

A non-perturbative open-shell theory for atomic and molecular systems : Application to transbutadiene

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Abstract. A non-perturbative theory is proposed in this article in which an energy independent effective Hamiltonian is obtained for open-shell systems. We have given a diagrammatic version of theory to facilitate the analysis of the problem. The theory has been applied to a model $4-\pi$ electron problem, for calculating the lowest $\pi-\pi^*$ singlet and triplet energy levels of transbutadiene. Comparison with full CI calculation indicates the excellent workability of the theory.

Keywords. Energy levels of atoms and molecules; non-perturbative open-shell theory.

1. Introduction

The usual procedure for the determination of accurate wavefunctions of finite many electron systems is the method of superposition of determinants. It is well known that by adding more and more determinants one may eventually converge to the true energy. The earliest method for determining the combination coefficients of the determinants uses the Ritz variation principle, and this is known as the configuration-interaction (CI) procedure. Another method is to choose a suitable model Hamiltonian and use its eigenfunctions as a basis in a perturbation calculation. In both of these methods one starts out with a limited number of determinants comprising a "reference" function, and builds up more and more accurate functions by bringing in the effects of more determinants.

It has become customary to classify the many-electron systems into two broad categories depending on the minimum number of determinants in the reference function that may adequately reflect the symmetry of the system. Systems with a single determinant as the reference function are called "closed shell" systems; similarly, systems for which a multi-determinant reference function is necessary are termed "open-shell" systems. The relevant perturbation techniques for these two classes of problems are rather different. A field theoretic version of perturbation theory for the closed shell case was first given by Goldstone (1957). The linked cluster nature of this theory and the use of a diagrammatic representation of the perturbation series simplified the calculation. A straightforward use of this treatment to open-shell cases, however, leads to divergence difficulties, as some of the energy denominators become zero. Recently these difficulties

have been removed by Brandow and others (Brandow 1967; Oberlechner *et al.* 1970; Johnson *et al.* 1971; Kuo *et al.* 1971) who have been able to formulate a linked cluster perturbation series appropriate for the open-shell case.

In the present paper we envisage another type of approach, neither variational nor perturbational, in which the wavefunction is written as an Ursell-type expansion about the reference function (Cizek 1966). The reference function will be taken to be multi-determinantal, so that the method is applicable to open-shell systems. The theory naturally goes over to the closed shell case when the reference function consists of only a single determinant, and this has been developed earlier by Cizek (Cizek 1966).

The outstanding merit of this kind of approach is that there are no energy denominators in the theory. Moreover, any specific N -body correlation effect can be isolated clearly, unlike the case in perturbation theory. In the following sections we give the derivation of this theory and show how it can be given a diagrammatic representation. Finally, the workability of this theory is described through a pilot numerical calculation in a 4 π -electron problem, transbutadiene.

2. Theory

2.1 General considerations

We want to build up our reference functions from a set of M linearly independent determinants ϕ_i , which may be said to span a "model space". We thus have M distinct reference functions ψ_0^k , which may be written as

$$\psi_0^k = \sum_i C_i^k \phi_i \quad (1)$$

Our object is to define an operator T , which acting on ψ_0^k generates all the "excited" determinants that enter the description of the problem. We now take that the exact wave functions ψ^k of the M energy levels of the system may be written as

$$\psi^k = e^T \psi_0^k \quad (2)$$

The Schrodinger equation then gives

$$H\psi^k = E^k \psi^k \quad (3 a)$$

or,

$$He^T \psi_0^k = E^k e^T \psi_0^k \quad (3 b)$$

If we can find an operator U such that

$$He^T = e^T U$$

then

$$He^T \psi_0^k = e^T U \psi_0^k = E^k e^T \psi_0^k \quad (4)$$

so that eqs (4) reduces to

$$U \psi_0^k = E^k \psi_0^k \tag{5 a}$$

or

$$U \sum_i C_i^k \phi_i = E^k \sum_i C_i^k \phi_i \tag{5 b}$$

The operator U obviously involves T , whose explicit construction has been dealt with in section 2.2.

Taking the scalar product of eq. (5 b) with any N particle determinant ϕ_l^* lying outside the model space, we have

$$\sum_i C_i^k \langle \phi_l^* | U | \phi_i \rangle = 0 \quad \text{for all } l. \tag{6}$$

Here we assume that each ϕ_i or ϕ_i^* is an antisymmetrized product of a selection of N spin-orbitals chosen from a complete set of orthonormal single-particle functions.

As mentioned before, in many atomic and molecular systems of interest, the reference functions ψ_0^k is multi-determinant as a consequence of symmetry. For example, with a spin-independent Hamiltonian, it is often necessary to combine a number of determinants to make ψ_0^k 's eigenfunctions of S^2 and S_z . If the total number of spin-eigenfunctions for the problem be equal to the dimension of the model space, then we may say that the problem is symmetry-degenerate. In this case, the combining coefficients C_i^k for the components ϕ_i in the reference functions ψ_0^k for the various spin eigenstates are determined entirely by the spin-coupling scheme. The coefficients C_i^k form an orthonormal, and therefore linearly independent set.

Hence, for the symmetry degenerate open shell case, we may replace eq. (6) by the simpler relation

$$\langle \phi_l^* | U | \phi_i \rangle = 0 \quad \text{for each } l \text{ and } i. \tag{7}$$

These equations are coupled simultaneous equations in the matrix elements of T appearing in U , by solving which T may be determined. Taking now the scalar product of eq. (5 b) with the functions ϕ_j of the model space, we have

$$\sum_i \langle \phi_j | U | \phi_i \rangle C_i^k = E^k C_j^k \quad \text{for each } \phi_j$$

In matrix notation, this may be written as

$$UC = CE \tag{8}$$

Putting in the matrix elements of T found from eq. (7) in eq. (8), we may find out the set of exact energies by solving the eigenvalue relation (8). Eq. (8) signifies that a single operator U generates the M exact energies E^k acting entirely within the model space. The operator U may thus be looked upon as a state independent effective Hamiltonian. In older perturbative developments of the open shell problems (Bloch and Horowitz 1958), one encounters effective Hamiltonians which depend parametrically on E^k , and thus may be called "state dependent". The later perturbative developments, however, do not share this shortcoming, and

in this sense our non-perturbative development is at least at par with these later theories. In many body language this state independence of E^k is often referred to as "energy independence". As we shall show in the following sections, U may be constructed so as to consist of linked terms only.

