PROBABILITY IN THEORETICAL CHEMISTRY.

A thesis presented for the degree of

Doctor of Philosophy

in the faculty of science of Leicester

University.

by

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September 1970.

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STATEMENT.

The work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester between October 1966 and September 1970.

The work has not been presented, and is not being concurrently presented, for any other degree.

Signed

B. Weiner.

September 1970.

ACKNOWLEDGEMENTS.

The author wishes to offer his thanks gratefully to:-

Dr. Tom.A.Claxton for his guidance and helpful advice.

Nigel Smith and Dr.D.McWilliams for use of their critical faculties.

Barbara Birch for the typing of this thesis.

Leicester University for providing a grant.

Dr J.Thompson of the University of Leicester Computing Laboratory for making facilities available for computations.

.....

And to Pamela.M.Jones for keeping me sane and being my friend.

ABREVIATIONS.

l.t.s--Linear Transformations.

l.i.---Linearly Independent.

l.d.---Linearly Dependent.

w.r.t.-with respect to.

s.t.---such that.

$\in$ ---Belonging to.

CONTENTS.

INTRODUCTION

Probability distributions due to the indeterministic nature of man's interaction with the micro-world, are inherent in the formulation of Quantum Mechanics. Probability distributions are also one of the main units of language in such widely dispersed fields as Economics, Psychology, Statistical Mechanics, and Control Theory. As here incomplete characterisation of the systems under study, due to the very large number of variables involved, lead to indeterminism.

A careful note must be made as to the different nature of the factors that cause probability distributions to play a centrol role in (a) Quantum Mechanics (b) Statistics (in general). In (a) determinism will never be attainable to man no matter how well he characterises the system under study, in (b) it is theoretically possible that a deterministic picture could be formed given all the pertinent variables.

Given that all these fields of study have such a common factor, is there a mathematical term that expresses such a link? Indeed there is - 'The Density Matrix', although known under different names in the varying disciplines its mathematical properties stay constant. Numerous reviews[1234] scan the usage, so only aspects that will be of relevance to the following pages will be mentioned.

In Quantum Mechanics we say that system under study can be described completely, within the limits imposed by the micro-world/macro-world interaction, by a set of pure state vectors

$\Psi_i, i=1,\ldots,\infty$ that exist in an infinite Hilbert Space. These vectors are eigenvectors of the Hamiltonian operator, that is represented by H in the Hilbert Space, (properties of which are discussed in many texts).

i.e. $H\Psi^i = E^i\Psi^i$

This operator commutes with a maximal set of other operators, the set of all operators that correspond to the maximum number of simultaneous observables of the system, and thus the eigenvectors Ψ_i are simultaneous eigenstates of the other operators[1]

In general the state of the system would be an incoherent superposition of eigenstates (pure states), i.e.

$$\Psi = \sum_i c^i \Psi^i$$

and the probability of observing any pure state in the mixture would be $|c^i|^2$, (only pure states can be observed). When this is so we have incomplete information about the system, i.e. it has not been prepared into a pure state by maximal set of measurements (the act of measurement being equivalent to filtering out a pure state of the system) so we have a statistical spread of states. When we make a measurement on such a system two different averaging concepts enter (i) the expectation value of the action of a given operator on a pure state - expressing the inherent uncertainty of the interaction of the micro and macro worlds, and (ii) the ensemble average of the expectation values due to the different states, the ensemble weighting factors being c^i . (i)

[1] Hermetian matrices that commute i.e.AB-BA=0 have simultaneous eigenvectors.

and (ii) correspond to (a) and (b) before, nothing can be done about (i) but it is possible to prepare the system so that it is in a definite state. [i.e. characterising the system completely, within the limitations mentioned].

That there are two different averaging concepts utilised is aesthetically unsatisfactory and leads to complexities, and a lack of clarity in actual computations. For this reason J. Von Neuman proposed, in 1927, an alternative method of characterising states, The Density Matrix

Following V.FANO,Rev Mod Phys,29,74,(1957) and P.ROMAN,Advanced Quantum Theory:-

Let our system be represented by a set of normalised pure states Ψ_i , and the normalised weight of each pure state be denoted by C_i , we can expand our pure state in terms of orthonormal eigenvectors $\{\chi_n\}$ of a maximal set of commuting operators. [not the same maximal set for which Ψ_i is a pure state]

$$\Psi_i = \sum_n a^n_i \chi_n \quad , \text{ with } \langle \chi_n | \chi^m \rangle = \delta^m_n$$
$$\sum_n |a^n_i|^2 = 1.$$

Then the expectation value of Ω in the pure state Ψ_i is

$$\langle \Omega \rangle_i = \sum_{nm}{}' a^{*i}_n a^i_m \langle \chi_n | \Omega | \chi^m \rangle = \sum_{nm}{}' a^{*i}_n a^i_m \Omega^m_n$$

Thus the grand average of the observable Ω would be

$$\langle \Omega \rangle = \sum_i{}' C_i \langle \Omega \rangle_i = \sum_{nm}{}' \{ \Omega^m_n \sum_i{}' C_i a^{*i}_n a^i_m \}$$

If we define Γ (The Density Matrix) as

$$\Gamma^n_m = \sum_i{}' C_i a^{*i}_n a^i_m$$

Then $\langle \Omega \rangle = \sum_{nm}{}' \Gamma^n_m \Omega^m_n = Tr\, \Gamma\Omega$

Here T and Ω are representations of the Density Matrix, and the operator in the bases $\{\chi_i\}$ of the Hilbert Space. Thus the grand average of Ω can be computed by knowing T. The diagonel elements of T have a direct physical meaning, the probability with which the base state χ_n occurs in the ensemble. i.e

$$T^N_N = \sum_i c_i |a^N_i|^2$$

Now $a^N_i = \langle \Psi_i | \chi^N \rangle$

So $T^N_M = \sum_i \langle \chi_M | \Psi^i \rangle c_i \langle \Psi_i | \chi^N \rangle$

Thus the operator $\hat{T}$ is given by

$$\hat{T} = \sum_i |\Psi^i\rangle c_i \langle \Psi_i|$$ i.e. it can be represented as a sum over projection operators.

The eigenvectors of T are the possible pure states the system can have, and the eigenvalues the corresponding statistical weights.

If the system is in a pure state (i.e. describable by a single state vector Ψ_i), then $c_i = 1$ and $c_k = 0$ for $k \neq i$.

and for that state $T_i = |\Psi^i\rangle\langle\Psi_i|$

Thus for a pure state the Density Matrix becomes a projection operator, with the related property of idempotency

$$T_i = T_i^2$$

and the expectation value of an observable for a pure state is given by $\langle \Omega \rangle = Tr\, T_i \Omega$ as it was for a mixed state, thus the same formalism can handle pure and mixed states.

The state vector or the Density Matrix for a particular system can be determined either analytically or experimentally. Analytically the state vector is a solution to the eigenvalue problem $H\Psi^i = E^i \Psi^i$, where H, the Hamiltonian of the system characterises the symmetry of the system to the fullest

extent. Experimentally it is determined by carrying out a maximal set of simultaneous measurements of all possible commuting observables on the system.

The Density Matrix is determined analytically by finding a matrix that commutes with the Hamiltonian of the system, where the Hamiltonian embodies the complete symmetry of the system, viz one finds a Υ s. $[H,\Upsilon] = 0$, the set of all solutions are the density matrices corresponding to the possible states of the system. Experimentally Υ is determined by making $N^2 - 2$ or $N^2 - 1$ independent measurements of the system, where N is the number of possible pure states the system could be in, if the system is actually in a pure state $N^2 - 2$ measurements are enough to completely determine the density matrix of that state[3].

A fundamental difference between the Density Matrix and the state vector description is apparent. State vectors can only be characterised for pure states and thus we can only predict the behaviour of a system in a pure state, while the Density Matrix can be characterised for a mixed state of the system, so we can predict the behaviour of mixed state systems, viz for the state vector description we have to have complete knowledge of the system, while in the Density Matrix scheme we can work with incomplete knowledge.

Further if we are only interested in certain properties of the system we can express the Density Matrix in a basis of the possible pure states of this property. If there are N such states, then we need only make $N^2 - 1$ independent measurements to determine the Density Matrix w.r.t. these properties. Such a Density Matrix is only valid in predicting

behaviour that is a function of these properties.

The behaviour of the system w.r.t. these properties of interest is thus predicted in the average field of the properties not of interest.

Analytically we can determine such a Density Matrix by finding Γ that commutes with H when the Hamiltonian only characterises those properties of interest.

When we have a N particle system and we are only interested in P particle properties we need only find a Density Matrix that commutes with a Hamiltonian that only expresses P particle properties. Such Density Matrices are called P^{th} Order Reduced Density Matrices. This is not possible in the state vector formalism, as state vectors are only defined for pure states of the system and have to be determined maximally.

Almost all chemical systems (and indeed most physical ones as well) are expressed in terms of two particle Hamiltonians, thus only two particle properties are of interest. (Two particle properties determine one particle ones). Hence to describe such systems the 2nd Order Reduced Density Matrix has to be determined, such that $[H^{(2)}, T^{(2)}] = 0$. Where $H^{(2)}$ embodies all 2 particle symmetries implicitly. If we define a Hamiltonian that only embodies energy properties, but not angular momenta or statistical, and if we are only interested in the S = 0 state of the system We have to determine [1] $\Gamma^{(2)}$

[1] W.A.BINGEL and W.KUTZELNIGG (Queens Papers No. 11).

where $[H^{(2)}, \Gamma^{(2)}] = 0 = [\Gamma^{(2)}, J^{(2)^2}] = [\pi, \Gamma^{(2)}] = 0$

s.t. $[H^{(2)}, J^{(2)^2}] = [H^{(2)}, \pi] = [J^{(2)^2}, \pi] = 0$

where $J^{(2)^2}$ embodies all angular momenta requirements, and π statistical (i.e. Fermi-Dirac, or Bose-Einstiens) requirements.

However analytically it has proved impossible to describe π completely, s.t. π represents the statistics of a 2 particle subsystem of a N particle system. This is known as the N representability problem.

In Part I of this thesis we will limit ourselves to systems that are in singlet spin states (this is for simplicity in the application of the probability constriants), and describe and analyse the mathematical structure of the representations of various N particle operators in (a) the continuous co-ordinate representation, and (b) the discrete functional representation of a Hilbert Space. This will be achieved by utilising the notation developed in Chapter 1 which is, due to the lack of space and direct relevance to this thesis of many ancillary topics, of a rather truncated and abrupt form. However it is important to refer one's concepts to a general mathematical structure rather than develope notions in vacuum.

Chapter 2, 3 and 4 will deal with various properties of the representations of operators, with particular concentration on the 2nd Order Reduced Density Matrix andits eigenfunctions. Also rather intensively developed will be the sub space structure of the functional representations and their associated spin symmetry. In chapter 5 we will interpret the 2nd Order Reduced Density Matrix, and its relation to other orders of Density

Matrices, probabilistically. Thus trying to find conditions that $\Gamma^{(2)}$ has to obey so that it does correspond to a description of two particle properties of a system of N identical Fermions. Hence trying to find some partial solution to the N representability problem. In Chapter 6 we describe the application of the previous chapters to a practical approach, using a computer program that has been written along the structure presented in this chapter. The results achieved by restricting possible $\Gamma^{(2)}$'s by various constriants are discussed and given.

To people involved with the efficient production of mathematical results that can be applied to chemical systems that the experimenter has characterised, the N representability problem and its attempts at solution would seem to appear rather esoteric, and in fact it cannot be claimed that an efficient method of furnishing a mathematical parameterization of an experimental system has ever been developed through the approach of trying to determine directly the Reduced Second Order Density Matrix of a system. However one can never feel satisfied with the cruder approximation that, although superficially predicts results in qualitative agreement with some experimental parameter, often at the same time predict parameters that are wildly in disagreement. Thus doubt exists as to whether one has characterised the structure of the physical system mathematically or whether one has just fortutiously computed a parameter that happens to agree with experiment but for the wrong reasons.

So a balance must be sought and mathematical analysis must extend from both ends of approximation, one end at which theoretical rigour is maintained and the other where refinements

to a gross approximation are developed.

Thus in Part II we look at two extensions of the independent particle model (where we do not limit ourselves to singlet states of systems), i.e. where we characterise only 1 particle properties of the system, and hence all predictions are based upon the 1st Order Reduced Density Matrix. The first extension is that of partial Configuration Interaction. In a full CI calculation one determines the coefficients of a full Slater Determinental expansion of the N particle wavefunction - (which in fact is an expansion over the exterior product functional space $\bigwedge^N_N F^{(2M)}$), i.e. one solves the eigenvalue problem $H\Psi^i = \epsilon^i \Psi^i$ where the Hamiltonian and wavefunction are represented in $\bigwedge^N_N F^{(2M)}$, which does in fact solve the N representability problem but only does so at an 'overwork' cost. For our Hamiltonian usually only embodies at most two particle operators, and we are determining an N particle wavefunction (or in fact its discrete representation). To shorten the work involved we truncate our CI expansion to a fixed number of terms and try and construct an optimum partial basis to $\bigwedge^N_N F^{(2M)}$. This is known as the Multi-configuration Self consistant Field Method (MCSCF). This does improve upon the basic independent particle model but not very efficiently.

Chapter 1 (in Part II) deals with the MCSCF method and presents some computational results and comparisons with other approximations

≠ See chapters 1,2,3,4 for usage of notation.

