

Lawrence Berkeley National Laboratory

Recent Work

Title

A GENELOGICAL ELECTRONIC COUPLING PROCEDURE INCORPORATING THE HARTREE-FOCK INTERACTING SPACE AND SUITABLE FOR DEGENERATE POINT GROUPS. APPLICATION TO EXCITED STATES OF BH₃

Permalink

<https://escholarship.org/uc/item/3913w4wd>

Author

Swope, W.C.

Publication Date

1979-08-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Submitted to the Journal of Chemical Physics

A GENEALOGICAL ELECTRONIC COUPLING PROCEDURE INCORPORATING
THE HARTREE-FOCK INTERACTING SPACE AND SUITABLE FOR
DEGENERATE POINT GROUPS. APPLICATION TO EXCITED STATES OF
 BH_3

W. C. Swope, H. F. Schaefer III, and D. R. Yarkony

August 1979

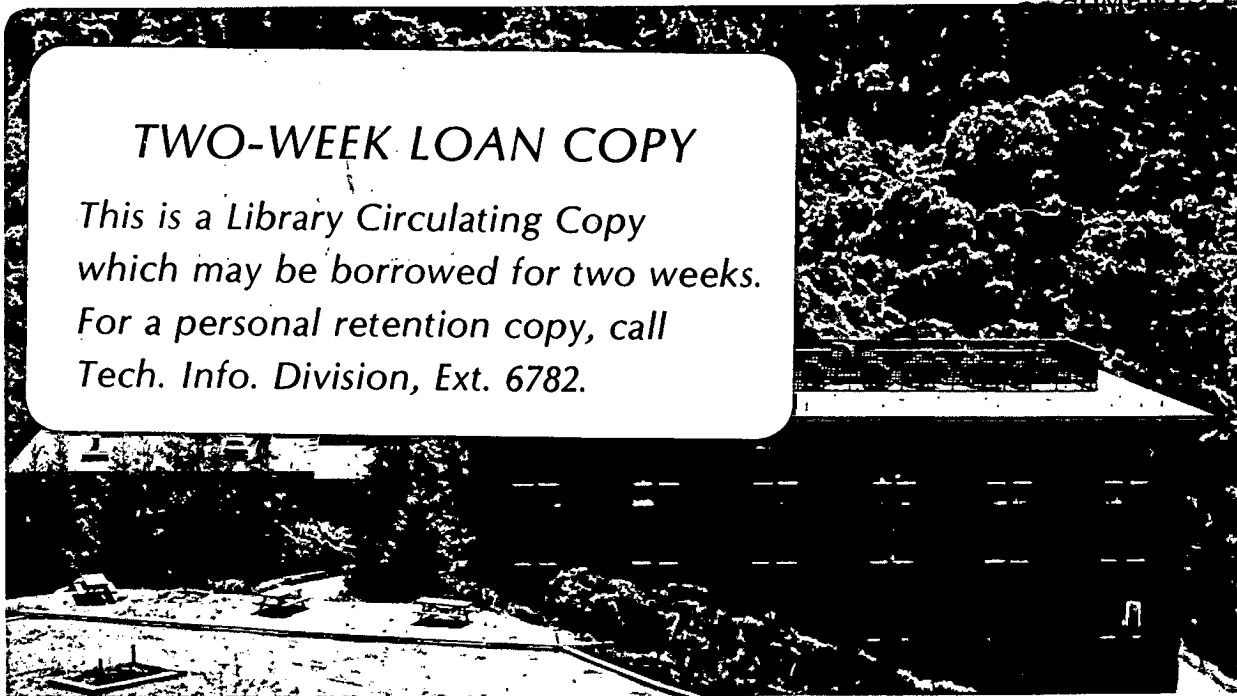
RECEIVED
LAWRENCE
BERKELEY LABORATORY

JAN 31 1980

LIBRARY AND
DOCUMENTS SECTION

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*



LBL-9580e.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

A GENEOLOGICAL ELECTRONIC COUPLING PROCEDURE INCORPORATING
THE HARTREE-FOCK INTERACTING SPACE AND SUITABLE
FOR DEGENERATE POINT GROUPS. APPLICATION TO EXCITED STATES
OF BH_3

W. C. Swope, H. F. Schaefer III,

Department of Chemistry and Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, University of California,
Berkeley, California 94720

and

D. R. Yarkony

Department of Chemistry
Johns Hopkins University
Baltimore, Maryland 21218

Abstract

The use of Clebsch-Gordan type coupling coefficients for finite point groups is applied to the problem of constructing symmetrized N-electron wavefunctions (configurations) for use by the Hartree-Fock SCF and CI methods of determining electronic wavefunctions for molecular systems. The configurations are eigenfunctions of electronic spin operators, and transform according to a particular irreducible representation of the relevant group of spatial operations which leave the Born-Oppenheimer Hamiltonian invariant. The method proposed for constructing the configurations involves a geneological coupling procedure. It is particularly useful for studies of molecules which belong to a group which has multiply degenerate irreducible representations. The advantage of the method is that it results in configurations which are real linear combinations of determinants of real symmetry orbitals.

This procedure for constructing configurations also allows for the identification of configurations which have no matrix element of the Hamiltonian with a reference configuration. It is therefore possible to construct a Hartree-Fock interacting space of configurations which can speed the convergence of a CI wavefunction.

The coupling method is applied to a study of the ground and two excited electronic states of BH_3 in its D_{3h} geometry. The theoretical approach involved Hartree-Fock SCF calculations followed by single and double substitution CI calculations, both of which employed double-zeta plus polarization quality basis sets. The B-H bond length was found to be 1.194 Å for the ground state, 1.26 Å for a ${}^1E''$ state lying 6.08 eV above the ground state, and 1.24 Å for a ${}^3E''$ state lying 5.48 eV above

the ground state. Energies were calculated only for D_{3h} geometries of the molecule, so the excited states may not be stable with respect to C_{2v} distortions. In fact, since both excited states are spatially degenerate, they are expected to exhibit Jahn-Teller distortion.

Finally, the effect of including only Hartree-Fock interacting configurations rather than all single and double substitution configurations in the CI calculation is demonstrated to be energetically quite small.

I. Introduction.

In the application of quantum mechanics to the study of the electronic structure of molecular systems, one is often confronted with the construction of N-electron functions which are symmetrized with respect to a group of operators which commute with the Born-Oppenheimer (B.O.) Hamiltonian. These functions are used as trial functions in variational procedures such as the self-consistent field molecular orbital (SCF-MO) method and the configuration interaction (CI) method. In both of these methods the N-particle trial functions are linear combinations of products of N single-particle symmetrized functions. In the SCF-MO procedure the best set of symmetrized single-particle functions (orbitals) is variationally determined with respect to the simplest possible symmetrized N-particle trial function constructed from these orbitals. In the CI procedure the best linear combination of symmetrized N-particle functions is determined with respect to a given set of symmetrized orbitals.

