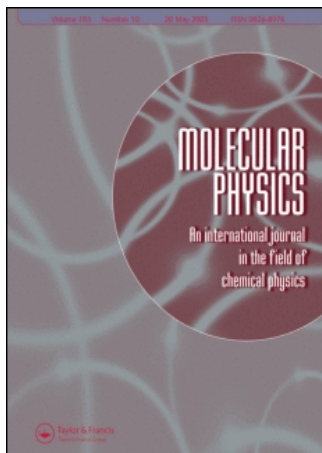


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Application of unitary group methods to configuration interaction calculations

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A computational approach to the *direct* configuration interaction method is described. The method is formulated using the calculus of the generators of the unitary group. The simple structure of the generator matrices within the harmonic excitation level scheme is exploited to give a computational method that is competitive with traditional approaches. A new scheme for basis set truncation in the case of partial configuration interaction is devised employing orbital populations. It is also shown that the block structure of the generator matrices leads to the definition of a new order parameter for perturbation methods which is both effective and convenient.

1. INTRODUCTION

There are two fundamentally different approaches to the method of configuration interaction (CI) in quantum mechanical studies of atoms and molecules (see [1] for a comprehensive review):

- (a) conventional CI, in which one computes the explicit numerical values of the matrix representation of the hamiltonian prior to the solution of the secular problem [1];
- (b) direct CI, in which the molecular integrals are processed directly in the solution of the secular problem [2, 3, 4].

The original formulation of the direct CI method by Roos [2] involved the use of *integral type symbolic references*. Each integral was identified by type and its contribution to the eigenvalue calculation evaluated by a table look-up procedure. This technique is only feasible when (a) the number of different types of matrix element is small (for example single and double substitutions from a closed-shell reference state) and/or (b) there exists a simple correspondence between the four index integral label and the configuration sequence numbers so that an explicit list of configurations is not required. With Roos' work came the development of the vector method by Whitehead [3], which has been subsequently adapted by Bender *et al.* [4]. In the vector method configurations can be associated easily with two electron integrals by writing the hamiltonian in second quantized form and using an occupation number representation for the configurations. Further it is possible to deal with an arbitrary reference space and there is no problem in dealing with higher than double excitations. The

major difficulty with this method is that it deals with Slater determinants and so the configuration space is much larger than necessary.

The development of unitary group methods by Paldus [5–9] provides the theoretical framework for an efficient implementation of direct CI in a very general way. At the most elementary level unitary group methods offer :

- (a) a group theoretical label for *each* spin-coupled state and thus an implicitly ordered list ;
- (b) a recipe for evaluating all matrix elements in terms of a few fundamental matrix elements (*via* the Lie algebra of the group).

However there remain many problems to be solved before an effective formalism for large scale electronic structure calculations is obtained.

Shavitt [10, 11] has recently developed a powerful graph-theoretical method for representing the canonically ordered set of spin-coupled states. This representation permits a direct computation of all the matrix elements required for a direct CI calculation. On the other hand it is possible to use the Lie algebra itself, in a brute force manner, to evaluate the necessary matrix elements. The optimum organization for this approach has been described previously by Downward and Robb [12] and forms the basis of the approach to be discussed here.

2. THEORY

2.1. The calculus of the unitary group

The discussion of the use of the theory of the unitary group in CI calculations has been the subject of two comprehensive reviews by Paldus [8, 9] ; thus we shall limit ourselves to a brief summary of the essential elements of the theory that relate directly to the computational approach to be discussed.

The spin-free form of the hamiltonian can be written as

$$H = \sum_{i,j} \langle i|h|j \rangle \mathbf{E}_{ij} + \frac{1}{2} \sum_{i,j,k,l} [ij|kl] \mathbf{E}_{ij} \mathbf{E}_{kl} - \delta_{jk} \mathbf{E}_{il}, \quad (1)$$

where the \mathbf{E}_{ij} are the generators of the unitary group $U(n)$ and n is the number of orbitals in the problem. The $\langle i|h|j \rangle$ and $[ij|kl]$ are the usual one- and two-electron integrals (charge cloud notation). The operators \mathbf{E}_{ij} are expressed in terms of fermion creation and annihilation operators $\eta_{i\sigma}^\dagger$, $\eta_{j\sigma}$ as

$$\mathbf{E}_{ij} = \sum_{\sigma} \eta_{i\sigma}^\dagger \eta_{j\sigma}, \quad (2)$$

where $\eta_{i\sigma}^\dagger$ creates an electron in orbital i with spin σ (α or β), similarly for $\eta_{j\sigma}$. The \mathbf{E}_{ij} satisfy the commutation relation

$$[\mathbf{E}_{ij}, \mathbf{E}_{kl}] = \delta_{jk} \mathbf{E}_{il} - \delta_{il} \mathbf{E}_{kj} \quad (3)$$

and the Hermitian condition

$$\mathbf{E}_{ij}^\dagger = \mathbf{E}_{ji} \quad (4)$$

and correspond to the Lie algebra of $U(n)$.

Any complete set of N particle basis states $|K\rangle$ give a representation of the Lie algebra and hence the matrix representation of the hamiltonian via equation (1). Thus

$$\langle K|H|L\rangle = \sum_{ij} \langle i|h|j\rangle \langle K|\mathbf{E}_{ij}|L\rangle + \frac{1}{2} \sum_{ijkl} [ij|kl] \langle K|\mathbf{E}_{ij}\mathbf{E}_{kl} - \delta_{jk}\mathbf{E}_{il}|L\rangle. \quad (5)$$

Further, we can factorize the products of generators in the second term to give

$$\langle K|\mathbf{E}_{ij}\mathbf{E}_{kl}|L\rangle = \sum_M \langle K|\mathbf{E}_{ij}|M\rangle \langle M|\mathbf{E}_{kl}|L\rangle. \quad (6)$$

However the generators are not independent. For $k=j$, $i \neq l$, equation (3) reduces to

$$[\mathbf{E}_{ij}, \mathbf{E}_{jl}] = \mathbf{E}_{il}. \quad (7)$$

Thus a knowledge of the matrix representation of the *elementary* generators $\mathbf{E}_{i,i+1}$ and the *weight* generators \mathbf{E}_{ii} is all that is required to compute the matrix representation of H , since all the remaining matrix elements of H can be constructed using equations (3) and (6). Paldus [5] has given simple formulae for the matrix elements of $\mathbf{E}_{i,i+1}$ in the Gelfand–Tsetlin basis (corresponding to the usual spin-coupled basis for an N -electron CI expansion of the wavefunction).

