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Commentationes

CI Method for the Study of General Molecular Potentials

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A method of configuration interaction designed for general molecular potentials is outlined. The technique employed to arrive at a symmetrized multideterminantal basis for such calculations relies heavily on certain properties of Abelian groups; in particular the M_L quantum number commonly employed in atomic structure calculations is replaced in the general molecular case by the index p which labels irreducible representations of some appropriate Abelian group. Formation of the desired symmetrized linear combinations of determinants is thereupon accomplished solely by means of a series of simple diagonalizations, a procedure which insures both the linear independence and the orthonormality of the resultant basis set. CI treatments involving the C_4H_4 isomer tetrahedrane (T_d point group) and the linear nitrous oxide NNO molecule are considered in some detail with a view toward illustrating the use of the techniques described herein. Finally, a survey of a series of recent calculations utilizing the CI method is made and it is concluded from these results that the effects of such treatment vary strongly from one system to another, depending in a very specific manner upon the individual characteristics of a given molecule.

Es wird eine Methode der Konfigurationswechselwirkung beschrieben, welche für allgemeine Molekülpotentiale bestimmt ist. Die Technik, die verwendet wird, um eine symmetrisierte Vieldeterminanten-Basis für solche Berechnungen zu erhalten, macht stark von bestimmten Eigenschaften Abelscher Gruppen Gebrauch; insbesondere wird die Quantenzahl M_L, welche üblicherweise in Atomstrukturberechnungen verwendet wird, im allgemeineren Fall der Moleküle durch eine Zahl p ersetzt, welche die irreduziblen Darstellungen einer geeigneten Abelschen Untergruppe der Gesamtgruppe des Moleküls bezeichnet. Die Bildung der gewünschten symmetrisierten Linearkombination von Determinanten wird daraufhin durch eine Reihe von einfachen Diagonalisierungen erreicht, einem Verfahren, das sowohl die lineare Unabhängigkeit als auch die Orthonormalität der entstehenden Basisfunktionen gewährleistet. CI-Verfahren für das tetraedrische C_4H_4 Isomer (T_d Punktgruppe) und das lineare Stickoxydul NNO werden ausführlicher behandelt, um die Anwendung der beschriebenen Arbeitsmethoden zu erläutern. Abschließend findet sich ein Überblick über eine Reihe von neueren Berechnungen mit der beschriebenen CI-Methode, aus deren Ergebnissen gefolgert wird, daß die Wirkungen solcher CI-Behandlungen von einem System zum anderen sehr variieren und in ganz bestimmter Weise von den einzelnen Eigenschaften eines gegebenen Moleküls abhängen.

Description d'une méthode d'interaction de configuration pour des potentiels moléculaires généraux. La technique utilisée pour obtenir une base symétrisée de déterminants repose fortement sur certaines propriétés des groupes abéliens; en particulier le nombre quantique M_L communément utilisé dans les calculs de structure atomique est remplacé dans le cas moléculaire général par l'indice p qui caractérise les représentations irréductibles de certains groupes abéliens appropriés. Une série de simples diagonalisations permet alors de former les combinaisons linéaires symétrisées de déterminants recherchées; ce procédé assure simultanément l'indépendance linéaire et l'orthonormalité de la base résultante. Ces techniques sont illustrées par l'I.C. sur le tétrahédrane, isomère de C_4H_4 (groupe ponctuel T_d) et la molécule linéaire d'oxyde nitreux NNO. Finalement on effectue une revue d'une série de calculs récents utilisant la méthode d'I.C. et on en conclue que les effets de tels traitements varient fortement d'un système à l'autre, avec une dépendance spécifique des caractéristiques moléculaires individuelles.

1. Introduction

The general technique of configuration interaction for generating electronic wavefunctions is a direct application of the variation principle for a linear trial function. From a computational point of view the most convenient basis set for carrying out a CI treatment consists of n-electron determinants constructed in the usual manner from a set of mutually orthonormal functions, each of which depends on the coordinates (spin and spatial) of only one electron; in this case the determinants so constructed are also mutually orthonormal and the form of their Hamiltonian[1] matrix elements is especially simple. For some time now adequate orthonormal one-electron basis sets have been readily available because of the ease with which SCF MO calculations for a general polyatomic system can be carried out. The present paper outlines a practical method for carrying out CI calculations which is especially designed for the treatment of general molecular potentials; in particular it presents a scheme for taking maximum advantage of the symmetry characteristics of such potentials. The method works equally well for closed and open shell SCF sets of molecular orbitals in a general n-electron formulation and can be modified quite simply to utilize any set of orthonormal one-electron functions.

2. Outline of the Method

To begin with, two mutually exclusive sets Φ_c and Φ_v, containing K and M elements respectively, are formed from the molecular orbitals of the parent SCF calculation. Ordinarily, the orbital energy ε_i is used as a criterion for the construction of these sets; thereby the most stable occupied orbitals are included in Φ_c (core), the remaining occupied and a certain number of the most stable virtual MO's are placed in Φ_v (valence), while the least stable unoccupied orbitals are usually ignored in the treatment. Each determinantal wavefunction is an antisymmetrized product of n distinct spin orbitals: these include all of the $2K$ spin orbitals associated with the fixed core Φ_c and v others $(n-2K)$ which are selected from those associated with the valence set Φ_v. Thus the total number of determinants comprised by the above prescription is $\binom{2M}{v}$. It proves convenient to require that the sets Φ_c and Φ_v each consist of complete shells of one-electron functions, so that their respective linear manifolds are invariant (stable) under the operations of the nuclear point group G (the complete set of spatial operators that commute with the Hamiltonian)[2].