Among the groups of operators which may commute with the B.O. Hamiltonian is the permutation group and the group of rotations of the spin coordinates of all electrons. Symmetrization with respect to the permutation group results in the N-particle functions being expressed as some linear combination of Slater determinants. Symmetrization with respect to rotations of electron spin coordinates results in linear combinations of determinants which are eigenfunctions of the operators S^2 and S_z .

In addition to the permutation and spin rotation groups, for a particular choice of nuclear coordinates there may exist a group of spatial symmetry operations which commute with the B.O. Hamiltonian. Groups of this nature

are the well-known point groups which are discussed at length in many quantum mechanics textbooks.¹

The smallest N-electron function which is symmetrized with respect to permutation, spin and space operations is called a "configuration function", or simply a "configuration". A configuration, therefore, is antisymmetric on particle exchange, and is characterized by its eigenvalues of S^2 and S_z as well as the component of the irreducible representation (IR) of the point group to which the molecule belongs. Configurations are defined with respect to an electron occupation (e.o.) which specifies how the electrons are distributed among the single particle spatial functions without reference to the component of the function if it transforms as a degenerate IR. An example of an e.o. is $1a'_1{}^2 2a'_1{}^2 3a'_1 le'^3$.

In general there are several determinants associated with a particular e.o. These determinants taken together constitute an invariant space under all the group operations. The configurations which can be constructed from this space of determinants allow for a partitioning of this space into smaller subspaces.

There are many procedures for constructing the configurations² associated with a particular e.o. from a set of symmetrized single-particle functions.³ Since the B.O. Hamiltonian does not involve the spin coordinates of the electrons, the spin and space parts of the configuration may be symmetrized separately. In fact there are many ways to construct spin eigenfunctions, the most common of which are the projection operator and the geneological coupling techniques.⁴ A geneological technique which uses Clebsch-Gordan coefficients to couple successive electron spins will be used here.

General procedures for constructing spatially symmetrized (i.e., with respect to the point group) N-electron functions² are less common. However, if the point group of the molecule is abelian, each determinant constructed from symmetrized orbitals is itself already symmetrized. The IR according to which such a determinant transforms has characters which are simply the products of the characters of the symmetrized orbitals which constitute it. Complications may arise even for abelian groups which have a higher than two-fold axis of symmetry. These groups, such as C_3 , do have all one-dimensional IRs, but these are complex. Since it may be computationally cumbersome to deal with complex orbitals (and, hence, complex integrals) it is common to use real orbitals which then form a basis for a real reducible representation. When this is done, however, individual determinants may no longer be symmetrized. Spatially symmetrized configurations are, in general, linear combinations of determinants.

General methods exist for treating the non-abelian axial point groups all of which have at most two-dimensional IRs. These groups include C_{nv} , D_n and D_{nh} (for $n > 2$), D_{nd} , $C_{\infty v}$ and $D_{\infty h}$. A method of constructing configurations symmetrized with respect to these groups has been presented by Gershgorin and Shavitt.⁵ Their method employs complex orbitals, yet they demonstrated that calculations using the resulting configurations need only real integrals. Furthermore, their method of constructing configurations can also be used for the abelian groups that have a higher than two-fold axis of symmetry (and hence one-dimensional IRs that are complex) as mentioned above.

The preceding method is not applicable to those groups with trebly degenerate IRs, the icosahedral and cubic point groups. A method for

constructing configurations symmetrized with respect to the operations of these point groups was developed and used by Buenker and Peyerimhoff.⁶ Their method relies on resolving the partners of a degenerate IR by the use of a differentiating abelian subgroup g of the full point group G . Configurations symmetrized with respect to g are constructed very easily. Linear combinations of these configurations are taken which are the eigenfunctions of some non-commuting operator R in G , which is not, of course, in g . Their method is quite general and can also treat molecules belonging to non-abelian axial groups.

In Sections II through IV we will discuss an alternative method of constructing configurations. The method is general enough to handle all the spatial symmetries discussed above as well as atomic symmetry. Although it is not restricted to real orbitals, if it employs real symmetrized orbitals it produces configurations that are real, obviating the use of complex arithmetic. The configurations which result may thus easily be used for developing energy expressions for use in open-shell SCF programs and as input to any CI procedure which can already utilize abelian (non-degenerate IRs) spatial symmetry. In Section V a method of identifying which configurations have vanishing Hamiltonian matrix elements between themselves and some reference (usually the SCF) configuration is presented. This method permits reduction of a list of configurations to the Hartree-Fock interacting space and can substantially reduce the size of the calculation with only a minimal loss of correlation energy.⁷

In Section VI the procedure is applied to the study of the electronic structure of the ground and some low-lying excited states of BH_3 in its D_{3h} geometry.

II. The Coupling Procedure.

The procedure is a genealogical coupling method analogous to the Clebsch-Gordan technique used to couple spins. In fact it relies on Clebsch-Gordan-like coefficients, coupling coefficients, for the various point groups. This method as applied to spatial symmetry has its roots in work already a decade old. In a 1969 paper Gabriel discussed this procedure as applied to CI calculations for molecules and showed its close relationship with Racah theory and its application to nuclear shell theory.⁸ Gabriel displayed coupling coefficients for two particles in atomic orbitals transforming as p_x , p_y and p_z . (The coupling coefficients for orbitals transforming as p_0 , p_{\pm} are the usual Clebsch-Gordan coefficients.) He also discussed permutational and spin symmetry.

The genealogical procedure was also discussed in 1973 in a paper by Wybourne.⁹ This paper did not discuss the derivation of coupling coefficients but did outline a method similar to that applied here. A general method for deriving coupling coefficients for finite point (and space) groups has been provided by Sakata.¹⁰ The coupling coefficients for the $C_{\infty v}$ group are presented elsewhere.¹¹

Because of this background we limit ourselves to a brief overview of the procedure providing specific details only for clarity or to explain the methodology which is unique to our approach.¹²

To construct a configuration of the desired space and spin symmetry from a particular electron occupation (e.o.) (a) one first places the shells of the occupations in some canonical order. This order will determine the

sequence in which the shells are successively coupled and will depend on whether the interacting space or the entire invariant subspace of configurations is to be retained. (See Section V.) Next, (b) the possible space-spin states consistent with fermion statistics that can arise from each of the shells are determined. (See Section IV.) Then, for the decided ordering of shells, (c) the direct products of the states of each shell with the states resulting from the cumulative coupling of all previous shells is decomposed. This decomposition can be done without regard for fermion statistics in contrast to (b). Furthermore, the space and spin parts may be decomposed separately. The intermediate couplings that result in a state of the desired symmetry are the geneologies. Next, (d) the geneologies are used along with the Clebsch-Gordan coefficients and the coupling coefficients associated with the point group to construct symmetrized (according to space and spin) shell functions. The geneological procedure insures that shell functions of the same symmetry arising from a given e.o. through different geneologies are orthogonal. Finally, (e) the resulting shell functions are expanded in terms of spin orbitals and antisymmetrized to yield the required configuration functions expressed as linear combinations of determinants.