The formula tape for direct CI will consist of a list of the values of the integrals $\langle i|h|j\rangle$ with their associated \mathbf{E}_{ij} matrices (non-zero elements only), followed by the two-electron integral values and their associated matrices $(\mathbf{E}_{ij}\mathbf{E}_{kl} - \delta_{jk}\mathbf{E}_{il})$. A procedure for generating such a formula tape based on equations (5), (6) and (7) is

- (i) construct the \mathbf{E}_{ii} , $\mathbf{E}_{i,i+1}$ matrices,
- (ii) calculate the \mathbf{E}_{ij} ($j > i+1$) by matrix multiplication using equation (7) (for example $\mathbf{E}_{i,i+2} = [\mathbf{E}_{i,i+1}, \mathbf{E}_{i+1,i+2}]$),
- (iii) calculate the $\mathbf{E}_{ij}\mathbf{E}_{kl}$ products for the unique integrals by matrix multiplication from the \mathbf{E}_{ij} constructed in step (ii).

Clearly there are severe practical problems involved in the use of equation (6). These arise because the generator matrices are very large and even though they are sparse they cannot be held in the high speed memory of current computers. The case of a partial CI expansion gives rise to a further difficulty, since the intermediate summation over $|M\rangle$ in equation (6) will extend outside the range of the subset of configurations forming the partial CI. Most of these difficulties are eliminated by grouping the basis states by harmonic levels. In the following paragraphs we describe the scheme [12] which we have found to be useful in practical calculations. This sort of scheme has also been discussed by Paldus [9] and Harter *et al.* [13].

2.2. Harmonic level basis states

We begin with the observation that the Gelfand–Tsetlin basis can be grouped into levels or sets where each member of a set is connected to at most two members of an adjacent set by the elementary generators $\mathbf{E}_{i,i+1}$. We denote an element of harmonic level T_P by a Weyl tableau

$$|m\rangle = |x_1 x_2 x_3 \dots x_r \dots x_l; y_1 y_2 \dots y_s \dots y_u\rangle, \quad (8)$$

where the x_i and y_i are the integers in the first and second columns. The level number is taken as the sum of the numbers in the Weyl tableau

$$T_P = \sum_i x_i + \sum_i y_i. \quad (9)$$

The level T_{P+1} is then derived from level T_P via operation with $\mathbf{E}_{i+1,i}$. Thus \mathbf{E}_{x_{r+1},x_r} operates on $|m\rangle$ to give

$$|m'\rangle = |x_1 \dots x_{r+1}, \dots x_l; y_1 \dots y_s \dots y_u\rangle \quad (10)$$

in level T_{P+1} , since $\mathbf{E}_{i+1,i}$ increases at most only one of the numbers in a column of a Weyl tableau. Thus $\mathbf{E}_{i,i+1}$ are strictly upper triangular matrices *in this basis* since $\langle m | \mathbf{E}_{i,i+1} | m' \rangle = \langle \mathbf{E}_{i+1,i} | m' \rangle$.

The generation of the configuration list by harmonic level numbers T_P is useful because we can compute the matrix elements of $\mathbf{E}_{i,i+1}$ as we generate the ordered list. Further the grouping drastically simplifies the later calculation of H because *all* the generators and bilinear forms take on a block structure, by T_P level

$$\langle m(T_P) | \mathbf{E}_{ij} | m(T_{P+r}) \rangle = 0 \text{ unless } j-i=r, \quad (11)$$

$$\langle m(T_P) | \mathbf{E}_{ij} \mathbf{E}_{kl} | m(T_{P+r}) \rangle = 0 \text{ unless } j-i+l-k=r. \quad (12)$$

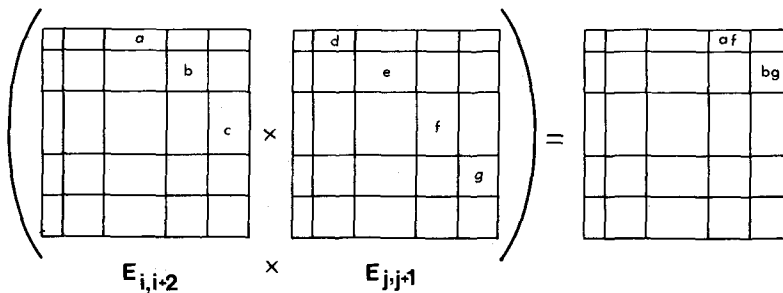


Figure 1. Pictorial representation of the multiplication of two generators with five harmonic levels.

Thus all manipulations of the generators may be performed with blocks that connect weights T_P and T_{P+r} , thus eliminating much searching that would otherwise be required during the manipulations. Figure 1 illustrates the product of $\mathbf{E}_{i,i+2}$ with $\mathbf{E}_{j,j+1}$ and shows the block structure of both the generators and the product. In the case of a total of five harmonic levels, $\mathbf{E}_{i,i+2}$ has three non-zero blocks; these are between levels T_1-T_3 (a), T_2-T_4 (b), T_3-T_5 (c). $\mathbf{E}_{j,j+1}$ has four such blocks (in accordance with equation (11)) and this gives rise to two blocks in the product, in accordance with equation (12). It can readily be seen that the matrix multiplication is formally similar to multiplication of vectors, the vectors having selected blocks of the generators as elements. In this example we have (a, b) from $\mathbf{E}_{i,i+2}$ and (f, g) from $\mathbf{E}_{j,j+1}$ to give (af, bg) as product. It is this reduction of the generators to *vector form* that considerably eases the computational problems.

2.3. Basis set completeness : partial CI

The problem of basis set completeness arises in the application of equation (6); the intermediate summation $|M\rangle$ must be complete. Thus $|M\rangle$ must include all spin-coupled states that can be connected to $|K\rangle$ or $|L\rangle$ by *any* generator, that is that differ from $|K\rangle$ or $|L\rangle$ by one spatial orbital. In general for a partial CI this summation would extend outside the range of configurations to be included in the final eigenvector calculation. For example if $|K\rangle$ and $|L\rangle$ are double substitutions relative to some reference function, then $|M\rangle$ must include all single and triple substitutions. Fortunately the problem can be avoided by reorganization of the bilinear terms in equation (5).

