An ab-initio derivation of the pi-electron hamiltonian by a non-perturbative open-shell formalism

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Abstract. A method for generating a pi-electron hamiltonian in an ab-initio manner using the non-perturbative open-shell many-body formalism recently developed by us is presented. The π-hamiltonian thus derived is energy-independent, and is also proved to be spin-independent. A recipe is given with the help of which Goldstone—like matrix-elements of H_π can be extracted up to three body terms. It has been demonstrated that the use of diagrammatics considerably simplifies the algebra and allows one to keep track of the various quantities involved. Up to a given order of approximation, an explicit form of H_π containing up to the three body terms has been given, and some of the important physical effects embedded in the hamiltonian are discussed. A comparative analysis of the various formalisms currently in use forms the concluding section of the paper.

Keywords. Many body theory; atoms and molecules; ab-initio π-electron theory.

1. Introduction

Considerable amount of theoretical studies have so far been made to explain and correlate various properties of planar conjugated systems. The various schemes—broadly classified as the ' semi-empirical Pariser-Parr-Pople (PPP) theories '—have been remarkably successful in predicting a wide range of phenomena associated with the low-lying energy levels of conjugated systems. All of them invoke the π-electron approximation. Lykos and Parr (1956) gave the form of the π-electron hamiltonian under the assumption that the σ-framework is fixed and the π-electron moves in the field of the σ-framework (the frozen core approximation). In concrete computational terms, only the minimal p_z basis-orbitals centred on each atom were used for constructing all the configurations in which σ-part is common and the π-part consisted of different selections of π/π^* orbitals and it was tacitly taken for granted that these configurations are the one which more or less describe the low-lying excitation features of conjugated systems. In practice, the various matrix-elements of the π-hamiltonian in the minimal p_z-basis are calibrated to fit the spectra of conjugated prototype systems, and duly adjusted for other systems according to some semi-empirical systematics. There are a plethora of such systematics, and they are of such varying nature that it is difficult to discern whether they are related or not, or even, whether some are consistent or not.

The success of the π-electron theories may at first sight seem to imply the correctness

P.—1

of the underlying assumptions. But, in reality, the excitation of π-electrons must invariably accompany σ-reorganisation with a consequent change of the σ-π interaction effects. Also, correlation of the π-electrons obviously of greater magnitude than that provided for by the minimal basis π/π^* orbitals. There is therefore little a priori reason that the π-hamiltonian derived after Lykos and Parr (1956) will provide as accurate a value of the low lying energy levels of conjugated systems as they do. The situation looks even more complicated if we recall Pariser's argument in favour of reduced values of repulsion integrals implying a correlation correction (Pariser 1953). Is there any guarantee that we would not be overcounting the correlation effect in a CI procedure designed to improve on the results? This calls for a deeper analysis of the basis of the π-electron approximation and motivates development of methods for deriving the π-electron hamiltonian in an ab-initio manner. One may then clearly see the effect brought out by σ-reorganisation effect (which may have been introduced in disguise during the empirical calibration of the matrix-elements) and the part of correlation introduced by Pariser's recipe, so that one stands on safer grounds and may eventually go in for a limited CI to incorporate features left out by the empirical systematics. However, the relaxation of the frozen σ-core could not in a straightforward way lead to a form of the π-hamiltonian following the procedure of Lykos and Parr (1956). It was nevertheless felt that an ab-initio derivation of the π-hamiltonian would lead one to look upon the π-electron theories as real microscopic theories with clearly defined theoretical assumptions.

In recent times, there have been renewed attempts to justify the use of a single π-hamiltonian for studies on conjugated systems by invoking the concept of an effective hamiltonian. There are presently several ways to construct an effective hamiltonian for any quantum mechanical systems (see e.g. Barrett and Kirson 1973, Jørgensen 1974, 1975 for recent references), although the basic underlying idea of all these techniques is the same: Given a hamiltonian H for a system of N interacting particles, how to derive a 'different' hamiltonian $\bar{H}$ which will act only on a smaller set of particles and will yield the same eigenvalues as some selected eigenvalues of H. The different formalisms implement this objective in different fashions.

Transcribed in the domain of the π-electron theory, it would mean that one seeks to obtain a π-hamiltonian H_π which will act within a restricted set of π/π^* configurations having the common core of occupied σ-orbitals and different selections of π/π^* orbitals, but which would nevertheless generate the low-lying eigen spectra of the full H as its eigenvalues. H_π would thus behave as conforming to the picture of frozen core but in reality would embody all the effects due to the σ-relaxation and the altered σ-π interaction following the relaxation. It would also have, as a built-in feature, a neat separation of the total π-electron correlation into a minimal basis π/π^* correlation induced by a CI through H_π and an external correlation implicitly present in H_π, as H_π would have to generate the exact eigenvalues of the full H. The first studies in this direction were initiated by Harris (1967), which were later extended and modified by Westhaus and others (1973, 1975). They approached the problem by transforming away the matrix-elements of H connecting configurations involving $\sigma \rightarrow \pi$ excitations and those containing only π-excitations. The method is essentially a Van Vleck unitary transformation of H, but due to the rather unwieldy nature of the attendant algebra they could not achieve a complete transformation. Linderberg and Ohrn (1968) and Shibuya et al (1975) used the Green's function formalism to

incorporate σ-π interaction effect in the π-electron spectra. Freed *et al* (1972, 1974) used a cluster decomposition of the low-lying eigenfunctions of H in the manner of Silverstone and Sinanoghu (1966) and Löwdin's partitioning technique (see Löwdin 1962, 1966, for detailed references) to construct a H_π acting within π-π^* configurations.

Kvasnicka (1975) used a quasidegenerate Rayleigh-Schrödinger perturbation theory through the third order to construct a H_π-and discussed the specific features that his formalism brings out. Freed (1973) published a review highlighting the then state of affairs and Kvasnicka (1975) also gave a brief perspective of his work against the background of other theories. Numerical investigations to calculate matrix-elements of H_π from first principles along some of the formalisms described above are also coming up (see e.g. Freed *et al* 1974, Westhaus *et al* 1975, 1976). During the preparation of the revised manuscript of the present paper, we came to know of Freed's latest work (1976) where he adapted generalised perturbation theory (Freed 1968) to Jørgensen formalism (1975) to generate H_π in a manner different from his earlier work.

The present paper serves to introduce yet another mode of derivation of H_π. This will be along the line of development that we recently followed to formulate a non-perturbative many-body theory for open-shell systems (Mukherjee *et al* 1975a, 1975b)†. The procedure looks like a one-shot unitary transformation of H to eliminate the matrix-elements connecting σ-excitations with π-excitations to any desired accuracy, but the transformation is followed through an algebraic-cum-diagrammatic formalism. We hope to demonstrate that the present approach leads to an expression of H_π in occupation number representation just like an ordinary hamiltonian and is suitably tailor-made to bring out the contribution of zero, one, two, ... many-body terms in H_π. It will be shown that diagrammatic representation of the mathematical quantities involved will simplify the attendant algebra to a great extent and allow us to separate various equations properly. It will allow us also to discuss the relatively unexplored domains like the importance of three and higher body terms of H_π, the symmetry properties of H_π or its spin-independence. In section 2, we briefly describe the desirable properties of a bona fide H_π, in sections 3 and 4 we develop the theory, in section 5 we give an explicit expression of H_π to a certain order of approximation. Finally, in section 6 we indicate the relation of the present theory with the existing theories.

2. Criterion for a good H_π

Let us now lay down the general properties that a good H_π is expected to satisfy. This is essential for an appraisal of the performance of a particular effective hamiltonian formalism, otherwise we might ascribe physical significance to certain peculiarities of H_π which are due to some special artifice of a particular theory.

1. Firstly, we demand that our H_π should be hermitian—otherwise one of the vital interpretative aspects, that eigen function of H_π would behave as wave-functions of the π-π^* states, would be lost.

2. Secondly, we demand that H_π should not involve in it the state-energy E para-

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†We shall henceforth refer to these two papers as I and II respectively. The key argument leading to H_π by the present formalism is mentioned at the end of I.

metrically—as any true hamiltonian can be defined only with respect to a complete basis-set, and cannot involve state energies parametrically.

3. Thirdly, we want to have a tractable expression for H_π, embodying a large part of the effect of σ-relaxation and σ-π interaction effects as compactly as possible. By compactness, we mean that the H_π should include a reasonable amount of σ-effects by a combination of rather few-body operators—preferably up to two, and at most up to three-body terms. Otherwise H_π would be too complicated to be of any practical utility.

4. We also demand that H_π should have the same symmetries as that of the full H—i.e., for a spin-independent H, H_π should be spin-independent and should be invariant under all the symmetry operations belonging to the point group of the molecule.

It may well turn out that all these together might impose restrictions which are too stringent for a workable H_π, and then one has to abandon one or the other criterion in favour of workability. But then one would know where one stands and also would have in mind how much one can and should abandon.

Besides these, we may have in mind more or less aesthetic criterion like (5) transferrability of the matrix-elements of H_π. This is however best studied only in connection with the numerical illustrations involving a series of compounds and we do not attempt to look into this feature in the present work.

3. The algebraic structure of H_π

The full hamiltonian H for the conjugated systems may be written in occupation number representation as (I, II)

$$H = \sum_{I, J} \langle I | h | J \rangle X_I^+ X_J + \frac{1}{(2!)^2} \sum_{I, J, K, L} \langle IJ | V | KL \rangle_a X_I^+ X_J^+ X_L X_K \quad \text{(1a)}$$

$$= \sum_{I, J} \langle I | h | J \rangle X_I^+ X_J + \frac{1}{2} \sum_{I, J, K, L} \langle IJ | V | KL \rangle X_I^+ X_J^+ X_L X_K \quad \text{(1b)}$$

I, J, etc. refer to spin-orbitals (SO). Each SO can be written as $I = i \cdot \gamma_i$, where i stands for the space part and γ_i is the corresponding spin function. The quantities $\langle IJ | V | KL \rangle_a$ and $\langle IJ | V | KL \rangle$ are the Hugenholtz-type and Goldstone-type matrix-elements respectively. We have written H in two different ways as we shall have occasions to use both of them in our subsequent derivations.

For an N-electron conjugated system having N_π π-electrons, we choose on the basis of chemical intuition a set of N-electron determinants, in all of which there is a common set of N_σ σ-orbitals $(N_\sigma = N - N_\pi)$, and a selection of N_π π-orbitals from a set of M_π π-type orbitals $(M_\pi \geqslant N_\pi)$. These determinants may be said to span an N_π-electron model space of dimension $D_\pi = M_\pi! / N_\pi! (M_\pi - N_\pi)!$, containing N_σ σ-electrons and N_π π-electrons. We want our H_π to operate on these configurations and generate the low-lying eigenvalues of H. Besides these, we shall have other N-electron determinants built up from the set of σ-SO's and π-SO's as well as from a set of other

excited SO's (all of them together comprising a complete set) in which electrons would either occupy orbitals other than those considered in the determinants of model-space, or occupy the same σ-and π-SO's as in the model-space, but the number of π-electrons differ from N_π. These may be termed 'the excited configurations' for the N-electron system, and they would bring in σ-relaxation, external π-correlations and σ-π interaction effects. We shall designate the N-electron determinants of the model space as ϕ_i, and the excited determinants as ϕ_i^*.

