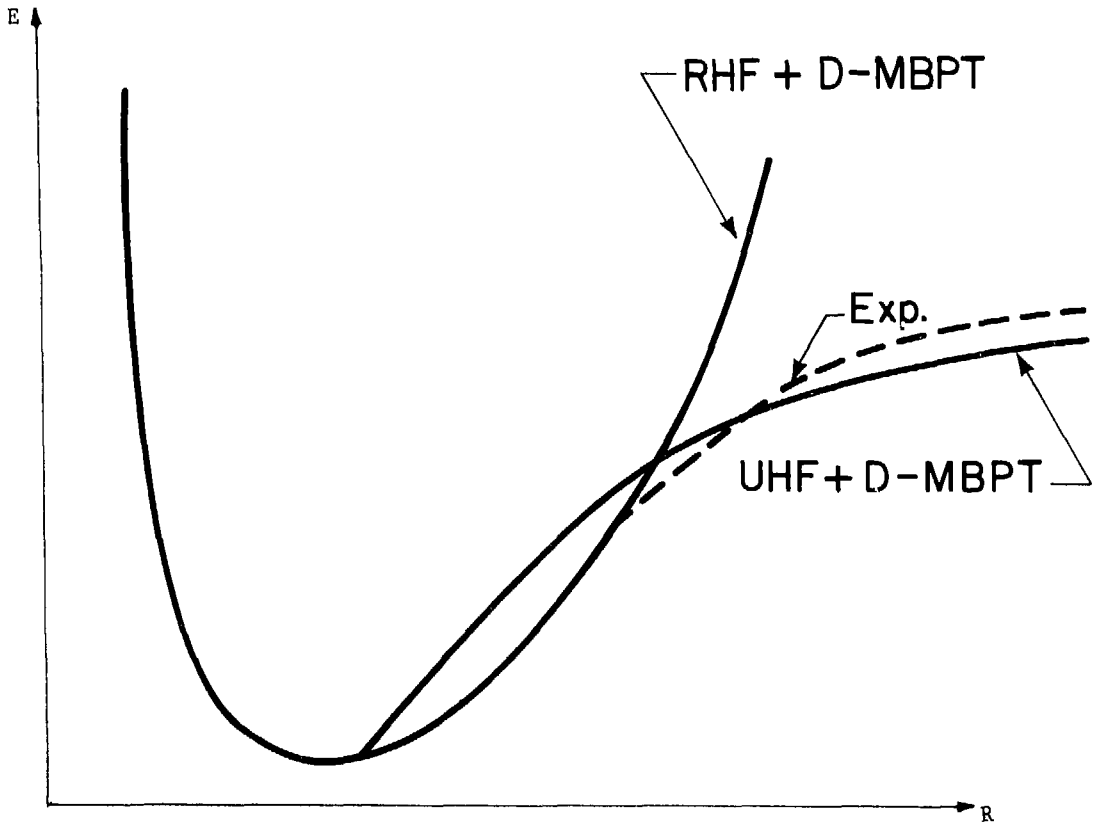
b) Transition state geometry is taken from the SCF calculations of Liskow et al.[7]

c) Units for energy differences are kcal/mole.

d) Estimated zero-point correction is included, ~0 for ΔE (isomerization) and ~5-6 for the activation barrier (see text).

e) See Refs. 5 and 3.

N_2 potential curve



Disadvantages of MBPT (as used here)

- Limitation to a single reference determinant.
  - RHF is fine near equilibrium for many molecules.
  - UHF is often suitable for open shells (high spin cases) and for breaking a single bond into open-shell fragments.
  - UHF has problems in describing multiple bond breaking.

  (A multiconfigurational generalization of MBPT has been given by Brandow and used in calculations on H_2 and BH by Kaldor.)
- Exclusion of triple excitations.

Advantages of MBPT

1) All properties are evaluated by summing products of molecular integrals, which is a conceptually simple procedure that lends itself to efficient computer algorithms particularly suited to vector machines. (No configurations need be considered.)
2) The cancellations that occur in full CI among different levels of excited configurations, like double and quadruple excitations, are already incorporated into the linked-diagram expansion. Hence, approximations to the linked-diagram expansion can benefit from higher excitation effects automatically.
3) MBPT provides properly size-consistent results due to 2).
4) As long as an entire diagram is computed, MBPT results are invariant to unitary transformations among degenerate orbitals.
5) The diagrammatic summation of MBPT may be computed recursively to all orders in many cases. The closed form equivalent of the most important MBPT summations are found in the coupled-cluster formulation of Coester, Kümmel, and Čížek.

Survey of Some Current Work in PT (necessarily incomplete!)

I. Potential Surface Problem

- MBPT including all single, double, quadruple excitation effects to fourth-order, higher-order double and quadruple terms: UHF reference function [Bartlett, Pople].
- Multi-reference function MBPT to third-order [Kaldor].
- GVB reference function RSPT to second-order [Kirtman].
- Multi-reference function CI-RSPT to fourth-order [Davidson, Bender].

II. Ionization Potentials (Double Perturbation Theory)

- Third-order RSPT [Chong, Simons].
- "Transition State" and second-order PT for correlacion [Goscinski, Öhrn].
- Many propagator studies use PT to solve for Green's function [Cederbaum].

III. Second-Order Properties (Double Perturbation Theory)

- Coupled Hartree-Fock and second-order correlation [Adamowicz, Sadlej].
- Coupled Hartree-Fock and high-order correlation [Bartlett, Purvis].

IV. Excitation Energies

- PT of excitation energies discussed by Paldus, Čižek
- Most applications use PT to evaluate polarization propagator [Yeager, Freed, Linderberg, Jorgenson, many others].

V. Miscellaneous

- Direct determination of conformational barrier in ethane using PT [Nee, Parr, and Bartlett].

SOME RECENT PAPERS OF INTEREST

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ALTERNATIVE INITIAL APPROXIMATIONS IN PERTURBATION THEORY

Comments by Bernard Kirtman

In the table, two alternatives to the Hartree-Fock (HF) initial approximation in perturbation theory are evaluated. One is the generalized valence bond (GVB) model;[1] the other is a limited multiconfiguration wavefunction. In ψ_{GVB} the spin function S is a linear combination of independent bonding structures. For a perfectly paired (PP) molecule it has the form shown. To make the VB calculations practical one must use either a strong orthogonality approximation[2] or a method based on overlap expansions.[3] In either case the zeroth-order treatment involves $\underline{O}(NK^4)$ steps, where N is the number of electrons and K the dimension of the basis. Several advantages of GVB with respect to HF are listed, along with the disadvantages, in the table. These advantages follow from the improved approximation [cf. items (a) and (b)] and the spatially localized [cf. item (c)], quasiatomic [cf. item (d)] character of the VB orbitals. Under item (b) the example is based on preliminary calculations[4] which indicate that the second-order VB energy may be as accurate as third-order HF. The possibility that basis sets may be avoided with an atoms-in-molecules type approach [see item (d)] rests on being able to suitably adapt Kelly's[5] numerical perturbation techniques.

A limited multiconfiguration initial approximation is required for excited states with open shells where there is an exact zeroth-order degeneracy and also in many instances of quasidegeneracy as well. Several appropriate degenerate perturbation methods,[6,7] which (usually) yield the entire set of strongly interacting states, are available. All need to be more thoroughly explored, although Brandow's expansion does seem to represent a distinct improvement[8] over the Bloch-Horowitz procedure from which it is derived. For one particular method, namely generalized Van Vleck, we have given the most time-consuming computational steps (in third-order) beyond those present in a non-degenerate treatment. The parameter $\underline{r}$, here, is the number of virtual orbitals in the set of zeroth-order configurations, divided by N.

Only single substitutions are taken into account, but one or two doubles would make no difference. The first and last steps listed each correspond to a single elementary sum; the middle one to two such sums. For $r = 1$, say, the extra computational effort is comparable to that of an ordinary ground state calculation.