In the general open shell case, the coefficients C_i^k are not symmetry determined, and a possible method of handling this case is discussed in section 4.

2.2 Construction of U

Let us first classify the single particle orbitals from which the determinants ϕ_i and ϕ_i^* are built. The orbitals which appear in all the ϕ_i 's of the model space will be called hole orbitals and will be labelled as α, β, \dots , etc. The orbitals that are not present in any ϕ_i will be called particle orbitals and will be indicated by p, q, \dots , etc. The remaining orbitals which appear in some ϕ_i 's but not in all of them at a time will be called valence orbitals, and will be denoted by the letters \bar{p}, \bar{q}, \dots , etc. An unspecified orbital will be labelled by the letters A, B, \dots , etc.

The Hamiltonian for the system may be written in occupation number representation (Schweber 1961) as

$$H = \sum_{A, B} \langle A | h | B \rangle X_A^\dagger X_B + \frac{1}{(2!)^2} \sum_{A, B, C, D} \langle AB | g | CD \rangle_a X_A^\dagger X_B^\dagger X_D X_C \quad (9)$$

where X_A^\dagger and X_B are the creation and destruction operators for the states A and B respectively. The suffix "a" indicates an antisymmetrized matrix element (Cizek 1969). We may also express each function ϕ_i as

$$\phi_i = \Omega_i^\dagger | 0 \rangle \quad (10 a)$$

where Ω_i^\dagger is an appropriate product of valence creation operators acting upon the "core" part consisting only of the occupied hole states. We use the convention of taking the core part as the vacuum, and designate it as $| 0 \rangle$.

With respect to this vacuum, we may write eq. (9) in normal order (Cizek 1966) as

$$H = \langle 0 | H | 0 \rangle + \sum_{A, B} \langle A | f | B \rangle N [X_A^\dagger X_B] + \frac{1}{(2!)^2} \sum_{A, B, C, D} \langle AB | g | CD \rangle_a N [X_A^\dagger X_B^\dagger X_D X_C] = \langle 0 | \bar{H} | 0 \rangle + F + V \quad (11)$$

with

$$\langle A | f | B \rangle = \langle A | h | B \rangle + \sum_\alpha \langle A\alpha | g | B\alpha \rangle_a \quad (12)$$

We now make the canonical transformations

$$\left\{ \begin{matrix} Y_a^\dagger = X_a \\ Y_a = X_a^\dagger \end{matrix} \right\}, \quad \left\{ \begin{matrix} Y_p = X_p \\ Y_p^\dagger = X_p^\dagger \end{matrix} \right\}, \quad \left\{ \begin{matrix} Y_p = X_p \\ Y_p^\dagger = X_p^\dagger \end{matrix} \right\} \quad (13)$$

so that

$$Y_A | 0 \rangle = 0, \quad \text{for any } A. \quad (14)$$

Equation (11) may be written down entirely in terms of the Y -operators. It is not necessary, however, to give here the transformed expression.

We now define T [eq. (2)] to be a sum of 1, 2, ..., N body operators

$$T = \sum_p T_p \quad (15 a)$$

where T_p is of the form

$$T_p = \frac{1}{(p!)^2} \sum \langle \dots \bar{p}\bar{q} \dots uv | t_p | \dots \bar{r}\bar{s} \dots \alpha\beta \rangle_a \quad (15 b)$$

$$N [\dots Y_p^\dagger Y_q^\dagger \dots Y_u^\dagger Y_v^\dagger Y_r^\dagger Y_s^\dagger \dots Y_\alpha Y_\beta \dots]$$

We place the restrictions that (a) the value taken up by any label on the right of a matrix element must not coincide with any on the left, and (b) the matrix elements which cause scattering only within the model space are to be excluded. The suffix a once again indicates an antisymmetrized matrix element. It can be easily checked that this form for T generates all the configurations ϕ_i lying outside the model space.

Featurewise, the operators F , V and T have one property in common, namely, each of them is a sum containing products of even number of creation and destruction operators in normal order. For convenience, we shall refer to such operators as "objects". Consider the product of any two objects A and Ω . Using Wick's theorem, we may write

$$A\Omega = (A\Omega)_0 + \overline{A\Omega} \quad (16 a)$$

where $(A\Omega)_0$ is the collection of all terms in normal order containing no contractions, and $\overline{A\Omega}$ is the collection of all terms containing at least one contraction (Schweber 1961) or more. We call \square to be the pairing symbol. Thus a paired set of objects $\overline{A\Omega}$ represents a collection of many contracted terms, and one must not confuse it with a single contracted term. Making a similar expansion for $\overline{\Omega A}$, we have,

$$\Omega A = (\Omega A)_0 + \overline{\Omega A} \quad (16 b)$$

Evidently $(A\Omega)_0 = (\Omega A)_0$ and hence

$$A\Omega = \Omega A + \overline{A\Omega} - \overline{\Omega A} \quad (16 c)$$

or, for two objects Γ and T , where Γ is either F or V ,

$$\Gamma T = T\Gamma + \overline{\Gamma T} - \overline{T\Gamma} \quad (17)$$

We then have, using eq. (17),

$$\begin{aligned}
 \Gamma T^2 &= (T\Gamma + \overleftarrow{T\overline{T}} - \overline{T\overline{T}}) T \\
 &= T^2\Gamma + T\overleftarrow{T\overline{T}} - T\overline{T\overline{T}} + T\overleftarrow{T\overline{T}} + \overleftarrow{T\overline{T\overline{T}}} - \overline{T\overline{T\overline{T}}} \\
 &\quad - T\overline{T\overline{T}} - \overleftarrow{T\overline{T\overline{T}}} + \overleftarrow{T\overline{T\overline{T}}} \\
 &= T^2\Gamma + 2T(\overleftarrow{T\overline{T}} - \overline{T\overline{T}}) + \overleftarrow{T\overline{T\overline{T}}} - (\overline{T\overline{T\overline{T}}} + \overleftarrow{T\overline{T\overline{T}}}) \\
 &\quad + (\overleftarrow{T\overline{T\overline{T}}}) \tag{18}
 \end{aligned}$$