If the basis states are generated by harmonic level as described previously then all the generator matrices are either strictly upper triangular (\mathbf{E}_{ij} , $i < j$), strictly lower triangular (\mathbf{E}_{ij} , $i > j$) or diagonal (\mathbf{E}_{ii}), and are referred to as raising, lowering and weight generators, respectively. Now, let us suppose we have a partial set of states that is complete with respect to raising generators. This set of states will also be complete with respect to the commutation relation given in equation (7) for $i < l$, since multiplication of two raising generators must give a strictly upper triangular matrix. However, the evaluation of the bilinear terms in equation (5) will also involve the product of raising generators on the left and lowering generators on the right and in this case the partial set is not complete.

To avoid this problem, where we have lowering operators on the right, we write the hamiltonian defined by equation (5) such that these products do not occur. The removal of this type of product is accomplished using the commutation relationships given in equation (3). Thus, for $i < j$ and $k > l$ the product $\mathbf{E}_{ij}\mathbf{E}_{kl}$ is replaced by $\mathbf{E}_{kl}\mathbf{E}_{ij} + \delta_{jk}\mathbf{E}_{il} - \delta_{il}\mathbf{E}_{jk}$, where the first term now involves a lowering operator multiplied by a raising operator. The bilinear terms for a summation over unique integrals with the raising-lowering combinations eliminated are given in table 1. The first column of this table lists the

Table 1. Block structure of bilinear forms for unique integral types.

| Integral type†‡ | Coefficient Γ_{ijkl} § | Block structure |
|-----------------|---|----------------------------------|
| $[ii ii]$ | $\frac{1}{4}\mathbf{E}_{ii}(\mathbf{E}_{ii} - 1)$ | $i - i$ |
| $[ii kk]$ | $\frac{1}{2}\mathbf{E}_{ii}\mathbf{E}_{kk}$ | $i - i$ |
| $[ij jj]$ | $\mathbf{E}_{jj}\mathbf{E}_{ji}$ | $i - j$ |
| $[ij kk]$ | $\mathbf{E}_{kk}\mathbf{E}_{ji}$ | $i - j$ |
| $[ii il]$ | $\mathbf{E}_{ii}\mathbf{E}_{li}$ | $i - l$ |
| $[ii kl]$ | $\mathbf{E}_{ii}\mathbf{E}_{lk}$ | $k - l$ |
| $[ij ij]$ | $\frac{1}{2}\{(\mathbf{E}_{ij} + \mathbf{E}_{ji})\mathbf{E}_{ji} - \mathbf{E}_{ii}\}$ | $i - i, 2i - 2j$ |
| $[il kl]$ | $(\mathbf{E}_{il} + \mathbf{E}_{li})\mathbf{E}_{lk} - \mathbf{E}_{ik}$ | $i - k, i + k - 2l$ |
| $[ik kl]$ | $(\mathbf{E}_{ik} + \mathbf{E}_{ki})\mathbf{E}_{lk}$ | $i - l, 2k - i - l $ |
| $[ij il]$ | $(\mathbf{E}_{ij} + \mathbf{E}_{ji})\mathbf{E}_{li}$ | $j - l, 2i - j - l$ |
| $[ij kl]$ | $(\mathbf{E}_{kl} + \mathbf{E}_{lk})\mathbf{E}_{ji}$ | $i + k - j - l, i - j - k + l $ |

† $i \geq j, k \geq l, i(i-1)/2 + j \geq k(k-1)/2 + l$.

‡ $[ij|kl] \equiv \int i(1)j(1)r_{12}^{-1}k(2)l(2)dr$.

§ The full coefficient is given by $\Gamma_{ijkl} + \tilde{\Gamma}_{ijkl}$.

|| This column gives the block structure of the bilinear terms, for example for $[ij|jj]$ only levels differing by $i - j$ may have non-zero matrix elements.

11 unique integral types. The second column lists the coefficients of these unique integrals, the coefficients being a sum of the non-unique contributions of the bilinear terms in equation (1). It turns out that all the expressions are of the form $\mathbf{\Gamma}_{ijkl} + \tilde{\mathbf{\Gamma}}_{ijkl}$ and thus we need only compute $\mathbf{\Gamma}_{ijkl}$ explicitly. ($\tilde{\mathbf{\Gamma}}_{ijkl}$ is the transpose of $\mathbf{\Gamma}_{ijkl}$ obtained by simply transposing the matrix representation of $\mathbf{\Gamma}_{ijkl}$.) The block structure of each of the types is listed in the third column; we use the notation $i-j$ to denote that only levels differing by exactly $i-j$ may have non-zero elements. Note that five of the types allow a level to have matrix elements with two other levels. Thus all the unique one- and two-electron integral coefficients are banded matrices with either two or four bands of submatrices.

We can now state the essential theorem regarding basis set completeness: any partial set of spin-coupled configurations that is complete with respect to the raising generators will also be complete for the evaluation of the bilinear terms in the hamiltonian. Having established this theorem we proceed to show that most of the partial CI wavefunctions of interest fall into a class that is complete in this respect.

Of most general interest is a partial CI wavefunction using a multidimensional reference space. Let us distinguish three ordered sets of orbitals, a set of *core* orbitals which are doubly occupied in all the reference configurations, a set of *valence* orbitals which have all possible occupancies in the reference configurations and, complementary to these two sets, a set of *virtual* or *unoccupied* (in the reference states) orbitals. The reference space is a full valence shell CI expansion. Any configuration may be classified according to the core orbital population P_c the valence orbital population P_v and the virtual orbital population P_u , where P_c is the number of core orbitals in the configuration and similarly for P_v , P_u . Further, if we use N_c to denote the number of core electrons, N_v to denote the number of valence electrons and t_u to denote the maximum virtual

Table 2. Orbital populations for complete sets of configurations.

| Set | Core orbital population, P_c | Valence orbital population, P_v | Unoccupied or virtual orbital population, P_u |
|----------|--------------------------------|-----------------------------------|---|
| A_1 | $N_c - t_u$ | N_v | t_u |
| A_2 | | $N_v + 1$ | $t_u - 1$ |
| A_3 | | $N_v + 2$ | $t_u - 2$ |
| \vdots | | \vdots | \vdots |
| A_n | | $N_v + t_u$ | 0 |
| B_1 | $N_c - t_u + 1$ | $N_v - 1$ | t_u |
| B_2 | | N_v | $t_u - 1$ |
| \vdots | | \vdots | \vdots |
| B_n | | $N_v + t_u - 1$ | 0 |
| Z_1 | N_c | $N_v - t_u$ | t_u |
| Z_2 | | $N_v - t_u + 1$ | $t_u - 1$ |
| \vdots | | \vdots | \vdots |
| Z_n | | N_v | 0 |

N_c =number of core electrons, N_v =number of valence electrons, t_u =maximum occupancy of unoccupied orbitals (for example $t_u=2$ for double substitutions).

orbital population, then possible *complete* sets of configurations can be classified as in table 2. Referring to the table the sets of configurations labelled A_1 to Z_n are defined by the parameters P_c , P_v , P_u for some fixed N_c , N_v , t_u . The full set of configurations A_1 – Z_n is complete with respect to the raising generators. The subset of A_2 – Z_n is also complete, as is A_3 – Z_n . Similarly B_1 – Z_n is complete. In other words we can truncate the CI expansion with respect to minimum core orbital population demanded P_c^{\min} or maximum virtual orbital population t_u or both, where

$$P_c^{\min} \geq N_c - t_u \quad (13)$$

and Z_n is obviously the set of reference configurations.