In summary, the potential advantages — and, often, necessity — of the alternative initial approximations presented here are such as to warrant further careful investigation.

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4. B.Kirtman and S.J.Cole, J. Chem. Phys (to be published).
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6. There are a number of exchange perturbation theories. The one that we have used in correlation calculations is due to D. M. Chipman, J. Chem. Phys. 66, 1830 (1977), particularly his most flexible primitive function. The latter yields just one of the degenerate states at a time.
7. (a) C.Bloch and J.Horowitz, Nucl. Phys. 8, 91 (1958);
   (b) B.H.Brandow, Rev. Mod. Phys. 39, 771 (1967); Lect. Theor. Phys. B11, 55 (1968);
   (c) B.Kirtman, J. Chem. Phys. 49, 3890 (1968) and work in progress.
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Alternative Initial Approximations in Perturbation Theory

I. Generalized Valence Bond (GVB)

$$\Psi_{GVB} = \mathcal{A}\, \phi_a(1)\phi_b(2)\phi_c(3)\ldots \mathcal{S}(1,2,3,\ldots)$$

$$\Psi_{GVB}^{PP} : \mathcal{S} = \Delta(1,2)\Delta(3,4)\ldots ; \quad \Delta(i,j) = \alpha(i)\beta(j) - \alpha(j)\beta(i)$$

practical approx: strong orthogonality[2] (SO-VB) or overlap expansions[3] (DOS-VB)

<u>disadvantages</u>

(a) NK^4 vs. K^4 for Hartree-Fock

(b) non-symmetric (exchange) PT[6]

<u>advantages</u>

(a) required near dissociation limit

possibly:

(b) faster convergence $\Longrightarrow$ greater accuracy/effort

e.g. $\underbrace{\text{3rd-order HF}}_{N^2K^4}$ vs. $\underbrace{\text{2nd-order VB}}_{NK^4}$

(c) weak correlation between well-separated electrons $\Longrightarrow$ negligible or simple approximation

(d) atoms-in-molecules $\Longrightarrow$ avoid basis set

II. Limited Multiconfiguration

use IVO's for good zeroth-order excited states

<u>disadvantages</u>

(a) complex PT

exact degeneracy: exchange PT[6]

general: Block-Horowitz,[7a] Brandow,[7b] (generalized) Van Vleck[7c]

(b) evaluate entire secular matrix

$(r = N_v/N)$ $\quad rN^2K^4,\ rN^3K^3,\ r^2N^3K^3$ 3rd order

<u>advantages</u>

(a) required for exact and (some) quasidegeneracy

(b) all states obtained simultaneously

Comments by E. R. Davidson

VECTORIZED PERTURBATION THEORY

Given vector space $|\underline{f}\rangle = (|f_1\rangle, |f_2\rangle \ldots)$

Element $|\phi\rangle = |\underline{f}\rangle\, \underline{\phi}$ $\quad \underline{\phi} = \begin{pmatrix} \phi_1 \\ \phi_2 \\ \vdots \end{pmatrix}$

Vector method gives $\langle \underline{f}|H|\phi\rangle$ without forming matrix $\langle \underline{f}|H|\underline{f}\rangle$

If $|0\rangle$ is an approximate eigenvector involving several reference configurations, RSPT gives $|1\rangle$ and $|2\rangle$ by easy vector operations

F_2 $\quad \ldots \sigma_g^{\,2} + \ldots \sigma_u^{\,2}$ reference for U(R)

Mg_2 $\quad 4e^-$ problem

$^1\Sigma_g^+$, 2 $^1\Sigma_g^+$, $^1\Sigma_u^+$, $^1\pi_g$, $^1\pi_u$ states U(R)

All single and double excitations in minimum NO space in $|0\rangle$

Conclusion: with good $|0\rangle$, 4th order gives chemical accuracy. Calculation beyond 3rd order does not gain absolute accuracy unless triple and quadruple excitations are included

---

E. R. Davidson and C. F. Bender, Chem. Phys. Lett.

STEPS IN MULTICONFIGURATION/EXCITED STATE PERTURBATION THEORY CALCULATIONS

1. Define $\underset{\sim}{C}^0_A$; $\underset{\sim}{H}_{AA}\underset{\sim}{C}^0_A = \underset{\sim}{E}^0\underset{\sim}{C}^0_A$

2. For each root of interest

   a. form $H\psi^0_P$ --- 1
      i. calculate E^2
      ii. calculate C^1

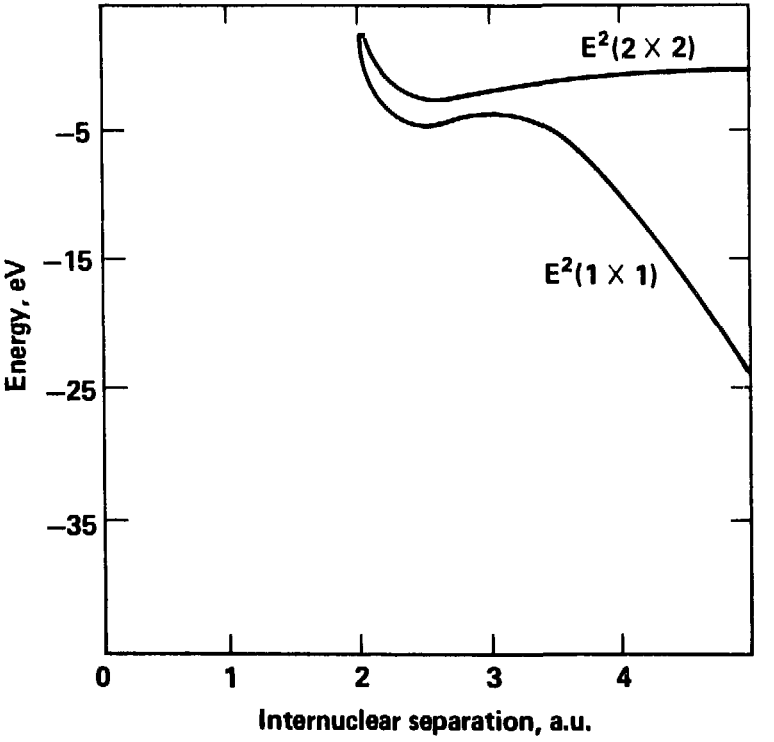
   b. form $H\psi^1_P$ --- 2
      i. calculate E^3
      ii. calculate C^2
      iii. calculate E^4

   c. $\psi^A_P = \psi^0_P + \psi^1_P + \psi^2_P$

   d. form $H\psi^A_P$ --- 3
      i. calculate $E_{AVE} = \langle\psi^A_P|H\psi^A_P\rangle$

POTENTIAL CURVES – PERT

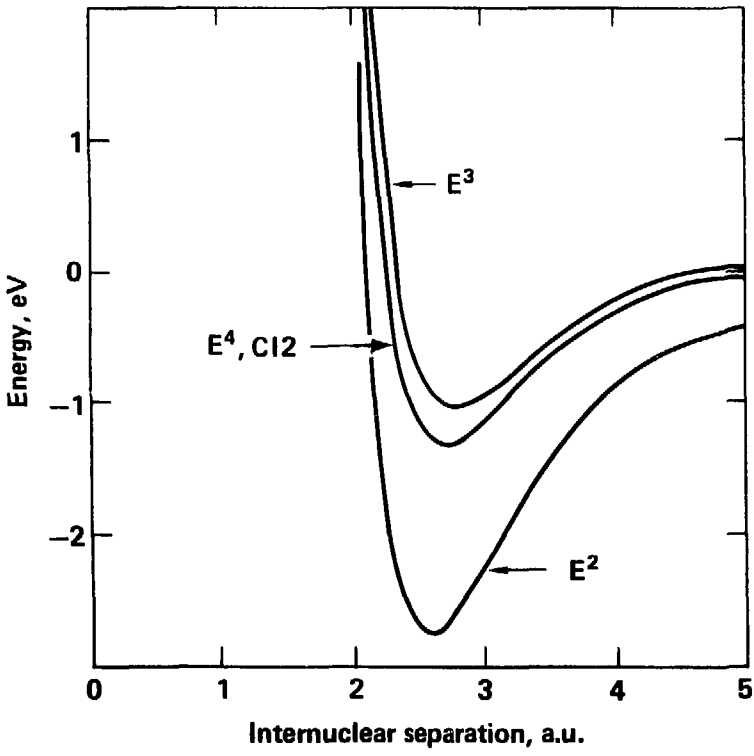
F_2: energy up to second order



(1 × 1) 1 configuration reference space
(2 × 2) 2 configuration reference space

POTENTIAL CURVES – CI PERT

F_2: total energy up to 2nd, 3rd, and 4th order without quadruples (2 configuration reference space)