Let us now introduce the idea of a linked term. Suppose we are given a product of k_1 number of T operators to the left of Γ and k_2 number of T operators on the right of it,

$$T^{k_1} \Gamma T^{k_2}$$

By a linked term $(T^{k_1} \Gamma T^{k_2})_L$ we mean the sum of all terms generated from this product by pairing Γ with a T on its immediate right or left first, then the paired object $\overleftarrow{T\overline{T}}$ or $\overline{T\overline{T}}$ with another T to its immediate right or left, and so on for all objects T , without skipping any intermediate T in the process. For example,

$$\begin{aligned}
 (\Gamma T)_L &= \overleftarrow{T\overline{T}}; & (T\Gamma)_L &= \overline{T\overline{T}} \\
 (\Gamma T^2)_L &= \overleftarrow{T\overline{T\overline{T}}}; & (T^2\Gamma)_L &= \overleftarrow{T\overline{T\overline{T}}} \\
 (T\Gamma T)_L &= \overleftarrow{T\overline{T\overline{T}}} + \overleftarrow{T\overline{T\overline{T}}}, \text{ etc.}
 \end{aligned}$$

The total number of paired terms in a linked term $(T^{k_1} \Gamma T^{k_2})_L$ is $(k_1 + k_2)! / k_1! k_2!$. We may now write eq. (18) in the condensed notation

$$\Gamma T^2 = \sum_{k=0}^2 \binom{2}{k} T^{2-k} \sum_{\substack{k_1, k_2 \\ k_1+k_2=k}} (-1)^{k_1} (T^{k_1} \Gamma T^{k_2})_L \tag{19}$$

We now assume the validity of this form for ΓT^n , i.e. we write

$$\Gamma T^n = \sum_{k=0}^n \binom{n}{k} T^{n-k} \sum_{\substack{k_1, k_2 \\ k_1+k_2=k}} (-1)^{k_1} (T^{k_1} \Gamma T^{k_2})_L \tag{20}$$

and show that this indeed is the correct choice. We proceed by the method of induction. Each linked term is also an object, and from their definition we have the basic recursion relations,

$$(T^{k_1} \Gamma T^{k_2})_L = T \overbrace{(T^{k_1-1} \Gamma T^{k_2})_L} + \overbrace{(T^{k_1} \Gamma T^{k_2-1})_L} T \tag{21 a}$$

for k_1 or $k_2 > 0$,

and

$$(\Gamma)_L = \Gamma \tag{21 b}$$

for $k_1 = k_2 = 0$.

A linked term vanishes for negative powers of T on either side of Γ . It then follows that

$$\sum_{\substack{k_1, k_2 \\ k_1+k_2=k}} (-1)^{k_1} [-\overbrace{T(T^{k_1} \Gamma T^{k_2})_L} + \overbrace{(T^{k_1} \Gamma T^{k_2})_L T}] = \sum_{\substack{k_1, k_2 \\ k_1+k_2=k+1}} (-1)^{k_1} (T^{k_1} \Gamma T^{k_2})_L \tag{22}$$

We then have

$$\begin{aligned} \Gamma T^{n+1} &= \left\{ \sum_{k=0}^n \binom{n}{k} T^{n-k} \sum_{\substack{k_1, k_2 \\ k_1+k_2=k}} (-1)^{k_1} (T^{k_1} \Gamma T^{k_2})_L \right\} T \\ &= \sum_{k=0}^n \binom{n}{k} T^{n+1-k} \sum_{\substack{k_1, k_2 \\ k_1+k_2=k}} (-1)^{k_1} (T^{k_1} \Gamma T^{k_2})_L \\ &\quad + \sum_{k=0}^n \binom{n}{k} T^{n-k} \sum_{\substack{k_1, k_2 \\ k_1+k_2=k}} (-1)^{k_1} [\overbrace{(T^{k_1} \Gamma T^{k_2})_L} T - T \overbrace{(T^{k_1} \Gamma T^{k_2})_L}] \\ &= \sum_{k=0}^n \binom{n}{k} T^{n+1-k} \sum_{\substack{k_1, k_2 \\ k_1+k_2=k}} (-1)^{k_1} (T^{k_1} \Gamma T^{k_2})_L \\ &\quad + \sum_{k=0}^n \binom{n}{k} T^{n-k} \sum_{\substack{k_1, k_2 \\ k_1+k_2=k+1}} (-1)^{k_1} (T^{k_1} \Gamma T^{k_2})_L \end{aligned} \tag{23 a}$$

Putting $k' = k + 1$ in the second term and using the relations

$$\binom{n}{k} + \binom{n}{k-1} = \binom{n+1}{k}; \quad \binom{n}{n+1} = \binom{n}{-1} = 0.$$

we may now combine the two terms, and have

$$\Gamma T^{n+1} = \sum_{k=0}^{n+1} \binom{n+1}{k} T^{n+1-k} \sum_{\substack{k_1, k_2 \\ k_1+k_2=k}} (-1)^{k_1} (T^{k_1} \Gamma T^{k_2})_L \tag{23 b}$$

Since relation (20) is valid for $n = 1$ and 2 and $n + 1$ it is also valid for all n . We then have

$$\begin{aligned} \Gamma e^{\Gamma} &= \sum_{n=0}^{\infty} \Gamma \frac{T^n}{n!} \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \sum_{k=0}^n \binom{n}{k} T^{n-k} \sum_{\substack{k_1, k_2 \\ k_1+k_2=k}} (-1)^{k_1} (T^{k_1} \Gamma T^{k_2})_L \end{aligned}$$

$$= \sum_{n=0}^{\infty} \sum_{k=0}^n \frac{T^{n-k}}{(n-k)!} \cdot \frac{1}{k!} \cdot \sum_{\substack{k_1, k_2 \\ k_1+k_2=k}} (-1)^{k_1} (T^{k_1} \Gamma T^{k_2})_L \tag{24 a}$$