A. Calculation of Integrals over Molecular Orbitals

The integrals over molecular basis functions Φ_i which are necessary for the calculation of Hamiltonian matrix elements between determinants can be divided into three categories:

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[1] In this paper only purely electrostatic Hamiltonians are considered.

[2] In this connection it can also be assumed without loss of generality that each element in Φ_c and Φ_v transforms according to one of the irreducible representations of G, i.e. is a pure symmetry orbital [1, 2] of G.

1. all distinct electron repulsion integrals involving MO's belonging to the valence set Φ_v,

$$[mn|m'n'] \equiv \left\langle \varphi_m(1)\,\varphi_n(2)\,\frac{1}{r_{12}}\,\varphi_{m'}(1)\,\varphi_{n'}(2)\right\rangle,$$

the total number of such integrals being

$$\binom{\binom{M+1}{2}+1}{2};$$

2. the $\binom{M+1}{2}$ integrals describing the interaction of the valence MO's with the core,

$$P_{mm'} = \left\langle \varphi_m \middle| -\frac{1}{2}\nabla^2 - \sum_a \frac{Z_a}{r_a} \middle| \varphi_{m'} \right\rangle + \sum_k^{\Phi_c} \{2[mk|m'k] - [mk|km']\};$$

and 3. the contribution of the core orbitals to the total electronic energy of each determinant

$$E_{\text{core}} = 2\sum_k^{\Phi_c} \left\{ \left\langle \varphi_k \middle| -\frac{1}{2}\nabla^2 - \sum_a \frac{Z_a}{r_a} \middle| \varphi_k \right\rangle \right\} + \sum_{k,l}^{\Phi_c} (2J_{kl} - K_{kl}),$$

where J_{kl} and K_{kl} are Coulomb and exchange integrals respectively.

The diagonal energy of each determinant is then equal to the sum of E_{core} and the nuclear repulsion V_N plus appropriate combinations of diagonal P matrix elements plus certain Coulomb and exchange integrals which are to be found among the quantities in the first category described above. The off-diagonal Hamiltonian matrix elements between pairs of determinants which differ by exactly one spin orbital (m and m') is equal to $P_{mm'}$ plus some combination of electron repulsion integrals involving only valence MO's; corresponding Hamiltonian off-diagonal matrix elements between determinants which differ by exactly two spin orbitals can always be expressed in terms of integrals in the first category. Hamiltonian matrix elements between determinants differing by more than two spin orbitals vanish[3].

All the integrals discussed above can be obtained in a straightforward manner by summing over the appropriate products of MO expansion coefficients and corresponding integrals over atomic basis functions; because of the symmetry properties of the molecular orbitals, however, considerable simplification in this procedure is readily available. Since the operators involved in the electron repulsion integrals and in the P matrix elements (since Φ_c consists of complete shells) belong to the fully symmetric representation of the nuclear point group G, each of these integrals must vanish whenever the direct product of the irreducible representations for all the MO's involved does not contain the fully symmetric representation of G. Utilization of this group theoretical property is especially

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[3] All of these results of course arise from the determinantal form of the wavefunctions under consideration and the orthonormality of the MO basis set from which they are constructed.

simple if G is Abelian, since in this case the direct product of any two irreducible representations is itself an irreducible (one-dimensional) representation. Also for this reason, if G is non-Abelian, it is useful to employ an MO basis set consisting of functions which are pure symmetry orbitals not only of G but also of g, one of its Abelian subgroups (as can be done without loss of generality). Thereupon a given molecular integral is set equal to zero unless the direct product of the representations for the MO's involved is the fully symmetric representation of the subgroup g. Such a procedure within a CI treatment does not in general exhaust the possible simplifications available through application of group theoretical techniques but it has the advantage of eliminating the great majority of unnecessary computations which arise in a straight-forward evaluation of the necessary integrals while requiring a minimum input of symmetry characteristics for the valence MO's. In a typical case, for which C_{2v} is used as the Abelian subgroup, this method eliminates the direct computation of approximately 75% of the molecular integrals required for the CI treatment.

B. Generation and Classification of Determinantal Wavefunctions

Once the necessary integrals over molecular basis functions have been computed the determinantal wavefunctions to be considered are generated by constructing all possible combinations of v $(n-2K)$ occupied valence (from Φ_v) spin orbitals, with each distinct combination representing a single determinant, as discussed in Sect. 2*A*. The determinants are each classified according to the following four characteristics in order to facilitate their arrangement into symmetrized linear combinations: 1. their M_s eigenvalue (since the determinants so constructed are eigenfunctions of S_z); 2. an index p indicating according to which irreducible representation of g the generated determinants transform[4]; 3. an index v denoting to which excitation class (relative to the SCF ground state wavefunction) the determinants belong; and 4. an index γ denoting the electronic configuration to which the determinants belong, i.e. a unique index is assigned to each distinct set of occupation numbers for the valence shells[5]. While this classification is being carried out it is also useful to compute the diagonal energy for each of the generated determinants according to the formulae discussed in Sect. 2*A*.

The determinantal wavefunctions are next arranged into symmetrized linear combinations, that is, the total linear space of determinants is partitioned into irreducible invariant subspaces of both spin and spatial point groups. It is well known that an electronic configuration is a linear space which is invariant under the application of all the symmetry operations of the combined spin and spatial point groups. Consequently, one need not consider symmetrized multideterminantal functions which are linear combinations of determinants arising from different configurations, i.e. possessing different configuration indices γ[6]. Further-

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[4] In what follows it is assumed, as in Sect. 2*A*, that each valence MO transforms according to one of the irreducible representations of g, an Abelian subgroup of G. Consequently, any product of these functions (and therefore each determinant) is a basis function for an irreducible representation of g.