CI2 = CI curve, 2 configuration reference space

Mg_2 CALCULATION DESCRIPTION

- Basis functions: [11s,7p] $\longrightarrow$ (4s,3p)
- SCF on $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 3\sigma_u^2 1\pi_g^4 1\pi_u^4 4\sigma_g^2 4\sigma_u^2$
- Molecular orbital basis: occupied .. canonical SCF, unoccupied .. ICSCF
- Configurations: frozen $1\sigma_g - 3\sigma_g$, $1\sigma_u - 3\sigma_u$, $1\pi_u$, $1\pi_g$
  1. (SCF + singles into $5\sigma_g$, $5\sigma_u$, $2\pi_g$, $2\pi_u$)$_{S+D}$
  2. (SCF + singles and doubles into $5\sigma_g$, $5\sigma_u$, $2\pi_g$, $2\pi_u$)$_{S+D}$
  3. SCF + full CI (quadruple excitations)
- Internuclear separation .. R = 6.00 a.u.
- Calculations: CI1, CI2, CI3, PERT1, PERT2, PERT3(2)
  Energies: ($^1\Sigma_g^+$, $2^1\Sigma_g^+$, $^1\Sigma_u^+$, $^1\pi_g$, $^1\pi_u$) transition moments

DOMINANT CONFIGURATIONS MUST BE IN C_A

$1^1\Sigma_g^+$	$\underset{\sim}{C}_A \in$ set 1	$\underset{\sim}{C}_A \in$ set 2
E^0	−399.174861	−399.216385
E^2	−399.245243	−399.238777
E^3	−399.241270	−399.239939
E^4	−399.242091	−399.240635
E^A	−399.237797	−399.240471
E^{CI}	−399.240599	
$2^1\Sigma_g^+$		
E^0	−398.969015	−399.071118
E^2	−396.734690	−399.093093
E^3	−397.967954	−399.092813
E^4	BANG	−399.094385
E^A	−398.966258	−399.093317
E^{CI}	−399.093978	

E^{CI} = energy of full 4 electron CI

CONVERGENCE OF PERTURBATION ENERGIES TO CI ENERGIES

Wavefunction 2 [a)]	$^1\Sigma_g^+$	$2^1\Sigma_g^+$	$^1\Sigma_u^+$	$^1\Pi_g$	$^1\Pi_u$
E^0	0.0239	0.0227	0.0383	0.0295	0.0213
E^2	0.0015	0.0007	-0.0009	0.0004	0.0016
E^3	0.0004	0.0010	1×10^{-5}	0.0002	0.0005
E^4	-0.0001	-0.0004	-0.0004	-0.0003	-0.0001
E^{CI}	-399.2403	-399.0938	-399.0963	-399.1347	-399.1004
Wavefunction 3 [b)]					
E^0	0.0242	0.0229	0.0386	0.0301	0.0216
E^2	0.0018	0.0009	-0.0007	0.0009	0.0019
E^3	0.0007	0.0012	0.0003	0.0011	0.0008
E^4	-4×10^{-5}	-0.0004	-0.0005	-0.0003	-0.0001
E^{CI}	-399.2406	-399.0940	-399.0966	-399.1352	-399.1008

a) (SCF + S + D into valence orbitals as reference space) + doubles only beyond 2^d order

b) (SCF + S + D into valence orbitals as reference space) + up to quadruples beyond 2^d order

COMPARISON OF TRANSITION MOMENTS

Wavefunction		Type	CI	Perturbation [a)]
2	$^1\Sigma_u^+ - {}^1\Pi_g$	x	0.42	0.40
2	$^1\Sigma_g^+ - {}^1\Pi_u$	y	0.49	0.48
2	$2^1\Sigma_g^+ - {}^1\Pi_u$	y	0.28	0.30
2	$^1\Sigma_g^+ - {}^1\Sigma_u^+$	z	3.69	3.72
2	$2^1\Sigma_g^+ - {}^1\Sigma_u^+$	z	0.37	0.34
3	$^1\Sigma_u^+ - {}^1\Pi_g$	x	0.43	0.40
3	$^1\Sigma_g^+ - {}^1\Pi_u$	y	0.50	0.48
3	$2^1\Sigma_g^+ - {}^1\Pi_u$	y	0.28	0.30
3	$^1\Sigma_g^+ - {}^1\Sigma_u^+$	z	3.69	3.72
3	$2^1\Sigma_g^+ - {}^1\Sigma_u$	z	0.38	0.34

a) Calculated with 2nd order wavefunction

B_K Approximation

Variation-perturbation expansion method

Z. Gershgorn & I. Shavitt, Int. J. Quantum Chem. 2, 751 (1968).

L. E. Nitzsche & E. Davidson, J. Chem. Phys. 68, 3103 (1978).

G. A. Segal & R. W. Wetmore, Chem. Phys. Lett. 32, 556 (1974).

L. E. Nitzsche & E. Davidson, J. Am. Chem. Soc. in press.

K. Freed, work in progress.

McMurchie & Davidson, W.I.P.

Partition Space

P Important (small #)
Q Less important (large #)

Approximate: $H \cong \tilde{H}$

$$\tilde{H}\begin{pmatrix} C_P \\ C_Q \end{pmatrix} = \begin{pmatrix} H_{PP} & H_{QP} \\ H_{PQ} & D_Q \end{pmatrix} \begin{pmatrix} C_P \\ C_Q \end{pmatrix} = \tilde{E} \begin{pmatrix} C_P \\ C_Q \end{pmatrix}$$

$$D_Q = \text{Diagonal of } H_{QQ}$$

$$[H_{PP} - H_{PQ}\,(\tilde{E}-D_Q)^{-1}\,H_{QP}]\;C_P = \dot{\tilde{E}}\;Cp$$

$$C_Q = (\tilde{E} - D_Q)^{-1}\;H_{QP}C_P$$

$$\tilde{E} = E^o + \delta$$

$$(E-D_Q)^{-1} \cong (E^o-D_Q)^{-1} - \delta(E^o-D_Q)^{-2}$$

$$[H_{PP}-E_o + H_{PQ}(E_o-D_Q)^{-1}\,H_{QP}]\;C_P = \delta[1 + H_{PQ}(E_o-D_Q)^{-2}\;H_{QP}]C_p$$

or

$$H_{eff}\;C_P = \delta\;S_{eff}\;C_p$$

$$H_{eff} = (1_{PP}\;H_{QP}(E_o-D_Q)^{-1})\;\tilde{H}\;\begin{pmatrix} 1_{PP} \\ (E_o-D_Q)^{-1}\;H_{PQ} \end{pmatrix}$$