Since $\frac{1}{(n-k)!} = 0$ for $n < k$, we have

$$\Gamma e^T = e^T \sum_{k=0}^{\infty} \frac{1}{k!} \sum_{\substack{k_1, k_2 \\ k_1+k_2=k}} (-1)^{k_1} (T^{k_1} \Gamma T^{k_2})_L \tag{24 b}$$

Taking

$$\Gamma = \langle H \rangle + F + V,$$

we have

$$He^T = e^T U, \tag{25 a}$$

where

$$U = \sum_{k=0}^{\infty} \frac{1}{k!} \sum_{\substack{k_1, k_2 \\ k_1+k_2=k}} (-1)^{k_1} (T^{k_1} (\langle H \rangle + F + V) T^{k_2})_L \tag{25 b}$$

Thus U consists of a sum of linked terms, and eq. (25 b) gives the factors accompanying each of them for each pair of values k_1 and k_2 . Since each T is a sum of T_p 's, and since $\Gamma = \langle H \rangle + F + V$ every linked term in eq. (25 b) may be broken up into its components in terms of all possible selections of T_p and any of F, V or $\langle H \rangle$. We may represent the operators T_p , as in figure 1, where we use the Hugen-

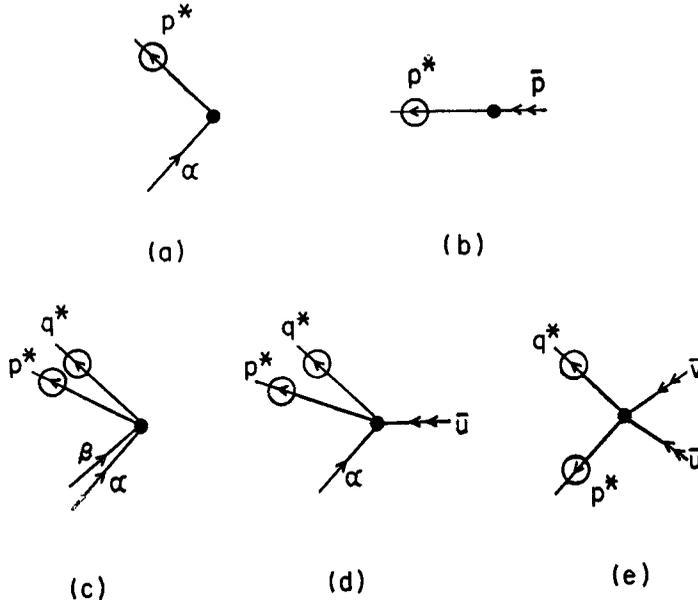


Figure 1. All possible shapes of T_1 (a and b) and T_2 (c, d and e) operators. A circle around an arrow indicates that the line can take up both valence and particle labels. We indicate this by putting a star on the label.

holtz convention for drawing the particle and hole lines (Hugenholtz 1957). The valence lines are treated in the same way as particle lines, they being distinguished by the placement of a double arrow on a line. The F and V operators may be represented by analogous diagrams, with vertices represented by open circles. A linked term like $(T^{k_1} F T^{k_2})_L$ will then give rise to a number of linked diagrams containing a string of k_1 T_p -vertices to the left of an F or a V vertex, and k_2 T_p -vertices to the right, they being paired with each other in all possible ways consistent with the pairing sequences present in the linked term. In this manner one can give a diagrammatic representation of U to any order of approximation desired. We may call the diagrams representing the operator U to be the U -diagrams.

The structure of the U -diagrams simplify considerably when we consider the closed-shell case. Here we have no valence lines in a diagram, and thus there are no T_p -vertices with lines to the right. Moreover, we cannot now join any T_p -vertex directly with another T_p -vertex, nor can we have a T_p -vertex connected to the left of a F or V vertex. The U diagrams then reduce to the same set of diagrams as obtained earlier by Cizek in his discussion of the closed-shell theory (Cizek 1966, 1969).

We may now proceed to calculate the matrix elements $\langle \phi_i | U | \phi_i \rangle$ and $\langle \phi_i^* | U | \phi_i \rangle$ appearing in eqs (8) and (7). Each of the ϕ_i 's and ϕ_i^* 's may be written as

$$\phi_i = \Omega_i^\dagger | 0 \rangle \quad (10 a)$$

$$\phi_i^* = A_i^\dagger | 0 \rangle \quad (10 b)$$

where Ω_i^\dagger and A_i^\dagger are appropriate sets of creation operators. If we consider only the *distinct* determinantal states ϕ_i and ϕ_i^* that may be built out of our starting set of single-particle orbitals, then in each of the representations (10) for these determinants the creation operators appear in a certain fixed order, which we call the "standard" order. In actual applications using the states ϕ_i and ϕ_i^* we shall always have in mind this particular order of creation operators.

In any matrix element like $\langle \phi_i^* | U | \phi_i \rangle$, only those U -diagrams contribute which cause a scattering from the group of single particle states present in ϕ_i to those in ϕ_i^* . If we compare the array of single particle labels in Ω_i^\dagger with the array of labels in A_i^\dagger , then we may find some common valence labels, say q in number. The remaining labels in Ω_i^\dagger and A_i^\dagger are all distinct from one another. The most elementary kind of U -diagrams connecting ϕ_i and ϕ_i^* will be those which cause scattering only between the distinct single particle states present in Ω_i^\dagger and A_i^\dagger . Next we have U -diagrams, which apart from causing scattering between the distinct single particle states, cause scattering from a single valence state in Ω_i^\dagger to another valence state in A_i^\dagger having the same label. We may then say that the U -diagrams concerned cause a "passive" valence-valence scattering. Continuing in this manner we have groups of U -diagrams which cause one, two ..., up to a maximum of q passive valence-valence scattering, over a background of scattering processes between the distinct single particle states in ϕ_i and ϕ_i^* .