We also classify all the orbitals $\{I\}$ that build up the functions ϕ_i and ϕ_i^* as follows:

(i) the set of σ-orbitals which are common to all the determinants ϕ_i are the core orbitals —to be labelled as σ_I, σ_J, etc.;

(ii) the set of M_π π-orbitals, which appear in some ϕ_i, but not in all of them at a time are the valence or π-orbitals—labelled as π_I, π_J, etc., and

(iii) the remaining are particle orbitals and are labelled as P_I, P_J, etc.†

The orbitals σ_I may be found from an ab-initio σ-basis-set limit calculation involving the ground state of the N-electron problem, with π-orbitals constructed from a minimal Lowdin-orthogonalised p_z basis-set. The orbitals π_I are the occupied and virtual π-orbitals coming out of this HF calculation. Orbitals P_I are the virtual σ^* and more diffused π^*-type orbitals—the latter augmenting the minimal p_x-basis and properly orthogonalised.†† In the semi-empirical π-electron systematics, the nature of the π-orbital basis is never explicitly spelled out—so that the above choice of the orbitals entails no difficulty, and may even be replaced by better working sets without affecting the physical conclusions derived from the formalism. (We may even replace the orthogonal valence orbitals by the non-orthogonal AO type orbitals at the end— the resulting modification of the relevant expressions and diagrammatics involved is straightforward)§.

We now define the vacuum state $|0\rangle$ as the one in which all the σ-SO's are occupied and all other SO's are empty. The state $|0\rangle$ is clearly the frozen-core N_σ-electron determinant. With respect to this vacuum, we may write H in normal order (I, II) as

$$H = \langle 0|H|0\rangle + F + V \tag{2a}$$

where

$$F = \sum_{I, J} \langle I|f|J\rangle N[X_I^+ X_J] \tag{2b}$$

with

$$\langle I|f|J\rangle = \langle I|h|J\rangle + \sum_K \langle I\sigma_K|v|J\sigma_K\rangle_a \tag{2c}$$

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†In our terminology, π_I, π_J include what are conventionally called π^* orbitals in semi-empirical π-electron theories.

††In our terminology, the π^* orbitals would refer to those π-orbitals that are contained in the particle basis-set.

§The choice of the orbital basis in π-hamiltonian has not been fully explored as yet. For concrete numerical applications, we refer to Freed (1974), Westhaus *et al* (1975, 1976).

and

$$V=\frac{1}{2!^2}\underset{\substack{I,J\\K,L}}{\Sigma}\langle IJ|\,v\,|KL\rangle_a N[X_I^+X_J^+X_LX_K]$$

We now define the canonical hole-particle type of transformations:

$$Y_\sigma=X_\sigma^+;\ \ Y_\pi=X_\pi;\ \ Y_p=X_p \tag{3}$$

along with their conjugate relations. All the determinants ϕ_i and $\phi_i{}^*$ may now be written in terms of $|0\rangle$ as

$$\phi_i=\Omega_i^+\,|0\rangle;\ \ \phi_i{}^*=\Lambda^+{}_{i*}|0\rangle, \tag{4}$$

where Ω_i^+ and $\Lambda^+{}_{i*}$ are appropriate products of valence and particle creation operators Y^+ written in the normal order.

For the model space, we may define D_π linear combinations $\psi_0{}^k$ of the functions ϕ_i as

$$\psi_0{}^k=\overset{D_\pi}{\underset{i=1}{\Sigma}}C_{ki}\phi_i,\ k=1,\,D_\pi \tag{5}$$

where the coefficients C_{ki} are now kept unspecified, but would be so chosen that $\psi_0{}^k$ would become eigen functions of H_π.

We now define a *unitary cluster expansion operator*[†] e^S, with S an anti-hermitian operator such that D_π low-lying exact wave-functions of H for the N-electron system may be written as

$$\psi^k=e^S\psi_0{}^k;\ k=1,\,D_\pi \tag{6}$$

Further we wish to separate the core energy of the system entirely from the π-energy and the π-σ interaction energy, so that core-correlation may never enter in our calculation. For this purpose, we shall demand further, that e^S converts the vacuum state $|0\rangle$ to the exact correlated N_σ-electron core-function ψ_c:

$$\psi_c=e^S|0\rangle. \tag{7}$$

We choose our operator S to be given by

$$S=T-T^+ \tag{8}$$

where T is a sum of one, two, ... N-body excitation operators:

$$T=\overset{N}{\underset{p=1}{\Sigma}}T_p. \tag{9}$$

[†]Van Vleck was the first to advocate use of unitary transformation of a hamiltonian to bring out certain physical effects in a more transparent manner (see e.g. Jørgensen 1975 for a detailed discussion). Westhaus (1975) calls his unitary operator a ' Van Kampen cluster expansion ' operator. Recently Girardeau (1975) considered a unitary operator similar to ours in a different context, which he called a ' tani transformation operator '.

Now we have to choose T in such a way that S can generate all the excited configurations ϕ_i^* by operating on ϕ_i's, and in addition all the excited configurations $\phi_{l*}^{N_\sigma}$ for a N_σ-electron problem by operating on $|0\rangle$. This of course means that all possible pure core-excitation operators must be present in T, irrespective of whether or not they will correspond to any physical excitation of the N-electron problem. This situation may arise because for the pure core problem, it is possible to excite electrons from σ-orbitals to π-orbitals which will be occupied for the N-electron model-space determinants ϕ_i. The inclusion of such excitations in T would never cause any problem, because the Pauli principle would be automatically taken care of by the anti-commutation property of the Fermion operators Y and Y^+.

T_p in general, will thus be of the form:

$$T_p = \frac{1}{p!^2} \Sigma \langle ..\pi_I\pi_J..P_PP_Q..|t_p|..\pi_K\pi_L..\sigma_A\sigma_B..\rangle_a$$

$$N[...Y^+_{\pi_I}Y^+_{\pi_J}...Y^+_{P_P}Y^+_{P_Q}...Y^+_{\sigma_B}Y^+_{\sigma_A}...Y^+_{\sigma_L}Y_{\pi_K}...] \tag{10a}$$

$$= \frac{1}{p!} \Sigma \langle ..\pi_I\pi_J..P_PP_Q..|t_p|..\pi_K\pi_L..\sigma_A\sigma_B..\rangle X$$

$$N[..Y^+_{\pi_I}Y^+_{\pi_J}..Y^+_{P_P}Y^+_{P_Q}..Y^+_{\sigma_B}Y^+_{\sigma_A}..Y_{\pi_L}Y_{\pi_K}..] \tag{10b}$$

As T_p is a p-fold excitation operator, T_p^+ is destined to serve as a p-fold de-excitation operator. The matrix-elements like $\langle..\pi_K..\pi_L..\sigma_A\sigma_B|t_p^+|..\pi_I\pi_J..P_PP_Q\rangle_a$ is equal to $\langle..\pi_I\pi_J..P_PP_Q..|t_p|..\pi_K\pi_L..\sigma_A\sigma_B..\rangle_a$, so that we may take the matrix-elements of T_p for all p as the only variables of the problem. We shall discuss more about the matrix-elements of T_p in section 4.

We look for an operator $\bar{H}$, such that

$$H e^S = e^S \bar{H} \tag{11}$$

As e^S is unitary, we have

$$\bar{H} = e^{-S}He^S = (e^S)^+He^S \tag{12}$$

$\bar{H}$ being a unitary transform of H, is hermitian.

We have recently shown (I, II) that, for fermion systems, the form of $\bar{H}$ can be found out by using the Generalised Wick Theorem (GWT) and the concept of generalised contraction (which we call pairing). Adopting the same notations as in I, we may write $\bar{H}$ as

$$\bar{H} = \sum_{k=0}^{\infty} \frac{1}{k!} \sum_{\substack{k_1,k_2 \\ k_1+k_2=k}} (-1)^{k_1} (S^{k_1}(\langle 0|H|0\rangle + F + V) S^{k_2})_L \tag{13a}$$

with

$$\Gamma = \langle 0|H|0\rangle + F + V. \tag{13b}$$

For the proof of this relation, we refer to I. $(S^{k_1} \Gamma S^{k_2})_L$, we called linked term (I). $(S^{k_1} \Gamma S^{k_2})_L$ is a sum of all terms having k_1 number of S operators on the left of Γ, k_2 number of S operators on the right, in each of which there are subterms consisting of all possible contractions between groups of creation—annihilation operators in Γ and S on either side of Γ following a specific rule. The rule states that the sets of contractions would start from Γ and would proceed both to the left and right of it without skipping any intermediate S in the process. All the terms in $(S^{k_1} \Gamma S^{k_2})_L$ are linked in the way as dictated by the rule, and this is why we called $(S^{k_1} \Gamma S^{k_2})_L$ as a linked term in I.

From (13), $\bar{H}$ also thus consists of linked terms only. As $\bar{H}$ contains all the subterms containing zero, singly, doubly, ... contracted creation—annihilation operators, N, $N-1$, ..., two, one and zero pairs of creation—annihilation operators remain uncontracted. They constitute the N, $N-1$, ..., two, one and zero body operators of $\bar{H}$.

Let us now consider the Schrödinger equation for the K low lying states of the N-electron problem:

$$H \psi^k = E^k \psi^k; \ k=1, D_\pi. \tag{14}$$

Using the definition of ψ^k from eq. (6) and the relation (11) we have

$$\bar{H} \psi_0^k = E^k \psi_0^k; \ k=1, D_\pi. \tag{15}$$

Projecting (15) on to the excited ϕ_{l*}, and using the linear independence of the coefficients C_{ki} in (5), we have:

$$\langle \phi_{l*} \mid \bar{H} \mid \phi_i \rangle = 0 \text{ for all } i \text{ and } l. \tag{16}$$

Similarly, projecting (15) on to the model space, we have

$$\sum_i \langle \phi_j \mid \bar{H} \mid \phi_i \rangle C_{ki} = E^k C_{kj}; \text{ for all } j, k. \tag{17}$$

Similarly, for the N_o-electron core-problem, we may get:

$$\bar{H} \mid 0 \rangle = E^c \mid 0 \rangle. \tag{18}$$

Projecting on to the N_o-electron excited states $\phi_{l*}^{N_o}$, we have

$$\langle \phi_{l*}^{N_o} \mid \bar{H} \mid 0 \rangle = 0; \text{ all } l \tag{19}$$

and

$$E^c = \langle 0 \mid \bar{H} \mid 0 \rangle \tag{20}$$

substituting eq. (13) in eqs (16) and (19), we get a set of coupled equations in the matrix-elements of T_p (and T_p^+), which would furnish the matrix-elements of T_p and

$T_p{}^+$, and hence of S. The solution of (10) and (19) would thus determine S completely.