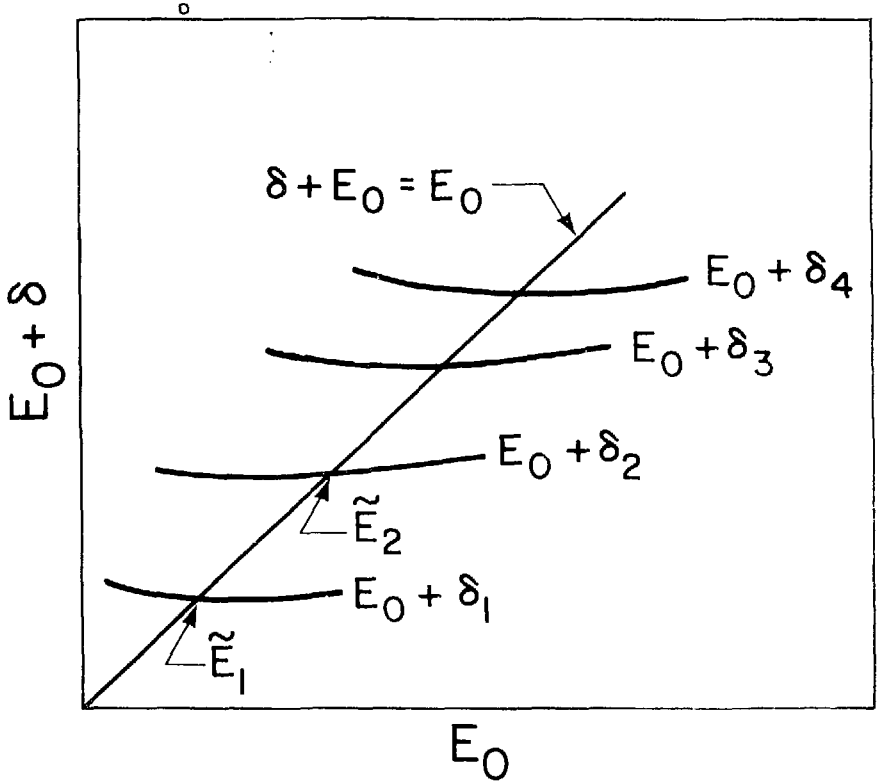
$$S_{eff} = (1_{PP}\;H_{PQ}(E_o-D_Q)^{-1})\;\begin{pmatrix} 1_{PP} \\ (E_o-D_Q)^{-1}\;H_{PQ} \end{pmatrix}$$

So for all E_o

$$E_o + \delta \geqslant \tilde{E}$$

and

$$E_o = \tilde{E} \quad \text{for} \quad \delta = 0$$



Because of variational property $E_o + \delta$ varies by $\sim 10^{-8}$ when E_o is changed by 10^{-1}

Practical

For a grid in E_o over range of spectrum compute $H_{eff}(E_o)$ and $S_{eff}(E_o)$ for all E_o

Simultaneously

$$S_{ij}^{eff} = S_{ij} + \sum_{k \in Q} \frac{H_{ki} H_{kj}}{(E_o - H_{kk})^2} \qquad k,j \in P$$

$$H_{ij}^{eff} = H_{ij} + \sum_{k \in Q} \frac{H_{ki} H_{kj}}{(E_o - H_{kk})} \qquad i,j \in P$$

weighted scalar product H_{Qi} "sparse"

$H_{K_1,1}$	$H_{K_1,2}$
$H_{K_2,1}$	$H_{K_2,2}$
.	$H_{K_3,2}$
.	.
.	.
.	.
.	.
All non-zero connections to 1	All non-zero connections to 2

"matches" (common connections)

$$K_{i,1} = K_{j,2}$$

<u>All</u>: connection lists "ordered" alphabetical

Compute

$$C_Q = (\tilde{E} - D_Q)^{-1} H_{QP} C_P$$

if any C_Q are "Large" ($> \varepsilon$) change P and repeat

Repeat for decreasing ε until C and E converge

Little experience yet. Probable $\varepsilon \approx 10^{-2}$ for acceptable accuracy

$P \sim 10^1 - 10^2$ independent of N for Quantum Chem.

Cost $\sim P^2 N$ (CPU and I/O) Faster than N^2!

IX. COUPLED CLUSTER THEORY

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Presentation by J. A. Pople

COUPLED CLUSTER THEORY

Configuration Interaction (limited to double substitutions) is not size-consistent.

Perturbation Theory (Møller-Plesset) may converge slowly.

Coupled cluster theory (limited to double substitutions) is size-consistent and is equivalent to configuration interaction for a two-electron system. However, it is not variational (does not lead to an energy upper bound).

COUPLED CLUSTER THEORY WITH DOUBLE SUBSTITUTIONS (CCD)

Configuration Interaction:

$$\Psi(\mathrm{CID}) = (1 + \hat{T}_2)\ \Psi_o$$

$$\hat{T}_2 = \frac{1}{4} \sum_{ij} \sum_{ab} a_{ij}^{ab}\ \hat{t}_{ij}^{ab}$$

CID Not size consistent.

$$\Psi(\mathrm{CCD}) = \exp\ (\hat{T}_2)\ \Psi_o$$

$$= (1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2\ \hat{T}_2 + \cdots\ )\ \Psi_o$$

CCD Is size-consistent for separate closed-shell systems since

$$\exp\ (\hat{T}_2^A + \hat{T}_2^B)\ \Psi_o \approx \left[\exp\ (\hat{T}_2^A)\Psi_o^A\right]\left[\exp\ (\hat{T}_2^B)\ \Psi_o^B\ \right]$$

CCD WAVEFUNCTION

$$\Psi(CCD) = \Psi_o + \frac{1}{4} \sum_{ijab} a_{ij}^{ab} \Psi_{ij}^{ab}$$

$$+ \frac{1}{32} \sum_{ijab} \sum_{k\ell cd} a_{ij}^{ab} a_{k\ell}^{cd} \Psi_{ijk\ell}^{abcd} + \cdots\cdots$$

Coefficients a_{ij}^{ab} and energy E to be determined.

Variation approach impractical.

a_{ij}^{ab} is an array with $O(n^2N^2)$ elements where

n = number of electrons

N = number of basis functions

CIZEK EQUATIONS

$$\langle\Psi_o|H-E|\Psi(CCD)\rangle = 0$$

$$\langle\Psi_{ij}^{ab}|H-E|\Psi(CCD)\rangle = 0 \qquad \text{all } ijab$$

These suffice to determine E and a_{ij}^{ab}

First of these equations gives E,

$$E = E_{HF} + \frac{1}{4} \sum_{ijab} a_{ij}^{ab} (ij||ab)$$

$$(ij||ab) = \iint \chi_i^*(1)\chi_j^*(2)(1/r_{12}) \left[\chi_a(1)\chi_b(2) - \chi_b(1)\chi_a(2)\right] d\tau_1 \, d\tau_2$$

EQUATIONS FOR a-VECTOR

$$\langle \Psi_{ij}^{ab} | H-E | \Psi_o + \hat{T}_2 \Psi_o + \frac{1}{2} \hat{T}_2 \hat{T}_2 \Psi_o \rangle = 0$$

Put

$$H = H_o + V$$

where H_o is a Fock Hamiltonian, and V is perturbation in a Møller-Plesset expansion

$$(ab||ij) + a_{ij}^{ab} \Delta_{ij}^{ab} + u_{ij}^{ab} + v_{ij}^{ab} = 0$$

where u_{ij}^{ab} and v_{ij}^{ab} depend on a_{ij}^{ab}

Use ijab as array suffix and iterate

$$\underline{a} = -\underline{\underline{\Delta}}^{-1} (\underline{c} + \underline{u} + \underline{v})$$

$$\underline{u} = \underline{\underline{\bar{V}}}\, \underline{a}$$

$$\underline{v} = \underline{\underline{W}}\, \underline{a}\, \underline{a}$$

$\underline{\underline{\Delta}}$ is diagonal matrix

Vector $\underline{a}$ is given by

$$\underline{a} = - \underline{\underline{\Delta}}^{-1} (\underline{c} + \underline{u} + \underline{v})$$

$$\Delta_{ij}^{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$$

$\underline{u}$-vector is <u>linear</u> in $\underline{a}$

$$u_{ij}^{ab} = \frac{1}{2} \sum_{cd} (ab \| cd)\, a_{ij}^{cd} + \frac{1}{2} \sum_{k\ell} (k\ell \| ij) a_{k\ell}^{ab}$$

$$+ \sum_{kc} \Big\{ -(kb \| jc)\, a_{ik}^{ac} + (ka \| jc)\, a_{ik}^{bc}$$

$$- (ka \| ic)\, a_{jk}^{bc} + (kb \| ic)\, a_{jk}^{ac} \Big\}$$

EQUATIONS FOR a-VECTOR (cont)

Use of the large set of transformed integrals $(ab \| cd)$ can be avoided by transformation of a_{ij}^{cd} and u_{ij}^{ab} to the original atomic basis functions.