Each collection of U -diagrams, having a common disposition of the external lines, may be represented by what may be called a G -block (figure 2). In a G -block, corresponding to every U -diagram there may be other diagrams giving the same contribution. These are the diagrams which may be brought into coincidence with one another by suitable topological deformations. It suffices, therefore, to take only the topologically inequivalent diagrams in a G -block, and multiply the contribution of each by a suitable factor called the "weight" which is just the number of diagrams topologically equivalent to a given diagram. To obtain the contribution of a G -block to $\langle \phi_i^* | U | \phi_i \rangle$, we must calculate the contribution of each topologically inequivalent U -diagram separately. To do this, we proceed systematically in the following manner. First we mark the operators

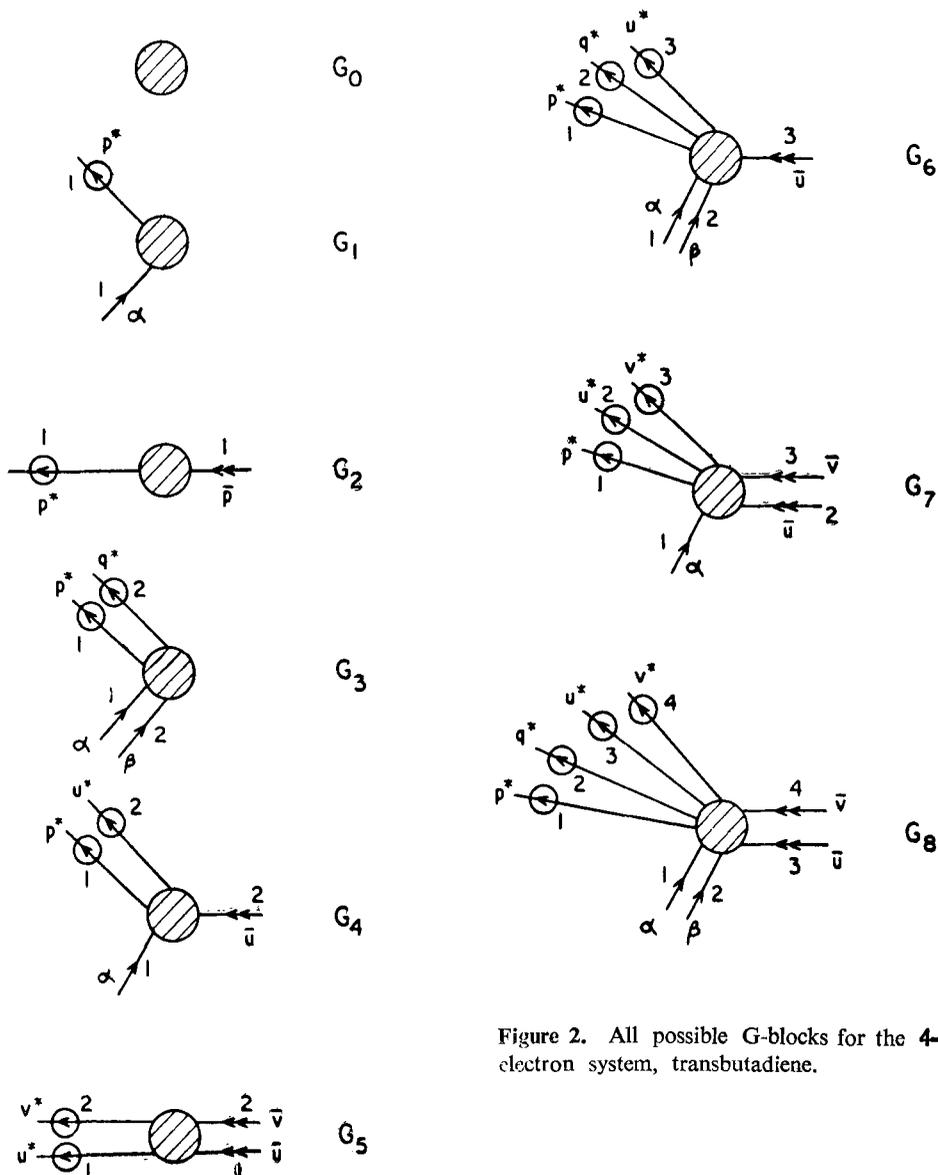


Figure 2. All possible G -blocks for the 4-electron system, transbutadiene.

appearing in each of Ω_i^\dagger and A_i^\dagger by the numbers 1, 2, ... sequentially from left to right. We now place the labels of the creation operators present in Ω_i^\dagger on the ingoing lines of the U -diagram in a manner compatible with the geometrical orientation and the arrow placings of the lines, and also put the markings alongside the labels. In this process, of course, all the labels present in Ω_i^\dagger may not be required. In a similar manner we put the labels and the markings corresponding to the operators in A_i^\dagger such that the ingoing line marked by a particular number traverses a continuous path within the diagram and goes out along a line with the same number. The whole length of such a line is marked by the same number marking its external segments. The remaining internal lines from closed loops in the sense that if one starts out from a vertex, one returns to it via some continuous path. Each loop again, is characterized by a certain number.*

We now evaluate the contribution of a U -diagram by using the following set of rules.

- (i) Assign the weight ω of a diagram.
- (ii) Assign the factor $1/k!$, where k is the number of T_p -vertices present, and the factors $1/(p!)^2$ for each T_p . If a V -vertex be present, then also include the factor $1/(2!)^2$.
- (iii) Assign the factor $(-1)^{l+h+k_1}$, where l is the number of loops, h the number of hole lines, and k_1 is the number of T_p -vertices appearing on the left of the F or V vertex.
- (iv) Label the internal lines appropriately, and write down the matrix elements for the scatterings at each vertex. Now sum over all internal lines.
- (v) Let us call the quantity obtained by using rules (i)–(iv) as c . If the U -diagram has n_1 outgoing particle and valence lines, n_2 ingoing hole lines and n_3 ingoing valence lines, then c is a function of these variables

$$C \equiv C(p_1, \dots, p_{n_1}; \alpha_1 \dots \alpha_{n_2}; \bar{p}_1, \bar{p}_2 \dots \bar{p}_{n_3}).$$

The total contribution of the U -diagram to the matrix element is then given by the formula

$$d(p_1 \dots p_{n_1}; \alpha_1 \dots \alpha_{n_2}; \bar{p}_1 \dots \bar{p}_{n_3}) = \sum (-1)^\epsilon (n_1, n_2, n_3) P(p_1 \dots p_{n_1}) \\ \times P(\alpha_1 \dots \alpha_{n_2}) P(\bar{p}_1 \dots \bar{p}_{n_3}) c(p_1 \dots p_{n_1}; \alpha_1 \dots \alpha_{n_2}; \bar{p}_1 \dots \bar{p}_{n_3}),$$

where P 's are the permutations for the labels indicated, and $\epsilon(n_1, n_2, n_3)$ is the parity for the whole permutation. The summation runs over all permutations, the parity of the identity permutation being unity.