[5] In the case of an atom, for example, the 270 possible determinants with a $3p^5 3d^2$ electronic configuration, and only those, would possess a given configuration index γ.

[6] Also, per force, one need not consider combinations of determinants belonging to different excitation classes.

more, it is not necessary to consider linear combinations which mix determinants with different eigenvalues of M_s since the Hamiltonian under discussion does not explicitly contain spin coordinates. For even-electron systems one need only be concerned with determinants having $M_s = 0$ because of the existence of step-up and step-down spin angular momentum operators (with similar remarks for $M_s = 1/2$ in the treatment of odd-electron molecules). It is also clear that sets of determinants with the same values of M_s and γ can be further divided without additional calculation into non-interacting subsets according to the g irreducible representation label p.

It is then useful to divide the total linear space of determinants into subspaces denoted hereafter as Ω', each of which consists of elements possessing the same values of M_s, p and γ (and per force ν). It is always possible to obtain an orthonormal basis for each Ω' subspace which consists of eigenvectors of the spin operator S^2 because each of these subspaces is invariant under the operations of the full spin rotation group, and S^2 itself is Hermitian. Therefore one need only diagonalize the matrix of S^2 over the initial (orthonormal) determinantal basis of Ω' in order to obtain the desired spin eigenfunctions with eigenvalues $S(S+1)$; methods for determining S^2 matrix elements over determinantal functions are well known [3] and involve only a minor amount of computation.

C. Symmetrized Multi-Determinantal Functions for Non-Abelian Groups

If the spatial point group G of the system under consideration is Abelian (only non-degenerate irreducible representations) the transformation to a basis of S^2 eigenfunctions for each Ω' subspace represents the ultimate length to which group theoretical techniques may be carried to simplify the diagonalization of the full Hamiltonian matrix. For non-Abelian G it is possible to proceed further by dividing each Ω' space into non-interacting subspaces Ω'' consisting of elements possessing the same value of S as well as of M_s, p, γ and ν. It is then possible[7] to obtain a new multi-determinantal basis for each Ω'' subspace consisting of elements which are not only eigenfunctions of S^2 but which also transform according to one of the irreducible representations of G. By analogy to the method of obtaining S^2 eigenfunctions one attempts to arrive at such a basis by diagonalizing some appropriate symmetry operator. Such a procedure would then replace standard projection operator methods [4] and related techniques which in practice involve a more formidable computational scheme than is required in the diagonalization method proposed herein.

In searching for an operator in G suitable for this purpose it is clear that none of those in the Abelian subgroup g is adequate since matrices for these operators over any basis for a general Ω'' subspace are scalar multiples of the identity matrix. At the same time none of the non-commuting elements of G appears strictly analogous to S^2 in the spin case because of the following two factors: 1. such operators are not in general Hermitian and 2. an Ω'' subspace is not in general closed under such operations since other partners in the basis for a given degenerate irreducible representation of G may well possess different values of the index

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[7] This follows from the fact that one need not consider symmetrized functions which mix determinants belonging to different Ω'' subspaces.

p, i.e. transform according to different irreducible representations of g, than do the elements of Ω''.

Closer examination, however, discloses a definite possibility that the *matrix* associated with a non-commuting element R of G relative to a given basis of Ω'' is capable of undergoing diagonalization to produce the desired symmetrized multi-determinantal functions. To investigate this point it is useful to consider the matrix $\mathbf{M}(R)$ for a non-commuting operator R over an orthonormal basis for Ω'' consisting of symmetrized functions of G. It can be shown that $\mathbf{M}(R)$ will be diagonal if no more than one partner for any given irreducible representation of G is present in Ω''; for under these circumstances it follows that

$$\begin{aligned} M_{ij}(R) = \langle f_i^{\alpha',p'}, R f_j^{\alpha,p}\rangle &= \Gamma^{\alpha}_{pp}(R)\,\langle f_i^{\alpha',p'}, f_j^{\alpha,p}\rangle \\ &= \Gamma^{\alpha}_{pp}(R)\,\delta_{ij}, \end{aligned} \tag{1}$$

where $f_j^{\alpha,p}$ is the j-th basis function for Ω'' transforming according to both of the irreducible representations Γ^α of G and Γ^p of g, with the index p now labelling rows of Γ^α of G as well as irreducible representations of g (Sect. 2*B*). In order to insure this condition for every Ω'' subspace it is sufficient that every irreducible representation of G decomposes into distinct irreducible representations of the Abelian subgroup g; for in this case all partners for a given irreducible representation of G can be distinguished from one another strictly on the basis of the index p and therefore each of them will be found in a different Ω'' subspace.

Investigation of the finite non-Abelian spatial point groups shows that all those in the categories D_n, C_{nv}, D_{nh} and D_{nd} possess at least one Abelian subgroup with the required property, namely that every irreducible representation of the non-Abelian group decomposes into distinct irreducible representations of the subgroup. Particular decompensations are given in Table 1 for each of these groups, as well as for the important special groups T, T_h, T_d, O and O_h. For every case there exist several suitable subgroups, each of which is hereafter referred to as a *differentiating* Abelian subgroup. Nor is the existence of such subgroups restricted to finite non-Abelian groups; for example, inspection of Table 1 shows that $D_{\infty h}$ and $C_{\infty v}$ are simply limiting cases for the D_{nh} and C_{nv} series in this respect. Finally, it can be shown that the two-dimensional rotation group is a differentiating Abelian subgroup of the full rotation group[8]. Thus, when applied to spherical potentials (atoms), the present method for obtaining symmetrized multi-determinantal functions employs a one-electron basis set which consists of symmetry orbitals of the two-dimensional rotation group, more commonly referred to as eigenfunctions of the spatial angular momentum operator L_z; in this case the quantum number M_L serves the same purpose as the general index p discussed above. The desired multi-determinantal functions can then be obtained by diagonalizing the Hermitian operator L^2 for each Ω'' subspace, a procedure which is of course well known [3]. This observation helps to identify the present method as a generalization of familiar techniques used in the treatment of atomic structure