Step (b) above insures that each geneology results in a configuration which is not annihilated by the antisymmetrizer in step (e). The necessity for consideration of fermion statistics at this point only is a result of the fact that the Pauli exclusion principle will exclude particular couplings of electrons in the same shell, but not of electrons in different shells. An example of this is that for two s-type electrons as in He, the $1s^2$ e.o. gives rise to only a 1S state whereas the $1s2s$ e.o. gives rise to both a 1S and a 3S state.

To illustrate, consider an e.o. of BH_3 $1a'_1{}^2$ $2a'_1{}^2$ $3a'_1$ $2e'$ $1e'{}^2$. (In what follows, the primes will be dropped for typographical convenience.) Suppose that configurations of space-spin symmetry 3A_2 are desired. The possible space-spin states for each shell that are consistent with fermion statistics are $a_1{}^2: {}^1A_1$; $a_1: {}^2A_1$; $e: {}^2E$; and $e{}^2: {}^1E, {}^1A_1$ and 3A_2 . For the ordering of shells as above, the first two shells can be coupled only one way, to a resultant 1A_1 . This may then be coupled only one way with the third shell to give a resultant 2A_1 . This may then be coupled two ways with the fourth shell to give 1E and 3E . Finally, coupling 1E with the possible states of the last shell results in ${}^1E, {}^1A_1, {}^1A_2, {}^1E$ and 3E , and coupling 3E with the possible states of the last shell results in ${}^3E, {}^3A_1, {}^3A_2, {}^3E, {}^5E, {}^3E$ and 1E . There is, therefore only one geneology resulting in the desired 3A_2 symmetry.

The possible couplings arising from this occupation are illustrated in the figure. Lines connect intermediate cumulative couplings and above each line is listed the coupling of each shell. The decomposition of direct products of spin IRs is given by the Clebsch-Gordan series $S = |S_1+S_2|, \dots, |S_1-S_2|$, and the decomposition of direct products of spatial IRs is given by the usual expression¹³

$$a_j = \frac{1}{h} \sum_k \chi^{(j)}(C_k)^* \chi(C_k) N_k \quad , \quad (1)$$

where a_j is the frequency index for the j^{th} IR, $\chi^{(j)}(C_k)$ is the character of the j^{th} IR for the k^{th} class C_k of N_k elements in an h element group. $\chi(C_k)$ is the character of the reducible representation for the k^{th} class obtained by multiplying the characters of the two IRs whose direct product is being decomposed.

$$\begin{aligned}
 S_2(e_x \otimes |00\rangle) &= \frac{1}{2} \{ [e_x \otimes |\frac{1}{2} \frac{1}{2}\rangle] [e_x \otimes |\frac{1}{2} -\frac{1}{2}\rangle] - [e_x \otimes |\frac{1}{2} -\frac{1}{2}\rangle] [e_x \otimes |\frac{1}{2} \frac{1}{2}\rangle] \\
 &\quad - [e_y \otimes |\frac{1}{2} \frac{1}{2}\rangle] [e_y \otimes |\frac{1}{2} -\frac{1}{2}\rangle] + [e_y \otimes |\frac{1}{2} -\frac{1}{2}\rangle] [e_y \otimes |\frac{1}{2} \frac{1}{2}\rangle] \} \\
 S_2(e_y \otimes |00\rangle) &= \frac{1}{2} \{ -[e_x \otimes |\frac{1}{2} \frac{1}{2}\rangle] [e_y \otimes |\frac{1}{2} -\frac{1}{2}\rangle] + [e_x \otimes |\frac{1}{2} -\frac{1}{2}\rangle] [e_y \otimes |\frac{1}{2} \frac{1}{2}\rangle] \\
 &\quad - [e_y \otimes |\frac{1}{2} \frac{1}{2}\rangle] [e_x \otimes |\frac{1}{2} -\frac{1}{2}\rangle] + [e_y \otimes |\frac{1}{2} -\frac{1}{2}\rangle] [e_x \otimes |\frac{1}{2} \frac{1}{2}\rangle] \} .
 \end{aligned}
 \tag{7}$$

which transform as $e_x \otimes |S=0\rangle$ and $e_y \otimes |S=0\rangle$, i.e., as the components of 1E .

When one combines these two-particle functions with the six particle function above according to the coupling rule (3) one obtains an eight particle transforming as 3A_2 :

$$\begin{aligned}
 S_8(a_2 \otimes |11\rangle) &= \frac{1}{\sqrt{2}} \{ S_6(e_x \otimes |11\rangle) \cdot S_2(e_y \otimes |00\rangle) \\
 &\quad - S_6(e_y \otimes |11\rangle) \cdot S_2(e_x \otimes |00\rangle) \} .
 \end{aligned}
 \tag{8}$$

Finally, the above function must be expanded in terms of spin orbitals and antisymmetrized to yield the required configuration. Substitution of spin orbitals into (6), (7) and (8) yields

$$\begin{aligned}
 A \left[\frac{1}{\sqrt{2}} 1a_1^2 (\alpha\beta - \beta\alpha) \right] [2a_1^2 (\alpha\beta - \beta\alpha)] [3a_1 \alpha] \\
 \times \frac{1}{\sqrt{2}} \{ [2e_x \alpha] \left[-\frac{1}{\sqrt{2}} (1e_x 1e_y + 1e_y 1e_x) \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha) \right] \\
 - [2e_y \alpha] \left[\frac{1}{\sqrt{2}} (1e_x^2 - 1e_y^2) \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha) \right] \} .
 \end{aligned}
 \tag{9}$$

A has been used to denote the antisymmetrizer. Eq. (9) reduces (up to a normalization constant) to

$$\psi_{3A_2} = \frac{1}{2} (D_1 - D_2 + D_3 - D_4) \quad (10)$$

where

$$\begin{aligned} D_1 &= A[(1a_1^2 \alpha\beta)(2a_1^2 \alpha\beta)(3a_1 \alpha)(2e_x \alpha)(1e_x 1e_y \alpha\beta)] \\ D_2 &= A[\quad \quad \quad (2e_x \alpha)(1e_x 1e_y \beta\alpha)] \\ D_3 &= A[\quad \quad \quad (2e_y \alpha)(1e_x^2 \alpha\beta)] \\ D_4 &= A[\quad \quad \quad (2e_y \alpha)(1e_y^2 \alpha\beta)] \end{aligned} \quad (11)$$

The importance of the relative phases of the component functions transforming as degenerate IRs, as in (4)-(7), cannot be overemphasized. The minus sign of the e_y component of function (4) eventually resulted in the phases of determinants in equation (10). The coupling method requires the partially coupled shells to transform in exactly the same way as the basis functions of the IRs. Related to this point is the requirement that all degenerate pairs of orbitals transform the same way. Particular attention must be paid to this point because many SCF-MO procedures generate orbitals with random phases.