Hence the contribution of a G-block to the matrix element is the sum of all such d 's, and will be denoted by D . In this manner the contribution of every G-block to the matrix element $\langle \phi_i^* | U | \phi_i \rangle$ is found. The evaluation of the matrix elements $\langle \phi_i | U | \phi_i \rangle$ is made in the same way.

3. Application to a 4- π electron problem: transbutadiene

To test the applicability of the non-perturbative open-shell theory (NPOST)

* For an algorithm to calculate the weight of a diagram, see our forthcoming paper (Mukherjee *et al.*; to be published).

described in the preceding section, we have made an application to a 4- π electron problem, transbutadiene, using the PPP parametrisation (Parr 1964). Our object is to calculate the energies of the lowest π - π^* singlet and triplet states of this molecule. These energies are then compared with the model exact answer by carrying out a full CI calculation in the chosen basis. We use two sets of orbitals, one obtained by diagonalizing the core Hamiltonian f , and the other by carrying out a SCF calculation for the ground state.

The two components of the model space for this problem are

$$\begin{aligned}\phi_1 &= \mathcal{A} [1\bar{1}2\bar{3}] \\ \phi_2 &= \mathcal{A} [1\bar{1}3\bar{2}]\end{aligned}\quad (26)$$

so that the reference singlet and triplet functions are given by

$$\begin{aligned}\Psi_0^s &= \frac{1}{\sqrt{2}} \{ \mathcal{A} | 1\bar{1}2\bar{3} | + \mathcal{A} | 1\bar{1}3\bar{2} | \} \\ \Psi_0^t &= \frac{1}{\sqrt{2}} \{ \mathcal{A} | 1\bar{1}2\bar{3} | - \mathcal{A} | 1\bar{1}3\bar{2} | \}\end{aligned}\quad (27)$$

This is a symmetry determined case and the coefficients for Ψ_0^s and Ψ_0^t are $\pm 1/\sqrt{2}$. The vacuum state is given by

$$|0\rangle = \mathcal{A} [1\bar{1}]\quad (28)$$

1 and $\bar{1}$ are therefore hole orbitals. There are a total of 8 spin-orbitals in this problem, built out of 8 spin-AO's. The orbitals 2, $\bar{2}$, 3 and $\bar{3}$ are the valence orbitals and 4 and $\bar{4}$, which do not appear in the ϕ_i 's are the particle orbitals. The orbitals 1, 2, 3, 4 are numbered in order of increasing energies.

In this calculation we have confined ourselves to the linear approximation in U . Thus U is approximated as

$$U = \langle 0 | H | 0 \rangle + F + V + (FT)_L + (VT)_L - (TF)_L - (TV)_L\quad (29)$$

For the present 4-electron problem $T = \sum_{p=1}^4 T_p$. We have listed all the non-vanishing matrix elements of t_p up to $p = 4$ in table 1. All U -diagrams containing a single T_p -vertex may be classified into G-blocks, which are displayed in figure 2. As an example, we have reproduced all the topologically inequivalent diagrams belonging to block G_5 in figure 3. Equations (7) in this case become the following set of 14 simultaneous equations.

CLASS I: Scattering of the type $a \rightarrow p^*$

$$D_1(3; 1) + \sum_{\bar{v}=2, \bar{3}} D_4(3, \bar{v}; 1; \bar{v}) + D_7(3, 2, \bar{3}; 1; 2, \bar{3}) = 0\quad (30 a)$$

CLASS II: Scattering of the type $\bar{u} \rightarrow p^*$

$$D_2(4; 2) + D_5(4, \bar{3}; 2, \bar{3}) = 0\quad (30 b)$$

CLASS III: Scattering of the type $\left. \begin{matrix} a \\ \beta \end{matrix} \right\} \rightarrow \left\{ \begin{matrix} p^* \\ q^* \end{matrix} \right\}$

$$D_3(4, \bar{2}; 1, \bar{1}) + \sum_{\bar{u}=2, \bar{3}} D_6(4, \bar{2}, \bar{u}; 1, \bar{1}; \bar{u}) + D_8(4, \bar{2}, 2, \bar{3}; 1\bar{1}; 2, \bar{3}) = 0\quad (30 c)$$

Table 1. The T -matrix elements for the π - π^* singlet and triplet states of trans-butadiene

No.	Matrix element	Value	
		HF* orbitals	Core diagonal orbitals
1.	$\langle 3 t_1 1 \rangle = \langle \bar{3} t_1 \bar{1} \rangle$	0.01450	0.1690
2.	$\langle 4 t_1 2 \rangle = \langle 4 t_1 \bar{2} \rangle$	0.0145	-0.0294
3.	$\langle 4\bar{2} t_2 1\bar{1} \rangle_a = \langle 24 t_2 1\bar{1} \rangle_a$	0.0161	-0.0281
4.	$\langle 44 t_2 1\bar{1} \rangle_a$	-0.0475	-0.0464
5.	$\langle 24 t_2 13 \rangle_a = \langle \bar{2}4 t_2 \bar{1}\bar{3} \rangle_a$	0.2772	0.2718
6.	$\langle 4\bar{2} t_2 1\bar{3} \rangle_a = \langle 24 t_2 3\bar{1} \rangle_a$	0.1746	0.1749
7.	$\langle 34 t_2 2\bar{3} \rangle_a = \langle 4\bar{3} t_2 3\bar{2} \rangle_a$	0.0832	0.0908
8.	$\langle 34 t_2 12 \rangle_a = \langle \bar{3}4 t_2 \bar{1}\bar{2} \rangle_a$	0.0225	0.0185
9.	$\langle 3\bar{2} t_2 2\bar{1} \rangle_a = \langle 2\bar{3} t_2 1\bar{2} \rangle_a$	0.0909	-0.0788
10.	$\langle 44 t_2 1\bar{3} \rangle_a = \langle 44 t_2 3\bar{1} \rangle_a$	-0.0161	-0.0010
11.	$\langle 34 t_2 2\bar{3} \rangle_a = \langle 4\bar{3} t_2 3\bar{2} \rangle_a$	-0.0909	0.0897
12.	$\langle 3\bar{2}4 t_3 1\bar{1}\bar{3} \rangle_a = \langle 24\bar{3} t_3 13\bar{1} \rangle_a$	-0.0291	0.0214
13.	$\langle 4\bar{2}4 t_3 2\bar{1}\bar{3} \rangle_a = \langle 244 t_3 13\bar{2} \rangle_a$	-0.0291	0.0181
14.	$\langle 34\bar{2}4 t_4 12\bar{1}\bar{3} \rangle_a = \langle 24\bar{3}\bar{4} t_4 13\bar{1}\bar{2} \rangle_a$	-0.0015	-0.0016