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[8] Proof of this statement can be found by examining the traces of the D_L (L being the total angular momentum quantum number) irreducible representation matrices corresponding to operators in the C_{2L+1} subgroup; these are found to be $(2L+1)$ for the identity operation and 0 for all other elements in the subgroup. Therefore, because of the Celebrated Theorem [5], D_L decomposes into *each* of the $2L+1$ one-dimensional irreducible representations of C_{2L+1}, which is itself a subgroup of the two-dimensional rotation group.

Table 1. *Correlation of the irreducible representation Γ of the commonly occurring non-Abelian point groups G with those of an Abelian subgroup g. The notation employed is that of Ref.* [6]. *In all cases each $\Gamma(G)$ decomposes into distinct irreducible representations of g; all other Abelian subgroups g′ which bear the same relationship to a given G are listed in the last column*

G	g	$\Gamma(G)$	$\Gamma(g)$		g'
D_n(n odd, $\geqq 3$)	C_2	A_1	A		C_n
		A_2	B		
		$E_j\left(j=1,\frac{n-1}{2}\right)$	$A+B$		
D_n(n even, $\geqq 4$)	D_2	A_1	A	A[a]	C_2, C_n
		A_2	B_1	B_1	
		B_1	A	B_2	
		B_2	B_1	B_3	
		$E_j\left(j=1,\frac{n}{2}-1\right)$	odd j B_2+B_3	B_2+B_3	
			even j $A+B_1$	$A+B_1$	
C_{nv}(n odd, $\geqq 3$)	C_s	A_1	A'		C_n
		A_2	A''		
		$E_j\left(j=1,\frac{n-1}{2}\right)$	$A'+A''$		
C_{nv}(n even, $\geqq 4$)	C_{2v}	A_1	A_1	A_1[a]	C_s, C_n
		A_2	A_2	A_2	
		B_1	A_1	B_1	
		B_2	A_2	B_2	
		$E_j\left(j=1,\frac{n}{2}-1\right)$	odd j B_1+B_2	B_1+B_2	
			even j A_1+A_2	A_1+A_2	
D_{nh}(n odd, $\geqq 3$)	C_{2v}	A'_1	A_1		C_{nh}, C_n C_2, C_s
		A'_2	B_2		
		$E'_j\left(j=1,\frac{n-1}{2}\right)$	A_1+B_2		
		A''_1	A_2		
		A''_2	B_1		
		$E''_j\left(j=1,\frac{n-1}{2}\right)$	A_2+B_1		
D_{nh}(n even, $\geqq 4$)	D_{2h}	A_{1g}	A_g	A_g[a]	C_2, C_s, C_n D_2, C_{2v}, C_{2h}, C_{nh}, S_n
		A_{2g}	B_{1g}	B_{1g}	
		B_{1g}	A_g	B_{2g}	
		B_{2g}	B_{1g}	B_{3g}	
		$E_{jg}\left(j=1,\frac{n}{2}-1\right)$	odd j $B_{2g}+B_{3g}$	$B_{2g}+B_{3g}$	
			even j A_g+B_{1g}	$Ag+B_{1g}$	
		A_{1u}	A_u	A_u	
		A_{2u}	B_{1u}	B_{1u}	
		B_{1u}	A_u	B_{2u}	
		B_{2u}	B_{1u}	B_{3u}	
		$E_{ju}\left(j=1,\frac{n}{2}-1\right)$	odd j $B_{2u}+B_{3u}$	$B_{2u}+B_{3u}$	
			even j A_u+B_{1u}	A_u+B_{1u}	

[a] This column refers to cases in which $\frac{n}{2}$ is odd, while the preceding column deals with the $\frac{n}{2}$ even case.

Table 1 (continued)

G	g	$\Gamma(G)$	$\Gamma(g)$	g'
D_{nd}(n odd, $\geqq 3$)	C_{2h}	A_{1g}	A_g	$C_2, C_s, C_n,$ S_{2n}
		A_{2g}	B_g	
		$E_{jg}\left(j=1, \frac{n-1}{2}\right)$	A_g+B_g	
		A_{1u}	A_u	
		A_{2u}	B_u	
		$E_{ju}\left(j=1, \frac{n-1}{2}\right)$	A_u+B_u	
D_{nd}(n even, $\geqq 2$)	C_{2v} $(C_2 \equiv C_n^{n/2})$	A_1	A_1	$C_2, C_s, D_2,$ S_{2n}
		A_2	A_2	
		B_1	A_2	
		B_2	A_1	
		$E_j\,(j=1, n-1)$	odd j B_1+B_2	
			even j A_1+A_2	
T	C_3	A	A	D_2
		E_+	E_+	
		E_-	E_-	
		T	$A+E_++E_-$	
T_h	C_3	A_g	A	D_2, C_{2v}, D_{2h} S_{2n}
		E_{g+}	E_+	
		E_{g-}	E_-	
		T_g	$A+E_++E_-$	
		A_u	A	
		E_{u+}	E_+	
		E_{u-}	E_-	
		T_u	$A+E_++E_-$	
T_d	C_{2v}	A_1	A_1	C_3, S_4
		A_2	A_2	
		E	A_1+A_2	
		T_1	$A_2+B_1+B_2$	
		T_2	$A_1+B_1+B_2$	
O	D_2	A_1	A	C_3
		A_2	B_1	
		E	$A+B_1$	
		T_1	$B_1+B_2+B_3$	
		T_2	$A+B_2+B_3$	
O_h	D_{2h}	A_{1g}	A_g	$C_3, D_2, C_{2v},$ C_4, C_{4h}, S_4, S_6
		A_{2g}	B_{1g}	
		E_g	A_g+B_{1g}	
		T_{1g}	$B_{1g}+B_{2g}+B_{3g}$	
		T_{2g}	$A_g+B_{2g}+B_{3g}$	
		A_{1u}	A_u	
		A_{2u}	B_{1u}	
		E_u	A_u+B_{1u}	
		T_{1u}	$B_{1u}+B_{2u}+B_{3u}$	
		T_{2u}	$A_u+B_{2u}+B_{3u}$	