III. The Coupling Coefficients.

In order to use the method of coupling successive orbitals to produce an N-particle function which transforms according to a particular representation, a set of coupling coefficients is needed. The coupling coefficients, denoted $c_{kli}^{\alpha\beta\gamma}$, are defined by

$$f_i^\gamma = \sum_{k,l} c_{kli}^{\alpha\beta\gamma} f_k^\alpha \otimes f_l^\beta \quad (12)$$

where f_i^γ is a function which transforms as the i^{th} component of the γ^{th} IR. The coupling coefficients are defined with respect to a group and a set of IRs for the group. (The IRs must be the ones that describe the transformation properties of the single particle functions.) If the group is the full rotation group and the representations are those provided by the rotation of angular momentum vectors, the c's are the familiar Clebsch-Gordan coefficients. These are tabulated in most quantum mechanics textbooks. No such information exists for the finite point groups, however.

The coupling coefficients for the finite point groups can be derived once the representation matrices are known. The method of Sakata¹⁰ involves a series of matrix multiplications and is easily programmed for use by a computer. (The coupling coefficients derived by Sakata for the finite point groups were complex because he used complex representations. The couplings used here are real, but the same technique may be used to generate them.) The coupling coefficients used in our algorithm were, however, derived by a related technique which exploits the Van Vleck projection operator formalism.^{1,3}

Recall that for a symmetrized single-particle function, P_R is defined by

$$P_R f_i^\alpha = \sum_{j=1}^{m(\alpha)} f_j^\alpha \Gamma_{ji}^\alpha(R) \quad (13)$$

for every operation R in the group. In this equation $\Gamma_{ji}^\alpha(R)$ is a matrix element of the matrix that represents element R as described by the α^{th} IR of degeneracy $m(\alpha)$. It is a consequence of the great orthogonality theorem that

$$P_{ij}^\alpha f_k^\beta = \delta_{jk} \delta_{\alpha\beta} f_i^\alpha, \quad (14)$$

where P_{ij}^α is given by

$$P_{ij}^\alpha = \frac{m(\alpha)}{h} \sum_R \Gamma_{ij}^\alpha(R) P_R \quad (15)$$

P_{ij}^α is called a projection operator because it projects out of an arbitrary function the part which corresponds to the i^{th} component of the α^{th} IR if the function contains a component which transforms like the j^{th} component of the α^{th} IR.

To extend this technique to a two-particle function space, we need only observe that on a direct product space

$$P_R (f_i^\alpha \otimes f_k^\beta) = \sum_{j=1}^{m(\alpha)} \sum_{\ell=1}^{m(\beta)} (f_j^\alpha \otimes f_\ell^\beta) \Gamma_{ji}^\alpha(R) \Gamma_{\ell k}^\beta(R) \quad (16)$$

For example, if the operations have been defined such that for some R ,

$$P_R e_x = -\frac{1}{2} e_x - \frac{\sqrt{3}}{2} e_y \text{ and } P_R e_y = \frac{\sqrt{3}}{2} e_x - \frac{1}{2} e_y, \text{ then}$$

$$\begin{aligned} P_R e_x(1) e_y(2) &= \left[-\frac{1}{2} e_x(1) - \frac{\sqrt{3}}{2} e_y(1) \right] \left[\frac{\sqrt{3}}{2} e_x(2) - \frac{1}{2} e_y(2) \right] \\ &= \frac{1}{4} \left[-\sqrt{3} e_x(1) e_x(2) + e_x(1) e_y(2) - 3 e_y(1) e_x(2) + \sqrt{3} e_y(1) e_y(2) \right]. \end{aligned} \quad (17)$$

If one uses the projection operator technique to determine the coupling coefficients, care must be taken to use the transverse projection operator (P_{ij}^α , where $i \neq j$) to determine the correct relative phases (as in equation 4) of functions transforming as components of a multiply degenerate IR.

The task of determining the coupling coefficients is readily programmable and needs to be done only once for each point group. In fact, there are many groups which have the same coupling coefficients because they are isomorphic. Thus, the C_{3v} and D_3 groups have identical coupling coefficients.

Real coupling coefficients have been determined for point groups C_{6v} , C_{4v} , $C_{\infty v}$, D_4 , D_6 , D_{2h} , D_{3h} , D_{2d} , $D_{\infty h}$, and T_d .¹² Of course, this also establishes the couplings for the various subgroups associated with the above as well as other groups which are isomorphic with them. Thus, once the coefficients for the C_{6v} group are determined, one has them immediately for C_2 , C_{2v} and C_{3v} (subgroups) as well as for D_6 (isomorphic) and its subgroups. The results for the $C_{\infty v}$ group have been applied to a study of sulfur oxide which is presented elsewhere.¹¹

IV. The Allowed Intrashell Couplings.

Not all N-particle functions are allowed by fermi statistics. Consider the case of two equivalent e-type electrons in a molecule of D_{3h} symmetry. Without regard for fermi statistics, six states can be constructed. They are 1A_1 , 3A_1 , 1A_2 , 3A_2 , 1E , and 3E . The corresponding wavefunctions may be constructed from coupling coefficients like those listed in equations 2, 3 and 4.