* HF stands for Hartree-Fock.

$$D_3(4, \bar{4}; 1, \bar{1}) + \sum_{\bar{u}=2, \bar{3}} D_6(4, \bar{4}, \bar{u}; 1, \bar{1}; \bar{u}) + D_8(4, \bar{4}, 2, \bar{3}; 1\bar{1}; 2, \bar{3}) = 0 \tag{30 d}$$

CLASS IV: Scattering of the type $\left. \begin{matrix} a \\ \bar{u} \end{matrix} \right\} \rightarrow \left\{ \begin{matrix} p^* \\ q^* \end{matrix} \right.$

$$D_4(\bar{4}, \bar{2}; \bar{1}; \bar{3}) + D_7(\bar{4}, \bar{2}, 2; \bar{1}; \bar{3}, 2) = 0 \tag{30 e}$$

$$D_4(4, \bar{2}; 1; \bar{3}) + D_7(4, \bar{2}, 2; 1; \bar{3}, 2) = 0 \tag{30 f}$$

$$D_4(\bar{4}, 3; \bar{1}; 2) + D_7(\bar{4}, 3, \bar{3}; \bar{1}; 2, \bar{3}) = 0 \tag{30 g}$$

$$D_4(4, 3; 1; 2) + D_7(4, 3, \bar{3}; 1; 2, \bar{3}) = 0 \tag{30 h}$$

$$D_4(\bar{2}, 3; \bar{1}; 2) + D_7(\bar{2}, 3, \bar{3}; \bar{1}; 2, \bar{3}) = 0 \tag{30 i}$$

$$D_4(4, \bar{4}; 1; \bar{3}) + D_7(4, \bar{4}, 2; 1; \bar{3}, 2) = 0 \tag{30 j}$$

CLASS V: Scattering of the type $\left. \begin{matrix} \bar{u} \\ v \end{matrix} \right\} \rightarrow \left\{ \begin{matrix} u^* \\ v^* \end{matrix} \right.$

$$D_6(3, \bar{4}; 2, \bar{3}) = 0 \tag{30 k}$$

CLASS VI: Scattering of the type $\left. \begin{matrix} a \\ \beta \\ \bar{u} \end{matrix} \right\} \rightarrow \left\{ \begin{matrix} p^* \\ q^* \\ u^* \end{matrix} \right.$