Time required is $O(n^2N^4)$

$$\underline{a} = - \underline{\underline{\Delta}}^{-1} (\underline{c} + \underline{u} + \underline{v})$$

$\underline{v}$-vector is quadratic in $\underline{a}$ (see Hurley, ref. 3)

$$v_{ij}^{ab} = \frac{1}{4} \sum_{k\ell cd} (k\ell \| cd) \Big\{ a_{ij}^{cd} a_{k\ell}^{ab} - 2 a_{ij}^{ac} a_{k\ell}^{bd} + a_{ij}^{bd} a_{k\ell}^{ac}$$

$$-2 \left(a_{ik}^{ab} a_{j\ell}^{cd} + a_{ik}^{cd} a_{j\ell}^{ab}\right) + 4\left(a_{ik}^{ac} a_{j\ell}^{bd} + a_{ik}^{bd} a_{j\ell}^{ac}\right) \Big\}$$

Each part of the summation can be split into two operations, e.g.

$$X_{ia\ell d} = \sum_{kc} (k\ell \| cd) \; a_{ik}^{ac}$$

followed by

$$\sum_{k\ell cd} (k\ell \| cd) \; a_{ik}^{ac} a_{j\ell}^{bd} = \sum_{\ell d} X_{ia\ell d} \; a_{j\ell}^{bd}$$

Time required is $O(n^3N^3)$

COMPUTATIONAL TIMES FOR MØLLER-PLESSET THEORY

n = Number of electrons

N = Number of basis functions

				VAX TIME (min) n=10, N=40
	Calculated Integrals		$O(N^4)$	10
	Hartree-Fock SCF		$O(N^4)$	5
	Integral Transformation		$O(nN^4)$	5
Repeated for each iteration of CCD	Second Order		$O(n^2N^2)$	1
	Third Order		$O(n^2N^4)$	10
	Fourth Order	S	$O(n^2N^3)$	1
		D	$O(n^2N^2)$	1
		T	$O(n^3N^4)$	-
		Q	$O(n^3N^3)$	8
				41

References on Coupled-Cluster Theory

1. J. Cizek, J. Chem.Phys. 45, 4256 (1966).

2. J. Cizek and J. Poldus, Int.J.Quant.Chem. 5, 359 (1971).

3. A. C. Hurley, 'Electron Correlation in Small Molecules', Academic Press (1976).

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6. J. Paldus, J. Cizek and I. Shavitt, Phys.Rev. A5, 50 (1972).

7. J. A. Pople, R. Krishnan, H. B. Schlegel and J. S. Binkley, Int.J. Quant.Chem. (to be published).

8. R. J. Bartlett and G. D. Purvis, Int.J.Quant.Chem. (to be published).

Comments by J. Paldus

The spin-adapted form of the coupled-cluster equations[1-4] was extended from the CPMET[5] to the ECPMET for the closed-shell case.[6] The most complicated triexcited-triexcited term is shown. Note that the pertinent coefficients are always expressible through a simple quantity $D_K^{(Z)}(X,Y)$, which is tabulated. The quantity $\Delta^Z(X,Y)$ is defined as

$$[X] = 2X + 1$$

where

$$[X,Y,Z,\ldots] = [X][Y][Z] \ldots$$

and

$$\Delta^Z(X,Y) = [X,Y]^{\frac{1}{2}} \begin{Bmatrix} \frac{1}{2} & Z & X \\ \frac{1}{2} & \frac{1}{2} & Y \end{Bmatrix} ,$$

They satisfy the Racah-Elliot sum rule

$$\sum_Y (-)^Y \Delta^Z(X,Y)\Delta^Z(Y,X') = (-)^{X+X'} \Delta^Z(X,X') ,$$

which in fact is an expression of group-theoretical orthogonality relations for the representation metrices $D_k^{(S)}$ of S_3. The triexcited configurations used are essentially the singlet hole-particle Gelfand states.

The same formulas can be used in direct CI approach of Roos and Siegbahn[7]. Hopefully, a similar approach could also be used for Hausman and Bender's[8] direct CI.

ECPMET (or CIMI)

$$\sum_{j=0}^{i_{max}} \Lambda_{S_I}^{(i,j)} (a^1,\dots,a^i \,|\, a_1 \dots a_i)^{\{S^1,\dots,S^{i-2}\}}_{\{s_1,\dots,s_{i-2}\}} = 0 \quad ; \quad i=1,2,\dots,i_{max}.$$

Triexcited-triexcited part

$$\Lambda_{\tilde{S}_I}^{(3,3)} (a^1a^2a^3|a_1a_2a_3)^{\tilde{S}^{12}}_{\tilde{S}_{12}} =$$

$$- \sum_{\kappa=1}^{3}\sum_{S^{12}} D_\kappa^{(\tilde{S}_I)}(\tilde{S}^{12},S^{12}) \Big[\sum_{b^1} \langle a^{\kappa+1}|f|b^1\rangle\langle b^1a^{\kappa+2}a^\kappa|\underline{t}^{(3)}(\tilde{S}_I)|a_1a_2a_3\rangle^{S^{12}}_{\tilde{S}_{12}}$$

$$+ \sum_{b^1b^2} \langle a^{\kappa+1}a^{\kappa+2}|v|b^1b^2\rangle\langle b^1b^2a^\kappa|\underline{t}^{(3)}(\tilde{S}_I)|a_1a_2a_3\rangle^{S^{12}}_{\tilde{S}_{12}}\Big]$$

$$+ \sum_{\kappa=1}^{3}\sum_{S_{12}} D_\kappa^{(\tilde{S}_I)}(\tilde{S}_{12},S_{12}) \Big[-\sum_{b_1} \langle b_1|f|a_{\kappa+1}\rangle\langle a^1a^2a^3|\underline{t}^{(3)}(\tilde{S}_I)|b_1a_{\kappa+2}a_\kappa\rangle^{\tilde{S}^{12}}_{S_{12}}$$

$$+ \sum_{b_1b_2} \langle b_1b_2|v|a_{\kappa+1}a_{\kappa+2}\rangle\langle a^1a^2a^3|\underline{t}^{(3)}(\tilde{S}_I)|b_1b_2a_\kappa\rangle^{\tilde{S}^{12}}_{S_{12}}\Big]$$

$$- \sum_{b^1b_1}\sum_{\kappa,\lambda=1}^{3}\sum_{S_{12}S^{12}} D_\kappa^{(\tilde{S}_I)}(\tilde{S}^{12},S^{12}) D_\lambda^{(\tilde{S}_I)}(\tilde{S}_{12},S_{12})$$

$$\times \langle a^{\kappa+1}b_1|v|b^1a_{\lambda+1}\rangle\langle b^1a^{\kappa+2}a^\kappa|\underline{t}^{(3)}(\tilde{S}_I)|b_1a_{\lambda+2}a_\lambda\rangle^{S^{12}}_{S_{12}}$$

$$+ \sum_{b^1b_1}\sum_{\kappa,\lambda=1}^{3}\sum_{S_IS_{12}} [\tilde{S}_I,S_I]^{1/2}[S_{12}]^{-1} D_\kappa^{(\tilde{S}_I)}(\tilde{S}^{12},S_{12}) D_\lambda^{(\tilde{S}_I)}(\tilde{S}_{12},S_{12})$$

$$\times \langle a^\kappa b_1|v|a_\lambda b^1\rangle\langle a^{\kappa+1}a^{\kappa+2}b^1|\underline{t}^{(3)}(S_I)|a_{\lambda+1}a_{\lambda+2}b_1\rangle^{S_{12}}_{S_{12}} .$$

where

κ	$D_\kappa^{(Z)}(X,Y)$
1	$(-1)^Y\Delta^Z(X,Y)$
2	$(-1)^X\Delta^Z(X,Y)$
3	$\delta(X,Y)$