If we now insert the values of matrix-elements of S into the expression (17), the matrix-elements $\langle \phi_j \mid \bar{H} \mid \phi_i \rangle$ become known, and the solution of the eigenvalue eq. (20) would provide us with D_π exact energies E^k of the N-electron problem. Hence, $\bar{H}$ may be naturally thought of as a hermitian, state-independent operator which generates the low-lying exact energies E^k of the N-electron problem by acting entirely within the restricted set of π/π^* configurations with a common σ-core. $\bar{H}$ thus satisfies one of the basic requirements of a true H_π, and henceforth we shall identify $\bar{H}$ simply as H_π.

4. Diagrammatic construction of H_π

4.1. *Construction of block of H_π*

One of the most convenient ways of handling the matrix-elements of H_π appearing in (16), (17) and (19) is to use a diagrammatic approach of the type given in I, II. We would first transcribe all the terms of H_π in terms of Hugenholtz diagrams (Hugenholtz 1957) in the spin-orbital basis and later go over to spin-free diagrams for actual solution. Unlike that in perturbation theory, the conversion of one methodology to the other is a non-trivial problem in the non-perturbative frame-work.

A general linked term like $(S^{k_1} \Gamma S^{k_2})_L$ of H_π consists of all the quantities that can be formed from all possible selection of k_1 T_p and $T_p{}^+$ operators on the left of Γ, and all possible selection of $k_2 T_p$ and $T_p{}^+$ operators on the right of Γ, which are contracted in all possible ways in accordance with the rules of contraction laid down in the definition of a linked term. By definition, $(S^{k_1} \langle 0 \mid H \mid 0 \rangle S^{k_2})_L = \langle 0 \mid H \mid 0 \rangle$ for $k_1 = k_2 = 0$, and $= 0$ for any of k_1, $k_2 \neq 0$, so that we need not draw any diagram for such terms; $\langle 0 \mid H \mid 0 \rangle$ is merely a number. The overall sign of a linked term is $(-1)^{n_q}$, where n_q is the number of $T_p{}^+$ operators. Diagrammatically a linked term like $(T_{n_1} T_{n_2}{}^+ \cdots T_{n_{k_1}} V T_{n_{k_1}+1} \cdots T_{n_{k_1}+n_{k_2}})_L$, say, will give rise to a set of diagrams, all linked, which together comprise all the diagrams that could have been generated by joining all the $(k_1 + k_2 + 1)$—vertices with one another in all possible ways, conforming to the definition of a linked term as given in I. As a result, we shall have sets of linked diagrams differing in the number of external lines. We may say that each linked term yields a set of different n-body operators. The collection of all these diagrams may be called the H_π-diagrams.

First of all, we separate the H_π-diagrams into various groups according to the number of external lines. In each group again, we collect the set of diagrams having the same disposition and orientation of the external lines together in one G-block (I, II). In this manner, we classify all the diagrams into various G-blocks.

If we now specify the determinants ϕ_i and $\phi_i{}^*$ in eq. (17) by indicating the creation operators in $\Omega_i{}^+$ and $\Lambda^+{}_{i*}$, this automatically fixes the labels that can be attached to the external lines and at the same time fixes the shapes of G-blocks that can really cause a scattering of electrons from ϕ_i to $\phi_i{}^*$. For a scattering involving σ_A, σ_B and π_A to P_A, P_B and P_C, say, the G-block will look like the one shown in
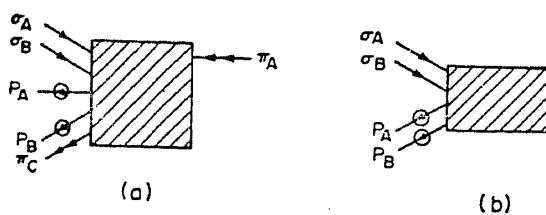
Figure 1. *G*-blocks showing particular scattering events.

figure 1(a). The contribution of this *G*-block may be evaluated using the recipe given in I, II†, and may be compactly written as

$$B\,(P_A P_B \pi_C,\ \sigma_A\, \sigma_B;\ \pi_A)\ D\,(P_A P_B \pi_C;\ \sigma_A\, \sigma_B;\ \pi_A),$$

where *D* is a function depending on the order of the arguments and *B* is a composite permutation operator generating the sum of all terms that can be obtained by permuting groups of spin-orbitals $(P_A,\ P_B,\ \pi_C)$, and $(\sigma_A,\ \sigma_B)$ in all possible ways, with a pairty factor $(-1)^\varepsilon$. ε is odd or even, depending on the parity of the permutation.

If there are sets of excited determinants $\phi_l *$, $\phi_m *$, etc. which are obtained by lifting electrons out of the same set of orbitals from the respective model space determinant ϕ_i, ϕ_j, say, and putting them in the same set, then we should somehow label the corresponding excitation operators in such a way that we can distinguish the two scattering events as distinct. The simplest way of doing this is to artificially increase the rank of the corresponding T_p operator by throwing in orbitals which would distinguish the two scattering processes (Mukherjee *et al* 1977). Thus, if for the states considered above, the electrons are lifted from σ_I, σ_J, say, to P_I and P_J, then we should consider the associated *T* operator as one not of rank 2, but greater—the actual number depending on the specification of extra labels that would uniquely distinguish the two scattering processes $(\phi_l \rightarrow \phi_l *;\ \phi_j \rightarrow \phi_m *)$. Thus if, for example, the two model space determinants ϕ_i and ϕ_j are such that one contains a π-orbital π_k, while the other does not contain it, but instead has another orbital π_L, it would then suffice to introduce two T_3—operators for the two scattering events:

(i) $\langle P_I P_J \pi_K \,|\, T_3 \,|\, \sigma_I \sigma_J \pi_K \rangle_a\ N\left[Y^+{}_{P_I}\, Y^+{}_{P_J}\, Y^+{}_{\pi_K}\, Y_{\pi_K}\, Y^+{}_{\sigma_J}\, Y^+{}_{\sigma_I} \right]$

(ii) $\langle P_I P_J \pi_L \,|\, T_3 \,|\, \sigma_I \sigma_J \pi_L \rangle_a\ N\left[Y^+{}_{P_I}\, Y^+{}_{P_J}\, Y^+{}_{\pi_L}\, Y_{\pi_L}\, Y^+{}_{\sigma_J}\, Y^+{}_{\sigma_I} \right]$

Thus, the two events in this case can be distinguished by increasing the rank of the T_p operator from two to three—and extra pair of creation—anihilation operators inserted due to this expansion of rank causes a passive scattering of an electron from π_K to π_K or from π_L to π_L, as the case may be. The above argument can be generalised in a straightforward manner.

If $\phi_l *$ is such that there are certain valence-lines in common with ϕ_l, then there will be certain other *G*-blocks, having less number of common lines which will also contribute to the matrix-element $\langle \phi_l * \,|\, \bar{H} \,|\, \phi_l \rangle$. Thus, for the block shown in

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†The details of the recipe is not necessary in what follows.

figure 1(a), if $\pi_c = \pi_A$ for certain ϕ_{l*} and ϕ_l, then in addition to the block 1(a) with $\pi_c = \pi_A$, a block of the type shown in figure 1(b) will also contribute. In general, for states with r valence-lines in common, there will be in total $(r+1)$—G-blocks showing explicitly the passive scattering of $0, 1, 2, ..., r$ valence lines respectively. We may call the G-block with no passive valence-valence scattering as the irreducible one, while the others may be called reducible G-blocks. Let us now see how the equations for T_p and T_p^+ are set up. We start with the core-part $|0\rangle$ of the N-electron problem. The excited configurations $\phi_{l*}^{N\sigma}$ for this problem are the $N\sigma$-electron determinants that are obtained by lifting $1, 2, ..., N\sigma$ electrons from $|0\rangle$ to all possible particle and valence states. Thus, written in terms of the G-blocks, contributing to the matrix-elements of H_π, the equation (19) would take the form as shown in figure 2. We now come to the full N-electron problem. Here again, the set of eqs (16) could diagrammatically be represented by a sum of G-blocks. Some typical diagrammatic equations will look like those shown in figure 3.

In these equations, the excitation is such that the labels on the ingoing valence lines are different from the outgoing ones. If, however, for certain choice of ϕ_{l*}, π_A coincides with any of π_I, π_J, etc., then in place of figure 3, we shall have contribution from

(2)

(a)　　　　(b)　　　　(c)

(3)

(a)　　　　(b)

(4)
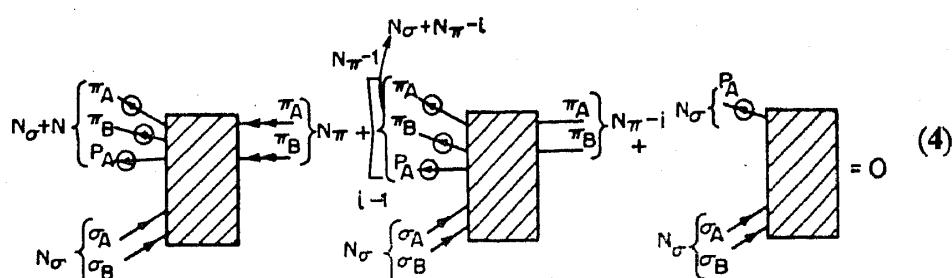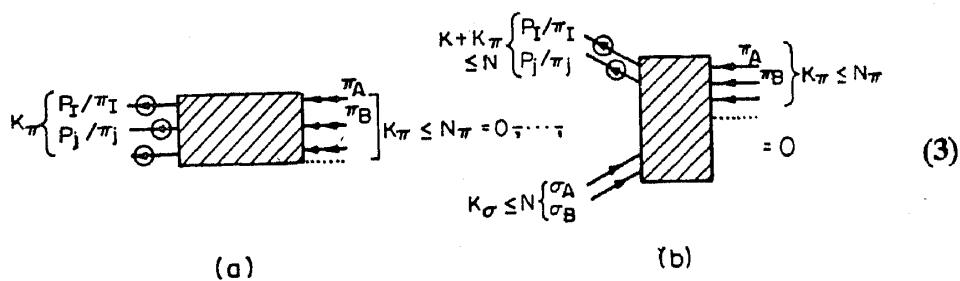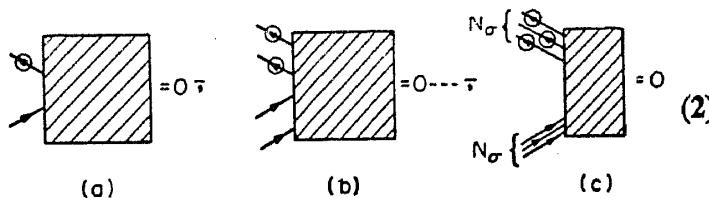
Figure 2. Core-excitation diagrams. B operator is assumed to be operative on the external lines in these diagrams.