It remains to demonstrate completeness under the raising generators. We will distinguish six types of raising generator, $\mathbf{E}_{cc'}$, \mathbf{E}_{cv} , \mathbf{E}_{cu} , $\mathbf{E}_{vv'}$, \mathbf{E}_{vu} , $\mathbf{E}_{uu'}$, where for example \mathbf{E}_{cv} is the class of generators \mathbf{E}_{ij} with i chosen from the core set and j from the valence set ($i < j$). To demonstrate completeness we must examine the result of the action of the corresponding *lowering* generator \mathbf{E}_{ji} on any of the configuration sets $|m\rangle$ of table 2 since we have $\langle m | \mathbf{E}_{ij} m' \rangle = \langle \mathbf{E}_{ji} m | m' \rangle$ for $i > j$.

Clearly $\mathbf{E}_{c'c}$, $\mathbf{E}_{v'v}$ and $\mathbf{E}_{u'u}$ cannot change P_c , P_v or P_u and thus the configuration resulting from the operation must remain in the same set. \mathbf{E}_{vc} decreases P_c by one and increases P_v by one leaving P_u unchanged. Similarly \mathbf{E}_{uv} decreases P_v and increases P_u , and \mathbf{E}_{uc} decreases P_c and increases P_u . Thus operation on a member of the subset B_i by \mathbf{E}_{uv} takes it into a member of subset B_{i-1} but no raising operator on set B_{i-1} will generate a member of B_i . Similarly \mathbf{E}_{vc} or \mathbf{E}_{uc} takes one from C_i to B_i or B_{i-1} but no raising generator can take one from B_i to C_i . Finally \mathbf{E}_{uc} on subset A_1 generates a member of a configuration set with $P_v = t_u + 1$ and no subsequent raising operation on this set can generate a member of A_1 .

The classes of configurations given in table 2 cover most situations one is likely to encounter in partial CI calculations. The full set A_1 – Z_n gives all t_u level substitutions with respect to a multidimensional reference space corresponding to a full CI in the valence orbitals. The case $t_u = 1$ corresponds to the first order wavefunction proposed by Schaefer *et al.* [14].

Table 3. Orbital populations for double substitution configuration interaction.

| Configuration Set | P_c | Orbital populations P_v | P_u |
|-------------------|-----------|---------------------------|-------|
| A_1 | $N_c - 2$ | N_v | 2 |
| A_2 | $N_c - 2$ | $N_v + 1$ | 1 |
| A_3 | $N_c - 2$ | $N_v + 2$ | 0 |
| B_1 | $N_c - 1$ | $N_v - 1$ | 2 |
| B_2 | $N_c - 1$ | N_v | 1 |
| B_3 | $N_c - 1$ | $N_v + 1$ | 0 |
| C_1 | N_c | $N_v - 2$ | 2 |
| C_2 | N_c | $N_v - 1$ | 1 |
| C_3 | N_c | N_v | 0 |

The class of configuration for $t_u=2$ is of particular practical importance. (The configuration sets in this case are tabulated in table 3.) The full set A_1-C_3 corresponds to all single and double excitations from a reference space (set C_3) which includes a full CI in the valence orbitals. The configuration sets C_2 and C_1 contain the single and double replacements of the valence orbitals only and these give the valence contribution to the correlation energy. The sets B_3 and B_2 contain single excitations of core electrons to valence and virtual orbitals respectively and account for core polarization while set B_1 contains double excitations from a core and a valence orbital and gives rise to valence-core correlation. Finally sets A_1-A_3 contain double excitations of the core-orbitals and give the core correlation energy.

There is a second class of complete sets of configuration that is contained *within* the scheme just outlined. This class is defined by excitation level truncation. The set of configurations that differ from the minimal state (that is the state of lowest harmonic level number) by less than a chosen excitation level t_e ($t_e=2$ corresponding to double substitutions) are complete with respect to raising generators. This is apparent from the fact that any lowering operation on a t_e excited state must generate either a t_e excited state or a state with t_e increased by one. This truncation scheme would be useful for CI calculation where one desired a reference space that was t_e level excited with respect to the minimal state.

An example of the combined use of t_u and t_e occurs in the calculation of particle-hole excitation energies from a HF closed-shell reference function. Here one could divide the valence orbitals into valence holes (occupied in the minimal state) and valence particles (unoccupied in the minimal state). One would then wish to truncate with respect to double substitutions relative to a reference space consisting of all single valence hole-valence particle excitations. The choice of $t_u=2$ allows all double excitations from a full valence shell CI. The choice of $t_e=3$ truncates at triple substitutions with respect to the minimal state and thus double substitutions with respect to *any* of the single valence hole-valence particle excited states. The two independent truncations can then be combined to provide the required configuration list.

Finally, we come to the problem of dealing with arbitrary configuration sets that are *not* complete with respect to the raising generators. If we define the reference space as the primary space and the partial set of configurations required in the eigenvector problem as the secondary space then the remaining configurations that are required only in the intermediate summation of equation (6) we can call the tertiary space. The tertiary space is used in the computation of generator products and thereafter neglected. In this way it is possible to deal with arbitrary sets of configurations. Of particular interest in this regard are configuration sets that have been truncated with respect to point group symmetry. If a configuration does not contribute to the final eigenvector calculation because it does not contain any components which belong to the same irreducible representation as the desired eigenvalue then it can be moved from the secondary to the tertiary space.