X	Y	Z	$\Delta^Z(X,Y)$
0	0	$\frac{1}{2}$	$-\frac{1}{2}$
0	1	$\frac{1}{2}$	$\frac{\sqrt{3}}{2}$
1	0	$\frac{1}{2}$	$\frac{\sqrt{3}}{2}$
1	1	$\frac{1}{2}$	$\frac{1}{2}$
1	1	$\frac{3}{2}$	-1

and

$$[S] = 2S+1$$

$$[S_1,\dots,S_i] = \prod_{k=1}^{i} [S_k]$$

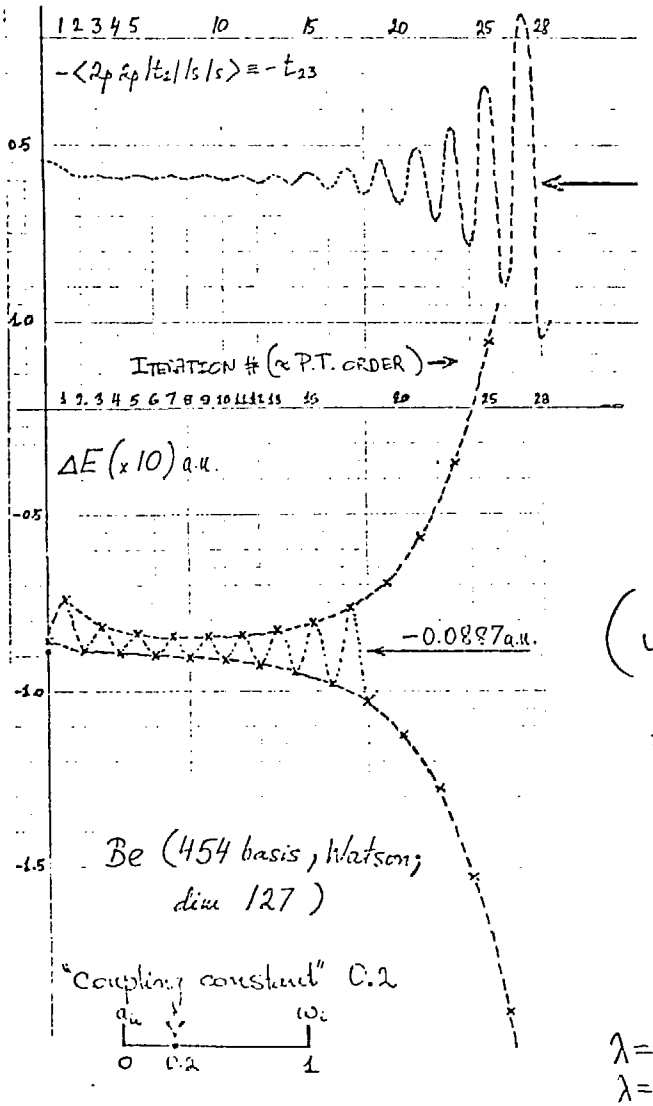
Figure 1. Extended coupled pair many-electron theory (ECPMET) or configuration interaction with molecular integrals (CIMI).

Recently, the size-consistent fourth-order iterative perturbative approaches to the correlation energy calculations were applied to many small and medium sized molecules by Bartlett et al.[9] and Pople et al.[10] These approaches can be regarded as an approximate solution to the CPMET equations[1] (1st Eq. in Fig. 2), which may be written in a form suitable for an iterative solution[5] (2nd Eq. in Fig. 2). However, a zero-order iterative process for the CPMET equations often diverges as in the case shown in Fig. 2, which indicates the values of the largest $\hat{t}_2$ matrix element and of correlation energy ΔE as a function of iteration number for Be atom, using Watson's basis[11] with four s, five p and four d AO's[6]. All 127 biexcited cluster components were considered. While this iterative process converged for smaller bases, this was the first basis for which divergence occured. Nevertheless, the values of the energy and cluster components, corresponding to the second iteration (which corresponds roughly to the fourth order PT) are very close to the exact values, obtained by solving the CPMET equations using Newton-Raphson iterative scheme. One may thus speculate, that the fourth order PT result is very close to the exact result even in the case that the PT approach diverges. One can give a deeper interpretation to these results relying on the theory of asymptotic series[12].

CPMET
(iterative sol^n)

$$v_i = \sum_j a_{ij} t_j + \sum_{j \le k} b_{ijk} t_j t_k$$

$$\Rightarrow \quad \boxed{t_i^{(n+1)} = \frac{1}{a_{ii}^{(1)}} \left[v_i - a_{ii}^{(2)} t_i^{(n)} - \sum_{j(\neq i)} a_{ij} t_j^{(n)} - \sum_{j \le k} b_{ijk} t_j^{(n)} t_k^{(n)} \right]}$$



0th iteration:

$$t_i^{(0)} = \frac{v_i}{a_{ii}^{(1)}}$$

$\Rightarrow$ 2nd order ΔE

$\sim$

$$a_{ii} \equiv a_{ii}^{(1)} + a_{ii}^{(2)}$$

$$= \omega_i + d_i$$

$$\left(\omega_i = \sum_{a'} \varepsilon_{a'}^{HF} - \sum_{a_1} \varepsilon_{a_1}^{HF} \right)$$

$\Rightarrow$

$$a_{ii}^{(1)} = \omega_i + (1-\lambda) d_i$$

$$a_{ii}^{(2)} = \lambda d_i$$

$$\lambda \in [0, 1]$$

$\lambda = 0$ Epstein-Nesbet
$\lambda = 1$ Møller-Plesset

Figure 2. Iterative solution of CPMET equations and PT approaches.

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X. LOGISTICS AND PROGRAM DESIGN

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PROGRAM LOGIC AND STRUCTURE

Presentation by G. H. F. Diercksen

Problem: Build a program system by linking different programs, *under the condition that programs/subprograms/math. algorithms/coding blocks* can easily be *updated/modified/substituted.*

Key Words: Modularization, Data Interfaces.
These terms are neither new nor original, but they are adapted from Information Science.