problems; it should be emphasized, however, that in general the matrix which is to be diagonalized need not correspond to an Hermitian operator.

The matrix $\mathbf{M}(R)$ is related by a unitary transformation to every matrix $\mathbf{M}'(R)$ corresponding to the same operator R and defined with respect to some orthonormal basis of Ω''. Diagonalization of $\mathbf{M}'(R)$ leads uniquely to the eigenvalues of diagonal $\mathbf{M}(R)$ which, according to Eq. (1), are equal to particular diagonal elements of the irreducible representation matrices of G; it is easily shown that these diagonal matrix elements are in turn uniquely specified by the condition that each irreducible representation of G decomposes into distinct irreducible representations of g[9].

The eigenvectors of $\mathbf{M}'(R)$ in general differ from those of $\mathbf{M}(R)$ by a linear transformation which also must be unitary; unless this transformation mixes $\mathbf{M}(R)$ eigenvectors belonging to different irreducible representations of G, however, the eigenvectors of $\mathbf{M}'(R)$ still must be properly symmetrized multideterminantal functions. Such mixing can occur if and only if eigenvectors corresponding to different irreducible representations of G posses a common eigenvalue; from Eq. (1) it follows that this condition implies the existence of equal diagonal matrix elements belonging to rows of different irreducible representations of G but to the same irreducible representation of g[10]. Table 2 demonstrates for each of the groups considered in Table 1 that it is possible to find at least one differentiating Abelian subgroup which leads to representation matrices for some group element whose diagonal elements do not exhibit such equalities[11].

Thus at least for all the groups discussed above it is always possible to obtain a basis set for each Ω'' subspace consisting of symmetrized multi-determinantal functions solely by means of a series of simple diagonalizations; in turn, the set of groups considered herein exhausts the list of those commonly ocurring in the study of molecular potentials. In this manner, ultimately one can form an orthonormal basis of symmetrized functions for both spin and spatial point groups which spans the entire linear space of determinantal wavefunctions. At least one major advantage in the utilization of a diagonalization procedure for this purpose is that it automatically insures both the linear independence and the orthonormality of the resultant multi-determinantal basis vectors.

D. Final Stage of the CI *Treatment*

Once a properly symmetrized set of multi-determinantal functions has been determined, it is a three-step process to complete the CI calculation. First, Hamiltonian matrices over single determinants are constructed from the molecular integrals discussed in Sect. 2*A*, one matrix for each pair of values of M_s and p represented in the total secular equation[12]. Next, each of these arrays is used to form smaller Hamiltonian matrices over symmetrized multi-determinantal functions obtained previously for each irreducible representation of the combined spin and spatial point groups involved in the treatment. Finally, each of the

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[9] The condition allows the freedom of only diagonal unitary transformations among basis partners.

[10] That is, it implies that $\Gamma^{\alpha}_{pp}(R)=\Gamma^{\alpha'}_{pp}(R)$ for $\alpha\neq\alpha'$.

[11] Clearly not every differentiating Abelian subgroup possesses this property.

[12] Only determinants with $M_s=0$ in the even- and $M_s=1/2$ in the odd-electron case need be considered.

Table 2. *Diagonal irreducible representation matrix elements $\Gamma^{\alpha}_{pp}(R)$ for all the non-Abelian groups G listed in Table 1. The indices α and p are labels for the irreducible representations of G and g respectively, while R denotes an element of G; otherwise the notation is the same as that employed in Table 1. For a given G the Abelian subgroup g and the operator R are chosen such that no two diagonal matrix elements corresponding to the same value of p but to different values of α are equal. (Note that each $\Gamma^{\alpha}_{pp}(R)$ is uniquely specified by the condition that its corresponding basis vector transform according to the p-th irreducible representation of the subgroup g)*

<table>
<tr><th>G</th><th>g</th><th>R</th><th>$\Gamma^{\alpha}_{pp}(R)$</th></tr>
<tr><td>D_n(n odd, $\geqq 3$)</td><td>C_2</td><td>C_n</td><td>
<table>
<tr><th>$\alpha \backslash p$</th><th>A</th><th>B</th></tr>
<tr><td>A_1</td><td>1</td><td></td></tr>
<tr><td>A_2</td><td></td><td>1</td></tr>
<tr><td>$E_j\left(j=1,\frac{n-1}{2}\right)$</td><td>$c$</td><td>$c$</td></tr>
</table>
</td></tr>
<tr><td>D_n(n even, $\geqq 4$)</td><td>D_2</td><td>C_n</td><td>
<table>
<tr><th>$\alpha \backslash p$</th><th>A</th><th>B_1</th><th>B_2</th><th>B_3</th><th>A</th><th>B_1</th><th>B_2</th><th>B_3[a]</th></tr>
<tr><td>A_1</td><td>1</td><td></td><td></td><td></td><td>1</td><td></td><td></td><td></td></tr>
<tr><td>A_2</td><td></td><td>1</td><td></td><td></td><td></td><td>1</td><td></td><td></td></tr>
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<tr><td>C_{nv}(n odd, $\geqq 3$)</td><td>C_s</td><td>C_n</td><td>
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<table>
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<tr><td>D_{nh}(n odd, $\geqq 3$)</td><td>C_{2v}</td><td>C_n</td><td>
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</table>

[a] This column refers to cases in which $\frac{n}{2}$ is odd, while the preceding column deals with the $\frac{n}{2}$ even case.