2.4. The eigenvector problem

The objective of direct CI methods is to avoid the requirement to assemble the matrix representation of the hamiltonian and instead process the molecular

integrals directly in the solution of the eigenvalue problem. Of the many diagonalization methods available only those that employ simultaneous relaxation of eigenvector components may be used. Such techniques include the Lanczos method [15] and variation-perturbation theory (for example the Davidson method [16]); those that require sequential relaxation such as those proposed by Shavitt *et al.* [17] or Nesbet [18] cannot be used. The disadvantage of variation-perturbation methods is that one cannot determine many eigenvalues simultaneously. For this reason we have chosen to use a form of energy-independent quasi-degenerate Rayleigh-Schrödinger perturbation theory originally developed by Brandow [19]. The details of the method have been published elsewhere [20] so here we give only a brief summary.

The explicit matrix representation of the hamiltonian can be written in partitioned form as

$$\left[\begin{array}{c|c} \mathbf{H}^0 + \mathbf{V}^1 & \mathbf{Z}^\dagger \\ \hline \mathbf{Z} & \mathbf{W} \end{array} \right] \left[\begin{array}{c} \mathbf{A}_\alpha \\ \hline \mathbf{B}_\alpha \end{array} \right] = E_\alpha \left[\begin{array}{c} \mathbf{A}_\alpha \\ \hline \mathbf{B}_\alpha \end{array} \right], \quad (14)$$

where \mathbf{H}^0 and \mathbf{V}^1 are the diagonal and off-diagonal components of that part of the representation of \mathbf{H} defined to be the reference space, \mathbf{W} contains the representation of \mathbf{H} in the secondary space and \mathbf{Z} , \mathbf{Z}^\dagger contain matrix elements between reference and secondary configurations.

The eigenvalues are obtained from the solution of an energy independent eigenvalue problem

$$\tilde{\mathbf{H}}\mathbf{A}_\alpha = E_\alpha \mathbf{A}_\alpha, \quad (15)$$

where $\tilde{\mathbf{H}}$ has the form

$$\tilde{\mathbf{H}}_{AB} = (\mathbf{H}^0 + \mathbf{V}^1)_{AB} + \mathbf{Z}_A^\dagger \mathbf{C}_B + \sum_{C \neq B} \mathbf{R}_{AC} \mathbf{G}_{CB}, \quad (16)$$

where the subscripts A , B refer to reference space states. The vector \mathbf{Z}_A^\dagger is the A th row of \mathbf{Z} . The vector \mathbf{C}_A is the energy independent projection of the eigenvector component \mathbf{B}_α onto the secondary space and is determined from the matrix equation

$$\mathbf{Z}_A + [(E_A + \Delta E_A) \cdot \mathbf{1} - \mathbf{W}] \mathbf{C}_A = 0 \quad (17)$$

with

$$E_A = (\mathbf{H}^0 + \mathbf{V}^1)_{AA} \quad (18)$$

and

$$\Delta E_A = (\tilde{\mathbf{H}} - \mathbf{H}^0)_{AA}. \quad (19)$$

The matrix \mathbf{G} has elements

$$\mathbf{G}_{CB} = (\tilde{\mathbf{H}} - \mathbf{H}^0)_{CB}. \quad (20)$$

The matrix \mathbf{R} has elements

$$\mathbf{R}_{AC} = \mathbf{C}_A^\dagger \mathbf{C}_C. \quad (21)$$

The equation system defined by equation (17) is solved using the usual Gauss-Seidel iteration for which the n th order iterate is

$$\mathbf{C}_A^{(n)} = (E_A + \Delta E_A^{(n)} - \mathbf{W}_1)^{-1} \mathbf{Z}_A^\dagger + (E_A + \Delta E_A^{(n)} - \mathbf{W}_1)^{-1} \mathbf{W}_2 \mathbf{C}_A^{(n-1)} \quad (22)$$

with

$$\Delta E_A^{(n)} = \mathbf{Z}_A^\dagger \mathbf{C}_A^{(n-1)}, \quad (23)$$

$$\Delta E_A^{(1)} = 0, \quad (24)$$

$$\mathbf{C}_A^{(0)} = 0. \quad (25)$$

The partition of \mathbf{W} into \mathbf{W}_1 and \mathbf{W}_2 is arbitrary but for computational convenience \mathbf{W}_1 is constrained to be diagonal. Thus the eigenvalue procedure is as follows.

(1) Construct explicitly \mathbf{Z}_A , E_A , \mathbf{W}_1 and the A th row of \mathbf{V}^1 from the integral values and matrix elements of \mathbf{E}_{ij} and \mathbf{T}_{ijkl} found on the formula tape. Simultaneously, prepare a shortened form of the formula tape containing only those matrix elements contributing to \mathbf{W}_2 .

(2) Construct the vector $\mathbf{C}_A^{(1)} = (E_A - \mathbf{W}_1)^{-1} \mathbf{Z}_A^\dagger$.

(3) Compute $\sigma_A^{(n)}$ using the shortened formula tape via

$$[\sigma_A^{(n)}]_m = \sum_n \sum_{i,j} \langle i|h|j \rangle \{ [\mathbf{E}_{ij}]_{mn} + [\mathbf{E}_{ij}]_{nm} \} [\mathbf{C}_A^{(n-1)}]_n \\ + \sum_{ijkl} [ij|kl] \{ [\mathbf{T}_{ijkl}]_{mn} + [\tilde{\mathbf{T}}_{ijkl}]_{nm} \} [\mathbf{C}_A^{(n-1)}]_n,$$

where \mathbf{T}_{ijkl} is defined in table 1. The summations extend over all the unique integral labels.

(4) Compute $\mathbf{C}_A^{(n)}$ using

$$\mathbf{C}_A^{(n)} = (E_A + E_A^{(n)} - \mathbf{W}_1)^{-1} (\mathbf{Z}_A^\dagger + \sigma_A^{(n)}).$$

(5) Compute $\Delta E^{(n+1)}$ by vector product (equation (23)).

(6) Iterate steps 3, 4, 5 until $(\Delta E^{(n+1)} - \Delta E^{(n)})$ is less than some threshold.

(7) Repeat steps 1-6 for each reference function $|A\rangle$.

(8) Compute the first two terms of $\tilde{\mathbf{H}}$ in equation (16) using the converged coefficients obtained from step 5.

(9) Construct \mathbf{R} of equation (21) using the same coefficients.

(10) Compute the full effective hamiltonian $\tilde{\mathbf{H}}$ in equation (16).

(11) Iterate step 10 (since \mathbf{G} is a function of $\tilde{\mathbf{H}}$).

(12) Diagonalize $\tilde{\mathbf{H}}$ to give eigenvectors projected onto the reference space and the eigenvalues.