$$^1A_1: \frac{1}{2} [e_x(1)e_x(2)+e_y(1)e_y(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)]$$

$$^3A_1: \frac{1}{\sqrt{2}} [\quad \quad \quad][\alpha(1)\alpha(2)]$$

$$^1A_2: \frac{1}{2} [e_x(1)e_y(2)-e_y(1)e_x(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)]$$

$$^3A_2: \frac{1}{\sqrt{2}} [\quad \quad \quad]\alpha(1)\alpha(2)$$

$$^1E: \begin{cases} \frac{1}{2} [e_x(1)e_x(2)-e_y(1)e_y(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)] \\ \frac{1}{2} [-e_x(1)e_y(2)-e_y(1)e_x(2)] \quad \quad \quad " \end{cases}$$

$$^3E: \begin{cases} \frac{1}{2} [e_x(1)e_x(2)-e_y(1)e_y(2)]\alpha(1)\alpha(2) \\ \frac{1}{2} [-e_x(1)e_y(2)-e_y(1)e_x(2)] \quad \quad \quad " \end{cases}$$

Operation on these functions by the antisymmetrizer annihilates all except the 1A_1 , 3A_2 and 1E functions, leaving

$${}^1A_1: \frac{1}{\sqrt{2}} [A(e_x e_x \alpha\beta) + A(e_y e_y \alpha\beta)]$$

$${}^3A_2: A(e_x e_y \alpha\alpha)$$

and

$${}^1E: \left\{ \begin{array}{l} \frac{1}{\sqrt{2}} [A(e_x e_x \alpha\beta) - A(e_y e_y \alpha\beta)] \\ -\frac{1}{\sqrt{2}} [A(e_x e_y \alpha\beta) + A(e_x e_y \beta\alpha)] \end{array} \right\}$$

Therefore, the only states allowed from the e^2 occupation are the above three. It is these states to which step b of Section II refers.

The coupling procedure requires either a tabulation of the allowed intrashell couplings for partially occupied shells or a fast and systematic way to determine them. Like the coupling coefficients themselves, these need only be determined once for a given point group.

A simple method for the determination of the allowed couplings of a shell occupation has been presented by Goscinski and Ohrn.¹⁴ Their method, which uses a generalization of equation 1 where the frequency index a_j lists the frequency of states which are symmetrized with respect to space and spin as well as antisymmetric with respect to particle exchange, is exploited by our algorithm.

V. The Hartree-Fock Interacting Space of Configurations.

Discussions concerning the Hartree-Fock (HF) interacting space of configurations were first presented by Bunge and Bunge⁷ and later by McLean and Liu.⁷ The idea is to delete certain configurations from a list which do not "interact" with one or more reference configurations. Two configurations are said to interact if there is a non-zero matrix element of the Hamiltonian between them. The non-interacting configurations are not expected to contribute substantially to a CI wavefunction or its corresponding energy since these configurations do not contribute in a first (for energy and wavefunction) or second (for energy) order Rayleigh-Schrödinger perturbation series expansion.

The configuration list used for the atomic CI calculations of Bunge and Bunge was generated by the application of projection operators to a list of determinants. The determinants were obtained from electron occupations which in turn were generated as single and double substitutions of electrons from the HF occupation. Some of the determinants so generated differed by more than two spin orbitals from any determinant of the HF configuration. It was found that some configurations projected from these non-interacting determinants consisted entirely of non-interacting determinants themselves. These were the non-interacting configurations. The maximum non-interacting space of Bunge was the one projected from the particular choice of determinants which yielded the largest number non-interacting configurations. It is important to note, however, that some of the determinants of Bunge's interacting space of configurations were non-interacting.

McLean and Liu prescribed a procedure for constructing a smaller interacting space of configurations all of whose determinants interact with

the reference determinants. Their procedure cannot be used with the geneological procedure discussed here.

All configurations generated from occupations that are single or double substitutions from a closed-shell reference occupation are interacting with respect to the reference configuration. If the reference is an open-shell configuration coupled with space-spin symmetry, say, S_A an interacting configuration arising from a given occupation is determined in this work as one which, if it has as part of its open shell exactly the same orbitals and occupation numbers as the reference, has the coinciding open shells coupled with the same space-spin symmetry (S_A) as the reference. (By "the same space-spin symmetry," it is meant to include not only the total spin (S) and spatial IR designation but also the component of spin (m_s) and IR when the IR is degenerate.) To perform this selection, the shells of the occupation are ordered so that those open shells which coincide with the open shells of the reference are last. The geneologies which are kept (which produce the interacting configurations) are those which have a cumulative space-spin coupling up to, but not including, the coinciding open shells which are the same as that for the reference.

An example will serve to clarify this process. Consider a calculation of the low-lying 3E state of BH_3 arising from an occupation $1a_1^2 2a_1^2 3a_1 1e^3$. If this occupation is used as a reference occupation in a CI calculation, an occupation which would appear in a list of single and double substitutions is $1a_1^2 3a_1 1e^3 2e^2$. For the purpose of constructing the geneologies, the shells are reordered to $1a_1^2 2e^2 3a_1 1e^3$ so that the shells which appear also in the reference are coupled last. From this occupation there are four

geneologies which would yield 3E configurations. However, there is only one geneology which yields a potentially interacting configuration. This is the geneology which has $1a_1^2 2e^2$ coupled to the same space-spin symmetry as $1a_1^2 2a_1^2$ in the reference, namely 1A_1 . It is easily verified that the other three configurations are non-interacting.

This criterion for selecting an interacting space of configurations sometimes produces configurations with determinants which differ by more than two spinorbitals from the reference determinants. It is, therefore, a larger interacting space than that formulated by McLean and Liu and one of roughly the same size as that of Bunge.

This simple criterion for dropping non-interacting configurations can reduce the number of configurations by as much as a half with only a small cost in correlation energy. The reason for the large reduction is two-fold. First, since the number of open-shell electrons is usually much smaller than the number of closed-shell electrons for an open-shell reference configuration, there is usually a larger number of occupations part of whose open shells match the open shells of the reference than there are occupations whose open shells are completely different than those of the reference. In a singles and doubles substitution CI, these occupations are obtained from substitutions of electrons from the closed shell to the virtual orbitals; substitutions which leave the open shell occupations as they are in the reference. It is to all these occupations that the criterion for selecting the interacting space can be applied. Secondly, for these same types of occupations there are, in general, the largest number of geneologies resulting in the correct space-spin symmetry because these occupations usually have more open shells.

Another advantage of using the interacting space is that the non-interacting configurations are often (for the same reasons as mentioned above) longer, in terms of the number of determinants they contain, than the interacting configurations. Because of this the fraction of time to generate the formulas for the CI Hamiltonian matrix elements is even smaller than the square of the ratio of the number of interacting configurations to the total number of configurations.