Another type of extension of the independent particle model is the U.H.F. (unrestricted Hartree Fock) method which, although very efficient (usually) and improves upon the Restricted Hartree Fock Method, suffers from the limitation that wavefunctions it predicts are not eigenfunctions of the total spin angular momentum operator S^2, and thus the associated Full Density Matrix does not commute with the representations of S^2. Chapter 2 hence deals with methods attempting to constrain solutions to the UHF method so that they are eigenfunctions of S^2.

In appendix 4 there is an example that, it is hoped, illuminates some of the mathematical forms described in general in Chapter 1.

References to Part I are of such general applicability to all of Part I, they are collected at the end of this introduction with relevant remarks.

References

D. Ter Haar, 'Theory and Applications of the Density Matrix', Reports on Progress in Physics Vol. XXIV, 1961.

V. Fano, Rev. Mod Phys., 29, 74, 1957.

R. McWeeny, Rev. Mod Phys., 32, 355, 1960.

P. Roman, 'Advanced Quantum Theory' (Addison-Wesley, Library of Congress Catalog No. 65 - 16887, 1964).

Reduced Density Matrices with Applications to Physical and Chemical Systems. Editors - A.J. Coleman and R.M. Erdahl. (Queens Papers on Pure and Applied Mathematics - No. 11, 1968). This contains a general survey of the state of Reduced Density Matrix Theory up to 1968 and stimulates many ideas.

H.C. Longuet-Higgins 'Second Quantisation in the Electronic Theory of Molecules'. Quantum Theory of Atoms, Molecules and Solid State. Editor - P.O. Lowdin. (Academic Press N.Y. 1966). Even though 2nd Quantisation has not been mentioned explicitly in the text it is a very useful equivalent formalism to that used.

Frank Weinhold and E. Bright Wilson Jr., J. Chem. Phys., 47, 7,2298, 1968. This article, coupled with their contribution to Queens Paper No. 11, originated my interest in the probablistic approach to N-Representability.

Reference Books on Probability Theory -

Drake, Fundamentals of Applied Probability Theory (McGraw Hill,1967)

P.L. Meyer, Introductory Probability and Statistical Applications (Addison-Wesley, 1965).

A. Yaspan, Essentials of Probability (Prindle, Weber and Schmidt Library of Congress Catalog Card No. 68-12612, 1968).

Reference Books on Matrix Theory -
Marcus Ming, A Survey of Matrix Theory and Matrix in Equalities (Allyn and Bacon, 1964).

Eisenschitz, Matrix Algerbra for Physicists, (Heinemann, 1966).

Reference Books on Algerbra -
Greub, W.H., Multilinear Algerbra (Springer-Verlag Berlin-Heidelberg 1967)(Library of Congress Card No. 67-14017).
Chapter 1 is based mainly on this book. Any fallacies are probably due to my misinterpretation of the Algerbraic symbolism.

Reference Books on Linear Programming -
Simmonard, Linear Programming (Prentice Hall, 1966)
(Library of Congress Catalog Card No. 66-19887).

Duffin, Peterson, Zener, Geometric Programming (J. Wiley and Sons, 1966) (Library of Congress Catalog Card No. 66-21053).

B. Noble, Applied Linear Algerbra (Prentice-Hall, 1969).

W.I. Zangwill, Non Linear Programming (Prentice-Hall, 1969)
(Library of Congress Catalog Card No. 69-10606).

PART ONE.

CHAPTER ONE.

Notation and Algebra play an important part in Quantum theoretical discussions, and for convenience this chapter collects together basic definitions and algebraic relationships used in other parts of this thesis.

Vector and Tensor Products

Strictly, the following applies to vectors referred to a discrete basis. However, with certain qualifications the relationships can be extended to vectors referred to a continuous basis i.e. functions. As these qualifications do not affect the essence of the definitions and relationships they will not be explicitly stated.

The following notations are used in this section:-

$E^{(m)}$ - an m-dimensional contravarient Euclidoan vector space (space of Tensor rank 1)

$E_{(m)}$ - " " covarient " vector space (space of Tensor rank 1)

S_m - symmetric group of degree m.

$Q_{k,m}$ - totality of strictly increasing sequences of k integers chosen from 1,....m. The number of such sequences, i.e. order of $Q_{k,m}$ is ${}^{m}C_{k}$.

$S_{k,m}$ - Totality of sequences of k integers chosen from 1,....m.

$G_{k,m}$ - Totality of non-decreasing sequences of integers chosen from 1,...m.

σ_γ - a sequence $\in \left\{Q_{k,m},\ S_m,\ S_{k,m},\ \text{or } G_{k,m}\right\}$

$\sigma_\gamma \equiv \left\{\sigma_{\gamma_1}, \ldots\ldots\ldots \sigma_{\gamma_k}\right\}$ each σ_{γ_i} being an integer, i.e. $\sigma_{\gamma_k} = i_k$.

Any vector $x_j \in E_{(m)}$ can be expressed as a linear sum

$x_j = \sum_{i=1}^{i=m} x_j^i \, e_i$ where $\left\{ e_i \right\} i = 1, \ldots\ldots m$ is a basis of $E_{(m)}$

where $x_j^i \quad i = 1, \ldots\ldots n$ are components of the covarient vector x_j.

In Dirac Notation, a covarient vector is symbolised by $\langle x_j |$ and a contravarient vector by $| x^j \rangle$.

The spaces $E^{(m)}$ and $E_{(m)}$ are called dual spaces, and a unique scalar can be associated with a pair of vectors, one from $E^{(m)}$ and one from $E_{(m)}$. This association is called a scalar product and is denoted by $\langle x_i \mid x^j \rangle$, and is defined in terms of components as:-

$$\langle x_i \mid x^j \rangle = \sum_k^m x_i^k \, x_k^j$$

The two spaces $E^{(m)}$ and $E_{(m)}$ are isomorphic and to every vector $\in E^{(m)}$ there is a vector associated with it in $E_{(m)}$, i.e.

These vectors are dual to each other, and the relationship between the components is:-

$$x_i^j = x_j^{i\,*}$$ where * indicates complex conjugate,

hence the scalar product $\langle x_i | x^j \rangle$ could be written as:-

$$\langle x_i | x^j \rangle = \sum_k^m x_i^k \, x_j^{k\,*}$$

A scalar product is also known as an Inner Product.

An Outer Product or Tensor Product, is symbolised by $\otimes$ and is defined as $W_{ij} = x_i \otimes x_j$, where the components of W_{ij} are $W_{ij}^{\;ke} = x_i^k x_j^e$. This is a covarient Tensor product and the space of all such products is denoted by $\otimes_2 E_{(m)}$, The contravarient tensor product is defined as:-

$W^{ij} = x^i \otimes x^j$, and the components are defined as:-

$W^{ij}{}_{ke} = x_k^i \, . \, x_e^j$, the space of all such products being $\otimes^2 E^{(m)}$

and the mixed contra-covarient product being

$W_j^i = x^i \otimes x_j$, the components are $W_{j\,e}^{i\,k} = x_e^i \, . \, x_j^k$, and the space of all products being $\otimes_1^1 E^{(m)}$. The spaces $\otimes^2 E^{(m)}$ and $\otimes_2 E_{(m)}$ are dual, and the space $\otimes_1^1 E^{(m)}$ is dual to itself, the tensor W_j^i being dual to W_i^j.

In general, a covarient Tensor space of rank p and dimension m is written as $\otimes_p E_{(m)}$ and is a p-linear map of the space $E_{(m)}$ and contains tensors of the form

$$W = x \otimes \dots \otimes x_p = \prod_1^p \otimes x_i \qquad W \in \otimes_p E_{(m)}$$

Similarly, the contravarient Tensor space of rank p and dimension m is written as $\otimes^p E^{(m)}$ and contains tensors of the form

$$W = x' \otimes \dots \otimes x^p = \prod_i^p \otimes x^i,$$

and the mixed Tensor product space of covarient rank p and contravarient rank q is written as $\otimes_p^q E^{(m)}$ and contains tensors of the form

$$W = x' \otimes \dots \otimes x^q \otimes y_1 \otimes \dots \otimes y_p .$$

From now on for the sake of simplicity, we will only refer to mixed spaces of the form $\otimes_p^p E^{(m)}$ i.e. equal contra- and covarient rank.

A basis for $\otimes^p E^{(m)}$ (whatever property $\otimes^p E^{(m)}$ has is reflected in $\otimes_p E_{(m)}$ and sometimes $\otimes_p^p E^{(m)}$).

can be formed by the M^p Tensors formed by the products

$$e^{\sigma_{\nu_1}} \otimes \dots \otimes e^{\sigma_{\nu_p}} = \prod_i^p \otimes e^{\sigma_{\nu_i}} \qquad \sigma_\nu \in S_{p,m}$$

and any Tensor $W \in \otimes^p E^{(m)}$ can be expressed uniquely as a linear sum

$$W = \sum_{\sigma_\nu \in S_{p,m}} w_{\sigma_\nu} \prod_i^p e^{\sigma_{\nu_i}} \quad , \text{ as } W \text{ is a tensor product}$$

then $W = x' \otimes \dots \otimes x^p$

and $W_{\sigma_\nu} = W_{\sigma_{\nu_1} \dots \sigma_{\nu_p}} = x^1_{\sigma_{\nu_1}} \cdot x^2_{\sigma_{\nu_2}} \dots x^p_{\sigma_{\nu_p}}$.

where $x^j_{\sigma_{\nu_i}}$ is the component of the j^{th} vector along the axis marked by the basis vector $e^{\sigma_{\nu_i}}$.

Each product $\prod_{i=1}^p \otimes e^{\sigma_{\nu_i}}$ can be thought of as denoting a particular tensor axis in the m-dimensional p-rank Tensor space $\otimes^p E^{(m)}$.

In Dirac Notation, a Tensor Product can be written as

$|x^1\rangle |x^2\rangle \ldots . |x^p\rangle ; \langle x^1|\langle x^2|\ldots . \langle x^p|$, or

$|x^1\rangle |x^2\rangle \ldots . |x^p\rangle \langle y^1|\langle y^2\ldots . \langle y^q|$ depending on

whether the products are contravarient, covarient or mixed.

The inner product between two tensors ω^j and $\omega_k \in \otimes^p E^{(m)}$ and $\otimes_p E_{(m)}$

is defined as

$$\langle \omega_j | \omega^k \rangle = \sum_{\sigma_\nu \in S_{p,m}} \omega_j^{\sigma_\nu} . \omega^k_{\sigma_\nu}$$

$$= \sum_{\sigma_\nu \in S_{p,m}} x_1^{\sigma_{\nu_1}} . x_2^{\sigma_{\nu_2}} \ldots . x_p^{\sigma_{\nu_p}} . y'_{\sigma_{\nu_1}} \ldots . y^p_{\sigma_{\nu_p}}$$

$$= \sum_{i}^{m} \ldots . \sum_{i_p}^{m} (x_{i_1}^{i_1} . y'_{i_1}) (x_2^{i_2} . y^2_{i_2}) \ldots . (x_p^{i_p} . y^p_{i_p})$$

$$= \langle x_1 | y' \rangle \ldots . \langle x_p | y^p \rangle$$

where $\omega_j = x_1 \otimes \ldots \otimes x_p$

and $\omega_k = y_1 \otimes \ldots . \otimes y_p$

Now if we define the basis vectors of $E^{(m)}$ and $E_{(m)}$ to have the

property $\langle e_i | e^j \rangle = \delta_i^j$ i.e. to be <u>orthonormal</u>

then the inner product between two bases Tensors $\in \otimes^p E^{(m)}$ and

$\otimes_p E_{(m)}$ is

$$\langle \pi_i^p \otimes e_{\sigma_{\nu_i}} | \pi_i^p \otimes e^{\mu_{\nu_i}} \rangle = \langle e_{\sigma_{\nu_1}} | e^{\mu_{\nu_1}} \rangle \ldots . \langle e_{\sigma_{\nu_p}} | e^{\mu_{\nu_p}} \rangle$$

$$= \delta^{\mu_{\nu_1}}_{\sigma_{\nu_1}} \ldots . \delta^{\mu_{\nu_p}}_{\sigma_{\nu_p}}$$

$$= \delta^{\mu_\nu}_{\sigma_\nu}$$

Thus the base tensors of $\otimes^p E^{(m)}$ and $\otimes_p E_{(m)}$ are orthonormal.

A basis for $\otimes_p^p E^{(m)}$ can be formed by the $[2m]^p$ Tensor products

$$e^{\sigma_{\nu_1}} \otimes \ldots . \otimes e^{\sigma_{\nu_p}} \otimes e_{\sigma_{\mu_1}} \otimes \ldots . e_{\sigma_{\nu_p}} = \pi_i^p \otimes e^{\sigma_{\nu_i}} \otimes \pi_i^p \otimes e_{\sigma_{\nu_i}} .$$

Then we see that $\otimes_p^p E^{(m)}$ can be decomposed as

$$\otimes_p^p E^{(m)} = \otimes^p E^{(m)} \otimes \otimes E_{(m)}$$

and any tensor $\in \otimes_p^p E^{(m)}$ as a product of tensors $x \otimes y$,

$x \in \otimes^p E^{(m)}$ and $y \in \otimes_p E_{(m)}$.