2.5. Application of low order perturbation methods to configuration selection

The methods described in the previous sections could be criticized on the grounds that they are not suitable for approximate perturbation methods (for example second order) which are used for configuration selection. Having shown how arbitrary partial configuration sets may be handled using a tertiary space we now present a discussion of the problem of performing a second order perturbation theory calculation without the necessity of evaluating all the matrix elements of the hamiltonian.

Clearly a wide variety of perturbation theories can be shown to correspond to the choice of the $\mathbf{W}_1/\mathbf{W}_2$ partition in equation (22). For example, Epstein-Nesbet perturbation theory sets \mathbf{W}_1 to the diagonal elements of \mathbf{W} . A calculation truncated at $n=1$ in equation (22) does not require the calculation of the off-diagonal elements of \mathbf{W} and corresponds to the type of second order perturbation theory that might be used for configuration selection. If we compute

just the diagonal elements of \mathbf{W} then we can use Epstein–Nesbet perturbation theory for configuration selection. However, because of the recursive nature of the matrix element evaluation of the generators, the evaluation of solely the diagonal elements of \mathbf{W}_1 cannot be implemented efficiently. Thus we must modify low order perturbation theory methods to suit the present method of matrix element evaluation.

The generation of the basis states by harmonic level with the resultant block structure of the generator matrices provides an excellent starting point for such a perturbation theory. As pointed out by Paldus [9], if the energies of all single particle states were equidistant then all states in the k th harmonic level would have the same energy, namely $k\Delta$ where Δ is the energy separation of the single particle states. Even though the assumption of equidistant orbital energies is not exact one may expect that the energy difference between any two states will be approximately proportional to the difference in their level numbers.

Thus it would appear that one may be able to truncate the CI expansion by harmonic level number. However, as we shall presently demonstrate numerically, this is not very practical. The reason for this is that the number of states in each level increases towards the middle level and then decreases. Thus, while the contribution to the total energy from each configuration decreases with increasing level number, the number of such configurations increases. An example of basis function distribution is shown in figure 2. This plots the number of configurations per level versus the level number for the singlet state of H_2O and clearly shows the rapid increase in the density of configurations in each level. On the other hand, as we now show, the third order contribution to the energy from a pair of configurations is proportional to the *difference* in their harmonic level numbers and thus harmonic level differences provide a new order parameter for perturbation theory.

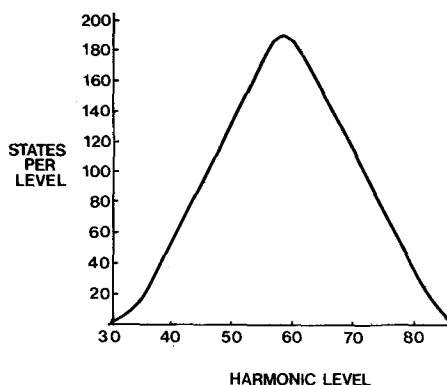


Figure 2. Distribution of configurations for a CI wavefunction for H_2O ($t_u=2$).

Consider the correction ΔC_{AX} to the X th element of the vector \mathbf{C}_A obtained from the second order iterate ($n=2$) of equation (22)

$$\Delta \mathbf{C}_{AX} = \frac{\mathbf{W}_{XY} \mathbf{Z}_{AX}}{(\mathbf{E}_A - \mathbf{W}_{XX})(\mathbf{E}_A - \mathbf{W}_{YY})}, \quad (26)$$

which can be rearranged to give

$$\Delta C_{AX} = \frac{1}{\mathbf{W}_{XX} - \mathbf{W}_{YY}} \left[\frac{1}{E_A - \mathbf{W}_{XX}} - \frac{1}{E_A - \mathbf{W}_{YY}} \right] \mathbf{W}_{XY} \mathbf{Z}_{XA}.$$

Clearly $\mathbf{W}_{XX} - \mathbf{W}_{YY}$ will be approximately proportional to differences in level number. Hence it becomes possible to define orders of perturbation theory based on harmonic level *blocks*. The lowest order corresponds to the inclusion of harmonic level blocks that contain matrix elements between configurations that do not differ in level number. This obviously includes second order of ordinary perturbation theory. Since all matrix elements are computed by harmonic level blocks, naturally, it is feasible to construct a partial formula tape containing only blocks between harmonic levels that differ by some integer and of course all blocks contributing to \mathbf{Z}_A^\dagger , \mathbf{Z}_A .

At lowest order the above method should yield a better result than ordinary second order perturbation theory and can form a basis for configuration selection. From a practical point of view one must still evaluate all the elementary generators but only selected parts of the bilinear terms in the hamiltonian need to be computed, to perform the low order perturbation calculation. Those configurations that do not contribute significantly to the energy can be moved to the tertiary space before the full calculation of the bilinear terms.

3. COMPUTATIONAL DETAILS

Since the configuration space will be relatively large it is not possible to store the complete generator matrices, even on external storage. Because the matrices are sparse it is possible to store explicitly just the non-zero elements as a list of matrix element indices and values. Thus the lists of generator matrices and the formula tape are kept to easily manageable sizes. However this does increase the complexity of the matrix multiplications although it simultaneously reduces the time spent performing them because of the relatively few stored elements. If the non-zero elements are stored sequentially by row then a matrix multiplication involves n passes through the second matrix where n is the number of stored rows in the first matrix, one row of the product being computed in each pass.

It is apparent that a considerable degree of data management is required to compute all the bilinear terms in the hamiltonian and since the generators cannot be kept in the central memory of the computer this is reflected in considerable file activity. Most large modern computers allow I/O operations to continue simultaneously with the execution of a program (although the popular programming language FORTRAN by definition prohibits users from taking advantage of this) and we have used this to improve the efficiency of the computation dramatically. A region of memory is set aside for use as a buffer and all I/O operations pass data through this buffer. When the buffer is either half-full or half-empty a request is made to the operating system to empty or refill (to or from specified sectors on disc) the half-buffer while the program can continue transferring data from the other half if needed or else continue with a matrix multiplication.

Many of the molecular integrals required in a calculation will either be zero by symmetry or small and thus there is no need to compute the bilinear terms

corresponding to these. Although this reduces the computation time dramatically it also destroys the sequential access of data from external storage. In order to avoid manipulating data that is not required we keep a record of the disc and buffer addresses of each block of each generator and in this way we have defined a random access file that operates most efficiently when accessed sequentially. The file is used in a random access mode to obtain the first block of any generator and then sequentially for the remaining blocks.