Lit: ? Folklore

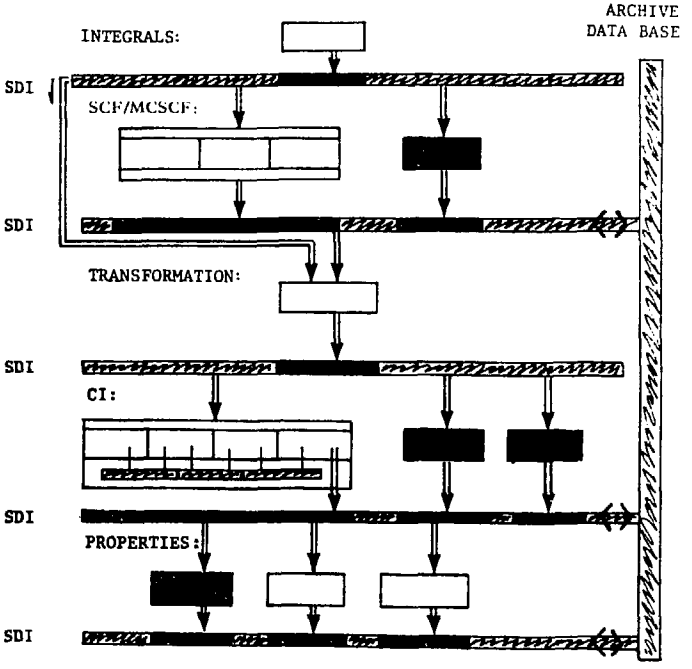


Figure 1. MUNICH molecular program system (MMPS)

MODULARIZATION :

Hierarchy Levels

I Program systems (e.g., MUNICH MPS)

II Programs + subprograms

definition: modules to and from which data are passed exclusively from and to data lists held on external storage.

(e.g. GAUSS, SCF, TRANSF, CI, CISD, ...

SCF: CSCF, OSCF, USCF, ...

CI: CONGEN, SYMGEN, SYMORD, NUMGEN, EIGEN, NATORB,...)

III {Math} algorithms

IV {Logical}blocks of coding "programming without GO TO"?

Advantages: on each level it's easy to update/modify/substitute.

Disadvantages: none?

DATA STRUCTURES:

Standard Data Interfaces (SDI)

A SDI contains the complete and self-content results of the calculation up to the point of generation.

Requirements:

- SDI locatable by name
- SDI logical data sublists locatable by name, to avoid "counting"
- SDI/SDI logical data sublists easily copyable without knowledge of contents

Key: Labelled SDI, SDI sublists, SDI records

Standard Data Interface (SDI) Structure

DEF: SDI = A sequence of any number of Standard Data Sections (SDS) preceded by and including a SDI label (the SDI is closed indirectly by the start of the next SDI or an EOF mark).

DEF: SDS = A sequence of any number of Standard Data Records (SDR) preceded by and including an SDS label (the SDS is closed indirectly by the start of the next SDS or an EOF mark).

DEF: SDR = A sequence of alphanumeric data preceded by and including an SDR label, written/read by one "write/read" statement in any suitable higher language.

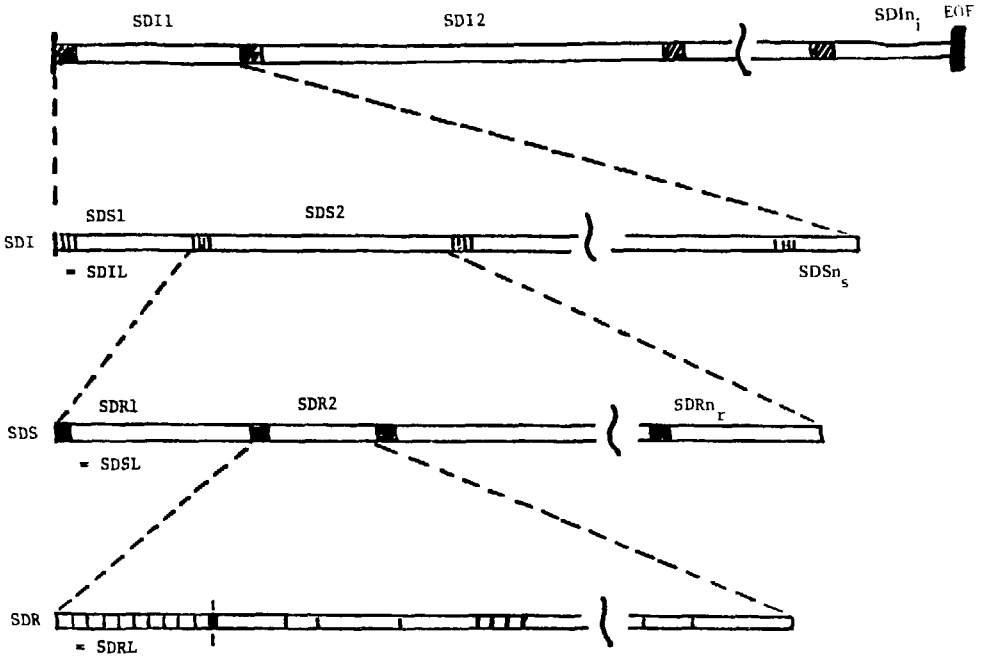
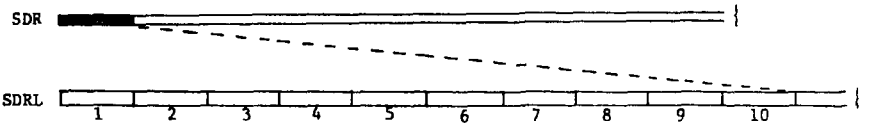


Figure 2

<u>Standard Data Record Label (SDRL)</u>

DEF: The SDR label consists of ten integers



SDRL(1) = LRF = logical record flag
= 0 default
= -1 SDSL
= 4 end of SDS, optional

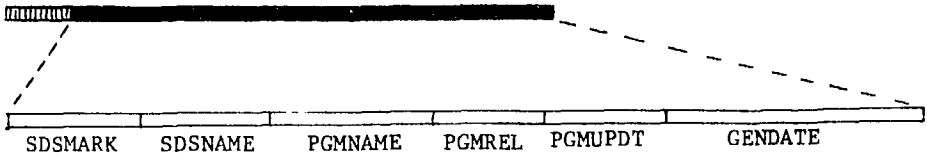
SDRL(2) = LRN = logical record number

SDRL(3) = LRL = logical record length (in standard units), not including the SDRL

SDRL(4) ↓ SDRL(10) } available to user/to be assigned

Standard Data Section Label (SDSL)

DEF: The SDS label consists of one SDR with logical record flag = -1.



SDSMARK = SDS mark

SDSNAME = SDS name

PGMNAME = generating program name

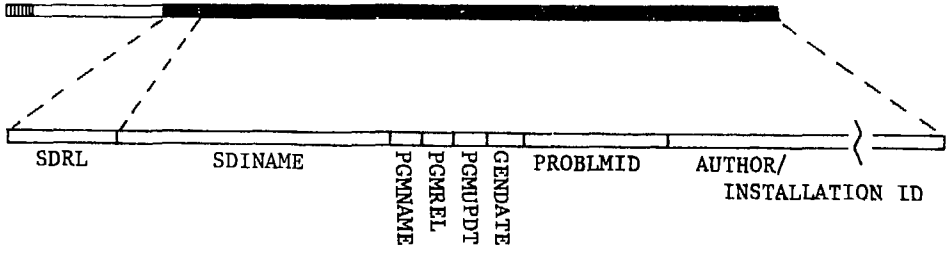
PGMREL = generating program release #

PGMUPDT = generating program update #

GENDATE = SDS generation date

Standard Data Interface Label (SDIL)

DEF: The SDI label consists of *one* SDS named ⟨ SDI label ⟩ which consists of *two* SDR. The first SDR contains the SDS label; the second SDR contains the SDI label.



SDRL = standard data record label

SDINAME = standard data interface name

PGMNAME = generating program name

PGMREL = generating program release #

PGMUPDT = generating program update #

GENDATE = SDI generating date

PROBLMID = problem identifier

MUNICH SDI's

SDI NAMES	SDS NAMES
GAUSSIAN INTEGRAL LIST SHORT LABELED	ASYSDEF GBASDEF GOVERL GKINET GNUCLE GEXELF GTWO
SELF CONSISTENT FIELD	ASYSDEF GBASDEF GSYSDEF EIGVAL EIGVEG
TRANSFORMED INTEGRAL LIST	ASYSDEF GBASDEF GSYSDEF EIGVAL EIGVEG TRANSDEF TOVERL
Etc.	etc.