Any Tensor $\omega \in \otimes_p^p E^{(m)}$ can be expressed uniquely as a linear sum

$$\omega = \sum_{\sigma_\nu, \mu_\nu \in S_{p,m}} \omega_{\mu_\nu}^{\sigma_\nu} \prod_i^p \otimes e^{\mu_\nu i} \otimes \prod_i^p \otimes e_{\sigma_\nu i}$$

and $\omega_{\mu_\nu}^{\sigma_\nu} = \omega_{\mu_{\nu_1} \cdots \mu_{\nu p}}^{\sigma_{\nu_1} \cdots \sigma_{\nu p}} = x^1_{\mu_{\nu_1}} \cdot x^2_{\mu_{\nu_2}} \cdots x^p_{\mu_{\nu p}} \cdot y_1^{\sigma_{\nu_1}} \cdots y_p^{\sigma_{\nu p}}$

$$= (x^1_{\mu_{\nu_1}} \cdot y_1^{\sigma_{\nu_1}})(x^2_{\mu_{\nu_2}} \cdot y_2^{\sigma_{\nu_2}}) \cdots (x^p_{\mu_{\nu p}} \cdot y_p^{\sigma_{\nu p}})$$

Thus $\omega = Z_1 \otimes \cdots \otimes Z_p$ where $Z_i = x^i \otimes y_i$ and $Z_i \in \otimes_1^1 E^{(m)}$

The inner product in $\otimes_p^p E^{(m)}$ is defined as

$$\langle u | \omega \rangle = \sum_{\sigma_\nu, \mu_\nu \in S_{p,m}} u_{\mu_\nu}^{\sigma_\nu} \cdot \omega_{\sigma_\nu}^{\mu_\nu} \quad \text{where} \quad \langle u_{\mu_\nu}^{\sigma_\nu} | = | u_{\sigma_\nu}^{\mu_\nu} \rangle$$

$$= \sum_{i_1 \cdots i_p}^{m} \sum_{j_1 \cdots j_p}^{m} Z_{1 j_1}^{1 i_1} \cdot Z_{2 j_2}^{2 i_2} \cdots Z_{p j_p}^{p i_p} Q_{1 i_1}^{1 j_1} \cdots Q_{p i_p}^{p j_p}$$

$$= \sum_{i_1 \cdots i_p, j_1 \cdots j_p} (Z_{1 j_1}^{1 i_1} Q_{1 i_1}^{1 j_1}) \cdots (Z_{p j_p}^{p i_p} Q_{p i_p}^{p j_p})$$

$$= \langle Z_1^1 | Q_1^1 \rangle \cdots \langle Z_p^p | Q_p^p \rangle$$

and if $Z_i^i = x_i \otimes y^i$

and $Q_i^i = p^i \otimes q_i$

then $\langle Z_i^i | Q_i^i \rangle = \langle x_i | p^i \rangle \langle q_i | y^i \rangle$

and thus

$$\langle u | \omega \rangle = \langle x_1 | p^1 \rangle \langle q_1 | y^1 \rangle \cdots \langle x_p | p^p \rangle \langle q_p | y^p \rangle$$

and the inner product between base tensors gives

$$\langle \prod_i^p \otimes e_{\mu_{\nu i}} \otimes \prod_i^p \otimes e^{\sigma_{\nu i}} | \prod_i^p \otimes e^{\lambda_{\nu i}} \otimes \prod_i^p \otimes e_{\chi_{\nu i}} \rangle$$

$$= \langle e_{\mu_{\nu_1}} | e^{\lambda_{\nu_1}} \rangle \langle e_{\chi_{\nu_1}} | e^{\sigma_{\nu_1}} \rangle \cdots \langle e_{\mu_{\nu p}} | e^{\lambda_{\nu p}} \rangle \langle e_{\chi_{\nu p}} | e^{\sigma_{\nu p}} \rangle$$

$$= \delta_{\mu_{\nu_1}}^{\lambda_{\nu_1}} \cdot \delta_{\chi_{\nu_1}}^{\sigma_{\nu_1}} \cdots \delta_{\mu_{\nu p}}^{\lambda_{\nu p}} \cdot \delta_{\chi_{\nu p}}^{\sigma_{\nu p}}$$

$$= \delta_{\mu_\nu}^{\lambda_\nu} \cdot \delta_{\chi_\nu}^{\sigma_\nu} = \delta_{\mu_\nu \chi_\nu}^{\lambda_\nu \sigma_\nu}$$ so again the base tensors are orthonormal.

Another type of product can be defined in $\otimes_p^p E^{(m)}$ that

associates two Tensors $U, V \in \otimes_p^p E^{(m)}$ with a third $W \in \otimes_p^p E^{(m)}$

This product is called a Matrix Product and is defined as

$U.V = W$ where

$$W_{\sigma_\nu}^{\mu_\nu} = \sum_{\chi_\nu} U_{\sigma_\nu}^{\chi_\nu} V_{\chi_\nu}^{\mu_\nu} = \sum_{i_1 \ldots i_p}^{m} (Z_{1\sigma_{\nu_1}}^{1 i_1} . Q_{1 i_1}^{1 \mu_{\nu_1}}) \ldots . (Z_{p\sigma_{\nu_p}}^{p i_p} . Q_{p i_p}^{\mu_{\nu_p}})$$

where $Z_i^i, Q_i^i \in \otimes_1^1 E^{(m)}$

and if we define $R_i^i = Z_{i^o}^i Q_i^i$

then

$$W_{\sigma_\nu}^{\mu_\nu} = R_{1\sigma_{\nu_1}}^{1\mu_{\nu_1}} . R_{2\sigma_{\nu_2}}^{2\mu_{\nu_2}} \ldots\ldots\ldots R_{p\sigma_{\nu_p}}^{p\mu_{\nu_p}}$$

and thus $W = R_1^1 \otimes \ldots\ldots\ldots \otimes R_p^p$

The inner product $\langle U | V \rangle$ as defined in $\otimes_p^p E^{(m)}$ can be thought of as $\mathrm{Tr}\, W$, where $W = U.V$.

It is possible to define entities U, V, W, s.t.

$$U = \sum_{\substack{\sigma_\nu \\ \sigma_{\nu_\chi} \in S_{p,m}}} U_{\sigma_\nu} \prod_i^p \otimes e^{\sigma_{\nu_i}}$$

$$V = \sum_{\sigma_\nu \in S_{p,m}} V^{\sigma_\nu} \prod_i^p \otimes e_{\sigma_{\nu_i}}$$

$$W = \sum_{\sigma_\nu, \mu_\nu \in S_{p,m}} W_{\mu_\nu}^{\sigma_\nu} \prod_i^p \otimes e^{\mu_{\nu_i}} \otimes \prod_i^p \otimes e_{\sigma_{\nu_i}}$$

s.t. $U, V, W \in \otimes^p E^{(m)}, \otimes_p E_{(m)}$ and $\otimes_p^p E^{(m)}$

respectively, such entities U, V, W are not Tensors as they do not obey the Tensor Transformation Laws.

Only when

$$U_{\sigma_\nu} = x_{\sigma_{\nu_1}}^1 . x_{\sigma_{\nu_2}}^2 \ldots\ldots\ldots x_{\sigma_{\nu_p}}^p$$

$$V^{\sigma_\nu} = y_1^{\sigma_{\nu_1}} . y_2^{\sigma_{\nu_2}} \ldots\ldots\ldots y_p^{\sigma_{\nu_p}}$$

$$W_{\mu_\nu}^{\sigma_\nu} = Z_{1\mu_{\nu_1}}^{1\sigma_{\nu_1}} . Z_{2\mu_{\nu_2}}^{2\sigma_{\nu_2}} \ldots\ldots\ldots Z_{p\mu_{\nu_p}}^{p\sigma_{\nu_p}}$$

are U, V and W Tensors (as they then transform as Tensors).

LINEAR TRANSFORMATIONS

The spaces of l.t's that map $E^{(m)}$ onto $E^{(m)}$ and $E_{(m)}$ onto $E_{(m)}$ are denoted by $L(E^{(m)})$ and $L(E_{(m)})$ respectively. An l.t. that maps $x_i \in E_{(m)}$ into $y_i \in E_{(m)}$ is defined as having the following effect $y_i^j = \sum_k^m x_i^k u_k^j$ where $y = x.u$ and the elements of u are u_k^j, $u \in L(E_{(m)})$

and an l.t. that maps $x^i \in E^{(m)}$ into $y^i \in E^{(m)}$ is defined as $y_j^i = \sum_k^m u_j^k x_k^i$, $u \in L(E^{(m)})$

Every l.t. $\in L(E^{(m)})$ can be associated with an l.t. $\in L(E_{(m)})$ and the relationship is, if $u \in L(E^{(m)})$ and V is the corresponding l.t. $\in L(E_{(m)})$ then $u_j^i = V_i^{j*}$ or $u = V^+$

where $^+$ denotes the Hermetian transpose.

If we transform $E^{(m)}$ by u at the same time as we transform $E_{(m)}$ by w then

$$\langle xu \mid wy \rangle = \sum_i^m (xw)^i (wy)_i = \sum_i^m \sum_j^m \sum_k^m x^j u_j^i . w_i^k y_k$$

$$= \sum_j^m \sum_k^m \left\{ x^j \left(\sum_i^m u_j^i . w_i^k \right) y_k \right\}$$

Now if $\sum_i^m u_j^i w_i^k = \delta_j^k$ then the scalar product is equal to

$\sum_j^m x^j y_k = \langle x \mid y \rangle$ i.e. is left unchanged

We can see that δ_j^k can be thought of as the elements resulting from the Matrix product of u with w i.e.

$u.w = I$ where the element of $I = \delta_j^k$

I is known as the identity transformation and has the property of mapping vectors onto themselves.

When

$u.V = I$ where

$U \in L(E^{(m)})$, $V \in L(E_{(m)})$, then $U.V^{+} = I$

where $U \in L(E^{(m)})$ and $V^{+} \in L(E^{(m)})$

So we define $U^{-1}{}^{i}_{j} = V^{*j}_{i}$ thus $UU^{-1} = I$

where U, and $U^{-1} \in L(E^{(m)})$

Such a transformation U on $E^{(m)}$ and U^{-1+} on $E_{(m)}$ is known as a

Similarity Transformation.

If $U^{-1} = U^{+}_{,}$ (both $\in L(E^{(m)})$ then $UU^{+} = I$ we say that the transformation is Unitary.

The space $\otimes^{1}_{1} E^{(m)}$ is isomorphous to a subspace of $L(E^{(m)})$ and $L(E_{(m)})$, i.e. those l.t.s that can be decomposed into Tensor products from a subspace of $L(E^{(m)})$ and $L(E_{(m)})$.

Though all l.t.s can be expanded on the bases $\{e^{\mu_{\nu_1}} \otimes e^{\mu_{\nu_2}} \otimes e_{\sigma_{\nu_1}} \otimes e_{\sigma_{\nu_2}}\}$ for $L(E^{(m)})$

or the bases $\{e_{\mu_{\nu_1}} \otimes e_{\mu_{\nu_2}} \otimes e^{\sigma_{\nu_1}} \otimes e^{\sigma_{\nu_2}}\}$ for $L(E_{(m)})$ (as the bases are the same)

Where $\mu_\nu, \sigma_\nu \in S_{2,m}$, some are not Tensors.

Similarly l.t.s associated with $\otimes^{p} E^{(m)}$ i.e. $L(\otimes^{p} E^{(m)})$ and those associated with $\otimes_{p} E_{(m)}$ i.e. $L(\otimes_{p} E_{(m)})$ can be expanded on the bases

$$\left\{ \prod_{i}^{p} \otimes e^{\mu_{\nu_i}} \otimes \prod_{i}^{p} \otimes e_{\sigma_{\nu_i}} \right\} \equiv \left\{ \prod_{i}^{p} \otimes e_{\mu_{\nu_i}} \otimes \prod_{i}^{p} \otimes e^{\sigma_{\nu_i}} \right\}$$

respectively, but not all are Tensors.

Thus, any l.t. $U \in L(\otimes^{p} E^{(m)})$ and $L(\otimes_{p} E_{(m)})$ can be expanded so $U = \sum_{\sigma_\nu} \sum_{\mu_\nu} U^{\mu_\nu}_{\sigma_\nu} \cdot \prod_{i}^{p} \otimes e^{\sigma_{\nu_i}} \otimes \prod_{i}^{p} \otimes e_{\mu_{\nu_i}}$.

A sufficient condition for $U \in L(\otimes^{p} E^{(m)})$ and $L(\otimes_{p} E_{(m)})$ is that

$$U^{\mu_{\nu_1}}_{1\sigma_{\nu_1}} \cdot U^{\mu_{\nu_2}}_{2\sigma_{\nu_2}} \cdots\cdots U^{\mu_{\nu_p}}_{p\sigma_{\nu_p}} = U^{\mu_\nu}_{\sigma_\nu}$$

Transformations that do not have such a property might map tensors $\in \otimes^{p} E^{(m)}$ or $\otimes_{p} E_{(m)}$ into entities that have Non-Tensor character.

When $U = U_1 \otimes U_2 \otimes \ldots\ldots \otimes U_p$

then $U \in L(\otimes^p E^{(m)}),\ L(\otimes_p E_{(m)})$

where $U^{\sigma_\nu}_{\mu_\nu} = U_1{}^{\mu_{\nu_1}}_{\sigma_{\nu_1}} \cdot U_2{}^{\mu_{\nu_2}}_{\sigma_{\nu_2}} \ldots\ldots U_p{}^{\mu_{\nu_p}}_{\sigma_{\nu_p}}$,

and only when all the constituent l.t's $\in \otimes'_1 E^{(m)}$ does $U \in \otimes^p_p E^{(m)}$.