We have obtained timing data (via calls to the operating system) for the proportion of the total computation time spent in the matrix multiplier and the proportion spent in using the buffered files discussed above. Due to technical problems this data may only be reliable to within a relatively large error margin but is sufficient to indicate general trends. We observe that the time spent performing matrix multiplications increases at a rate slightly worse than n^2 where n is the number of states in the secondary space (with the tertiary space empty). Both the multiplication and IO data transfer times increase linearly with the number of non-zero integrals although we have not been able to deduce a clear relationship between the constants of proportionality and the factors affecting the calculation, for example the number of harmonic levels which determines the length of the vector multiplication.

4. RESULTS AND DISCUSSION

4.1. *Some numerical examples*

It is our intention in this section to illustrate the feasibility of the methods previously discussed in practical applications in quantum chemistry. We present some numerical examples and timing data associated with the computer programs that have been used.

As a first example we consider the calculation of the hamiltonian for the NH^+ molecule for the determination of the lowest $^2\Sigma^+$ eigenvalue. The objective is to compare the computer time required in this method with that of a standard CI package. We used a basis of 21 orbitals and chose to have one frozen 1s nitrogen core orbital, one core orbital (2σ) and four valence orbitals (1π , 3σ , 4σ). The three valence electrons and four valence orbitals give us twenty valence configurations, of which only six, corresponding to $(1\pi)^2 3\sigma$, $(1\pi)^2 4\sigma$, $(3\sigma)^2 4\sigma$, $3\sigma(4\sigma)^2$, will contribute to the $^2\Sigma^+$ state. Using the truncation scheme defined in table 2 with $t_u=2$ we obtain a total of 10 154 configurations, corresponding to the 20-dimensional reference space. Only 2701 of these configurations contribute to the $^2\Sigma^+$ eigenvalue by symmetry and thus the remaining 7453 configurations are moved to the tertiary space. However this does not in fact correspond to the normal configuration list in a conventional CI calculation, where only single and double substitutions relative to the six dimensional reference space are included. For example, the configuration $(\pi^2)(3\sigma^2)5\sigma$ would not be included since it is a triple excitation from the reference space. In our case it is also a double excitation from $(2\sigma)^2(3\sigma^2)\pi$, a reference configuration that does not contribute to the desired eigenvalue. If configurations of this type are also moved to the tertiary space we are left with a total of 1916 configurations leaving 8238 in the tertiary space.

The timing data (CDC 7600 CPU seconds) for the computation of the matrix elements of the hamiltonian are presented in table 4 along with the data

Table 4. Timing information (CPU seconds) for NH^+ calculations.

| | |
|-----------------------------|-----------------------|
| CI bonded functions† | |
| n_1 | 6 |
| n_2 | 1910 |
| Formula tape/s | 101.1 |
| Numerical matrix elements/s | 18.6 |
| CI using $U(n)$ ‡ | |
| n_1 | 6 |
| n_2 | 1910 |
| n_3 | 8238 |
| E_{ij}/s | Arith : 88, I/O : 64 |
| Γ_{ijkl}/s | Arith : 60, I/O : 127 |
| Total | 339 |

† Timings for SPLICE, Atlas Computing Division RL-77-110/b run on IBM 370/195.

‡ Timings for this work run on CDC 7600.

from a standard CI package (SPLICE, Atlas Computing Division, RL-77-110/B). Care must be taken in comparing the total times since the two sets of programs have been run on different computers. We have partitioned the total time for our programs into an arithmetic part and an I/O part. The arithmetic part includes the time spent executing the users program and the I/O part the time spent in performing physical data transfers to external storage. The overhead incurred in causing the multiprogramming operating system to reschedule the CPU is also included in the I/O part.

The conventional CI method appears to be approximately three times faster than the method described in this paper. However the example chosen is particularly perverse for unitary group methods since it is not possible to take full advantage of the high point group symmetry.

Table 5. Timing information for H_2O calculation. All times are given in CDC 7600 CPU seconds.

| | | | |
|---------------------------|------|------|-------|
| CI using $U(n)$ | | | |
| t_u | 2 | 4 | 6 |
| n_1 | 4 | 4 | 4 |
| n_2 | 189 | 625 | 684 |
| n_3 | 516 | 1711 | 1836 |
| E_{ij}/s | 3.5 | 13.6 | 16.0 |
| $\tilde{\Gamma}_{ijkl}/s$ | 4.5 | 18.0 | 20.0 |
| Vector/s | 7.9 | 32.9 | 37.5 |
| Total | 15.9 | 64.5 | 129.4 |
| Vector method (from [4]) | | | |
| $n_1 + n_2$ | 1051 | 7290 | 11149 |
| Vector/s | 387 | 683 | 1145 |

As a second example we consider the calculation of the 1A_1 Rydberg states of H_2O for comparison with the vector method [3]. For this example we use a total of 11 orbitals where we have one frozen core, one core orbital ($2a_1$) and six valence orbitals ($1b_2, 3a_1, 1b_1, 4a_1, 2b_2, 2b_1$) with six valence electrons. A calculation that corresponds to all double excitations from a reference space of single excitations of the minimal state ($\dots (1b_2)^2(3a_1)^2(1b_1)^2$) is obtained with $t_u=2$ and an overall truncation level truncation of $t_e=3$. In this case one obtains a total of 705 configurations of which 189 are required in the eigenvector calculation. The timing data is given in table 5. It is apparent that the present technique is about ten times faster than the vector method; however most of this presumably arises through the increased efficiency in using proper spin-coupled basis states rather than Slater determinants.

4.2. Harmonic level perturbation and truncation

As discussed in § 2 it is possible to truncate the CI expansion with respect to harmonic level and to define orders of perturbation theory with respect to harmonic level differences. In this section we present some numerical tests which illustrate the efficiency of such procedures.

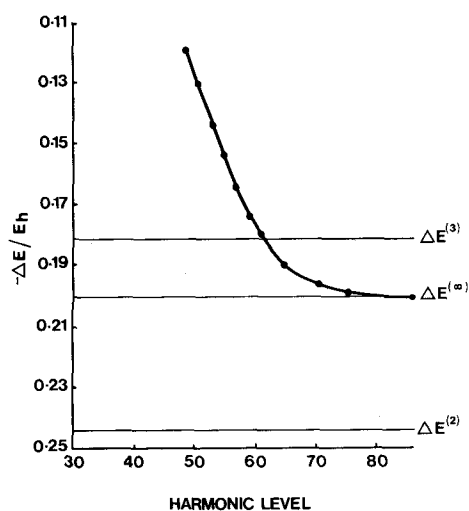


Figure 3. Truncation of a CI wavefunction for H_2O by harmonic level. $\Delta E^{(n)}$ represents the n th order perturbation energy.