Figure 3. Typical excitation diagrams from the model-space of $\pi_\sigma + N_\pi$ electron problem.

Figure 4. Typical excitation diagram showing scattering between ϕ and ϕ_l with all N_π-valence lines common.

both reducible and irreducible G-blocks. We have already discussed a typical case in figure 1(b) with $\pi_A = \pi_C$. In particular, for a scattering event with all N_π-valence lines in common, we shall have the diagrammatic equality as shown in figure 4. Since the block to the extreme right of the figure consists of a pure core-scattering event, its contribution is already zero from figure 2. Hence the contribution of all the reducible G-blocks taken together is zero. The same type of argument will hold good for scattering events having $r(<N_\pi)$ valence-lines in common, if the irreducible block ocrresponds to a pure core-scattering process. When the irreducible G-block for a particular scattering process does not correspond to a pure core-scattering, both the irreducible and the sets of reducible G-blocks together should be equated to zero.

Thus, we may write down the system of eqs (16) and (19) in terms of G-blocks. For all practical purposes equations have to be truncated, so that each G-block will contain only a limited number of T_p/T_p^+ vertices. Let us emphasise that a truncation of eq. (13) does not in general imply a truncation of the system of eqs (16) and (19); rather it implies a reduction in the number of diagrams entering the G-blocks.

Coming now to the matrix-elements $\langle \phi_j | \bar{H} | \phi_i \rangle$, we note that this will reduce to a sum of blocks, where the external lines will be labelled by valence-lines only. Blocks containing zero, one, two pairs of ingoing and outgoing lines would contribute respectively to zero, one, two, ... body terms of the π-hamiltonian. The zero-body term corresponds to the closed diagrams coming from $\langle 0 | \bar{H} | 0 \rangle$, and would cause a common shift of all the energy levels E^k, and may be entirely dropped. This will correspond to the elimination of the core-energy part entirely from our calculation.

From the structure of H_π, it is clear that it would contain three and higher body operators. In contrast, the conventional semi-empirical π-hamiltonian contains at best two-body operators. Another point to note is that the G-blocks contributing to $\langle \phi_j | \bar{H} | \phi_i \rangle$ are labelled by SO's, thus defining the matrix-elements of H_π with respect to SO's. However, the conventional π-hamiltonian is taken to be spin-independent and is defined entirely in terms of orbitals.

The following questions naturally emerge: (a) How far are the higher-body operators important vis-a-vis the semi-empirical π-hamiltonian? (b) How far can one consider the H_π to be spin-independent? (c) How would one correlate the quantities appearing in the ab-initio theory with the parameters of the semi-empirical theory? Of these, the answer to question (b) is already contained in our criteria, for a H_π : H_π has to be spin-independent. Thus at some stage we should try to get rid of the spin-variables. How far can one do this depends on the formalism adopted and any formalism which does not allow of a consistent description of H_π with spin-independent operators suffers from an obvious shortcoming. As to the question (a), we cannot at present furnish concrete answer, as this would require an extensive computation on prototpye systems. We shall however attempt to provide partial answer to (c); we shall moreover show that our formalism gives a two-body term in H_π which is richer than that found by others.

4.2. *Spin-independence of T and H_π*

Our first objective, however, is to examine the consistency of the assumption that H_π is spin-independent as implied by our theory. We shall prove by formal arguments that one can assume the operators T_p as spin-independent and still the system of equations determining T_p's are complete. Then the spin-independence of H_π would

automatically follow, as the matrix-elements of F and V are manifestly spin-independent.

Let us first remark that the assumption of the spin-independence of T_1 operators can be trivially represented as

$$\langle A \mid t_1 \mid B \rangle = \langle a \mid t_1 \mid b \rangle \; \delta(\gamma_a, \gamma_b). \tag{21}$$

On the other hand, the corresponding two and higher body operators cannot be so easily be taken off from the spin-variables and a more sophisticated analysis is necessary (Mukherjee and Bhattacharya 1977).

Let us start from a general two-body matrix-element $\langle AB \mid t_2 \mid CD \rangle_a$, and express left and right side of the anti-symmetrised two-electron functions in terms of spin-coupled functions. For a spin-independent T_2, we then have

$$\langle AB \mid t_2 \mid CD \rangle_a \equiv \left\langle \begin{array}{cc} a & b \\ m_a & m_b \end{array} \middle| t_2 \middle| \begin{array}{cc} c & d \\ m_c & m_d \end{array} \right\rangle a = \sum_{S, M} \{ ab \mid t_2 \mid cd \}_S \times$$

$$\langle \tfrac{1}{2} \tfrac{1}{2}; SM \mid \tfrac{1}{2} m_c \tfrac{1}{2} m_d \rangle \langle \tfrac{1}{2} m_a \tfrac{1}{2} m_b \mid \tfrac{1}{2} \tfrac{1}{2} SM \rangle \tag{22}$$

where we have explicitly indicated the associated spin-projections of the spin-orbitals, A, B, etc. and the quantities $\langle \tfrac{1}{2} \tfrac{1}{2} SM \mid \tfrac{1}{2} m_c \tfrac{1}{2} m_d \rangle$ are the Clebsch-Gordan $(C\text{-}G)$ coefficients. The quantity $\{ ab \mid t_2 \mid cd \}_s$—we would like to call as a reduced Hugenholtz matrix-element—depends only on *orbitals* a, b, c, d and a spin-index S, and not on spin-projections. Equation (22) is a consequence of the Wigner-Eckart theorem (Wigner 1959). S can take on values 0 and 1, so that for distinct orbitals a, b, c, d we should have two independent reduced Hugenholtz matrix-elements.

For the three particle operator, we can likewise define the corresponding reduced matrix-element as

$$\langle ABC \mid t_3 \mid DEF \rangle_a = \left\langle \begin{array}{ccc} a & b & c \\ m_a & m_b & m_c \end{array} \middle| t_3 \middle| \begin{array}{ccc} d & e & f \\ m_d & m_e & m_f \end{array} \right\rangle_a$$

$$= \sum_{\substack{S_i, S_j, S \\ M_i, M_j, M}} \{ (ab)_{S_i} \, c \mid t_3 \mid (de)_{S_j} f \}_S \; \langle (\tfrac{1}{2} \tfrac{1}{2}) S_j M_j, \tfrac{1}{2}; SM \mid \tfrac{1}{2} m_d \tfrac{1}{2} m_e \tfrac{1}{2} m_f \rangle \times$$

$$\langle \tfrac{1}{2} m_a \tfrac{1}{2} m_b \tfrac{1}{2} m_c \mid (\tfrac{1}{2} \tfrac{1}{2}) S_i M_i; \tfrac{1}{2}; SM \rangle \tag{23}$$

where the coupling scheme is to couple (A, B) to S_i, (C, D) to S_j and a final coupling of these pairs with C and F respectively to give a resultant S. The transformation coefficients are the generalized $C\text{-}G$ coefficients (see e.g. El Baz and Castel 1972). For distinct orbitals a, b, c, d, e and f there are five linearly independent matrix-elements. An analogous procedure may be followed for the higher-body operators, and we are not explicitly showing their forms. The quantities $\{ (ab)_{S_i} \, C \mid t_3 \mid (df)_{S_j} e \}_s$ can be written a linear combination of $\{ (ab)_{S_i}, C \mid t_3 \mid (de)_{S_j} f \}_s$ because of transformation properties of the generalised $C\text{-}G$ coefficients.

We shall now concretely demonstrate the elimination of spin-variables for the set

of equations containing up to three-body operators. The generalisation to higher-body operators is straightforward and is not particularly illuminating:
Consider all equations of the form

$$B_i \, D_i{}^a = 0; \quad i = 1, 2, 3. \tag{24}$$

where D_i stands for the contribution from the Gi-block containing i-pairs of external lines. The superscript a on a D_i is given to indicate that there may be more than one-G-block containing i-external lines. The equations contain Hugenholtz matrix-elements of T_1, T_2 and T_3 as variables. We shall now write these equations in terms of the reduced matrix-elements. For the sake of clarity, let us choose a specific example:

Pick out of the class of equations $B_2 D_2{}^a = 0$ for all a, a particular sub-set $B_2 D_2{}^b = 0$, say, in each of which the external spin-orbital labels carry the same space-parts. Moreover let us deal with the most general situation by choosing the ingoing and outgoing orbitals to be all different. The general form of the selected sub-set of equations would look like

$$B_2 \begin{pmatrix} c & d \\ m_c & m_d \end{pmatrix} \begin{matrix} a & b \\ m_a & m_b \end{matrix} D_2{}^b \begin{pmatrix} c & d \\ m_c & m_d \end{pmatrix} \begin{matrix} a & b \\ m_a & m_b \end{matrix} = 0 \tag{25}$$

for all choices m_a, m_b, etc.

From these equations let us construct the following equations

$$\sum_{\substack{m_a, m_b \\ m_c, m_d}} \langle \tfrac{1}{2} \tfrac{1}{2} SM | \tfrac{1}{2} m_c \tfrac{1}{2} m_d \rangle \langle \tfrac{1}{2} m_a \tfrac{1}{2} m_b | \tfrac{1}{2} \tfrac{1}{2} SM \rangle \, B_2 \begin{pmatrix} c & d \\ m_c & m_d \end{pmatrix} \begin{matrix} a & b \\ m_a & m_b \end{matrix}$$
$$D_2 \begin{pmatrix} C & d \\ m_c & m_d \end{pmatrix} \begin{matrix} a & b \\ m_a & m_b \end{matrix} = 0 \tag{26}$$

there would be two linearly independent equations for the two possible values of S. Now breaking up all Hugenholtz matrix-elements in terms of reduced matrix-elements in D_2, we arrive formally at equations of the type:

$$K_2{}^s(ab; \, cd) = 0; \quad S = 0, 1. \tag{27}$$

Now for a set of orbitals a, b, c, d there are two linearly independent reduced t_2-matrix-elements, and we thus have as many equations as there are unknowns. For the case $i = 3$, let us again choose a particular $D_3{}^a$. Again let us take all orbitals to be different, and select G-blocks with SO's which differ in spin-allocations only. We can likewise construct equations of the type.

$$\sum_{\substack{m_a, m_b, m_c \\ m_d, m_e, m_f \\ M_i, M_j}} \langle (\tfrac{1}{2} \tfrac{1}{2}) S_j M_j, \tfrac{1}{2}; SM | \tfrac{1}{2} m_d \tfrac{1}{2} m_e \tfrac{1}{2} m_f \rangle \langle \tfrac{1}{2} m_a \tfrac{1}{2} m_b \tfrac{1}{2} m_c | (\tfrac{1}{2} \tfrac{1}{2}) S_i M_i; \tfrac{1}{2}; SM \rangle$$
$$B_3 \begin{pmatrix} d & e & f \\ m_d & m_e & m_f \end{pmatrix} \begin{matrix} a & b & c \\ m_a & m_b & m_c \end{matrix} D_3{}^b \begin{pmatrix} d & e & f \\ m_d & m_e & m_f \end{pmatrix} \begin{matrix} a & b & c \\ m_a & m_b & m_c \end{matrix} = 0 \tag{28}$$

for all allowed S_i, S_j and S.