Throughout this Table $c = \cos\frac{2\pi j}{n}$ and $c' = \cos\frac{\pi j}{n}$.

Table 2 (continued)

G	g	R	$\Gamma^{\alpha}_{pp}(R)$
D_{nh}(n even, $\geqq 4$)	D_{2h}	C_n	$\begin{array}{r\|cccccccc} \alpha\backslash p & A_g & B_{1g} & B_{2g} & B_{3g} & A_u & B_{1u} & B_{2u} & B_{3u} \\ \hline A_{1g} & 1 & & & & & & & \\ A_{2g} & & 1 & & & & & & \\ B_{1g} & -1 & & & & & & & \\ B_{2g} & & -1 & & & & & & \\ E_{jg}\left(j=1,\frac{n}{2}-1\right)\ \text{odd}\ j & & & c & c & & & & \\ \text{even}\ j & c & c & & & & & & \\ A_{1u} & & & & & 1 & & & \\ A_{2u} & & & & & & 1 & & \\ B_{1u} & & & & & -1 & & & \\ B_{2u} & & & & & & -1 & & \\ E_{ju}\left(j=1,\frac{n}{2}-1\right)\ \text{odd}\ j & & & & & & & c & c \\ \text{even}\ j & & & & & c & c & & \end{array}$
			$\begin{array}{r\|cccccccc} \alpha\backslash p & A_g & B_{1g} & B_{2g} & B_{3g} & A_u & B_{1u} & B_{2u} & B_{3u}{}^{a} \\ \hline A_{1g} & 1 & & & & & & & \\ A_{2g} & & 1 & & & & & & \\ B_{1g} & & & -1 & & & & & \\ B_{2g} & & & & -1 & & & & \\ E_{jg}\left(j=1,\frac{n}{2}-1\right)\ \text{odd}\ j & & & c & c & & & & \\ \text{even}\ j & c & c & & & & & & \\ A_{1u} & & & & & 1 & & & \\ A_{2u} & & & & & & 1 & & \\ B_{1u} & & & & & & & -1 & \\ B_{2u} & & & & & & & & -1 \\ E_{ju}\left(j=1,\frac{n}{2}-1\right)\ \text{odd}\ j & & & & & & & c & c \\ \text{even}\ j & & & & & c & c & & \end{array}$
D_{nd}(n odd, $\geqq 3$)	C_{2h}	C_n	$\begin{array}{r\|cccc} \alpha\backslash p & A_g & B_g & A_u & B_u \\ \hline A_{1g} & 1 & & & \\ A_{2g} & & 1 & & \\ E_{jg}\left(j=1,\frac{n-1}{2}\right) & c & c & & \\ A_{1u} & & & 1 & \\ A_{2u} & & & & 1 \\ E_{ju}\left(j=1,\frac{n-1}{2}\right) & & & c & c \end{array}$
D_{nd}(n even, $\geqq 2$)	C_{2v}	S_{2n}	$\begin{array}{r\|cccc} \alpha\backslash p & A_1 & A_2 & B_1 & B_2 \\ \hline A_1 & 1 & & & \\ A_2 & & 1 & & \\ B_1 & & -1 & & \\ B_2 & -1 & & & \\ E_j(j=1,n-1)\ \text{odd}\ j & & & c' & c' \\ \text{even}\ j & c' & c' & & \end{array}$

Table 2 (continued)

<table>
<tr><th>G</th><th>g</th><th>R</th><th colspan="9">$\Gamma^{\alpha'}_{pp}(R)$</th></tr>
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matrices over symmetrized functions is diagonalized to obtain the final CI wavefunctions.

By far the most time-consuming step in the entire CI procedure described above involves the transformation from integrals over AO basis functions to those over

MO's required to construct the various Hamiltonian matrices. The majority of the remaining time necessary to complete the CI calculation is expended in carrying out the diagonalization of the Hamiltonian matrices over symmetrized functions. By contrast, the techniques involved in generating the determinantal wavefunctions, symmetrizing them and constructing the necessary Hamiltonian matrices from the molecular integrals constitute only a negligible part of the total computations for a given CI calculation. Ordinarily the total CI treatment involves considerably less computation than is required to obtain the AO integrals and the set of SCF MO's which is prerequisite to it.

3. Examples of the CI Method

The utility of the CI method discussed in the previous section can perhaps best be illustrated by examining two typical applications, one for the hypothetical C_4H_4 isomer tetrahedrane (T_d point group) and the other for the nitrous oxide molecule NNO in its linear equilibrium geometry ($C_{\infty v}$ point group).