In figure 3 we present the results for a 1420 configuration CI (double substitutions) calculation on H_2O (the basis set consists of 30 gaussian functions and is described in [22]). The correlation energy ($E_{CI}-E_{SCF}$) is plotted against the harmonic level number at which the calculation is truncated. The second and third order energies are shown for comparison. In this calculation there are 57 harmonic levels beginning at level 30. The configuration distribution by harmonic level for this calculation is illustrated in figure 2 and has been discussed in § 2.5. The correlation energy can be seen to converge linearly up to the middle level ($T_P=59$), then as the density of configurations in each level

decreases it rapidly converges to the final value. A calculation truncated at level 59 (approximately half of the configurations) yields a correlation energy which has approximately the same error as third order perturbation theory (10 per cent). By level 65 (1034 configurations) the error is 5 per cent. It is thus apparent that truncation by harmonic level could be an effective and simple

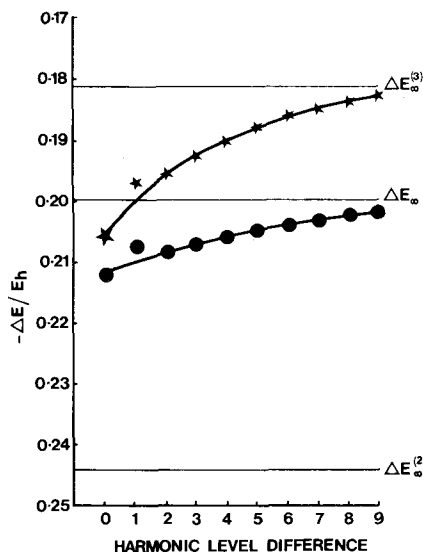


Figure 4. Convergence of perturbation theory using harmonic level difference as an order parameter for an H_2O CI calculation. The circles represent the convergence of the infinite order eigenvalue while the stars represent the convergence of the third order energy.

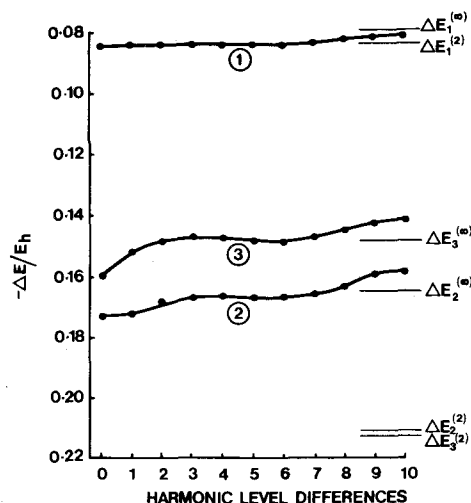


Figure 5. Convergence of perturbation theory using harmonic level difference as an order parameter for a C_2H_4 CI calculation. Curve 1 represents the ground state. Curves 2 and 3 represent the $\pi-\pi^*$ and $(\pi^*)^2$ states respectively.

method for CI truncation. This is much simpler than truncation by perturbation selection because it is defined at the outset of the calculation. However the error at the middle weight is too large to be useful in potential surface calculations.

In figure 4 we illustrate the convergence of harmonic level difference perturbation theory for the H_2O calculation just described. The correlation energy is plotted against the level differences. For comparison the second order energy is also included. It can be seen that even in zeroth order (only diagonal harmonic blocks), the error from second order perturbation theory is reduced from 22 per cent to 10 per cent. The correlation energy converges almost linearly with level differences and including up to nine level differences gives an error of only 1 per cent. One may conclude that this technique at zeroth order should provide a basis for configuration selection prior to a calculation proper.

In figure 5 we illustrate the convergence for a 5105 configuration term CI wavefunction corresponding to a multidimensional reference space $((\pi)^2, (\pi)(\pi^*), (\pi^*)^2)$ for C_2H_4 [21]. In this case we also observe a dramatic improvement of zeroth order over the result of ordinary second order perturbation theory. However here we can also see divergence after seven harmonic levels have been added.

5. CONCLUSIONS

In the previous sections we have given some discussion of a computational approach to direct CI calculations using the calculus of the unitary group. It would appear that this method is comparable in speed with conventional CI calculations yet also offers the advantages of direct CI.

The method discussed here is quite different from the elegant graph theoretical techniques of Shavitt [11]. It is thus important to make some brief comments on the differences. In Shavitt's method the formula tape contains only a small number of unique matrix elements for all \mathbf{E}_{ij} or $\mathbf{E}_{ij}\mathbf{E}_{kl}$ matrix. The upper walks required to resolve all the contributions of a generator are generated at each iteration of the eigenvalue routine. The unique matrix elements are computed directly using graph theoretical methods. In contrast the formula tape in the present work contains the complete \mathbf{E}_{ij} or $\mathbf{E}_{ij}\mathbf{E}_{kl}$ matrices for each integral so that there is no additional work to be done during the eigenvalue calculation. The formula tape could become prohibitively large as in conventional CI. However this problem is not as severe in direct CI since one never needs to assemble the matrix elements of the hamiltonian explicitly. It is clear that the extensive tree searching of Shavitt's method is replaced by the problem of organizing the extensive intermediate data in this method. However we believe that the block structure of the present calculations eliminates the major problems, but it is apparent that much of the computer time in this method is associated with data management.

After this work was submitted we became aware of recent developments in the graphical approach by Brooks and Schaefer [23]. These authors have developed a highly efficient solution to the upper walk problem and they reported their computation times were typically only 15 per cent of their conventional CI calculations. It would appear that the harmonic level approach is not quite competitive with the graphical methods of Shavitt. However, it does

provide some additional possibilities which may be difficult to implement in the graphical method.

Finally, we have demonstrated that the use of harmonic level difference as an 'order parameter' in perturbation methods gives a considerable increase in efficiency over the usual form of a second order perturbation theory (in the Epstein-Nesbet partition of the hamiltonian).

Note added in proof.—We should also refer the reader to a very recent development in the graphical approach to unitary groups by : SIEGHBACH, P. E. M., 1979, *J. chem. Phys.*, **70**, 5391 ; *Ibid.* (in the press). In this work the coupling coefficients required for direct CI are reduced to expressions involving the valence space only. In this manner the time-consuming upper walk problem is avoided.

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