After breaking up the Hugenholtz matrix-elements in D_3 in terms of the reduced matrix-elements, we get equations of the form

$$K_3^{S_i, S_j, S} (def; abc) = 0 \tag{29}$$

for all S_i, S_j, S.

For a fixed set $(def; abc)$, there are five reduced t_3 matrix-elements and we have corresponding five linearly independent eqs (29), so that we again have as many equations as are unknowns. This shows that it is possible to eliminate spin-variables from eqs (16, 19). The case of equations containing both reducible and irreducible blocks can be analogously treated. The same holds true also for higher body operators. For the representation of the matrix-elements $\langle \phi_j \mid \bar{H} \mid \phi_i \rangle$, we can follow the same procedure. We break up all the matrix-elements in terms of the corresponding reduced matrix-elements, and finally sum overall spin-projections to get the reduced matrix-elements of H_π. The above analysis proves that H_π can be written in a manifestly spin-independent manner.

Now we shall show, following a procedure of the type first used by Paldus *et al* (1972), that up to three-body terms the above problem can be cast in terms of Goldstone-like matrix-elements also. This would be of more practical value because of ease in computational procedure.

Equations (27) can be alternatively written as

$$d_2^b(cd; ab) - d_2^b(dc; ab) = 0$$

$$d_2^b(cd; ab) \qquad = 0 \tag{30}$$

$$d_2^b(cd; ba) \qquad = 0$$

d_2^b is a new functional of orbitals only obtained from D_2^b by spin-integration. From (30), it is obvious that two of these three equations are linearly independent and we choose the last two as our desired set. For the orbital set $(c, d; a, b)$ there are two distinct Goldstone matrix-elements $\langle cd \mid t_2 \mid ab \rangle$ and $\langle cd \mid t_2 \mid ba \rangle$ and we have as many unknowns as there are equations.

For $i=3$, similarly we can get eight equations for a fixed orbital set $(def; abc)$, as in (30), of which only five are linearly independent. We give below a particular choice;

$$d_3^b(def; abc) - d_3^b(fed; abc) = 0$$

$$d_3^b(fde; abc) - d_3^b(edf; abc) = 0$$

$$d_3^b(fde; abc) - d_3^b(dfe; abc) = 0$$

$$d_3^b(efd; abc) - d_3^b(fed; abc) = 0 \tag{31}$$

$$d_3^b(def; abc) - d_3^b(dfe; abc) + d_3^b(fde; abc) - d_3^b(fed; abc) + d_3^b(efd; abc)$$

$$- d_3^b(edf; abc) = 0$$

However, the number of Goldstone-type matrix-elements that can be formed from the set (*def; abc*) are six in number, so that we seem to have five equations in six unknowns. However, we can get around this difficulty by noting that each anti-symmetrised t_3 matrix-element is invariant under a common shift of all the Goldstone matrix-elements by x. From (31), we have

$$d_3^b \ (def; \ abc) = d_3^b(edf; \ abc) = d_3^b(dfe; \ abc) = d_3^b(fde; \ abc)$$

$$= d_3^b(efd; \ abc) = d_3^b(fed; \ abc) = y, \text{ say.} \tag{32}$$

Let us now choose our x in such a way as to make $y=0$. Then we have a set of six eqs (32) with $y=0$, and again we have as many equations as are unknowns. Such an analysis cannot however, be carried over to $T_p(p\geqslant4)$ operators.

This means that although $T_p \geq$ 4-body operators are spin-independent, a Goldstone representation for them is not straightaway possible. However, we have proved earlier that the present formalism embodies the folded diagram perturbation expansion of Brandow (II), which may be made spin-independent, the spin-independence of the t matrix-elements can be assumed as a consistent sufficiency condition:

$$d_p^b \ (s, \ t, \ \ldots; \ ab\ldots) = 0 \tag{33}$$

for all s, t, a, b, etc.

This again, just as in (30), would give us Goldstone matrix-elements to deal with. As we have proved the spin-independence of T, this seems to be consistent. In any case, up to T_3, we can generally write eqs (24) as

$$d_1^a \ (c, \ a) \ = 0; \ d_2^a \ (cd; \ ab) \ = 0; \ d_3^a \ (def; \ abc) \ = 0 \tag{34}$$

for distinct orbital lables and superscript labels.

We are now in a position to discuss the diagrammatic representation of eqs (34).

4.3. *Goldstone diagrammatics*

Following the convention of Goldstone (1957), we may represent each of the operators F, V, T_p and T_p^+—written in terms of the Goldstone matrix-elements—by Goldstone diagrams. As a typical example, we show in figure 5, some V, T_2 and T_2^+ operators.

Diagrammatic construction of the block d_t is straightforward, and parallels the recipe laid down for the Hugenholtz-block diagrammatics of 4.1. The external labels on the G-block should be such that it implies the same scattering event as that
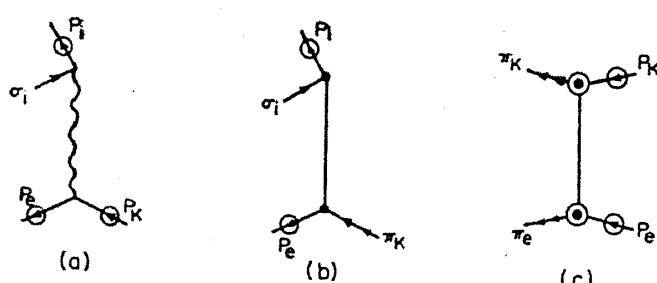

Figure 5. Some typical V, T_2 and T_2^+ Goldstone diagrams.

induced by the particular T_p matrix-element. In pratice, it will be possible to label the G-block in more than one way so that each represents the same type of scattering and we have to consider all such scattering events. For a T_p-diagram containing r passive valence-valence scattering lines, the corresponding equation will look like

$$\sum_{k=0} d'_{i+k} (uvw.., abc..) = 0 \qquad (35)$$

where $k=r$ term corresponds to the G-block having the same shape as the T_p diagram, and $k=1$ to r all correspond to reducible G-blocks. The $k=0$ terms is the irreducible ones and may or may not be present depending on whether or not it is a pure core—scattering event. The prime in d implies that the arguments u, v, etc. common with a, b, etc. have to be dropped suitably as k changes in the sum. To make the system of equations complete, we should not include in (35) reducible G-blocks carrying more than r passive valence lines. Thus, a truncation of $T = \sum_p T_p$ brings about a truncation of the possible G-blocks. We have given in appendix 1 the rules for the construction of d_i's. More explicitly, the system of eqs (34) will look like

$$\sum_j A_{ij} T(j) + \sum_{j,k} B_{ijk} T(j) T(k) + .. = \lambda_i \text{ for } i = 1 \text{ to } n_t \qquad (36)$$

n_t is the total number of distinct T_p matrix-elements, stored in a column like $T(i)$. The quantities λ_i come from $\bar{H}$ diagram having no T_p or $T_p{}^+$ vertices whatsoever; they therefore originate either from an F or from a V Goldstone diagram.

Returning now to eq. (17), we note that the non-vanishing Goldstone $\bar{H}$-diagrams contributing to $\langle \phi_j | \bar{H} | \phi_i \rangle$ can have only the valence labels on the external lines. Using the same considerations as we have done for $\langle \phi_i | \bar{H} | \phi_i \rangle$, all these diagrams may be grouped into various blocks, having various pairs of ingoing and outgoing valence lines with all possible valence labels put on them. The groups of labelled G-blocks containing p-pairs of ingoing and outgoing external lines may be identified with the p-body part of the H_π. Using the same rules as given in appendix 1, we may write down the corresponding expressions for the G-blocks, and as we know this time the values of the matrix-elements of T from (34) we may evaluate the matrix elements of $\bar{H}$, $\langle \phi_j | \bar{H} | \phi_i \rangle$.

5. Explicit expression for the matrix-elements of H_π: An analysis of the one, two and three body operators

In this section, we shall give an explicit expression of the matrix-elements of H_π within the approximation:

$$T = \sum_{p=1}^{3} T_p$$

All the different shapes of the T matrix-elements and G-blocks are shown in figure 6. We have omitted from our considerations all T_p matrix-elements that vanish due to σ-π symmetry.

P.—2
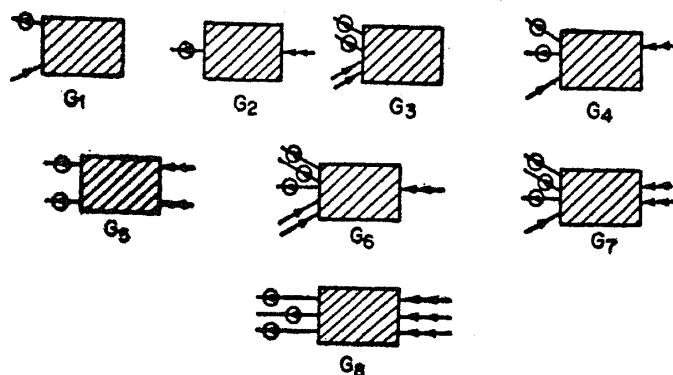
Figure 6. The shapes of all possible G-blocks that can be constructed under the approximations introduced in section 5.