Thus we have all linear transformations defined on the basis

$\left\{ \prod_i^{p\otimes} e^{\sigma_{\nu_i}} \otimes \prod_i^{p\otimes} e_{\mu_{\nu_i}} \right\}$ forming the space $GL(\otimes^p E^{(m)})$,

then we have those transformations that map $\otimes^p E^{(m)}$ onto $\otimes^p E^{(m)}$ forming the subspace $L(\otimes^p E^{(m)})$ of $GL(\otimes^p E^{(m)})$ and we have those l.t's. $\in L(\otimes^p E^{(m)})$ that are Tensors, which form a subspace of $L(\otimes^p E^{(m)})$ viz. $\otimes^p_p E^{(m)}$.

The matrix product between l.t's $\in L(\otimes^p E^{(m)})$ being defined as

$W = U.V.$

then

$$W^{\mu_\nu}_{\sigma_\nu} = \sum_{\substack{\chi_\nu \\ \chi_\nu \in S_{p,m}}} U^{\chi_\nu}_{\sigma_\nu} \cdot V^{\mu_\nu}_{\chi_\nu} .$$

and an inner product between l.t's can be defined as

$\langle U|V\rangle,\ U \in L(\otimes_p E_{(m)}),\ V \in L(\otimes^p E^{(m)})$

where $\langle U|V\rangle = \sum_{\sigma_\nu} \sum_{\substack{\mu_\nu \\ \sigma_\nu, \mu_\nu \in S_{p,m}}} U^{\sigma_\nu}_{\mu_\nu} \cdot V^{\mu_\nu}_{\sigma_\nu} = \sum_{\sigma_\nu} \sum_{\substack{\mu_\nu \\ \sigma_\nu, \mu_\nu \in S_{p,m}}} U^{\mu_\nu}_{\sigma_\nu} \cdot V^{\mu_\nu}_{\sigma_\nu}$

$U^+ \in L(\otimes^p E^{(m)})$ and $U^{+\sigma_\nu}_{\mu_\nu} = U^{\mu_\nu}_{\sigma_\nu}$.

Symmetric and Antisymmetric Tensors

If the linear mapping $\Pi_A = \frac{1}{p!} \sum_\sigma \varepsilon_\sigma \underline{\sigma}$ is defined where $\underline{\sigma} \in \underline{S}_p$ (S_p is the full symmetric group and $\underline{\sigma}$ is a permutation operator $\in \underline{S}_p$ with effect $\sigma_\nu\ (e_1 \otimes \ldots \otimes e_p) = e_{\sigma_{\nu_1}} \otimes \ldots \otimes e_{\sigma_{\nu_p}}$, , and ε_σ is the parity of the permutation).

Then the mapping $\Pi_A : \otimes^p E^{(m)}$ i.e. Π_A on every element of $\otimes^p E^{(m)}$ defines a subspace of $\otimes^p E^{(m)}$ that contains only antisymmetric tensors.

Π_A is a projection operator i.e. $\Pi_A^2 = \Pi_A$ and is known as the

Alternator or Antisymmetry Operator.

If $x \in \otimes^p E^{(n)}$ then $\Pi_A x$ is the antisymmetric part of x.

If $\Pi_A x = x$ then the Tensor is antisymmetric.

The inner product of antisymmetric parts of tensors, or antisymmetric tensors is given by

$$\langle \Pi_A (x_1 \otimes \ldots \otimes x_p) \mid \Pi^A (y^1 \otimes \ldots \otimes y^p) \rangle = \langle \Pi_A^2 (x_1 \otimes \ldots \otimes x_p) \mid y^1 \otimes \ldots \otimes y^p \rangle$$

$$= \langle \Pi_A (x_1 \otimes \ldots \otimes x_p) \mid y^1 \otimes \ldots \otimes y^p \rangle = \frac{1}{p!} \operatorname{Det} (\langle x_i \mid y^j \rangle)$$

If the linear mapping $\Pi_S = \frac{1}{p!} \sum_{\sigma \in S_p} \sigma$ is defined

then the mapping $\Pi_S \mid \otimes^p E^{(n)}$ defines a subspace of $\otimes^p E_{(n)}$ that contains only symmetric tensors; Π_S is also a projection operator $\Pi_S^2 = \Pi_S$ and is known as the symmetriser or Symmetry Operator.

If $x \in \otimes^p E^{(n)}$ then $\Pi_S x$ is the symmetric part of x and if $x = \Pi_S x$ then x is a symmetric tensor., and the inner product of the symmetric parts of two tensors or symmetric tensors $\in \otimes^p E^{(n)}$ and $\otimes^p E_{(n)}$ is given by

$$\langle \Pi_S (x_1 \otimes \ldots \otimes x_p) \mid \Pi^S (y^1 \otimes \ldots \otimes y^p) \rangle = \frac{1}{p!} \operatorname{Perm} (\langle x_i \mid y^j \rangle)$$

where Perm $\equiv$ Permanent, known sometimes as a positive Determinant, is defined as $\sum_{\sigma \in S_p} \sigma \, a_1^{\nu_1} a_2^{\nu_2} \ldots a_p^{\nu_p} = \operatorname{Perm}(A)$

where A is a $p \times p$ block of numbers with $(j, \nu_i)^{th}$ element $a_j^{\nu_i}$ $\quad j$ = row

ν_i = column

The Determinant is defined as

$$\sum_{\sigma \in S_p} \varepsilon_\sigma a_1^{\nu_1} a_2^{\nu_2} \ldots a_p^{\nu_p} = \operatorname{Det}(A)$$

where A is again a $p \times p$ block of numbers with $(j, \nu_i)^{th}$ element $a_j^{\nu_i}$.

The Antisymmetric subspace of $\otimes^p E^{(n)}$ is denoted by $\wedge^p (E^{(n)})$ and

the symmetric subspace as $Y^p(E^{(m)})$.

Hence $X^p(E^{(m)}) = I_m \pi^A$ (I_m = Image)

$Y^p(E^{(m)}) = I_m \pi^S$ where π^A and π^S are mappings defined on $\otimes^p E^{(m)}$.

A Tensor can be described completely by the sum of its symmetric and antisymmetric parts, i.e. if $x \in \otimes^p E^{(m)}$ then $x = \pi^A x + \pi^S x$

Thus $\pi^A + \pi^S = I$ (the identity map)

and $\otimes^p E^{(m)} = Y^p(E^{(m)}) + X^p(E^{(m)})$.

Exterior Powers

A skew-symmetric p-linear mapping of $E^{(m)}$ is called the p^{th} Exterior power of $E^{(m)}$ and is described by $\Lambda^p E^{(m)}$, The tensors $\in \Lambda^p E^{(m)}$ are exterior powers of the vector $\in E^{(m)}$. i.e.

If $\omega \in \Lambda^p E^{(m)}$ then $\omega = x^1 \wedge x^2 \ldots\ldots \wedge x^p$,

a basis for $\Lambda^p E^{(m)}$ can be formed from the basis of $E^{(m)}$ i.e.

$$\frac{1}{p!^{1/2}} \left\{ e^{\sigma_{\nu_1}} \wedge \ldots\ldots \wedge e^{\sigma_{\nu_p}} \right\} = \frac{1}{p!^{1/2}} \prod_i^p \wedge e^{\sigma_{\nu_i}}$$

where $\sigma_\nu \in Q_{p,m}$. The number of such sequences is ${}^mC_p$, thus there are ${}^mC_p$ bases Tensors in $\Lambda^p E^{(m)}$.

Any Tensor $\omega \in \Lambda^p E^{(m)}$ can be expressed uniquely as a linear sum

$$\omega = \sum_{\sigma_\nu \in Q_{p,m}} \omega_{\sigma_\nu} \frac{1}{p!^{1/2}} \prod_i^p \wedge e^{\sigma_{\nu_i}}$$

where $\omega_{\sigma_\nu} = (x^1 \wedge x^2 \ldots \wedge x^p)_{\sigma_{\nu_1} \sigma_{\nu_2} \ldots \sigma_{\nu_p}} = \frac{1}{p!^{1/2}} \text{Det} \begin{bmatrix} x^1_{\sigma_{\nu_1}} & \ldots\ldots & x^1_{\sigma_{\nu_p}} \\ \vdots & & \vdots \\ x^p_{\sigma_{\nu_1}} & \ldots\ldots & x^p_{\sigma_{\nu_p}} \end{bmatrix}$

and hence $\omega = x^1 \wedge x^2 \wedge \ldots\ldots x^p$.

ω_{σ_ν}'s that cannot be decomposed in this fashion correspond to ω's that are not <u>Tensors</u> $\in \Lambda^p E^{(m)}$.

The inner product between $U = x_1 \wedge \ldots\ldots \wedge x_p \in \Lambda_p E_{(m)}$ and $V = y^1 \wedge \ldots\ldots \wedge y^p \in \Lambda^p E^{(m)}$ is given by

$$\langle U|V\rangle = \langle x_1 \wedge \ldots \wedge x_p | y^1 \wedge \ldots \wedge y^p \rangle = \frac{1}{p!} \mathrm{Det}\,[\langle x_i | y^j \rangle]$$

and thus the scalar products between bases Tensors are given by:-

$$\frac{1}{p!}\left\langle \bigwedge_i^p e_{\mu\nu_i} \middle| \prod_i^p e^{\sigma\nu_i} \right\rangle = \frac{1}{p!} \mathrm{Det}\,(\langle e_{\mu\nu_i} | e^{\sigma\nu_i}\rangle) = \frac{1}{p!} \mathrm{Det}\,(\delta^{\sigma\nu_i}_{\mu\nu_j}) = \delta^{\sigma\nu}_{\mu\nu}.$$

A very important property of exterior products is that if the set of vectors $\{x_1, \ldots x_p\}$ are l.d. then $x_1 \wedge \ldots \wedge x_p = 0$.

Symmetric Tensor Product

A symmetric p-linear mapping of $E^{(m)}$ is called the p^{th} symmetric power of $E^{(m)}$ and is denoted by $V^p E^{(m)}$. The elements of $V^p E^{(m)}$ are symmetric powers of vectors $\in E^{(m)}$ viz.

$$W = x^1 V \ldots\ldots V x^p \qquad W \in V^p E^{(m)}.$$

The base Tensors of $V^p E^{(m)}$ can be defined as

$$\frac{1}{p!^{1/2}\sqrt{M(\sigma_\nu)}}\, e^{\sigma\nu_1} V \ldots\ldots e^{\sigma\nu_p} = \frac{1}{p!^{1/2}\sqrt{M(\sigma_\nu)}} \prod_{i=1}^{p} V\, e^{\sigma\nu_i}.$$

$\sigma_\nu \in C_{p,m}$ i.e. σ_ν are ordered sequences,

and each Tensor $\in V^p E^{(m)}$ can be expressed uniquely as a linear sum

$$W = \sum_{\nu=1}^{\nu=\binom{m+p-1}{m}} W_{\sigma\nu} \prod_i^p V\, e^{\sigma\nu_i} \cdot \frac{1}{\sqrt{M(\sigma_\nu)}\, p!^{1/2}}$$

Each component $W_{\sigma\nu}$ can be expressed in terms of the components of the vectors $\in W$, i.e. where $W = x^1 \wedge \ldots\ldots \wedge x^p$

$$W^{\sigma_\nu} = W^{\sigma\nu_1 \ldots \sigma\nu_p} = \frac{1}{\sqrt{M(\sigma_\nu)}} \cdot \frac{1}{p!}\, \mathrm{Perm} \begin{bmatrix} x^1_{\sigma\nu_1} & \cdots & x^p_{\sigma\nu_1} \\ \vdots & & \vdots \\ x^1_{\sigma\nu_p} & \cdots & x^p_{\sigma\nu_p} \end{bmatrix} = (x^1 V x^2 \ldots V x^p)_{\sigma\nu_1 \ldots \sigma\nu_p}$$

where $M(\sigma_\nu)$ is the multiplicity of the sequence which is defined as the product of the number of times any one integer appears in the sequence, viz.

If the sequence was $\sigma_\nu = (\sigma\nu_1 \ldots \sigma\nu_p) = (\underbrace{i_1, i_1, \ldots i_1}_{p/3}\ \underbrace{i_2 \ldots i_2}_{p/3}\ \underbrace{i_3 \ldots i_3}_{p/3})$

$$i_1 < i_2 < i_3 \qquad \text{(as they are different)}$$

then $M(\sigma_\nu) = \frac{p}{3} \cdot \frac{p}{3} \cdot \frac{p}{3} = \frac{p^3}{9}$

The inner product between $V \in V^p E^{(m)}$ and $U \in V_p E_{(m)}$ is given by

$$\langle u|v\rangle = \langle x_1 V \ldots V x_p | y' V \ldots V y^p \rangle = \frac{1}{p!\sqrt{M_x M_y}} \text{Perm}\left[\langle x_i | y^j \rangle\right]$$

M_x = number of repeated vectors in x

M_y = " " " " " y

and the scalar product between bases Tensors is thus

$$\frac{1}{p!\sqrt{M(\sigma_\nu)M(\mu_\nu)}} \left\langle \bigwedge_i^p e_{\sigma_{\nu i}} \middle| \bigwedge_i^p e^{\mu_{\nu i}} \right\rangle = \frac{1}{p!\sqrt{M(\sigma_\nu)M(\mu_\nu)}} \text{Perm}\left[\langle e_{\sigma_{\nu i}} | e^{\mu_{\nu i}} \rangle\right]$$

$$= \frac{1}{p!\sqrt{M(\sigma_\nu)M(\mu_\nu)}} \text{Perm}\left[\delta^{\mu_{\nu i}}_{\sigma_{\nu i}}\right]$$

$$= \delta^{\mu_\nu}_{\sigma_\nu}$$

The difference between $X^p(E^{(m)})$ and $\Lambda^p(E^{(m)})$ and $Y^p(E^{(m)})$ and $V^p(E^{(m)})$ being that X^p and Y^p are reducible while $\Lambda^p(E^{(m)})$ and $V^p(E^{(m)})$ are not.