A. Tetrahedrane: T_d

Tetrahedrane has the following ground state electronic configuration[13]:

$$1a_1^2 1t_2^6 2a_1^2 2t_2^6 3a_1^2 3t_2^6 1e^4 | 1t_1^0 .$$

A representative CI treatment for this system retains all the occupied MO's of a_1 and t_2 symmetry in the core Φ_c ($K = 12$) with the valence set Φ_v consisting of the $1e$ and $1t_1$ shells ($M = 5$). The number of valence electrons v is 4 and thus the total number of determinants involved in this calculation is $\binom{10}{4} = 210$. In this case each excitation class v constitutes one electronic configuration γ: ground state e^4, single excitation e^3t_1, double $e^2t_1^2$, triple et_1^3 and quadruple excitation t_1^4. From Tables 1 and 2 the differentiating Abelian subgroup g is selected to be C_{2v}[14], a choice which allows one to employ a real MO basis set: (e_a, e_b) for the le shell transforming according to the a_1 and a_2 irreducible representations respectively of C_{2v} and (t_{1a}, t_{1b}, t_{1c}) for the t_1 shell transforming as its a_2, b_1 and b_2 irreducible representations respectively. Of the 210 determinants 90 belong to the double excitation $e^2t_1^2$ configuration, which contains the following multiplets:

$$2\,{}^1A_1, {}^1A_2, 3\,{}^1E, {}^1T_1, 3\,{}^1T_2, {}^3A_2, {}^3E, 3\,{}^3T_1, 2\,{}^3T_2 \quad \text{and} \quad {}^5T_2 .$$

A schematic diagram depicting the partitioning of this configuration into its multiplets is given in Fig. 1. Attention is restricted to the 42 determinants in this excitation class with $M_s = 0$; of these 12 transform as the A_1, and 10 each as the A_2, B_1 and B_2 irreducible representations of the C_{2v} subgroup respectively (Table 1). Each of these four sets thus constitutes an orthonormal basis for a linear space of the type Ω' discussed in the previous section. New orthonormal bases of spin eigenfunctions can be obtained for all four Ω' spaces by diagonaliz-

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[13] Character table notation employed throughout this paper is that of Cotton [6].

[14] In general the largest available differentiating Abelian subgroup is taken in order to take maximum advantage of the partitioning method discussed herein.

ing S^2; for example, in the A_1 subspace the new basis consists of 8 singlets, 3 triplets and 1 quintuplet.

The linear manifold of the 8 ${}^1A_1$ functions constitutes a typical example of an Ω'' subspace. As indicated in Table 2, the final step in the symmetrization process is achieved by diagonalizing a C_3 matrix for all Ω'' subspaces. In the case of the ${}^1A_1$ subspace this procedure yields 3 eigenvectors transforming as ${}^1T_2$ (eigenvalue 0), 3 as ${}^1E$ (eigenvalue $-\frac{1}{2}$) and 2 as ${}^1A_1$ (eigenvalue 1); in a similar manner one obtains the other symmetrized functions desired as a basis for the $e^2t_1^2$ configuration. The entire process is then repeated for the e^3t_1, et_1^3 and t_1^4 configurations,

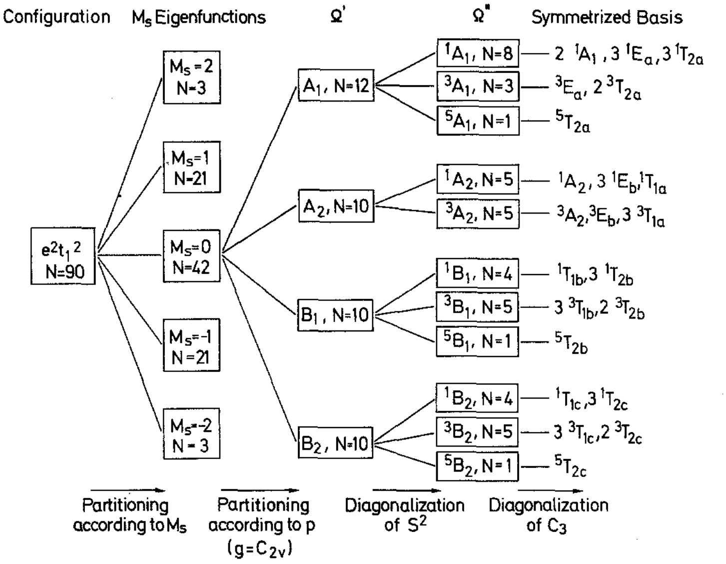

Fig. 1. Schematic diagram depicting the formation of a symmetrized multi-determinantal basis for a particular electronic configuration of the tetrahedrane molecule (T_d point group). In the last column the subscripts a, b and c are used to distinguish the spatial (orthonormal) components of a given multiplet

leading to the ultimate result of a properly symmetrized multi-determinantal basis for the set of wavefunctions ($M_s = 0$) considered in the CI treatment.

Four Hamiltonian matrices over single determinants ($M_s = 0$) are then constructed, one for each C_{2v} irreducible representation (28 functions in A_1, 24 each in A_2, B_1 and B_2). Within each of these symmetry categories several multiplet secular equations are solved by making use of the corresponding matrix elements and the expansion coefficients of the appropriate symmetrized functions.