Moreover, we shall work in the linear approximation, hence we shall omit from (36) all terms containing B_{ijk} and upwards. Equation (36), then, reduces to a system of linear simultaneous equations in matrix-elements of T. For our purpose, it is convenient to order the matrix-elements in such a way that for equation mumber i, the T-matrix-element, $T(i)$ appears in the ith row. The G-blocks in figure 6 will contain at best one T_p or $T_p{}^+$ Goldstone-vertex under the linear approximation. The values of the matrix-elements of T_p and $T_p{}^+$, when substituted in the G-blocks having external valence lines only, will give us the matrix-elements of H_π. Any p-body matrix-element $\langle uvw \mid H_\pi \mid abc.. \rangle$ will have the form

$$\langle uvw.. \mid H_{\pi_p} \mid abc..\rangle = \theta_H \sum_{p'} M_p \,(uvw..;abc) \tag{37}$$

where p' stands for all permutations interchanging $[(uvw..)$ and $(abc..)]$, θ_H stands for the operation of adding the hermitian conjugate of the expression $\sum_{p'} M_p(uvw..;abc..)$ to it. Diagrammatically, for every diagram contributing to $\langle uvw.. \mid H_{\pi_p} \mid abc..\rangle$, we shall have another which is its hermitian conjugate. The conjugate diagram looks like the mirror-image of the original, but the orientation of the arrows of the lines remains unaltered. The expressions of the quantities M_p for $p=1, 2, 3$ are given in appendix 2. In terms of these, H_π may be finally written as

$$H_\pi = \sum_{I,J} \langle \pi_I \mid H_{\pi_I} \mid \pi_J \rangle \, [Y^+{}_{\pi_I} \quad Y_{\pi_J}] + \frac{1}{2!} \sum_{\substack{I,J \\ K,L}} \langle \pi_I \pi_J \mid H_{\pi_2} \mid \pi_K \pi_L \rangle \times$$

$$[Y_I{}^+ Y_J{}^+ Y_L Y_K] + \frac{1}{3!} \sum_{\substack{I,J,K \\ L,M,N}} \langle \pi_I \pi_J \pi_K \mid H_{\pi_3} \mid \pi_L \pi_M \pi_N \rangle \times$$

$$[Y_I{}^+ Y_J{}^+ Y_K{}^+ Y_N Y_M Y_L] \tag{38}$$

with each H_{π_I} matrix-element having the property:

$$\langle \pi_I \pi_J... \mid H_{\pi_I} \mid \pi_K \pi_L..\rangle = \langle \pi_i \pi_J.. \mid H_{\pi_I} \mid \pi_k \pi_l..\rangle \,\delta(\gamma_i, \gamma_k)\,\delta(\gamma_J, \gamma_L). \tag{39}$$

In (39) spin-independence of H_π written in terms of Goldstone matrix-elements is manifest. As for valence labels, the operator X_I and Y_I are equivalent, we could have replaced Y and Y^+ by X and X^+, dropped the normal ordering operator N altogether, in that case H_π takes up exactly the same form as that of an ordinary hamiltonian.

In the construction of the G-blocks, whose contributions are shown in appendix 2, we have neglected further the contribution of T_3 matrix-elements involving only core-excitations. They are likely to be small, as the core wave-function $|0\rangle$ is a closed-shell system (Sinanoglu 1964). The matrix-elements of H_π are given by

$$\langle \pi_a | H_{\pi_1} | \pi_b \rangle = \langle \pi_a | f | \pi_b \rangle + \theta_H d_1 (\pi_a; \pi_b)$$

$$\langle \pi_a \pi_b | H_{\pi_2} | \pi_c \pi_d \rangle = \langle \pi_a \pi_b | v | \pi_c \pi_d \rangle + \theta_H (1 + P_{ab} P_{cd}) d_2 (\pi_a \pi_b; \pi_c \pi_d) \quad (40)$$

$$\langle \pi_a \pi_b \pi_c | H_{\pi_3} | \pi_d \pi_e \pi_f \rangle = \theta_H (1 + P_{ab} P_{de} + P_{ac} P_{df} + P_{bc} P_{ef} + P_{abc} P_{def} +$$

$$P_{cba} P_{fed}) d_3 (\pi_a, \pi_b, \pi_c; \pi_d, \pi_e, \pi_f)$$

where θ_H is the hermitiser introduced earlier, and P_{ij}, P_{ijk}, etc. are the permutation operators acting on the labels i, j, etc. The quantities d_1, d_2 and d_3 are given in the appendix 2. Some typical three body diagrams are shown in figure 7.
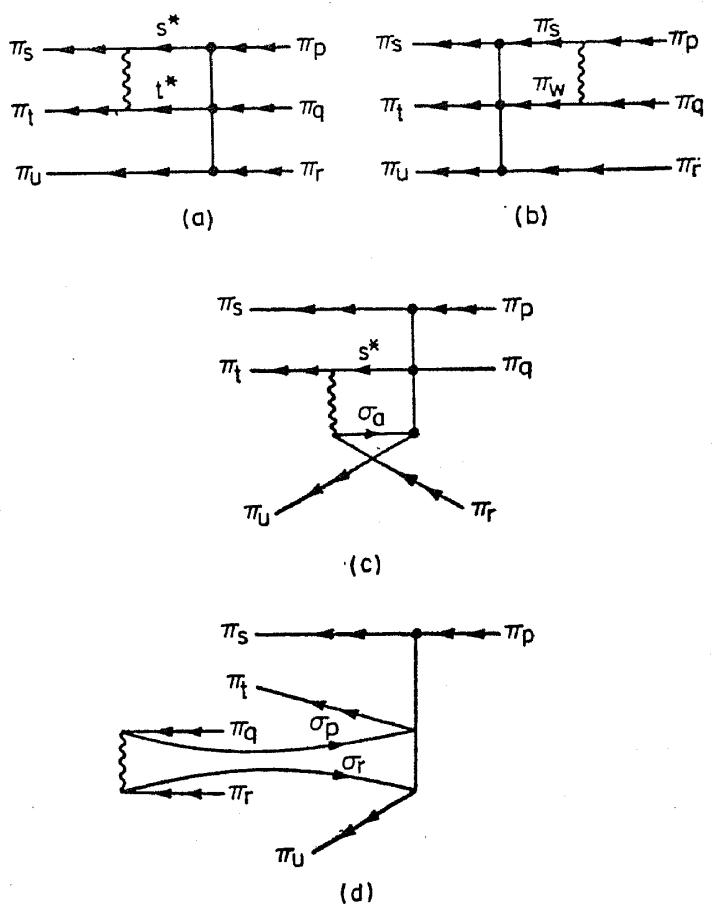

Figure 7. Some typical three-body diagrams of H_π.

We may now identify the matrix-elements $\langle \pi_a \mid H_{\pi_1} \mid \pi_b \rangle$ and $\langle \pi_a \pi_b \mid H_{\pi_2} \mid \pi_c \pi_d \rangle$ with the parameters β_{ab} and γ_{ab} of the semi-empirical π-electron theories. The other quantities neglected in the ZDO-approximation are not necessarily zero in the ab-initio formalism, and the validity of ZDO must be ascertained by an explicit ab-initio calculation.

To get an idea of the type of corrections brought about by the unitary operator e^S, it is instructive to decouple eqs (36) in the linear approximation, and attempt at an approximate solution of the matrix-elements of T as

$$T(i) = \frac{\lambda_i}{A(i,i)}. \tag{41}$$

Under this linear uncoupled approximation, all the T_3 matrix-elements are zero (as λ_i's for all the T_3 matrix-elements are zero), and the three-body part of H_π is constituted only by the T_1 and T_2 matrix-elements. Further for the matrix-elements in the HF basis λ_i's are zero for the T_1 matrix-elements, and thus under the approximation (41), all the T_1 matrix elements are also zero. The approximate expression for the one-centre repulsion parameter γ_{aa}, then, takes the form

$$\langle \pi_a \pi_a \mid H_{\pi_2} \mid \pi_a \pi_a \rangle = \langle \pi_a \pi_a \mid v \mid \pi_a \pi_a \rangle$$

$$+ \sum_{\sigma_b, \sigma_c} \frac{\langle \pi_a \pi_a \mid v \mid \sigma_b^* \sigma_c^* \rangle \langle \sigma_b^* \sigma_c^* \mid v \mid \pi_a \pi_a \rangle}{[\langle \sigma_b \mid f \mid \sigma_b \rangle + \langle \sigma_c \mid f \mid \sigma_c \rangle - 2 \langle \pi_a \mid f \mid \pi_a \rangle}$$

$$\frac{-\langle \pi_a \pi_a \mid v \mid \pi_a \pi_a \rangle - \langle \sigma_b \sigma_c \mid v \mid \sigma_b \sigma_c \rangle}{-\langle \pi_a \sigma_b \mid \bar{v} \mid \sigma_b \pi_a \rangle - \langle \pi_a \sigma_c \mid \bar{v} \mid \sigma_c \pi_a \rangle]}$$

$$+ \sum_{\sigma_b^*, \sigma_c^*} \frac{\langle \pi_a \pi_a \mid v \mid \sigma_b^* \sigma_c^* \rangle \langle \sigma_b^* \sigma_c^* \mid v \mid \pi_a \pi_a \rangle}{[2 \langle \pi_a \mid f \mid \pi_a \rangle - \langle \sigma_b^* \mid f \mid \sigma_b^* \rangle - \langle \sigma_c^* \mid f \mid \sigma_c^* \rangle + \langle \pi_a \pi_a \mid v \mid \pi_a \pi_a \rangle}$$

$$-\langle \sigma_b^* \sigma_c^* \mid v \mid \sigma_b^* \sigma_c^* \rangle]$$

$$+ \sum_{\pi_b, \pi_c} \frac{\langle \pi_a \pi_a \mid v \mid \pi_b \pi_c \rangle \langle \pi_b \pi_c \mid v \mid \pi_a \pi_a \rangle}{[2 \langle \pi_a \mid f \mid \pi_a \rangle - \langle \pi_b \mid f \mid \pi_b \rangle - \langle \pi_c \mid f \mid \pi_c \rangle + \langle \pi_a \pi_a \mid v \mid \pi_a \pi_a \rangle}$$

$$- \langle \pi_b \pi_c \mid v \mid \pi_b \pi_c \rangle] \tag{42}$$

The quantity $\bar{v} = v(2 - P_{12})$ includes the direct and exchange operators together. The starred orbitals are of particle type.

We find that the denominator in the second term of the eq. (42) is of the form $E_1 - E_2$, where E_1 and E_2 are respectively the average energy of the configurations $\phi_1 \sim Y^+_{\sigma_b} Y^+_{\bar{\sigma}_c} \cdots \mid 0 \rangle$ and $\phi_2 \sim Y^+_{\pi_a} Y^+_{\bar{\pi}_a} \cdots \mid 0 \rangle$ (the bar on the orbital labels denotes opposed spins). As ϕ_2 is obtained by lifting two electrons occupying σ_b and σ_c to π-orbitals π_a, the value of $E_1 - E_2$ will be negative. Physically speaking, this term represents the dielectric screening effect created by the σ-electrons on the coulomb repulsion of the π-electrons. Similarly, the denominators of the third and fourth

terms in (42) are dominated by the negative quantities $2\langle \pi_a | f | \pi_a \rangle - \langle \pi_b | f | \pi_b \rangle$ $- \langle \pi_c | f | \pi_c \rangle$, etc., and are also negative. These two terms represent the screening effect due to correlation of the π-electrons induced by the σ^* and π^* orbitals. These are external correlation effects. The internal correlation effects, i.e. the effect brought about by π-orbitals only, will be taken care of by the CI procedure implied by eq. (17). The formalism thus clearly separates the contribution of σ-electrons and excited configurations from the pure π-type corrections. The danger of double counting is thus completely avoided. In a similar manner, the effect of the σ-screening and the contribution of the configurations outside the model space to the two centre coulomb repulsion integral γ_{ab} can be found out.