VI. Application of the Coupling Procedure to the Study of Excited Electronic States of BH_3 in the D_{3h} Geometry.

There have been literally dozens of theoretical studies done on borane, BH_3 . The interest in this molecule is two-fold. Diborane, the borane dimer, is used by organic chemists as a standard reagent for hydroboration (cis-addition of H-OH to alkenes) as well as a powerful reducing agent.¹⁵ It is believed that in some cases the monomer is the reactive species in these processes.²⁵ Secondly, the dimerization to produce diborane is the simplest reaction that forms three-center (B-H-B) bonds from two center (B-H) bonds.¹⁶ Furthermore, the relatively small size of the molecules allows a fairly thorough theoretical treatment to be performed. Most studies to date, however, have been concerned with the dimerization reaction and have only treated the ground X^1A_1' state.

Of the many ab initio studies¹⁷ of borane which have been performed, perhaps the best which has been done at the Hartree-Fock level of theory was by Hall, Marynick and Lipscomb¹⁷ in 1972. Their treatment, which is near the Hartree-Fock limit, utilized a double zeta plus polarization basis of Slater-type orbitals on the hydrogen centers and a triple zeta plus polarization basis on the boron center. Their calculations yielded an energy of -26.4014 hartrees with a D_{3h} geometry and bond length of 2.25 a.u.

Considerable work has also been done in an attempt to treat the electron correlation energy contribution to the dimerization energy. There have been minimum basis configuration interaction calculations,¹⁸ valence bond calculations,¹⁹ and several studies²⁰ which determine electron pair correlation energies. Of the work

which treats electron correlation probably the most complete is that of Ahlrichs²⁰ presented in 1974 and that of Ahlrichs, et al.,²⁰ presented in 1975.

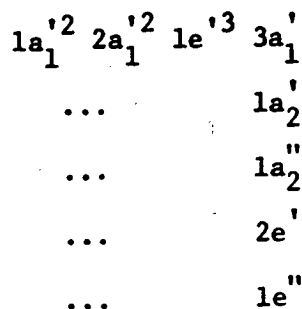
In his 1974 work Ahlrichs used a basis slightly larger than a double zeta plus polarization ([5s3p1d/2slp]) basis of gaussian type orbitals and obtained an SCF energy of -26.39697 hartrees at a D_{3h} geometry with a bond length of 2.25 a.u. His treatment of correlation energy involved the use of the independent electron pair approximation (IEPA) method, the pair natural orbital configuration interaction (PNO-CI) method, and the coupled electron pair approximation (CEPA) method. Of these, only the PNO-CI method is variational. The PNO-CI energy obtained in that work was -26.51107 hartrees which did not reflect the correlation of the $1a_1'$ ($\approx 1s$ on B) core electrons.

The work presented by Ahlrichs, et al., in 1975 used basis sets made larger than those in the 1974 work by the addition of more polarization functions ([5s3p2d1f/3s2p]). This extensive basis yielded an SCF energy of -26.39881 hartrees and a PNO-CI energy of -26.52325 hartrees when computed with a bond length of 2.25 a.u. As before, the core electrons were not correlated. The fact that all the extra functions resulted in an SCF energy that is lower by only 0.002 hartrees and yielded only 0.01 hartrees more correlation energy is significant. The reason that this large basis set did not yield an energy as close to the Hartree-Fock limit as that of Hall, et al., is that the latter, used a basis of Slater functions which describes the nuclear cusp of the orbitals better than a basis of Gaussian functions. This deficiency is not expected to affect the calculation of properties which will be discussed here.

All of the past theoretical studies have involved only the ground X^1A_1' state of borane which arises from the electron occupation $1a_1'^2 2a_1'^2 1e'^2$. Since borane is isoelectronic with methylene, which has a ground state symmetry of 3B_1 with low-lying states of 1B_1 and 1A_1 symmetry,²¹ it is interesting to determine if there are low-lying bound (with respect to D_{3h} stretch) electronic states of borane and, if so, how they relate to the electronic states of methylene.

The basis set used in this study consisted of a set (9s5p/4s) of primitive gaussian functions on the boron and hydrogen centers generated by Huzinaga and contracted to a slightly larger than double zeta set [4s3p/2s] by Dunning.²² This double zeta set was then augmented with d-type polarization functions on the boron center (zeta = 0.471) and p-type polarization functions on the hydrogen centers (zeta = 0.725). This double zeta plus polarization basis is almost of the quality of Ahlrich's 1974 work. In fact our basis yields an SCF energy only 0.0005 hartrees higher than Ahlrich's.

The strategy behind the search for higher bound electronic states involved performing a series of SCF calculations for the geometry 2.25 a.u. The SCF calculations utilized energy expressions which were obtained from symmetrized wavefunction forms which were constructed by the geneological procedure outlined in the earlier sections. The various symmetrized wavefunctions represented all space-spin couplings derived from electron occupations which were single substitutions of an electron from the orbital of the highest orbital energy of the ground state (the $1e'$ orbital) to the unoccupied orbital of lowest orbital energy of each symmetry type. The electron occupations produced by this procedure are



Of the states arising from these occupations the two of lowest energy at the SCF level have $1E''$ and $3E''$ symmetry and both arise from the third occupation.

It is not surprising that these occupations produce the lowest excited states for these geometries. The $1A_1'$ state is analogous to the $1A_1$ state of methylene which arises from an occupation $1a_1^2 2a_1^2 1b_2^2 3a_1^2$. If the IRs of D_{3h} are resolved into those of C_{2v} , $a_1' \rightarrow a_1$ and $e' \rightarrow (a_1, b_2)$, and it is easily seen that the two molecules actually have the same occupation in the lowest common point group. Similarly, $a_2'' \rightarrow b_1$ in going from D_{3h} to C_{2v} , and so the $1E''$ and $3E''$ states arise from an occupation that would be characterized $1a_1^2 2a_1^2 (3a_1 1b_2)^3 1b_1$ in C_{2v} . The ground $3B_1$ and the $1B_1$ states of methylene, in fact, arise from the occupation $1a_1^2 2a_1^2 1b_2^2 3a_1 1b_1$. It is unfortunate that this simple analysis does not predict the ordering of the states correctly; the ground state occupation of methylene corresponds to excited states of borane and vice versa.

The next step of the investigation involved performing single and double substitution configuration interaction (CI) calculations at various D_{3h} geometries on the ground and two excited states of the molecule. For this step the BERKELEY²³ system of CI programs was used together with the configuration generating procedure discussed above. Substitutions of all eight electrons were made into all available orbitals during the construction

of the configuration list. (I.e., no orbitals, occupied or virtual, were held frozen.) Only HF interacting configurations were generated. This procedure results in different numbers of configurations for each of the three electronic states, but treats them with comparable quality.

For each electronic state, energies were computed at several D_{3h} geometries. The resulting energies were fit to an analytic form. Not surprising for the ground state, but possibly surprising for the two excited states, all three states exhibit a local minimum in energy with respect to D_{3h} geometry distortions. The results are displayed in the table.