B. Nitrous Oxide NNO:C_{2v}

CI calculations on linear molecules (diatomics) have been carried out by several authors [7–10]. All these treatments are characterized by one-electron basis sets consisting of eigenfunctions of L_z (symmetry orbitals of the two-dimensional rotation group); while the present method is also applicable for such (imaginary) basis sets, it also allows for a treatment involving exclusively real one-electron functions with comparable facility, as is demonstrated in the following example. The NNO electronic configuration $1\pi^2 2\pi^2 3\pi^2 8\sigma^2$ (core Φ_c consists of seven doubly occupied σ MO's) gives rise to the following multiplets: $7\,{}^1\Sigma^+$, $4\,{}^1\Sigma^-$, $9\,{}^1\Delta$, $3\,{}^1\Gamma$, ${}^1\mathrm{I}$ ($M_L = 6$), $6\,{}^3\Sigma^+$, $9\,{}^3\Sigma^-$, $9\,{}^3\Delta$, $3\,{}^3\Gamma$, $3\,{}^5\Sigma^+$, $2\,{}^5\Sigma^-$, $3\,{}^5\Delta$ and ${}^7\Sigma^-$. The C_{2v} subgroup is chosen as the differentiating Abelian subgroup in order to enable the use of a real MO basis [π_x, π_y corresponding to the two C_{2v} symmetry planes $\sigma(xz)$ and $\sigma(yz)$ respectively]. Of the 216 determinants deriving from the $1\pi^2 2\pi^2 3\pi^2 8\sigma^2$ configuration 88 have $M_s = 0$ and these are divided equally among the A_1 and A_2 irreducible representations of C_{2v} (Table 1). In the usual manner a basis can be found for both the A_1 and A_2 subspaces (Ω' type) which consists of the following C_{2v} multiplets: $20\,{}^1A_1$, $18\,{}^3A_1$, $6\,{}^5A_1$, $17\,{}^1A_2$, $21\,{}^3A_2$, $5\,{}^5A_2$ and ${}^7A_2$ (${}^7\Sigma^-$), with each of these sets representing a basis for a subspace of Ω'' type. These subspaces can be further partitioned by diagonalizing, for example, a C_{12} (30° rotation) matrix for an orthonormal basis; for this operator the eigenvalues ε are related to M_L as follows:

$$\varepsilon(M_L) = \cos\frac{\pi M_L}{6}. \qquad (2)$$

Once the symmetrized multi-determinantal functions have been obtained for all configurations included in the treatment, the procedure for solving the secular equations for each symmetry type is essentially the same as that discussed above in the case of tetrahedrane.

4. Application of Configuration Interaction

Within the framework of the general description for carrying out a CI calculation given above the experimenter is left with several options, the most important of which are: accuracy of the MO basis set employed in the construction of the determinants, relative size of the valence and core sets of orbitals and method of selecting electronic configurations to be explicitly included in the calculation.

Generally speaking, of two sets of SCF MO's that which gives the lower ground state determinantal total energy is preferred in the CI treatment. There are, however, two comments relevant to this overall evaluation: the first is that the sensitivity of the CI treatment decreases fairly rapidly in practice as the MO basis set approaches Hartree-Fock accuracy, that is, the CI treatment has a compensating influence which tends to make the choice of SCF MO's less critical [11, 12]; the other is that obviously even the Hartree-Fock SCF orbitals are not optimum for a given CI expansion of the ground state since they have been optimized in the electronic field produced by a single determinantal wavefunction rather than for the field of the multi-determinantal ground state itself. The procedure of employing a set of orthonormal one-electron functions resulting from a multi-configuration SCF calculation [13] for the ground state as an MO basis for a CI calculation dealing with the entire electronic spectrum of this system is an attractive possibility for feature work.

Once an MO basis set has been selected, it is necessary to define realistic limits to the scope of the CI calculation undertaken both by restricting the size of the valence set employed and by omitting from consideration certain configurations arising from the higher excitations within this set. There are, of course, sound theoretical reasons motivating the latter simplification: triple and higher excitation configurations cannot interact directly with the ground state determinant and the spectrally important single excitation states bear the same relationship to configurations resulting from quadruple and greater excitations. In addition, the less stable of the triple excitation species are generally found to make only a minute contribution to the low lying states of a given system [14]. As a general rule, the more effective method of extending a CI treatment is to expand the valence set rather than to include a greater number of configurations involving excitations within the initial valence set[15].

At the same time experience indicates quite strongly that the nature of a given CI treatment must be determined to a large extent by the individual characteristics of the system under consideration. Indeed, this specificity constitutes one of the strongest arguments for the use of CI techniques to supplement the results of SCF calculations. It has been shown, for example, that while the common single excitation treatment of molecular electronic spectra [15, 16] has been of considerable use in demonstrating the applicability of modern theory to the study of these phenomena, its results are often dramatically different from those obtained from more complete CI calculations which include double and higher excitation configurations, as in the classic examples of benzene and *trans*-butadiene [17, 18]. The influence of triple excitation configurations is found to vary considerably among different systems, having a definite effect on the spectra of benzene [17] and nitrous oxide [14] but causing almost no change in the corresponding data for formic acid [19] and formaldehyde; finally, the ammonia borane molecule [20] shows negligible interaction between any of its configurations. In each of these cases, however, good agreement with experimental findings has been obtained.

In addition to its utilization in the study of vertical excitation spectra, configuration interaction also finds application for the description of molecular potential surfaces, especially when a major change in the electronic configuration of the ground state occurs as a result of variations in geometry; examples illustrating the effectiveness of CI techniques in this regard include studies of the ethylene rotational barrier [12], the rectangular deformation of cyclobutadiene [11] and the angular distortion of cyclopropane. In general, because of its potential for studying geometry changes in molecular excited states the CI method appears to be a valuable tool with which the experimentalist can investigate a wide area of spectroscopy which is virtually inaccessible by purely experimental means.

The ability of CI to introduce a certain amount of correlation into the ground state wavefunction also has other valuable effects; studies of nitrous oxide [14] and formic acid [19] in particular have shown that SCF molecular properties are definitely improved on emplyoment of CI. In summary, the case with which the CI techniques described herein can be handled and the effectiveness with which they can be applied provide compelling reasons for their use as a supplement to the SCF MO method.

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[15] In practice the valence set is usually composed of approximately equal numbers of occupied and virtual MO's.

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