Returning to eq. (36), if one goes beyond the zeroth order iterate, i.e. the linear uncoupled approximation, then one would generate matrix-elements of $T(i)$ which would embody not only the screening contributions included in the uncoupled approximation, but also their coupling effects as also various other types of coupling between the different T-operators. Direct solution of the eqs (36) would thus give matrix-elements of T which are equivalent to an infinitely summed up series involving many classes of diagrams. Let us emphasise that the construction of the coupled system of eqs (36) was remarkably simplified by introducing the diagrammatics and the notion of the division of diagrams into various G-blocks. In particular, the generation of the three-body terms of H_π containing genuine three-body operators like T_3 would have been extremely unwieldy in a purely algebraic approach. This is presumably the reason why a derivation of the three-body terms of H_π has been tried only very recently (Freed 1976). We came to know about Freed's work after the first draft of our paper was submitted for publication.

Besides the transformation of the full hamiltonian H to the model-space effective hamiltonian H_π, we have also to consider the transformation of other useful one- and two-particle operators. In particular, in the calculation of oscillator strengths of the allowed electronic transitions, the transformed operators corresponding to the electric and magnetic dipole operators d and μ would be extremely important. They may be obtained in a straightforward manner by substituting f everywhere by d or μ in the expression for H_π in eq. (37), and dropping the terms containing ν. It should be noted that, although the operators d and μ are one-particle types, the transformed operators d^π and μ^π would have to contain two, three... body terms. The situation parallels closely the case for H itself. The extent to which the higher body operators are important must be determined by a concrete calculation.

6. Discussion

We begin this section by indicating the relation of the present formalism with the other developments. Perhaps the formalism close in spirit and structure to ours is that of Westhaus (1973, 1975, 1976), developed along the earlier work of Harris (1967), and should be discussed first. Westhaus induced a canonical transformation on H by a unitary operator e^S with S chosen as $i s$ with s hermitian operator. This contrasts with a real representation of e^S in our case where we choose $S = T - T^+$ as an antihermitian operator. However, this difference of choice in the two methods is more apparent than real, as a real anti-hermitian operator is algebraically equivalent to i times a hermitian operator. The real difference lies in (a) his purely

algebraic manipulation without having recourse to a consistent use of occupation number representation and diagrammatics, (b) the truncation of the hierarchy of equations induced by the transformation in a way to decouple all matrix-elements of $T(i)$ and (c) not considering the core-valence separation theoretically in an explicit manner. In fact, due to a purely algebraic approach, a straightforward inclusion of more than linear terms in the transformation would be rather unwieldy. Our diagrammatic systematics however can avoid this problem by suitable book-keeping procedure. Furthermore, the use of the core part as the vacuum in our formalism automatically defines an effective one particle potential F which embodies scattering events under the vacuum sea and separates out the operator V free of such processes. This seems to be conceptually more transparent, as our one, two and three body operators really scatter one, two and three π-electrons. In contrast, Westhaus did not separate the passive core-core scattering events as we did and consequently classified some matrix-elements as three body forms which involve one or two core scattering events and are thus in effect not really three body terms. Westhaus did not include S_3 in his unitary operator and did not calculate real three body terms. It appears that the expressions of S_1 and S_2 given by Westhaus correspond essentially to a decoupled calculation of S_1 and S_2 as given in (41) of our formalism, with the difference that he worked with Hugenholtz matrix-elements and we worked with Goldstone matrix-elements, and in contrast to his—ours is a spin-independent representation. The decoupling implies an inconsistent truncation in the sense that H_π ceases to behave as a scalar in the symmetry group of the molecules. Westhaus and others (Westhaus *et al* 1975, Westhaus and Bradford 1976) in their calculation of the valence-shell hamiltonians of C, N and O atoms and some simple molecules did in fact obtain broken-symmetric solutions. But such truncations can easily be avoided by going over to a fully coupled solutions of the linearised equations of (36). We are at present investigating an alternative procedure in which only reduced matrix-elements, left out after the use of Wigner-Eckart theorem (Wigner 1967), of F, V, T and T^+ corresponding to any point-group symmetry would appear in the calculation, so that the inclusion of relevant symmetry can be accomplished right from the start (Mukherjee *et al*, to be published).

Linderberg and Ohrn's (1968) Green function approach is structurally very dissimilar to ours. The same can be said of the work of Shibuya *et al* (1975). In both these, the π-excitation spectra are calculated in such way that they avoid the explication of the underlying π-hamiltonian. In Shibuya's theory the formalism leads to a RPA like equation which is non-hermitian. In our view, an explicit formulation of the π-hamiltonian would be conceptually more transparent, and a non-hermitian formalism should be avoided as far as possible.

The earlier partitioning technique formulation of H_π by Freed (1972, 1974), and the consequent numerical applications are quite extensive and they bring out the various factors contributing to H_π. But the formalism had the disadvantage of leading to an energy-dependent hamiltonian. It seems that Freed considered the energy-dependence of H_π as both natural and unavoidable, but this feature is certainly due to the special formalism that he used. By adopting an alternative partitioning technique due to Coope (1970), for example, the energy dependence could have been avoided. After the submission of the first draft of our manuscript for publication, there has appeared another paper by Freed (1976), in which he shifts from his earlier view and gives an energy-independent formulation of H_π, much

along the same line as Jørgensen (1975). The generalised perturbation series that he builds up is structurally analogous to the simultaneous equation solution method of our theory (I, II), with the difference that explicit inversion of a set of matrices is needed to generate his series. Freed also discusses the question of core valence separation, and defines a suitable partition of the hamiltonian to achieve this. In contrast we achieve this by introducing T_p-matrix elements with passive valence-valence scatterings. The relative efficacies of the two formalisms remain to be tested. Freed also discusses three body terms of H_π which look quite similar to ours. Freed, however, does not discuss the elimination of spins, and this may pose non-trivial problem in an algebraic theory. In particular, the ladder terms that appear in the energy denominators of his perturbation series strongly resemble the Epstein-Nesbet perturbation series, which is known to be manifestly spin-dependent.

It should also be pointed out that numerical studies may indicate that the elimination of the energy dependence of H_π would lead to a slowly convergent expansion in which $p > 2$ body terms are also significant. In that case, one would say that the parametric dependence of H_π on E is a compact way of handling these latter terms. The situation is then comparable to that encountered in Green function type of formalism. But until a detailed numerical calculation settles the issue, we should suspend our judgement regarding this rather tricky question.

Kvasnicka (1975) used a third order degenerate Rayleigh-Schrödinger perturbation theory to derive a hermitian H_π. This formalism uses Goldstone diagrams right from the start, so that elimination of spin-variables is accomplished at the outset and the series is of such a structure that it can be used in a straighforward manner to generate the three and higher body spin-independent terms of H_π. In this sense, Kvasnicka's method is manifestly spin-independent. In contrast, the formalism of the present paper has the complexity that after the one body term, the spin-independence had to be proved. This is due to artifacts that are peculiar to the formalism. But, whereas it would be impossible in a perturbative formalism to include classes of diagrams which do not form well-defined algebraic series, in the non-perturbative formalism it is a built-in feature and in this sense yields a much more compact expression of H_π. In particular, the so-called off-diagonal ladder and ring diagram contributions cannot be included exactly by summing up any algebraic series, but are shown to be quite important in actual calculations on closed-shell systems (Davidson 1973; see e.g. Mukhopadhyay *et al* 1975 for an actual calculation). There is no reason to suppose that they will not be as important in open-shell cases. It also appears that the simple diagrammatic representation of the degenerate perturbation theory would be lost, if one goes beyond the third order (Kvasnicka 1975). No such limitations exist in the non-perturbative formalism.

We would like to conclude the comparative study of the various effective hamiltonian formalisms by drawing attention to an as yet untested but potentially very powerful formalism developed by Johnson and Baranger (1971). This formalism also generates a spin-independent hermitian effective hamiltonian, as in Kvasnicka's formalism, but the structure of the perturbation series is entirely different. Whereas in Kvasnicka's theory (K-theory in short), corresponding to each diagram in H_π, there is another which is hermitian conjugate to it (unless the diagram is self conjugate), each diagram of Johnson and Baranger formalism (JB in short) is intrinsically self-conjugate. To use a jargon from stereochemistry, K-theory yields a hermitian H_π by external compensation while JB-theory achieves the same property by internal com-

pensation. The number of terms in JB-series is less for a particular order of perturbation, and in this sense more compact than the K-series. Moreover, there is no difficulty of diagrammatic interpretation as one goes beyond the third order of perturbation.† The K-formalism was initially meant for nuclear structure calculations but has not yet been applied in either nuclear physics or molecular physics.

It appears now that we have quite a few theoretical apparatus at our disposal to tackle the π-electron problem in an ab-initio manner. It seems extremely worthwhile at this stage of development of π-electron theories to undertake a comparative ab-initio studies on prototype π-systems using the different formalisms that have been currently developed. A parallel study in nuclear structure calculations has already begun (see e.g. Barret *et al* 1975, Richert *et al* 1976).

Let us now discuss certain specific features of H_π as coming out of the present formalism. From eq. (42), it appears that the extent of screening of the π-electrons would depend on the dominance of contribution of certain terms in the sum. As the matrix elements appearing in (42) are of the dispersion type, they fall off rapidly with the distance of separation of σ, σ^* or π^* with π; thus only those σ, σ^* or π^* orbitals which are spatially closest to the π-orbitals concerned would give a sizeable contribution. It thus appears, that the extent of screening will be greater for π-electrons in atoms which have greater number of nearest neighbours. This gives us a physically appealing picture; for atoms with greater number of nearest neighbours would have to be in the interior of the molecule in some sense, and electrons sitting on them are likely to experience more screening, as they would be screened from all sides. In this sense, even for alternant hydrocarbons, the one-centre repulsion integrals γ_{aa} for C-atoms which are at the periphery are theoretically expected to be greater in magnitude than those for the interior C-atoms. This spells a breakdown of the Coulson-Rushbrook like theorems (see Parr 1963), and is a consequence of the effect of correlation and σ-screening. The two-centre repulsion integrals γ_{ab} would also be expected to display a similar site-dependence, being more screened in the interior than in the periphery. The conclusions would remain the same also for the more accurate coupled calculations [eq. (36)]. A similar conclusion to ours was also reached by Westhaus and Freed. Gutfreund and Little (1969) estimated in a purely empirical manner the extent of screening of the π-electrons for large condensed hydrocarbons by putting a probe-charge at various places, and also reached a similar conclusion.

The question of the transferability of the π-hamiltonian parameters must be regarded as *sub judice* till detailed numerical results become available. But in order to test this criterion, the π-hamiltonian must have to be formulated in terms of a non-orthogonal, slater-like, pz basis-set. The generation of such a H_π from an orthogonal basis set is straightforward. We start out with the Lowdin-orthogonalised pz basis-set, and end up with eqs (16) and (19). We next expand each orthogonal pz in terms of the non-orthogonal set, and generate for each block containing orthogonal orbitals as the external labels a sum of blocks labelled by various non-orthogonal orbitals in the external lines. As the non-orthogonal basis-set is lineraly independent, each such block in the sum must separately be zero. Thus, for equations corresponding to blocks labelled by orthogonal basis sets, we would have as many blocks labelled by non-orthogonal basis. Further, in the sum over internal valence-lines in a diagram, we can expand the orthogonal orbitals in terms of the non-orthogonal orbitals,

†The K-formalism is very general and, for example, may be used to generate natural orbitals of a system by a Green function formalism (Mukhopadhyay *et al* to be published).

and can retain terms up to any order of expansion by a slight modification of the diagrammatic rules. This is shown in the appendix 1.