ALCHEMY Program System
(IBM Computer)

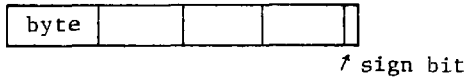
Comments by M. Yoshimine

Aim:
- Generality
- Open-ended

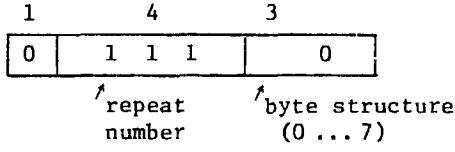
Program design:
- Modular structure
- Dynamic storage allocation
- I/O reduction
- efficient alogrithm

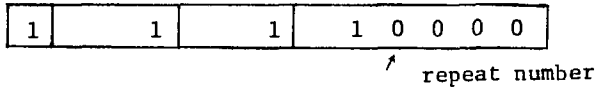
Packing of long data lists: [*A.D.McLean*] Floating point numbers to integer representation with code words.

number:

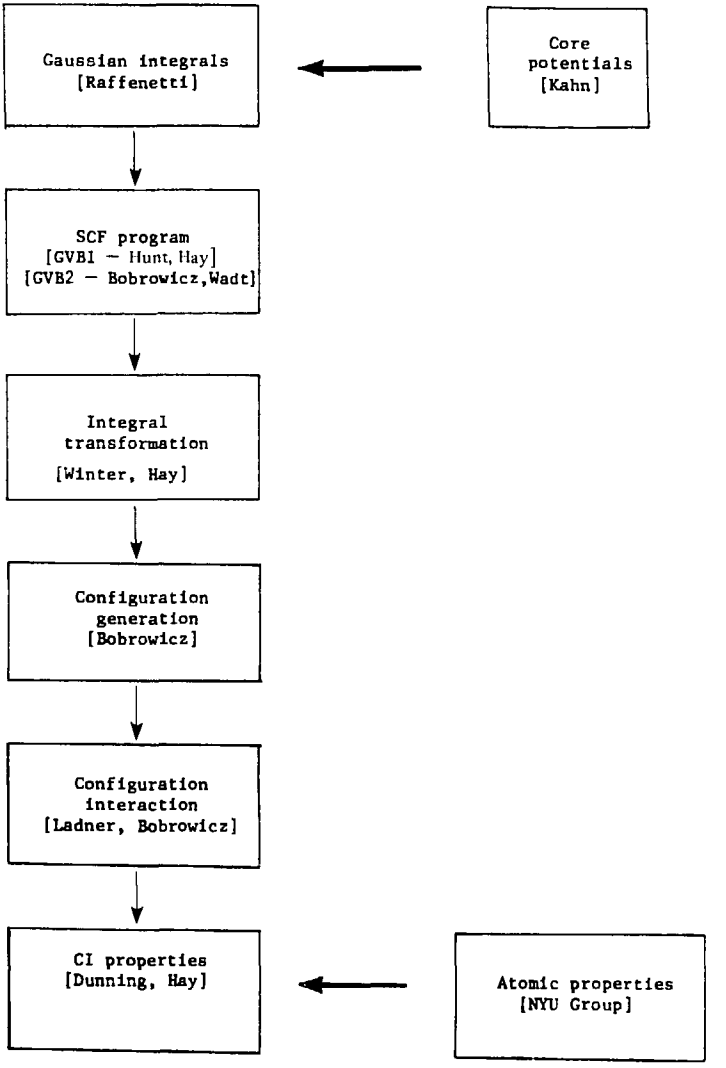


code word:





Comments by P. J. Hay



Characteristics of Bobrowicz CI Program at LASL (CDC 7600)

- Spin states — singlet ($S = 0$) through septet ($S = 3$).
- Flexibility in handling reference configurations and orbital restrictions in configuration generation.
- Use of symmetry for Abelian groups.
- Maximum of 48 MO's (60 MO's in slower version).
- Random access of transformed integrals in large core.
- Number of spin eigenfunctions 5000 for full matrix construction and extraction of several roots.
- A_k and B_k selection procedures.
- Shavitt and Davidson eigenvector algorithms.
- Example: HgCl $^2\Sigma^+$ state,

  17 electrons, 33 MO's

  1540 space and 4910 spin eigenfunctions

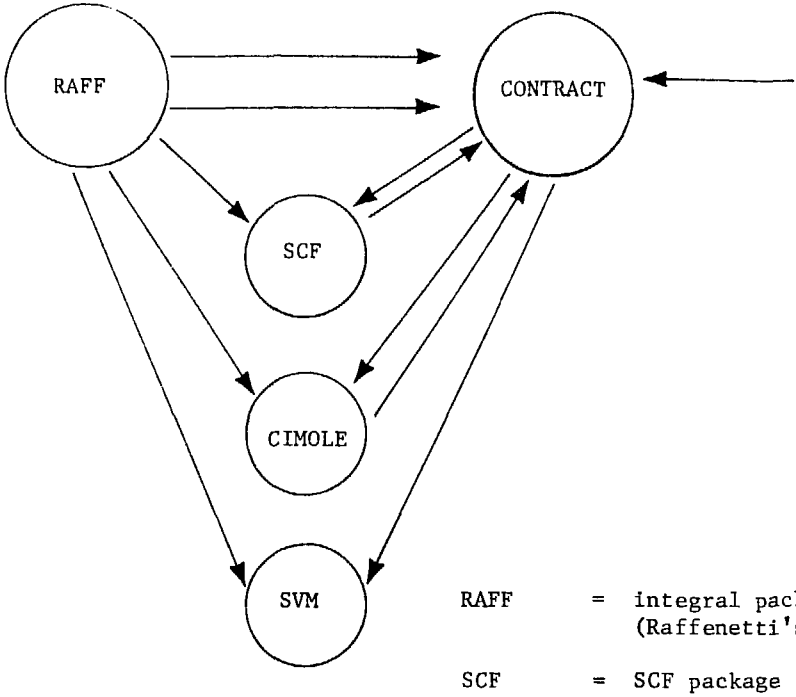
  Form CI matrix (946000 nonzero elements) 100 sec*

  Obtain 2 eigenvectors 187 sec

  *(CP + I/O time)

SCREEPER CODE OVERVIEW
(Lawrence Livermore Laboratory)

Comments by C. F. Bender



RAFF	=	integral package (Raffenetti's Polyatom)
SCF	=	SCF package
CONTRACT	=	integral transformation
CIMOLE	=	formula tape drive CI program
SVM	=	direct CI program

NASA Ames CI Program (CDC 7600)

Comments by S. R. Langhoff

Configuration generation

- Single and/or double excitations of a selected symmetry.
- Generation from up to 35 spatial occupancies.
- Can freeze any subset of the occupied or virtual orbitals
- Each configuration designated by two 60-bit words.

Configuration selection

- By a perturbation theory estimate of their energy contribution or coefficient.
- By diagonal elements.

Matrix element determination

- Number of non-coincidences and orbital differences determined by logic and bit counting procedures.
- Algorithm requires two passes through the configuration list:
  a) first pass determines a chained list of integrals
  b) second pass determines the matrix elements H_{IJ}
  c) non-zero matrix elements are written to disk with a label for each block
- Matrix elements are determined between Slater determinants and then expressed in terms of spin eigenfunctions.
- Largest amount of work is required in putting configurations in maximum coincidence and in determining the parity of the permutation.
- Spin information is stored in block data statements and loaded into fast core at execution.
- The J and K integrals are always held in fast core.

Program limitations

- 50 molecular orbitals.
- 9 open shells.
- 6000 spatial occupancies.
- $2^{15} - 1$ (32,383) maximum size of H matrix.
- All spin eigenfunctions must be kept for each spatial occupancy generated.

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