Mixed Exterior and Symmetric Tensors

The tensor product between tensors $\in \Lambda^p E^{(m)}$ and those $\in \Lambda_p E_{(m)}$ defines a space $\Lambda^p_p E^{(m)} = \Lambda^p E^{(m)} \otimes \Lambda_p E_{(m)}$ that contains tensors ω of the form

$$\omega = x' \wedge \ldots \wedge x^p \otimes y_1 \wedge \ldots y_p$$

The bases of such a space can be defined as

$$\frac{1}{p!} \left\{ \bigwedge_i^p e^{\sigma_{\nu i}} \otimes \bigwedge_i^p e_{\sigma_{\mu i}} \right\} \quad \sigma_\mu, \sigma_\nu \in Q_{p,m}$$

Any tensor $\omega \in \Lambda^p_p E^{(m)}$ can be expanded with reference to this basis:-

$$\omega = \sum_{\substack{\sigma_\nu, \mu_\nu \\ \mu_\nu, \sigma_\nu \in Q_{p,m}}} \omega^{\sigma_\nu}_{\sigma_\nu} \cdot \frac{1}{p!} \bigwedge_i^p e^{\sigma_{\mu i}} \otimes \bigwedge_i^p e_{\sigma_{\nu i}}$$

and $W^{\sigma_\nu}_{\mu_\nu}$ must be of the form

$$(x'\wedge\ldots\wedge x^\rho)_{\sigma_{\nu_1}\ldots\sigma_{\nu_\rho}}\cdot(y_1\wedge\ldots\wedge y_\rho)^{\sigma_{\nu_1}\ldots\sigma_{\mu_\rho}} \quad \text{i.e.}$$

$$W^{\sigma_\nu}_{\sigma_\mu} = \frac{1}{\rho!}\,\mathrm{Det}\begin{bmatrix} x'^{\sigma_{\nu_1}} & \ldots & x'^{\sigma_{\nu_\rho}} \\ \vdots & & \vdots \\ x^\rho_{\sigma_{\mu_1}} & \ldots & x^\rho_{\sigma_{\mu_\rho}} \end{bmatrix}\cdot\mathrm{Det}\begin{bmatrix} y_1^{\sigma_{\nu_1}} & \ldots & y_1^{\sigma_{\nu_\rho}} \\ \vdots & & \vdots \\ y_\rho^{\sigma_{\nu_1}} & \ldots & y_\rho^{\sigma_{\nu_\rho}} \end{bmatrix}$$

and components with such a property are components of Tensors $\in \Lambda^\rho_\rho E^{(m)}$

Inner and Matrix products are defined in an equivalent manner to that in $\bigotimes^\rho_\rho E^{(m)}$ viz.

$$\langle u|v\rangle = \sum_{\sigma_\nu}\sum_{\sigma_\mu,\,\sigma_\nu,\sigma_\mu\in Q_{\rho,m}} u^{\sigma_\nu}_{\sigma_\mu}\cdot V^{\sigma_\mu}_{\sigma_\nu}$$

and $w = u.v$ where

$$W^{\sigma_\rho}_{\sigma_\nu} = \sum_{\sigma_\chi\,\sigma_\mu,\sigma_\nu\in Q_{\rho,m}} u^{\sigma_\chi}_{\sigma_\nu}\cdot V^{\sigma_\mu}_{\sigma_\chi}$$

In an equivalent manner the space $V^\rho_\rho E^{(m)} = V^\rho E^{(m)}\otimes V_\rho E_{(m)}$ can be defined, and tensors $W\in V^\rho_\rho E^{(m)}$ are of the form

$$W = x'\vee\ldots\vee x^\rho\otimes y_1\vee\ldots\vee y_\rho$$

and the base is of the form

$$\frac{1}{\rho!\sqrt{M(\sigma_\mu)M(\sigma_\nu)}}\left\{\prod_i^\rho{}^{\vee} e^{\sigma_{\nu i}}\otimes\prod_i^\rho{}^{\vee} e_{\sigma_{\nu i}}\right\}\quad \sigma_\nu,\sigma_\mu\in G_{\rho,m}$$

Thus any $W\in V^\rho_\rho E^{(m)}$ can be expanded in the form

$$W = \sum_{\sigma_\nu,\mu_\nu\in G_{\rho,m}} W^{\sigma_\nu}_{\mu_\nu}\prod_i^\rho{}^{\vee} e^{\sigma_{\mu i}}\otimes\prod_i^\rho{}^{\vee} e_{\sigma_{\nu i}}$$

where the components must be of the form

$$W^{\sigma_\nu}_{\mu_\nu} = \frac{1}{\rho!\sqrt{M(\sigma_\nu)M(\mu_\nu)}}\,\mathrm{Perm}\begin{bmatrix} x'^{\sigma_{\nu_1}} & \ldots & x'^{\sigma_{\nu_\rho}} \\ \vdots & & \vdots \\ x^\rho_{\sigma_{\mu_1}} & \ldots & x^\rho_{\sigma_{\mu_\rho}} \end{bmatrix}\cdot\mathrm{Perm}\begin{bmatrix} y_1^{\sigma_{\nu_1}} & \ldots & y_1^{\sigma_{\nu_\rho}} \\ \vdots & & \vdots \\ y_\rho^{\sigma_{\nu_1}} & \ldots & y_\rho^{\sigma_{\nu_\rho}} \end{bmatrix}$$

and the Matrix and Inner products being defined equivalently to the other two cases.

<u>Exterior and Symmetric Products of Linear Transformations</u>

We define only the simplest case i.e.

$W = \underbrace{u\wedge u\wedge\ldots\wedge u}_{\rho}$ and $W = \underbrace{u\vee\ldots\vee u}_{\rho}$ where

$u\in L(E^{(m)})$ or $L(E_{(m)})$, then W in the first case $\in L(\Lambda^\rho E^{(m)})$

or $L(\Lambda_p E_{(m)})$ and in the second to $L(V^p E^{(m)})$ or $L(V_p E_{(m)})$

The components of $W = u \wedge \ldots\ldots \wedge u$ are given by

$$W^{\sigma_\nu}_{\sigma_\mu} = \underset{\sigma_\nu, \sigma_\mu \in Q_{p,m}}{} \text{Det} \begin{bmatrix} u^{\sigma_{\nu_1}}_{\sigma_{\mu_1}} & u^{\sigma_{\nu_2}}_{\sigma_{\mu_1}} & \ldots & u^{\sigma_{\nu_p}}_{\sigma_{\mu_1}} \\ \vdots & & & \vdots \\ u^{\sigma_{\nu_1}}_{\sigma_{\mu_p}} & \ldots\ldots & & u^{\sigma_{\nu_p}}_{\sigma_{\mu_p}} \end{bmatrix}$$

Any $W \in L(\Lambda^p E^{(m)})$ can be expanded so:-

$$W = \sum_{\sigma_\nu, \sigma_\mu \in Q_{p,m}} \sum_{\sigma_\mu} W^{\sigma_\nu}_{\sigma_\mu} \frac{1}{p!} \prod_i^p \wedge e^{\sigma_\mu} \otimes \prod_i^p \wedge e_{\sigma_{\nu_i}}$$

but only certain forms of $W^{\sigma_\nu}_{\mu_\nu}$ are allowable. For ones $\in L(\Lambda^p E^{(m)})$ the above one is the simplest, when W is made up of an exterior product of p 1.t's that are all the same.

The components of $W = u v \ldots\ldots v u$ are given by:-

$$W^{\sigma_\nu}_{\sigma_\mu} = \frac{1}{\sqrt{M(\sigma_\nu) M(\mu_\nu)}} \text{Perm} \begin{bmatrix} u^{\sigma_{\nu_1}}_{\sigma_{\mu_1}} & \ldots\ldots & u^{\sigma_{\nu_p}}_{\sigma_{\mu_1}} \\ \vdots & & \vdots \\ u^{\sigma_{\nu_1}}_{\sigma_{\mu_p}} & \ldots\ldots & u^{\sigma_{\nu_p}}_{\sigma_{\mu_p}} \end{bmatrix} \sigma_\nu, \sigma_\mu \in G_{p,m}$$

and any $W \in L(V^p E^{(m)})$ can be expanded so:-

$$W = \sum_{\sigma_\nu, \mu_\nu \in G_{p,m}} \sum_{\mu_\nu} W^{\sigma_\nu}_{\sigma_\mu} \frac{1}{p! \sqrt{M(\sigma_\mu) M(\sigma_\nu)}} \prod_i^p K e^{\sigma_{\mu_i}} \otimes \prod_i^p v e_{\sigma_{\nu_i}}$$

again with the above qualification.

The Matrix products are defined in an analagous way to that of 1.t's

$\in L(\otimes^p E^{(m)})$ or $L(\otimes_p E_{(m)})$.

Three important relationships follow from the properties of 1.t's previously discussed.

1. $u^1 x^1 \otimes u^2 x^2 \otimes \ldots\ldots \otimes u^p x^p = (u^1 \otimes \ldots\ldots \otimes u^p)(x^1 \otimes \ldots\ldots \otimes x^p)$

where $u^1 \ldots\ldots u^p \in L(E^{(m)})$

and $x^1, \ldots\ldots x^p \in E^{(m)}$

2. $u x^1 \wedge u x^2 \ldots\ldots \wedge u x^p = (\underbrace{u \wedge u \wedge \ldots\ldots \wedge u}_{p \rightarrow})(x^1 \wedge \ldots\ldots \wedge x^p)$

where $u \in L(E^{(m)})$ and $x^i \in E^{(m)}$.

$$3\cdot\, u x^1 \vee u x^2 \vee \ldots\ldots \vee u x^p = \underbrace{(u \vee u \vee \ldots\ldots \vee u)}_{p}(x^1 \vee \ldots\ldots \vee x^p)$$

$$u \in L(E^{(m)})$$
$$x^i \in E^{(m)}.$$

Contraction

An operation that can be defined over a mixed Tensor product space is one of contraction, which is a $(P + P)$- linear mapping of $\otimes^p_p E^{(m)}$ onto $\otimes^{p-1}_{p-1} E^{(m)}$.

The contraction operator is denoted by C^j_i and has the following effect:-

$$C^j_i [x^1 \otimes x^2 \otimes \ldots\ldots \otimes x^p \otimes y_1 \otimes \ldots\ldots \otimes y_p] = \langle x^j | y_i \rangle x^1 \otimes \ldots \otimes \hat{x}^j \otimes \ldots x^p \otimes y_p \otimes \ldots \otimes \hat{y}_i \otimes \ldots$$

C^j_i is called the contraction operator with respect to the pair (i,j).

when $j = i =$ we p/denote the operation by $C\,(= C^{p)}_{p\cdot})$

The contraction of the Tensor $u \in \otimes^p_p E^{(m)}$ is given by the expansion

$$C^j_i [u] = \sum_{\sigma_\nu, \sigma_\mu \in S_{p-1,m}} w^{\sigma_{\nu_1} \ldots \sigma_{\nu_{p-1}}}_{\sigma_{\mu_1} \ldots \sigma_{\mu_{p-1}}} \prod_i^p \otimes e^{\sigma_{\mu_i}} \otimes \prod_i^p \otimes e_{\sigma_{\nu_i}} \quad \therefore C^j_i [u] = w \in \otimes^{p-1}_{p-1} E^{(m)}$$

where $w^{\sigma_{\nu_1} \ldots \sigma_{\nu_{p-1}}}_{\sigma_{\mu_1} \ldots \sigma_{\mu_{p-1}}} = \sum_k^m u^{\sigma_{\nu_1} \ldots \sigma_{\nu_{p-1}} k}_{\sigma_{\mu_1} \ldots \sigma_{\mu_{p-1}} k}$

as $u^{\sigma_{\nu_1} \ldots \sigma_{\nu_p}}_{\sigma_{\mu_1} \ldots \sigma_{\mu_p}} = x^1_{\sigma_{\mu_1}} x^2_{\sigma_{\mu_2}} \ldots x^p_{\sigma_{\mu_p}} \cdot y_1^{\sigma_{\nu_1}} \ldots y_p^{\sigma_{\nu_p}}$

then $w^{\sigma_{\nu_1} \ldots \sigma_{\nu_{p-1}}}_{\sigma_{\mu_1} \ldots \sigma_{\mu_{p-1}}} = \sum_k x^1_{\sigma_{\mu_1}} \cdot x^2_{\sigma_{\mu_2}} \cdot \hat{x}^j_{\sigma_{\mu_j}} \cdot x^p_{\sigma_{\mu_{p-1}}} \cdot y_1^{\sigma_{\nu_1}} \ldots \hat{y}_1^{\sigma_{\nu_i}} \ldots y_p^{\sigma_{\nu_{p-1}}} \cdot x^j_k \cdot y^k_i$.