It is important to note that we have not referred to the energies and geometries of the E'' states as excitation energies (T_e) and bond lengths (r_e) because BH_3 in these electronic states may not be stable with respect to C_{2v} distortions, forming $H + BH_2$ or $H_2 + BH$. Furthermore, since these excited states are spatially degenerate, they are expected to show a Jahn-Teller distortion to a C_{2v} geometry ($E'' \rightarrow A_2 + B_2$) even if they are bound. An investigation of the C_{2v} geometries of the resulting four electronic states was felt to be beyond the scope of this work, which is concerned primarily with point groups involving degenerate IRs.

From the table it is clear that our lowest energy, -26.52872 a.u. for X^1A_1 at equilibrium, is significantly lower than that reported by Ahlrichs in 1974, -26.51107 a.u., even though the basis sets are comparable. This is due to the fact that our configuration lists allow for correlation of the $1a_1'$ core electrons whereas his did not.

The table displays a rather striking example of the considerable savings involved in using only HF interacting configurations in a CI calculation, particularly for the $^1E''$ state, where the interacting space

has only 62% as many configurations as the full space of single and double substituted configurations. Since the work involved in a CI calculation goes roughly as the square of the number of configurations, this saving is considerable. Moreover, the non-interacting configurations are usually the longest (more determinants) and so the effort saved by doing the smaller calculation is even more. One might well ask how much electronic energy this savings in effort has cost us. To determine this, a calculation was performed on the $^1E''$ state at the D_{3h} geometry with $R(B-H) = 2.373$ using all 4002 configurations constructed from the single and double substitutions. The larger calculation, which required more than four times the computational effort, yielded an energy of -26.30582, only 0.0006 hartrees lower than the more easily obtained energy. Although this difference is not expected to be constant over the range of geometries needed to compute vibrational frequencies, it is so small as to be inconsequential for our purposes.²⁴

Appendix: Coupling Coefficients for the D_{3h} Point Group

The coupling coefficients used in this study of the BH_3 molecule were derived by a projection operator technique from the following set of representations:¹

for the E'' representation,

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad \sigma_h = -E; \quad C_3 = \begin{pmatrix} -C & -S \\ S & -C \end{pmatrix}; \quad C_3^2 = \begin{pmatrix} -C & -S \\ -S & -C \end{pmatrix};$$

$$S_3 = -C_3; \quad S_3^2 = -C_3^2; \quad C_{2_1} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}; \quad C_{2_2} = \begin{pmatrix} C & -S \\ -S & -C \end{pmatrix};$$

$$C_{2_3} = \begin{pmatrix} C & S \\ S & -C \end{pmatrix}; \quad \sigma_{v_1} = -C_{2_1}; \quad \sigma_{v_2} = -C_{2_2}; \quad \sigma_{v_3} = -C_{2_3}$$

and for the E' representation

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad \sigma_h = E; \quad C_3 = \begin{pmatrix} -C & -S \\ S & -C \end{pmatrix}; \quad C_3^2 = \begin{pmatrix} -C & S \\ -S & -C \end{pmatrix};$$

$$S_3 = C_3; \quad S_3^2 = C_3^2; \quad C_{2_1} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}; \quad C_{2_2} = \begin{pmatrix} -C & S \\ S & S \end{pmatrix};$$

$$C_{2_3} = \begin{pmatrix} -C & -S \\ -S & C \end{pmatrix}; \quad \sigma_{v_1} = C_{2_1}; \quad \sigma_{v_2} = C_{2_2}; \quad \sigma_{v_3} = C_{2_3}$$

where $C = \cos\pi/3 = 1/2$ and $S = \sin\pi/3 = \sqrt{3}/2$. The representations for the one-dimensional representations are simply the characters and these may be found in any group theory text.¹

These representations are adequate to define the coupling coefficients for single particle functions which are symmetrized with respect to the representations.

The coupling coefficients for the direct products of functions transforming as the one-dimensional IRs may be trivially found from the character table. For the product of a function transforming as a one-dimensional IR with a function transforming as one component of a two-dimensional IR, there are two situations. If the one-dimensional IR is a_1' or a_2'' , the couplings are given as

$$\begin{Bmatrix} a & \otimes & e_x \\ a & \otimes & e_y \end{Bmatrix} \quad \text{transforms as} \quad \begin{Bmatrix} e_x \\ e_y \end{Bmatrix} ,$$

where e_i can be a component of either an e' - or e'' -type function. This situation describes $a_1' \otimes e' = e'$, $a_1' \otimes e'' = e''$, $a_2'' \otimes e' = e''$, and $a_2'' \otimes e'' = e'$. If the one-dimensional IR is a_2' or a_1'' , the couplings are given as

$$\begin{Bmatrix} a & \otimes & e_y \\ -a & \otimes & e_x \end{Bmatrix} \quad \text{transforms as} \quad \begin{Bmatrix} e_x \\ e_y \end{Bmatrix} .$$

This situation describes $a_2' \otimes e' = e'$, $a_2' \otimes e'' = e''$, $a_1'' \otimes e' = e''$. and $a_1'' \otimes e'' = e'$.

For the product of two functions each of which transforms as an e-type function, the couplings are given as

$$\frac{1}{\sqrt{2}} (e_x \otimes e_x + e_y \otimes e_y) \quad \text{transforms as} \quad a_1$$

$$\frac{1}{\sqrt{2}} (e_x \otimes e_y - e_y \otimes e_x) \quad \text{"} \quad a_2$$

$$\left\{ \begin{array}{l} \frac{1}{\sqrt{2}} (e_x \otimes e_x - e_y \otimes e_y) \\ \frac{1}{\sqrt{2}} (-e_x \otimes e_y - e_y \otimes e_x) \end{array} \right\} \quad \text{"} \quad \left\{ \begin{array}{l} e_x \\ e_y \end{array} \right\}$$

These last couplings are used for $e' \otimes e' = a_1' \oplus a_2' \oplus e'$, $e'' \otimes e'' = a_1' \oplus a_2' \oplus e'$, and $e' \otimes e'' = a_1'' \oplus a_2'' \oplus e''$.

Acknowledgments

This research at Berkeley was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. At Johns Hopkins DRY is pleased to acknowledge the partial support of the Research Corporation, the Donors of the Petroleum Research Fund, administered by the American Chemical Society and the National Science Foundation (grant CHE-7824153) during the course of this work.

We would also like to acknowledge the invaluable help of Dr. B. R. Brooks during the development and implementation of the CI programs used in this study.