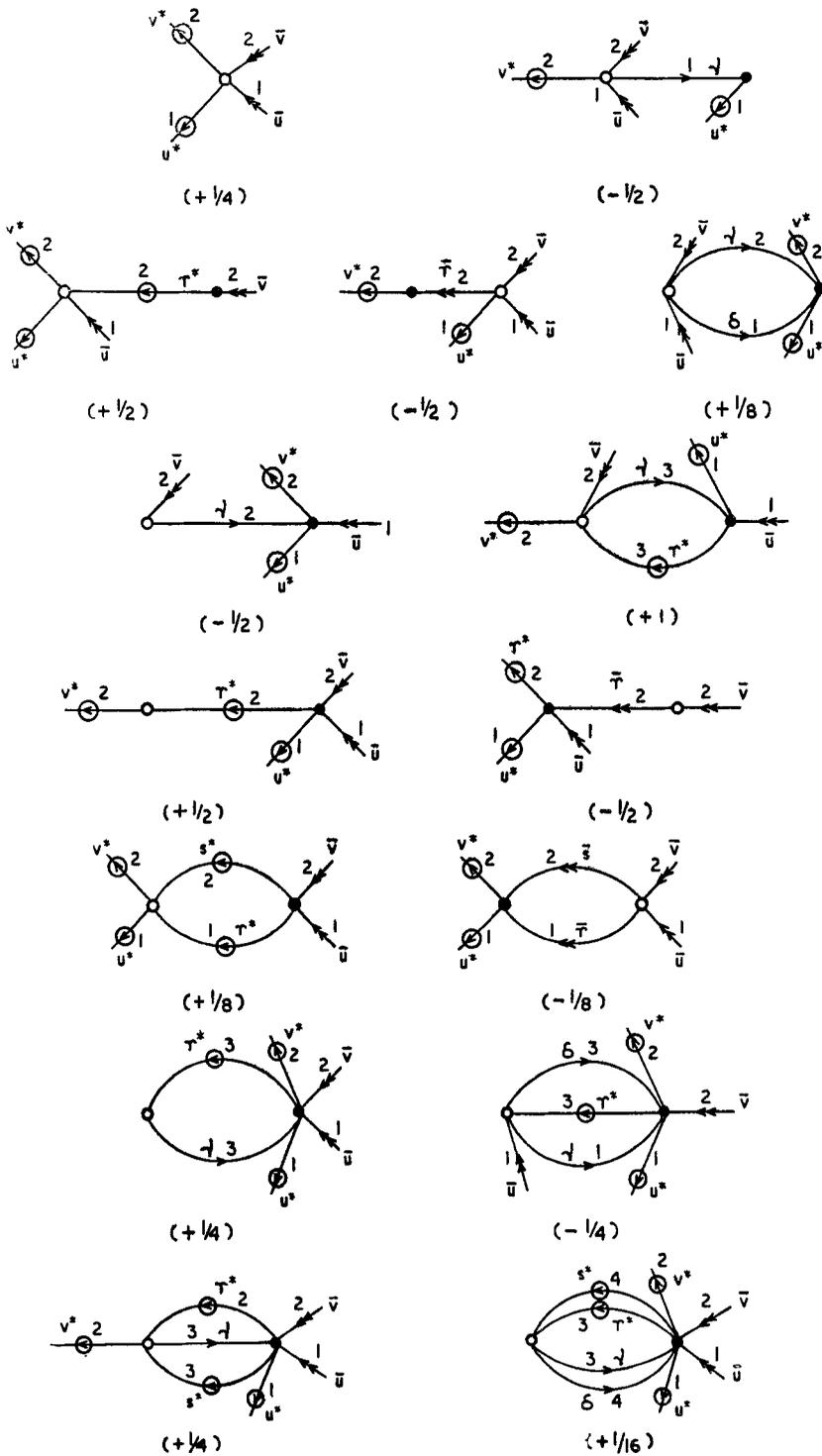


Figure 3. All the U -diagrams comprising the block G_6 . The weight and overall sign factors are also displayed with each diagram. The F and V vertices are designated by open circles. The diagrams contain all vertices up to T_4 .

$$D_6(3, \bar{2}, \bar{4}; 1, \bar{1}; \bar{3}) + D_8(3, \bar{2}, \bar{4}, 2; 1, \bar{1}; \bar{3}, 2) = 0 \quad (30 l)$$

CLASS VII: Scattering of type $\left. \begin{matrix} a \\ \bar{u} \\ \bar{v} \end{matrix} \right\} \rightarrow \left\{ \begin{matrix} p^* \\ u^* \\ v^* \end{matrix} \right.$

$$D_7(4, \bar{2}, \bar{4}; \bar{1}; 2, \bar{3}) = 0 \quad (30 m)$$

CLASS VIII: Scattering of the type $\left. \begin{matrix} a \\ \beta \\ \bar{u} \\ \bar{v} \end{matrix} \right\} \rightarrow \left\{ \begin{matrix} p^* \\ q^* \\ u^* \\ v^* \end{matrix} \right.$

$$D_8(3, 4, \bar{2}, 4; 1, \bar{1}; 2, \bar{3}) = 0 \quad (30 n)$$

where D_i is the contribution from block G_i . The energies are then given by

$$E^{s,t} = [D_0 + D_1(2; 2) + D_1(\bar{3}; \bar{3}) + D_5(2, \bar{3}; 2, \bar{3}) \pm D_5(2, \bar{3}; 3, \bar{2})] \quad (31)$$

where the + sign corresponds to the singlet and - sign to the triplet energy. The computed values of the matrix elements found from eqs (30) are given in table 1. In table 2 we give the calculated energies. A perusal of this table shows that even in this linear approximation the agreement between the results obtained from the present theory with the CI values is extremely good. The results can be improved by including the non-linear terms in the U -matrix elements, but the present results are sufficient demonstration of the workability of NPOST.

4. The general open shell case

We now come to the case of systems for which the combination coefficients C_i^k in the reference functions ψ_0^k are not determined by symmetry. In this case, one has to diagonalise eq. (8) to get the energies E^k as well as the coefficients C_i^k 's. As eigen-vectors of a matrix are linearly independent, we still have eqs (7) as the defining equations for T . However, the matrix U in this case is not hermitian in general, so that the functions ψ^k lose their interpretation as wavefunctions. If we want to retain the wavefunction interpretation, then we must find out a hermitian U . This may be attained by carrying out an alternative Ursell type expansion

Table 2. The π - π^* singlet and triplet energies for transbutadiene in eV

$T_1 + T_2$		$T_1 + T_2 + T_3$		Full ($T_1 + T_2 + T_3 + T_4$)		Full CI	
Singlet	Triplet	Singlet	Triplet	Singlet	Triplet	Singlet	Triplet

HF *								
orbital	-83.9462	-86.8177	-83.9617	-86.8273	-83.9629	-86.8256	-84.0013	-86.7060
Core diagonal orbitals	-83.9600	-86.7722	-83.9740	-86.7851	-83.9754	-86.7834	-84.0013	-86.7060

*HF stands for Hartree-Fock

of ψ^k -around ψ_0^k . We now set

$$\psi^k = e^s \psi_0^k \quad (32)$$

with

$$s = T - T^\dagger$$

T being given by eq. (15 b). We then have, using relation (24 b), which is also applicable here

$$He^s \psi_0^k = e^s U_H \psi_0^k = E^* e^s \psi_0^k \quad (33 a)$$

Hence

$$U_H \Psi_0^k = E \Psi_0^k \quad (33 b)$$

Also from eq. (33 a),

$$U_H = e^{-s} H e^s \quad (34)$$

since S by choice, is anti-hermitian,

$$(e^s)^\dagger = e^{s^\dagger} = e^{-s}$$

and hence

$$U_H^\dagger = (e^{-s} U_H e^s)^\dagger = U_H. \quad (35)$$

Thus U_H is a hermitian operator, and eq. (8) may be cast in the form

$$U_H C = C E \quad (36)$$

with C a square matrix whose columns are orthogonal to each other. Hence they are also linearly independent, and we have again

$$\langle \phi_l^* | U_H | \phi_i \rangle = 0 \quad \text{for all } l \text{ and } i. \quad (37)$$

The problem is now solved exactly as before. The diagrams for U_H are similar to those for U , except that we have, T_p^\dagger in addition to the T_p -vertices already present. The explicit construction of U_H will form the subject of later publications.

The fact that it is possible to construct a hermitian operator U_H has far reaching implications. One can, for example, now formulate the σ - π separability problem in conjugated molecular systems by being able to construct a hermitian π -electron effective Hamiltonian, which, acting entirely within the model space of the π - π^* configurations, generates all the low-lying energy levels of the system. The σ - π separability condition then reduces to the simple requirement that one may solve for the matrix elements of T_p constituting U_H and the relation (36) to find the energy eigenvalues.

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