Contraction operators can also be defined to map $\wedge^p_p E^{(m)}$ onto $\wedge^{p-1}_{p-1} E^{(m)}$ and $V^p_p E^{(m)}$ onto $V^{p-1}_{p-1} E^{(m)}$ but no particular vectors that make up the exterior, or symmetric product can be chosen to be contracted out, thus all contractions are denoted by C.

If $Z \in \wedge^p_p E^{(m)}$ then $W = C[Z] \in \wedge^{p-1}_{p-1} E^{(m)}$ has the components $w^{\sigma_{\nu_1} \ldots \ldots \sigma_{\nu_{p-1}}}_{\sigma_{\mu_1} \ldots \ldots \sigma_{\mu_{p-1}}}$ where σ_ν and $\sigma_\mu \in Q_{p-1,m}$ and the components are defined as:-

$$W^{\sigma_{\nu_1}\ldots\sigma_{\nu_{p-1}}}_{\sigma_{\mu_1}\ldots\sigma_{\mu_{p-1}}} = \sum_k^m Z^{k\sigma_{\nu_1}\ldots\sigma_{\nu_{p-1}}}_{k\sigma_{\mu_1}\ldots\sigma_{\mu_{p-1}}}$$

i.e. if $Z = x^1 \wedge \ldots \wedge x^p \otimes y_1 \wedge \ldots \wedge y_p$

then

$$W^{\sigma_{\nu_1}\ldots\sigma_{\nu_{p-1}}}_{\sigma_{\mu_1}\ldots\sigma_{\mu_{p-1}}} = \frac{1}{p!} \sum_{\substack{k \\ \sigma_\nu, \sigma_\mu \in Q_{p-1,m}}}^m \mathrm{Det}\begin{bmatrix} x^1_k & x^1_{\sigma_{\nu_1}} & \ldots & x^1_{\sigma_{\nu_{p-1}}} \\ \vdots & & & \vdots \\ x^p_k & x^p_{\sigma_{\nu_1}} & \ldots & x^p_{\sigma_{\nu_{p-1}}} \end{bmatrix}_s . \mathrm{Det}\begin{bmatrix} y_1^k & y_1^{\sigma_{\nu_1}} & \ldots & y_1^{\sigma_{\mu_{p-1}}} \\ \vdots & & & \vdots \\ y_p^k & y_p^{\sigma_{\mu_1}} & \ldots & y_p^{\sigma_{\mu_{p-1}}} \end{bmatrix}$$

and similarly if $Z \in V_p^p E^{(m)}$ then $W = c[Z] \in V_{p-1}^{p-1} E^{(m)}$

where W has the components $W^{\sigma_{\nu_1}\ldots\sigma_{\nu_{p-1}}}_{\sigma_{\mu_1}\ldots\sigma_{\mu_{p-1}}}$ $\sigma_\nu, \sigma_\mu \in G_{p-1,m}$ and

and the components are defined as

$$W^{\sigma_{\nu_1}\ldots\sigma_{\nu_{p-1}}}_{\sigma_{\mu_1}\ldots\sigma_{\mu_{p-1}}} = \sum_k^m Z^{k\sigma_{\nu_1}\ldots\sigma_{\nu_{p-1}}}_{k\sigma_{\mu_1}\ldots\sigma_{\mu_{p-1}}}, \text{ again if } Z = x^1 \vee \ldots x^p \vee \otimes y_1 \vee \ldots \vee y_p$$

then

$$W^{\sigma_{\nu_1}\ldots\sigma_{\nu_{p-1}}}_{\sigma_{\mu_1}\ldots\sigma_{\mu_{p-1}}} = \frac{1}{p!} \sum_k^m \frac{1}{\sqrt{M(\sigma_\nu : k) M(\sigma_\mu : k)}} \mathrm{Perm}\begin{bmatrix} x^1_k & x^1_{\sigma_{\nu_1}} & \ldots & x^1_{\sigma_{\nu_{p-1}}} \\ \vdots & & & \vdots \\ x^p_k & x^p_{\sigma_{\nu_1}} & \ldots & x^p_{\sigma_{\nu_{p-1}}} \end{bmatrix} . \mathrm{Perm}\begin{bmatrix} y_1^k & y_1^{\sigma_{\mu_1}} & \ldots & y_1^{\sigma_{\mu_{p-1}}} \\ \vdots & & & \vdots \\ y_p^k & y_p^{\sigma_{\mu_1}} & \ldots & y_p^{\sigma_{\mu_{p-1}}} \end{bmatrix}$$

where $\sigma_\nu, \sigma_\mu \in G_{p-1,m}$ but $\sigma_\nu : k, \sigma_\mu : k \in G_{p,m}$ and are the

sequences

$$\sigma_\nu : k = \{ k\sigma_{\nu_1} \ldots \sigma_{\nu_{p-1}} \}$$

$$\sigma_\mu : k = \{ k\sigma_{\mu_1} \ldots \sigma_{\mu_{p-1}} \}$$

Multilinear Functions as Tensors

If we consider the contravarient space $T^{(\infty)}$ and the covarient space $T_{(\infty)}$ of all continuous vectors, i.e. linear functions, we see that the bases linear functions can be $\{\delta(X - X')\}$ over all X' where $\delta(X - X')$ is a dirac delta function and has the property

$$\int f(X)\delta(X - X')dx = f(X'), \text{ and } \delta(X - X') = 1 \text{ if } X = X'$$
$$= 0 \text{ if } X \neq X'$$

Then any function $f^i \in T^{(\infty)}$ can be expanded as

$$f^i = \int f^i(X')\delta(X - X')dx'.$$

Inner products between elements of $T^{(\infty)}$ and $T_{(\infty)}$ are defined as:-

$$\langle f_i(x) | g^j(y) \rangle = \int f_i(x) g^j(x)\, dx$$

and each element of $T^{(\infty)}$ is associated with a unique element of $T_{(\infty)}$

viz. $g^j(y) \in T^{(\infty)} \sim g_i(y)^* \in T_{(\infty)}$

$f^i(y) \in T^{(\infty)} \sim f_i(y)^* \in T_{(\infty)}$

thus

$$\langle f_i(x) | g^j(x) \rangle = \int f^{i*}(x) g^j(x)\, dx. \qquad f^i, g^i \in T^{(\infty)}$$

The inner product between bases functions of $T^{(\infty)}$ and $T_{(\infty)}$ thus being

$$\langle \delta(x-x') | \delta(x-x'') \rangle = \int \delta(x-x')\delta(x-x'').dx = \delta(x'-x'').$$

Functions $\in \otimes^p T^{(\infty)}, \otimes_p T_{(\infty)}$ can be defined as

$W = f' \otimes \ldots \otimes f^p \quad W \in \otimes^p T^{(\infty)}$

and $W = f_1 \otimes \ldots \otimes f_p \quad W \in \otimes_p T_{(\infty)}$

each "component" of W thus being

$$f'(x').f^2(x^2)\ldots f^p(x^p) = W(x'x^2\ldots x^p)$$

each x^i being a particular value of the variable X^i over the interval in which the function f^i is defined. W can then be thought of as being a function of p variables $X', \ldots X^p$ which can have the values $X^i = [x_a^i, x_b^i]$, where $[x_a^i, x_b^i]$ is the interval over which the function is defined. Any $W \in \otimes^p T^{(\infty)}$ can then be expanded

$$W = \int W(x'\ldots x^p).\delta(X'-x').\delta(X^2-x^2)\ldots\delta(X^p-x^p).dx'dx^2\ldots dx^p$$

each "basis" function of $\otimes^p T^{(\infty)}$ being $\delta(X'-x')\delta(X^2-x^2)\ldots\delta(X^p-x^p)$ which is the $(x'\ldots x^p)^{th}$ base function. Quite often, as in the above, the tensor product of two functions $g(x') \otimes f(X^2)$ is written $g(x').f(X^2)$ i.e. as the product of two functions over every possible value of their variables.

The inner product between fuctions $U \in \otimes_p T_{(\infty)}$ and $W \in \otimes^p T^{(\infty)}$

is defined as:-

$$\langle u(x_1,\ldots x_p)|w(x'\ldots x^p)\rangle = \int u(x_1,\ldots x_p)\, w(x'\ldots x^p)$$
$$= \int u^*(x'\ldots x^p)\, w(x'\ldots x^p)\, dx'\ldots dx^p.$$

The symmetric and exterior powers of functions $\in T^{(\infty)}$ and $T^{(\infty)}$ form the tensor spaces $\Lambda^p T^{(\infty)}$, $\Lambda_p T_{(\infty)}$, $V^p T^{(\infty)}$ and $V_p T_{(\infty)}$, $w \in \Lambda^p T^{(\infty)}$ being defined as $w(x'\ldots x^p) = f^1(x') \wedge f^2(x^2) \ldots \wedge f^p(x^p)$

each "component" of $w(x'\ldots x^p)$ being defined as

$$w(x'\ldots x^p) = \frac{1}{p!} \mathrm{Det}\begin{bmatrix} f^1(x') f^1(x^2) \ldots f^1(x^p) \\ \vdots \\ f^p(x') \ldots f^p(x^p) \end{bmatrix}$$

with the assumtion that $x' < x^2 < \ldots < x^p$ and the functions $f^1, \ldots f^p$ are defined over the same interval.

Thus we can say that

$$= \frac{1}{p!^{1/2}} \mathrm{Det}\begin{bmatrix} f^1(x') \ldots f^1(x^p) \\ \vdots \\ f^p(x') \ldots f^p(x^p) \end{bmatrix}$$

where the values of $x', \ldots x^p$ are always different from each other.

The inner product in terms of the constituent functions is given by

$$\langle u(x_1,\ldots x_p)|w(x'\ldots x^p)\rangle = \frac{1}{p!} \mathrm{Det}\left[\langle g_i|f^j\rangle\right]$$

where $u(x_1,\ldots x_p) = \frac{1}{p!^{1/2}} \mathrm{Det}\begin{bmatrix} g_1(x_1) \ldots g_1(x_p) \\ \vdots \\ g_p(x_1) \ldots g_p(x_p) \end{bmatrix}$

The symmetric functions $w \in V^p T^{(m)}$ or $V_p T_{(m)}$ can be similarly defined as

$$w(x'\ldots x^p) = \frac{1}{p!^{1/2}} \mathrm{Perm}\begin{bmatrix} f^1(x') \ldots f^1(x^p) \\ \vdots \\ f^p(x') \ldots f^p(x^p) \end{bmatrix} \cdot \frac{1}{\sqrt{M(f)}}$$

where $M(f)$ is the product of the multiplicities of the functions constituting $w(x'\ldots x^p)$.

The spaces $\bigotimes_p^p T^{(\infty)}$, $\Lambda_p^p T^{(\infty)}$ and $V_p^p T^{(\infty)}$ can be defined in an analagous way as before.

Linear Mappings of $T^{(\infty)}$ and $T_{(\infty)}$ onto themselves

Mappings $\in L(T^{(\infty)})$ can be defined as $u(x_1 x^2)$ sometimes written as $u(x_1|x_2)$. These mappings have the effect

$$f(x_1) = \int u(x_1 x^2) g(x_2) dx_2, \quad f(x), g(x) \in T^{(\infty)}$$

and mappings $\in L(T_{(\infty)})$ as : $u(x'x_2)$ which have the effect

$$f(x') = \int u(x'x_2) g(x^2) dx_2, \quad f(x), g(x) \in T_{(\infty)}$$

Linear functions and linear transformations associated with linear functions have the properties:-

$$\alpha f(x) + \beta g(x) = h(x)$$

where the components of $h(x)$ are given by

$$h(x_1) = \alpha f(x_1) + \beta g(x_1).$$

$$\alpha u(x'|x_2) + \beta V(x'|x_2) = w(x'|x_2)$$

where the components of $w(x'|x_2)$ are given by

$$w(x'|x_2) = \alpha u(x'|x^2) + \beta V(x'|x_2)$$

In this very truncated section on multilinear functions as tensors no consideration has been given to the problems of convergence and other properties associated with the continuous and thus infinite dimensional "vectors" and Tensors, and thus the preceeding section is one of schematic understanding rather than of mathematical rigour.

Functional Vector and Tensor Spaces

Due to the linear nature of the functions we have previously been considering any linear function $f(x)$ can be expressed as a l.c. of other linear functions (of the same type i.e. covarient or contravarient). In general any $f^i(x) \in T^{(\infty)}$ can be expressed as an infinite sum

$$f^i(x) = \sum_i^{\infty} c^i_j e^j(x).$$

If we choose the functions $e^i(x)$ to be l.i. then any function $\in T^{(\infty)}$

can be expressed in terms of a unique linear sum of them, and thus the set of coefficients $\{c^i_j\}_{j=1,\ldots\ldots\infty}$ forms a unique characterisation of the function $f^i(x)$, and in fact we can say that the vector c^i represents the function $f^i(x)$ in the functional space $F^{(\infty)}$. There is a 1-1 correspondence between every function $\in T^{(\infty)}$ and every vector in $F^{(\infty)}$. Thus the space $T^{(\infty)}$ and $F^{(\infty)}$ are isomorphic. The set of functions $\{e^i(x)\}_{i=1,\ldots\ldots\infty}$ is a basis for $F^{(\infty)}$ and we can choose this set to be orthonormal.

i.e. $\int e^{i*}(x).e^j(x)dx = \delta^{ij} = \int e_i(x)e^j(x)dx$

When $e_i(x) \in T_{(\infty)}$ and $e^i(x) \in T^{(\infty)}$.

If we restrict the size of this base set to be m where m is finite then we only have an approximate representation of $T^{(\infty)}$ by $F^{(m)}$ i.e. $f^i(x) \simeq \sum_i^m c^i_j e^j(x)$.