References

1. The notation used will be consistent with that of M. Tinkham in Group Theory and Quantum Mechanics (McGraw-Hill, New York, 1964).
2. I. Shavitt in Modern Theoretical Chemistry, Vol. 3, edited by H. F. Schaefer (Plenum, New York, 1977).
3. For the construction of symmetry-adapted orbitals see, for example, G. Fieck, *Theoret. Chim. Acta* 44, 279 (1977) and, of course, F. A. Cotton, Chemical Applications of Group Theory (Wiley-Interscience, New York, 1971). In all discussion to follow, it will be assumed that the orbitals are symmetry-adapted.
4. R. Pauncz, Alternate Molecular Orbital Methods (W. B. Saunders Co., Philadelphia, PA., 1969).
5. Z. Gershgorin and I. Shavitt, *Intern. J. Quant. Chem.* 15 403 (1967).
6. R. J. Buenker and S. D. Peyerimhoff, *Theoret. Chim. Acta* 12, 183 (1968).
7. See A. D. McLean and B. Liu, *J. Chem. Phys.* 58, 1066 (1973) and C. F. Bunge and A. Bunge, *Intern. J. Quant. Chem.* 7, 927 (1973), and references therein.
8. J. R. Gabriel, *J. Chem. Phys.* 51, 3713 (1969).
9. B. G. Wybourne, *Intern. J. Quant. Chem.* 7, 1117 (1973).
10. I. Sakata, *J. Math. Phys.* 15, 1702 (1974).
11. W. C. Swope, Y.-P. Lee, and H. F. Schaefer, *J. Chem. Phys.* (to be published).
12. More detailed presentations may also be found in work of D. R. Yarkony, Ph. D. thesis, University of California, Berkeley, CA, 1975, and W. C. Swope, Ph.D. thesis, University of California, Berkeley, CA, 1979.

13. M. Tinkham, op. cit., p. 30.
14. D. Goscinski and Y. Ohrn, Intern. J. Quant. Chem. 2, 845 (1968).
15. R. T. Morrison and R. N. Boyd, Organic Chemistry, 2nd ed. (Allyn and Bacon, Boston, 1966), pp. 512-16.
16. W. N. Lipscomb, Science 196, 1047 (1977).
17. For examples of earlier ab initio studies of borane, see the following and references therein:
 - (a) W. E. Palke and W. N. Lipscomb, J. Chem. Phys. 45, 3948 (1966),
 - (b) S. D. Peyerimhoff, R. J. Buenker and L. C. Allen, J. Chem. Phys. 45, 734 (1966),
 - (c) J. J. Kaufman and L. A. Burnelle, RIAS Tech. Rep. 65, (1966),
 - (d) A. A. Frost, B. H. Prentice, R. A. Rouse, J. Am. Chem. Soc. 89, 3064 (1967),
 - (e) B. D. Joshi, J. Chem. Phys. 46, 875 (1967),
 - (f) S. D. Peyerimhoff, R. J. Buenker and J. L. Witten, J. Chem. Phys. 46, 1707 (1967),
 - (g) E. Switkes, R. M. Stevens and W. N. Lipscomb, J. Chem. Phys. 51, 5229 (1969),
 - (h) J. P. Petke and J. L. Witten, J. Chem. Phys. 51, 3166 (1969),
 - (i) M. E. Schwartz, Chem. Phys. Lett. 5, 50 (1970),
 - (j) M. Gelus, R. Ahlrichs, V. Staemmler and W. Kutzelnigg, Chem. Phys. Lett. 7, 503 (1970),
 - (k) P. T. van Duignen and D. B. Cook, J. Mol. Phys. 22, 637 (1971),
 - (l) J. H. Hall, D. S. Marynick, and W. N. Lipscomb, Inorg. Chem. 11, 3126 (1972),
 - (m) M. F. Guest, I. H. Hillier, V. R. Saunders, and M. H. Wood, Proc. Roy. Soc. A333, 201 (1973),

- (n) C. Edmiston and P. Lindner, Intern. J. Quant. Chem. 7, 309 (1973),
- (o) J. D. Dill, P. R. Schleyer and J. A. Pople, J. Am. Chem. Soc. 97, 3402 (1975),
- (p) A. D. Tait and M. Dixon, J. Mol. Phys. 29, 1353 (1975), and
- (q) V. I. Perevozchikov and L. A. Gribov, Opt. Spektrosk 42, 203 (1977).
18. A. Pipano and I. Shavitt, Intern. J. Quant. Chem. 2, 741 (1968).
19. J. M. Norbeck and G. A. Gallup, Intern. J. Quant. Chem., Symposium No. 7, 161 (1973) and R. MacLagan, J. Mol. Phys. 31, 1783 (1976).
20. See R. Ahlrichs, Chem. Phys. Lett. 19, 174 (1973); M. Gelus and W. Kutzelnigg, Theoret. Chim. Acta 28, 103 (1973); R. Ahlrichs, Theoret. 35, 59 (1974); and R. Ahlrichs, F. Driessler, H. Lischka, V. Staemmler and W. Kutzelnigg, J. Chem. Phys. 62, 1235 (1975), and references therein.
21. R. L. Lucchese, M. P. Conrad and H. F. Schaefer, J. Chem. Phys. 68, 5292 (1978).
22. T. H. Dunning, J. Chem. Phys. 53, 2823 (1970). A scaling factor of 1.2 was used for the hydrogen primitives.
23. R. R. Lucchese, B. R. Brooks, J. H. Meadows, W. C. Swope, and H. F. Schaefer, J. Comput. Phys. 26, 243 (1978); see also B. R. Brooks and H. F. Schaefer, Int. J. Quantum Chem. 14, 603 (1978).
24. The 0.0006 Hartree difference in electronic energy is comparable to the difference we have observed in unpublished calculations on O₂ and SO.
25. T. Clark and P.v.R. Schleyer, J. Organometallic Chem. 156, 191 (1978).

Table

<u>Electronic State</u>	<u>Size of D_{3h} CI Space</u>	<u>Size of CI Interacting Space</u>	<u>Minimum Energy[†] of D_{3h} Geometry</u>	<u>R(B-H) at This Energy</u>
$1E''$	4002/19608 [‡]	2485/12148	-26.30521	2.37 a.u.
$3E''$	6337/13658	3676/7982	-26.32745	2.34 a.u.
X $1A_1'$	774/4515	774 [‡] /4515	-26.52872	2.255 a.u.

[†] Energies are single and double substitution (HF interacting) CI energies in atomic units.

[‡] For closed-shell reference states, all single and double configurations are interacting.

[‡] Size is expressed as [the number of configurations used in the calculation]/[the number of unique determinants used to construct these configurations].

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720