We are currently undertaking a numerical investigation on the π-hamiltonian corresponding to $1s^2 \, 2s^2 \, p^2$ spectroscopic states of carbon using the formalism developed in the paper. Our aim is to provide theoretical values of the effective Slater-Condon parameters for the p-orbitals of carbon which would generate formally exact values for the energies of the spectroscopic states when calculated with the model space functions only.

Appendix I

Here we give the rules for finding out the expression corresponding to a Goldstone H_π-diagram in a G-block

(a) In a G-block only the topologically inequivalent diagrams should be included.

(b) For each diagram, label the external lines in such a way that the block implies the same scattering event as that implied by the corresponding T-matrix-element (see section 4.2).

(c) Label the internal lines appropriately, and sum over them.

(d) Attach a sign factor $(-1)^{n+h+l+m}$ to the diagram, where n is the number of T_p or T_p^+ operator on the left of an F or a V vertex, h is the number of hole lines, l is the number of loops and m is the number of T_p^+ operators in the diagram.

(e) Assign a factor $1/K!$ for each of K sets of equivalent vertices. Equivalent vertices are the ones in which equivalent lines enter and leave the same vertices.

In the diagram, there will be two types of strings formed by connecting T_p/T_p^+ vertices together. The first kind consists of strings which lie entirely on the left or right of an F or a V vertex. If n_l and n_r be respectively the number of T_p/T_p^+ vertices in any string lying on the left or right of the F or V vertex, then attach a factor $[(1/\pi n_l!) \, (1/\pi n_r!)]$, the product π goes over all such strings. The second kind of strings are those which extend to both sides of the F or V vertex. Draw an imaginary vertical line passing through the F or V vertex. Let n'_l and n'_r be the number of T vertices in the left and right segment of any such string. Attach a factor $(1/\pi n'_l!)$ $(1/\pi n'_r!)$, where the product goes over all strings of the second kind.

(f) collect the strings of T_p/T_p^+ vertices into classes, each class containing a set of equivalent strings. Let the number of strings in any class be n_c. Then attach a factor $(1/\pi n_c!)$, the product running over all classes.

For non-orthogonal valence lines, the rules for drawing and finding out the contribution of the diagram are practically the same, with the difference, that (a) each internal valence line is labelled by two distinct dummy valence labels and there is a two-fold sum over those two dummy labels. (b) If the overlap matrix S between the

non-orthogonal AO basis be written as $S = 1 + \vec{\Delta}$, then for each pair of valence labels (π_i, π_j) on any internal line, attach a factor $\sum\limits_{n_\nu=0}^{\infty} (-1)^{n_\nu} \, (\vec{\Delta}^{n_\nu})_{ij}$, where $(\vec{\Delta}^{n_\nu})_{ij}$ is the ij element of the $\vec{\Delta}^{n_\nu}$ matrix. For all practical purposes, the series has to be truncated after certain finite n_ν.

Appendix II

In this appendix we shall be giving expressions for the quantities d_1, d_2 and d_3 introduced in eq. (40):

$$d_1(\pi_a; \pi_b) = m_1(\pi_a; \pi_o) + \sum_{\sigma_b, \, \sigma_b^*} \langle \pi_a \sigma_b^* | v | \pi_b \sigma_b \rangle \langle \sigma_b | t_1^+ | \sigma_b^* \rangle \quad \text{(A1)}$$

where

$$m_1(\pi_a; \pi_b) = \sum_{\pi_b^*} \langle \pi_a | f | \pi_b^* \rangle \langle \pi_b^* | t_1 | \pi_b \rangle$$

$$+ \sum_{\sigma_b, \, \sigma_b^*} \langle \pi_a \sigma_b | \bar{v} | \pi_b \sigma_b^* \rangle \langle \sigma_b^* | t_1 | \sigma_b \rangle - \sum_{\sigma_b, \, \sigma_c, \, \pi_b^*} \langle \sigma_b \sigma_c | \bar{v} | \pi_b \pi_b^* \rangle$$

$$\langle \pi_a \pi_b^* | t_2 | \sigma_b \sigma_c \rangle + \sum_{\sigma_b, \, \sigma_b^*} \langle \sigma_b | f | \sigma_b^* \rangle \langle \pi_a \sigma_b^* | \bar{t}_2 | \pi_b \sigma_b \rangle$$

$$+ \sum_{\sigma_b, \, P_b^*, \, P_c^*} \langle \pi_a \pi_b | \bar{v} | P_c^* P_b^* \rangle \langle P_c^* P_b^* | t_2 | \pi_b \sigma_b \rangle$$

$$+ 2 \sum_{\sigma_b, \, \sigma_c, \, P_b^*, \, P_c^*} \langle \sigma_b \sigma_c | \bar{v} | P_b^* P_c^* \rangle \langle P_b^* P_c^* \pi_a | t_3 | \sigma_b \sigma_c \pi_b \rangle$$

$$- \sum_{\sigma_b, \, \sigma_c, \, P_b^*, \, P_c^*} \langle \sigma_b \sigma_c | \bar{v} | P_b^* P_c^* \rangle \langle P_b^* P_c^* \pi_a | t_3 | \pi_b P_c^* P_b^* \rangle \quad \text{(A2)}$$

$$d_2(\pi_a \pi_b; \pi_c \pi_d) = m_2(\pi_a \pi_b; \pi_c \pi_d) + \sum_{\pi_c^*} \langle \pi_c^* \pi_b | v | \pi_c \pi_d \rangle \times$$

$$\langle \pi_a | t_1^+ | \pi_c^* \rangle \quad \text{(A3)}$$

where

$$m_2(\pi_a \pi_b; \pi_c \pi_d) = - \sum_{\pi_c^*} \langle \pi_a \pi_b | v | \pi_c^* \pi_d \rangle \langle \pi_c^* | t_1 | c \rangle$$

$$+ \tfrac{1}{2} \sum_{\sigma_a, \, \sigma_b} \langle \sigma_a \sigma_b | v | \pi_c \pi_d \rangle \langle \pi_a \pi_b | t_2 | \sigma_a \sigma_b \rangle$$

$$+ \sum_{\sigma_a, \sigma_a^*} (\langle \sigma_a \pi_a \mid v \mid \sigma_a^* \pi_c \rangle \langle \sigma_a^* \pi_b \mid \overline{t_2} \mid \sigma_a \pi_c \rangle$$

$$- \langle \sigma_a \pi_a \mid v \mid \pi_c \sigma_a^* \rangle \langle \pi_b \sigma_a^* \mid t_2 \mid \pi_d \sigma_a \rangle)$$

$$+ \sum_{\sigma_a, \sigma_b, \pi_c^*} (\langle \sigma_a \sigma_b \mid \overline{v} \mid \pi_c^* \pi_d \rangle \langle \pi_a \pi_b \pi_c^* \mid t_3 \mid \pi_c \sigma_b \sigma_a \rangle$$

$$- \langle \sigma_a \sigma_b \mid v \mid \pi_c^* \pi_d \rangle \langle \pi_a \pi_b \pi_c^* \mid t_3 \mid \sigma_a \sigma_b \pi_c \rangle)$$

$$+ \sum_{P_c^*, P_d^*, \sigma_a} (\langle \pi_a \sigma_a \mid \overline{v} \mid P_c^* P_d^* \rangle \langle \pi_b P_c^* P_d^* \mid t_3 \mid \pi_d \pi_c \sigma_a \rangle$$

$$- \langle \pi_a \sigma_a \mid v \mid P_c^* P_d^* \rangle \langle \pi_b P_c^* P_d^* \mid t_3 \mid \sigma_a \pi_c \pi_d \rangle) \tag{A4}$$

$$d_3 (\pi_a \pi_b \pi_c; \pi_d \pi_e \pi_f) = m_3 (\pi_a \pi_b \pi_c; \pi_d \pi_e \pi_f)$$

$$+ \tfrac{1}{2} \sum_{\sigma_d^*, \sigma_c} \langle \pi_a \sigma_d^* \mid \overline{v} \mid \pi_d \sigma_c \rangle \langle \pi_b \pi_c \sigma_c \mid t_3^+ \mid \pi_e \pi_f \sigma_d^* \rangle$$

$$+ \tfrac{1}{2} \sum_{\sigma_c, \sigma_d} \langle \pi_b \pi_c \mid v \mid \sigma_c \sigma_d \rangle \langle \pi_a \sigma_c \sigma_d \mid t_3^+ \mid \pi_d \pi_e \pi_f \rangle \tag{A5}$$

where

$$m_3 (\pi_a \pi_b \pi_c; \pi_d \pi_e \pi_f) = \sum_{\pi_d^*} \langle \pi_a \pi_c \mid v \mid \pi_d^* \pi_f \rangle \langle \pi_d^* \pi_b \mid t_2 \mid \pi_d \pi_e \rangle$$

$$+ \tfrac{1}{2} \sum_{\pi_d^*} \langle \pi_a \mid f \mid \pi_d^* \rangle \langle \pi_d^* \pi_b \pi_c \mid t_3 \mid \pi_d \pi_e \pi_f \rangle$$

$$+ \tfrac{1}{2} \sum_{P_d^*, P_g^*} \langle \pi_a \pi_b \mid v \mid P_d^* P_g^* \rangle \langle P_d^* P_g^* \pi_c \mid t_3 \mid \pi_d \pi_e \pi_f \rangle$$

$$+ \sum_{\sigma_d^*, \sigma_c} (\langle \pi_c \sigma_c \mid \overline{v} \mid \pi_f \sigma_d^* \rangle \langle \pi_a \pi_b \sigma_d^* \mid t_3 \mid \pi_d \pi_e \pi_f \rangle$$

$$- \langle \pi_b \sigma_c \mid v \mid \sigma_d^* \pi_f \rangle \langle \pi_a \sigma_d^* \sigma_c \mid t_3 \mid \pi_d \pi_e \sigma_c \rangle$$

$$+ \langle \pi_c \sigma_c \mid v \mid \pi_f \sigma_d^* \rangle \langle \pi_a \sigma_d^* \pi_b \mid t_3 \mid \pi_d \pi_e \sigma_c \rangle)$$

$$+ \tfrac{1}{2} \sum_{\sigma_c, \sigma_d} \langle \sigma_c \sigma_d \mid \overline{v} \mid \pi_e \pi_f \rangle \langle \pi_a \pi_b \pi_c \mid t_3 \mid \pi_d \sigma_c \sigma_d \rangle \tag{A6}$$

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