The spaces are now homomorphic i.e approximations $f^i(x)$, $f^j(x)$,.... might be the same; thus the vector c^i might represent several true functions in $T^{(\infty)}$, but every tensor $\in T^{(\infty)}$ has only one representation in $F^{(m)}$, and $F^{(m)}$ is isomorphic to a subspace of $T^{(\infty)}$, signified by $F^{(m\infty)}$ i.e. to every vector $\in F^{(m)}$ there is one function $\in F^{(m\infty)}$ s.t. $g^i(x) = \sum_i^m c^i_j e^j(x) \simeq f^i(x)$.

The spaces of linear transformations $L(T^{(\infty)})$, $L(T_{(\infty)})$ are isomorphic to $L(F^{(\infty)})$ and $L(F_{(\infty)})$, and the l.t.s $\in L(F^{(m)})$ and $L(F_{(m)})$ map one approximation into another.

Another very important isomorphism exists. That of $E^{(m)}$ with $F^{(m)}$ and $E_{(m)}$ with $F_{(m)}$. For succinctness and brevity, we list here the following isomorphisms denoted by $\simeq$ and homomorphisms denoted by $\sim$.

$E^{(m)} \simeq F^{(m)} \simeq F^{(m\infty)} \sim T^{(\infty)}$; $L(E^{(m)}) \simeq L(F^{(m)}) \simeq L(F^{(m\infty)}) \sim L(T^{(\infty)})$

$E_{(m)} \simeq F_{(m)} \simeq F_{(m\infty)} \sim T_{(\infty)}$; $L(E_{(m)}) \simeq L(F_{(m)}) \simeq L(F_{(m\infty)}) \sim L(T_{(\infty)})$.

$\otimes^p E^{(m)} \simeq \otimes^p F^{(m)} \simeq \otimes^p F^{(m\infty)} \sim \otimes^p T^{(\infty)}$; $\otimes_p E_{(m)} \simeq \otimes_p F_{(m)} \simeq \otimes_p F_{(m\infty)} \sim \otimes_p T_{(\infty)}$.

$L(\otimes^p E^{(m)}) \simeq L(\otimes^p F^{(m)}) \simeq L(\otimes^p F^{(m\infty)}) \sim L(\otimes^p T^{(\infty)})$.

$L(\otimes_p E_{(m)}) \simeq L(\otimes_p F_{(m)}) \simeq L(\otimes_p F_{(m\infty)}) \sim L(\otimes_p T_{(\infty)})$.

$\otimes^p_p E^{(m)} \simeq \otimes^p_p F^{(m)} \simeq \otimes^p_p F^{(m\infty)} \sim \otimes^p_p T^{(\infty)}$.

The equivalent isomorphisms and homomorphisms are also true for the symmetric and exterior Tensor product spaces and their associated linear mappings.

Direct Product, Compound and Induced Matrices

It is possible to represent all multilinear mappings, (i.e. Tensor products, exterior products, symmetric products and contractions) as linear mappings between, in general, different dimensional spaces. In fact, multilinear maps are isomorphous to linear Maps viz.

$M(E^{(m)} \to \otimes^p E^{(m)}) \simeq L(E^{(m)} \to E^{(m^p)})$.

$M(E^{(m)} \to \wedge^p E^{(m)}) \simeq L(E^{(m)} \to E^{(mC_p)})$.

$M(E^{(m)} \to \vee^p E^{(m)}) \simeq L(E^{(m)} \to E^{(m+p-1C_p)})$.

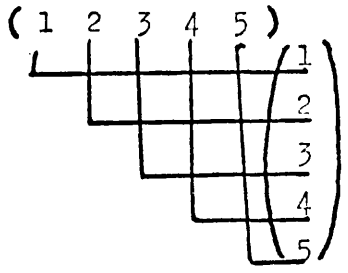
and multilinear mappings of the linear transformations associated with $E^{(m)}$ and $E_{(m)}$ are isomorphous to Direct, Compound or Induced Products of $\omega, u \in L(E^{(m)})$, $L(E_{(m)})$. The Direct Products are isomorphous to $L(\otimes^p E^{(m)})$, the Compound Products to $L(\wedge^p E^{(m)})$ and the Induced products to $L(\vee^p E^{(m)})$. The mappings $L(E^{(m)} \to E^{(mC_p)})$, $L(E^{(m)} \to E^{(mC_p)})$ and $L(E^{(m)} \to E^{(m+p-1C_p)})$ can also be thought of as special cases of Direct, Compound and Induced Products.

The above properties lead to a very useful way of conceptualising Tensors and the l.t's associated with Tensors.

Vectors $\in E^{(m)}$ or $E_{(m)}$ can be represented by a one-dimensional array of scalars, each scalar corresponding to a component of the

vector, we can arrange this 1-dimensional array either as a row or a column. We choose <u>contravarient</u> vectors $(E^{(m)})$ to be represented by a <u>column</u> of numbers and <u>covarient</u> $E_{(m)}$ by a <u>row</u>.

So we can write a scalar product as



the product being defined as the sum of the products of like positions in row and column.

l.t's $\in L(E^{(m)})$ or $L(E_{(m)})$ can be represented by a 2-dimensional array of scalars so

$$\begin{pmatrix} \cdots\cdots \vdots\, a^j_i \,\cdots\cdots \end{pmatrix}$$

i - denoting row

j - denoting column

An l.t. connecting two vectors $\in E^{(m)}$ is written as

$$\begin{pmatrix} \cdots\cdots \vdots\, a^j_i \,\cdots\cdots \end{pmatrix}\begin{pmatrix} \vdots \\ b_j \end{pmatrix} = \begin{pmatrix} \vdots \\ c_j \end{pmatrix}$$

each row of a acting as a row vector and forming an inner product with b to give each element c the element corresponding to that row of a used in the inner product.

An l.t. connecting two vectors $\in E_{(m)}$ is written as

$$(\cdots\cdots b^j \cdots\cdots)\begin{pmatrix} \cdots\cdots \vdots\, a^i_j \,\cdots\cdots \end{pmatrix} = (c^j \cdots\cdots).$$

This time, each column of a acting as a column vector forming a scalar product with b.

A Tensor product between vectors $u \in E^{(m)}$ and $v \in E_{(m)}$ can be represented as the <u>Direct Product</u>, so

$$\begin{pmatrix} \vdots \\ u^j \end{pmatrix} \otimes (\cdots v_i \cdots) = \begin{pmatrix} \cdots\cdots \vdots\, a^j_i \,\cdots\cdots \end{pmatrix} \quad \text{where} \quad a^j_i = u^j v_i$$

and thus $a \in \otimes_1^1 E^{(m)}$

A Tensor $\in \otimes^2 E^{(m)}$ can be represented by the Direct Product

$$\begin{matrix}\uparrow m \\ \downarrow\end{matrix}\begin{pmatrix}\vdots \\ u^j \\ \vdots\end{pmatrix} \otimes \begin{pmatrix}\vdots \\ v^i \\ \vdots\end{pmatrix} = \begin{pmatrix}\vdots \\ a^{ji} \\ \vdots\end{pmatrix}\begin{matrix}\uparrow \\ m^2 \\ \downarrow\end{matrix}$$

where $a^{ji} = u^j v^i$

and a Tensor $\in \otimes_2 E_{(m)}$ by the Direct Product

$$\underset{\longleftarrow m \longrightarrow}{(\ldots u^j \ldots\ldots)} \otimes \underset{\longleftarrow m \longrightarrow}{(\ldots v^i \ldots\ldots)} = \underset{\longleftarrow m^2 \longrightarrow}{(\ldots a^{ji} \ldots\ldots)}$$

where $a^{ji} = u^j v^i$

The Tensor Product of l.t's where $X \in L(E^{(m)}), Y \in L(E^{(m)})$

then $W = X \otimes Y$ is given by

$$\begin{matrix}\uparrow m \\ \downarrow\end{matrix}\underset{\longleftarrow m \longrightarrow}{\begin{pmatrix}\vdots \\ X_i^j \\ \vdots\end{pmatrix}} \otimes \underset{\longleftarrow m \longrightarrow}{\begin{pmatrix}\vdots \\ Y_e^k \\ \vdots\end{pmatrix}}\begin{matrix}\uparrow m \\ \downarrow\end{matrix} = \begin{bmatrix}\longleftarrow m^2 \longrightarrow \\ \ldots X_i^j (Y) \ldots\ldots \\ \vdots\end{bmatrix}\begin{matrix}\uparrow \\ m^2 \\ \downarrow\end{matrix} = \begin{bmatrix}\ldots W_{ie}^{jk} \ldots\ldots \\ \vdots\end{bmatrix}$$

where $W_{ie}^{jk} = X_i^j Y_e^k$.

The structure is exactly the same for $X \in L(E_{(m)})$ and $Y \in L(E_{(m)})$.

The above cases can easily be seen to be generalised to the general case for any p-linear Map (above case is when p = 2).

Exterior products of vectors $\in E^{(m)}$ can be represented in the following way

$$\underset{\longleftarrow m \longrightarrow}{(x_1)} \wedge \underset{\longleftarrow m \longrightarrow}{(x_2)} \ldots \wedge (x_p) = \underset{\longleftarrow {}^mC_p \longrightarrow}{(\ldots\ldots X \ldots\ldots)}$$

where the elements of X are defined as

$$X_{\sigma_\nu} = \frac{1}{p!^{1/2}} \operatorname{Det}\begin{bmatrix} x_1^{\sigma_{\nu 1}} \ldots\ldots x_1^{\sigma_{\nu p}} \\ \vdots \\ x_p^{\sigma_{\nu 1}} \ldots\ldots x_p^{\sigma_{\nu p}} \end{bmatrix} \quad \sigma_\nu \in Q_{p,m}.$$

$$(y^1) \wedge (y^2) \ldots\ldots \wedge (y^p)\begin{matrix}\uparrow \\ m \\ \downarrow\end{matrix}$$

has a corresponding definition.

Both these are special cases of the Compound Product defined for l.t's

$\in L(\Lambda^p E^{(m)})$ or $L(\Lambda_p E_{(m)})$.

If $U \in L(E^{(m)})$ then $\underbrace{U \wedge \ldots\ldots \wedge U}_{\longleftarrow p \longrightarrow}$ denoted by $C_p(U)$ is defined as

$$W = C_p(U) \quad (\text{thus } W \in L(\Lambda^p E^{(m)})$$

then W has the elements

$$W_{\mu_\nu}^{\sigma_\nu} = \text{Det}\left(U[\sigma_\nu | \mu_\nu]\right) \qquad \sigma_\nu, \mu_\nu \in Q_{p,m}$$

and $\text{Det}\left[U[\sigma_\nu|\mu_\nu]\right]$ is the Minor formed from elements

$$\begin{bmatrix} U_{\sigma_1}^{\sigma_{\mu_1}} & \ldots\ldots\ldots & U_{\sigma_1}^{\sigma_{\mu_p}} \\ \vdots & & \vdots \\ U_{\sigma_p}^{\sigma_{\mu_1}} & \ldots\ldots\ldots & U_{\sigma_p}^{\sigma_{\mu_p}} \end{bmatrix}$$

of U.

This is a special case of the compound product of a matrix $U(r \times m)$ i.e. a mapping $\in L(E^{(m)} \longrightarrow E^{(r)})$ in which case $W = C_p(U)$ is defined as having elements

$$W_{\mu_\nu}^{\sigma_\nu} = \text{Det}\left(U[\sigma_\nu | \mu_\mu]\right) \quad \begin{matrix} \sigma_\nu \in Q_{p,r} \\ \sigma_\mu \in Q_{p,m} \end{matrix}$$

Then the exterior product of vectors is generated when U is considered to be formed from the p-row vectors $x_1 \ldots\ldots x_p$ ($\therefore$ a $p \times m$ matrix). Then $C_p(U)$ is the product $p!^{1/2} x_1 \wedge \ldots\ldots \wedge x_p$ and row vector of dimension ${}^m C_p$ is formed, as there is only one sequence $\sigma_\nu \in Q_{p,p}$.

The Induced product of l.t's $U \in L(E^{(m)} \longrightarrow E^{(r)})$, U is an $r \times m$ matrix is defined as

$$P_p(U) = W,$$

and the elements of W as

$$W_{\mu_\nu}^{\sigma_\nu} = \frac{1}{\sqrt{M(\sigma_\nu) M(\mu_\nu)}} \text{Perm}\left[U[\sigma_\nu|\mu_\nu]\right]_{\substack{\sigma_\nu \in G_{p,r} \\ \sigma_\mu \in G_{p,m}}}$$

thus for $U \in L(E^{(m)})$, $W_{\mu_\nu}^{\sigma_\nu}$ has the same definition but $\sigma_\nu, \sigma_\mu \in G_{p,m}$ and then

$$P_p(U) = \underbrace{U \vee \ldots\ldots \vee U}_{\longleftarrow p \longrightarrow} = W$$

and $W \in L(\vee^p E^{(m)})$.

When we consider U to be made up of the p-row vectors $x^1 \ldots\ldots x^p \in E^{(m)}$ then $P_p(U) = p!^{1/2} x_1 \vee \ldots\ldots \vee x_p$.

as there is only one sequence $\sigma_\nu \underset{m+p-1}{\in} G_{p,p}$, $x_1 \vee \ldots\ldots \vee x_p$ is represented by a row vector with C_p components defined as

$$X_{\sigma\nu} = \frac{1}{p!\nu_2} \operatorname{Perm} \begin{bmatrix} x_1^{\sigma\nu_1} & \ldots\ldots & x_1^{\sigma\nu_p} \\ \vdots & & \vdots \\ x_p^{\sigma\nu_1} & \ldots\ldots & x_p^{\sigma\nu_p} \end{bmatrix} \quad \sigma_\nu \in G_{p,m}.$$

CHAPTER TWO.

Mathematical Structure of Density Matrices and wavefunctions of n identical particles with spin

Fermions are represented by antisymmetric wavefunctions and Bosons by symmetric wavefunctions (w.r.t. interchange of particle space-spin co-ordinates) These functions are Tensors $\in \Lambda^p T^\infty$ and $V^p T^\infty$ respectively. Systems of n Fermions or n Bosons could equally well be represented by Density Matrices defined in terms of the wave-functions thus:-

$$T_f^{(n)}(x_1' \ldots x_p' | x_1 \ldots x_p) = \Psi_f(x' \ldots x^{p'})\, \Psi_f(x_1 \ldots x_p)$$
$$= \Psi_f^*(x_1' \ldots x_p')\, \Psi_f(x_1 \ldots x_p)$$

where x_i are space-spin co-ordinates of the i^{th} particle.

$$T_B^{(n)}(x_1' \ldots x_p' | x_1 \ldots x_p) = \Psi_B^*(x_1' \ldots x_p')\, \Psi_B(x_1 \ldots x_p)$$

where f stands for Fermions and $\Psi_f(x' \ldots x^p) \in \Lambda^p T^\infty$
and B stands for Bosons and $\Psi_B(x' \ldots x^p) \in V^p T^\infty$
Thus $T_f^{(n)} \in \Lambda_p^p T^\infty$ and $T_B^{(n)} \in V_p^p T^\infty$
Wavefunctions could equally well be defined in terms of the Density Matrices, thus assigning the fundamental characterisation of the system to the Density Matrix rather than the wave-function.

From now on we will deal explicitly with Fermions.
We can approximately represent $\Psi(x_1 \ldots x_n)$ on $\Lambda_n F_{(2\infty)}$ and $T_{(n)}(x_1' \ldots x_p' | x_1 \ldots x_p)$ on $\Lambda_n^\wedge F^{(2\infty)}$. As $\Psi \in \Lambda_n F_{(2\infty)}$ it can be expressed as an exterior product of functions $\in F_{(2\infty)}$, i.e. $\Psi(x_1 \ldots x_n) = \chi_1(x_1) \wedge \chi_2(x_2) \ldots \wedge \chi_n(x_n)$ where $\chi_i(x_i) \in F_{(2\infty)}$
Now if we say that $F_{(2\infty)}$ is spanned by the orthonormal functions $\{\omega_i(x)\}_{i=1,\ldots,2}$, then a basis for $\Lambda_n F_{(2\infty)}$ can be written as $\{\hat{\Pi}_i^\wedge \omega_{\sigma v_i}(x_i)\}_{\sigma v \in Q_{n,2}}$. We can write the space-spin function $\omega_i(x)$ as a product of a

position space function and a spin space function i.e.

$\omega_i(x) = \sigma_k(r)\, S_e(\eta)$ $\quad r$ - position space variable

η - spin space variable

and $i \simeq (k, e)$.

Thus $F_{(z\infty)}$ can be decomposed as

$$F_{(z\infty)} = P_{(m\infty)} \otimes S_{(d\infty)}$$

where $(m\infty).(d\infty) = z\infty$.

For an electronic system $d\infty = 2\infty$, thus dimensions of F is $2m$

i.e. $F_{(2m\infty)} = P_{(m\infty)} \otimes S_{(2\infty)}$

and

$$\Lambda n F_{(2m\infty)} = (P_{(m\infty)} \otimes S_{(2\infty)}) \wedge (P_{(m\infty)} \otimes S_{(2\infty)}) \wedge \ldots \wedge (P_{(m\infty)} \otimes S_{(2\infty)})$$
$$= \Lambda_n (P_{(m\infty)} \otimes S_{(2\infty)})$$

We are mainly interested in the case of $n = 2$ so we will look at that in some detail.

$$\Lambda_2 F(2m\infty) = \Lambda_2 (P_{(m\infty)} \otimes S_{(2)}) = [P_{(m\infty)} \otimes S_{(2)}] \wedge [P_{(m\infty)} \otimes S_{(2)}]$$

This product can be shown to be equal to:-

$$\Lambda_2 P_{(m\infty)} \otimes V_2 S_{(2\infty)} \oplus V_2 P_{(m\infty)} \otimes \Lambda_2 S_{(2\infty)}.$$

Now the dimensions of $V_2 S_{(2)} = {}^3C_2 = 3$, (i.e. number of bases Tensors being 3).

If the base of $S_{(2)}$ (the functional discrete space) is $\{\alpha(\eta), \beta(\eta)\}$

α and β being orthonormal viz

$$\int \alpha(\eta)\beta(\eta)\, d\eta = 0, \quad \int \alpha^*(\eta)\alpha(\eta)\, d\eta = \int \beta^*(\eta)\beta(\eta)\, d\eta = 1$$

Then we can construct the bases Tensors of $V_2 S_{(2\infty)}$ to be

$$\alpha(\eta_1)\alpha(\eta_2),\ \beta(\eta_1)\beta(\eta_2) \text{ and } \frac{1}{\sqrt{2}}\{\alpha(\eta_1)\beta(\eta_2) + \alpha(\eta_2)\beta(\eta_1)\}$$

while $\Lambda_2 S_{(2\infty)}$ has only 1 independent Tensor, which we construct as

$$\frac{1}{\sqrt{2}}\{\alpha(\eta_1)\beta(\eta_2) - \alpha(\eta_2)\beta(\eta_1)\}$$

The bases of $\Lambda_2 P_{(m)}$ (the functional discrete space) is given by

$$\left\{ \hat{\prod_i}{}^{\wedge} \sigma(r)\sigma v_i \right\} \sigma_v \in Q_{n,m}$$

and the base of $V_2 P_{(m)}$ is given by

$$\left\{ \hat{\prod_i}{}^{v} \sigma(r)\sigma v_i \right\} \sigma_v \in G_{n,m}$$

$V_2 S_{(200)}$ can be decomposed in terms of a direct sum,

$$V_2 S_{(200)} = S^{\alpha\alpha}_{(100)} \oplus S^{\beta\beta}_{(100)} \oplus S^{\alpha\beta_t}_{(100)}$$

where $S^{\alpha\alpha}_{(100)}$ corresponds to the subspace generated by the basis tensor $\alpha(\zeta_1)\alpha(\zeta_2)$, etc.....,

and we can write $\Lambda_2 S_{(200)}$ as $S^{\alpha\beta_s}_{(100)}$

We thus can write

$$\Lambda_2 F_{(2m00)} = \Lambda_2 P^{\alpha\alpha}_{(m00)} \oplus \Lambda_2 P^{\beta\beta}_{(m00)} \oplus \Lambda_2 P^{\alpha\beta_t}_{(m00)} \oplus V_2 P^{\alpha\beta_s}_{(m00)}$$

Each subspace has a particular spin symmetry, thus within a subspace we can ignore the spin symmetry and say that the space is spanned by spinless Tensors $\left\{ \hat{\prod_i}{}^{\wedge} \sigma(r)\sigma v_i \right\} \sigma_v \in Q_{n,m}$ or $\left\{ \hat{\prod_i}{}^{v} \sigma(r)\sigma v_i \right\} \sigma_v \in G_{n,m}$ and we notice that $\Lambda_2 P^{\alpha\alpha}_{(m00)}$, $\Lambda_2 P^{\beta\beta}_{(m00)}$ and $\Lambda_2 P^{\alpha\beta_t}_{(m00)}$ are spanned by identical sets of Tensors.

The product $\Lambda_2 F_{(2m00)}$ can also be written as

$$\Lambda_2 F_{(2m00)} = \Lambda_2 (P_{(m00)} \otimes S^{\alpha}_{(100)}) \oplus \Lambda_2 (P_{(m00)} \otimes S^{\beta}_{(100)}) \oplus P_{(m00)} \otimes S^{\alpha}_{(100)} \wedge P_{(m00)} \otimes S^{\beta}_{(100)}$$

where $S_{(200)} = S^{\alpha}_{(100)} \oplus S^{\beta}_{(100)}$

The subspace $S^{\alpha}_{(100)}$ associated with the basis vector $\alpha(\zeta)$ and $S^{\beta}_{(100)}$ with the basis vector $\beta(\zeta)$

Now $\Lambda_2 (P_{(m00)} \otimes S^{\alpha}_{(100)}) = \Lambda_2 P_{(m00)} \otimes S^{\alpha\alpha}_{(100)} = \Lambda_2 P^{\alpha\alpha}_{(m00)}$

and $\Lambda_2 (P_{(m00)} \otimes S^{\beta}_{(100)}) = \Lambda_2 P_{(m00)} \otimes S^{\beta\beta}_{(100)} = \Lambda_2 P^{\beta\beta}_{(m00)}$

and we can write $\rho_{(m\infty)} \otimes S^{\alpha}_{(1\infty)} \wedge \rho_{(m\infty)} \otimes S^{\beta}_{(1\infty)} \equiv \rho^{\alpha\beta}_{(m\infty)}$

Thus $\Lambda_2 F_{(2m\infty)} = \Lambda_2 \rho^{\alpha\alpha}_{(m\infty)} \oplus \Lambda_2 \rho^{\beta\beta}_{(m\infty)} \oplus \rho^{\alpha\beta}_{(m\infty)}$

We note that $\rho^{\alpha\beta}_{(m\infty)}$ is not a factored position-spin space tensor space i.e. tensors $\in \rho^{\alpha\beta}_{(m\infty)}$ are not of the form $\chi(r) \textcircled{H} (s)$ where $\chi(r)$ is a space function and $\textcircled{H}(s)$ spin functions.

We know that $\Lambda_2 F_{(2m\infty)} \equiv \Pi_a (\otimes_2 F_{(2m\infty)})$

(though $\Lambda_2 F_{(2m\infty)}$ is an irreducible form of $\Pi_a (\otimes_2 F_{(2m\infty)})$).

and $\otimes_2 F_{(2m\infty)} = \otimes_2 (\rho_{(m\infty)} \otimes S_{(2)}) = \rho_{(m\infty)} \otimes S_{(2)} \otimes \rho_{(m\infty)} \otimes S_{(2)}$

$= \otimes_2 \rho_{(m\infty)} \otimes \otimes_2 S_{(2)} = \otimes_2 \rho_{(m\infty)} \otimes \left[{}^{\otimes}S^{\alpha\alpha}_{(1\infty)} \oplus^{\otimes} S^{\alpha\beta}_{(1\infty)} \oplus^{\otimes} S^{\beta\alpha}_{(1\infty)} \oplus^{\otimes} S^{\beta\beta}_{(1\infty)} \right]$

where ${}^{\otimes}S^{\alpha\alpha}_{(1\infty)}$ .... etc are the 4 subspaces associated with the 4 bases tensors that span $\otimes_2 S_{(2)}$, $\{\alpha(\eta_1)\beta(\eta_2), \alpha(\eta_1)\alpha(\eta_2), \beta(\eta_1)\beta(\eta_2), \beta(\eta_1)\alpha(\eta_2)\}$

Thus $\otimes_2 F_{(2m\infty)} = \otimes_2 \rho^{\alpha\alpha}_{(m\infty)} \oplus \otimes_2 \rho^{\alpha\beta}_{(m\infty)} \oplus \otimes_2 \rho^{\beta\alpha}_{(m\infty)} \oplus \otimes \rho^{\beta\beta}_{(m\infty)}$

Hence $\Lambda_2 F_{(2m\infty)} \equiv \Pi_a \left[\otimes_2 \rho^{\alpha\alpha}_{(m\infty)} \oplus \otimes_2 \rho^{\alpha\beta}_{(m\infty)} \oplus \otimes_2 \rho^{\beta\alpha}_{(m\infty)} \oplus \otimes_2 \rho^{\beta\beta}_{(m\infty)} \right]$

As $T^{(2)}(x_1' x_2' | x_1 x_2) \in \Lambda^2_2 F^{(2m\infty)}$ we can see that the spin factorisation (i.e. decomposition of $\Lambda^2_2 F^{(2m\infty)}$ into a direct sum of direct products of position space and spin space functions) will follow from that of $\Lambda_2 F_{(2m\infty)}$. Hence considering the 3 representations of $\Lambda_2 F_{(2m\infty)}$ we have for $\Lambda^2_2 F^{(2m\infty)}$ the following: -

(i) $\Lambda^2_2 F^{(2m\infty)} \equiv \left[\Lambda^2 \rho^{(m\infty)} \otimes V^2 S^{(2\infty)} \oplus V^2 \rho^{(m\infty)} \otimes \Lambda^2 S^{(2\infty)} \right] \otimes$
$\left[\Lambda_2 \rho_{(m\infty)} \otimes V_2 S_{(2\infty)} \oplus V_2 \rho_{(m\infty)} \otimes \Lambda_2 S_{(2\infty)} \right]$
$= \Lambda^2 \rho^{(m\infty)} \otimes V^2 S^{(2\infty)} \otimes \Lambda_2 \rho_{(m\infty)} \otimes V_2 S_{(2\infty)}$
$\oplus V^2 \rho^{(m\infty)} \otimes \Lambda^2 S^{(2\infty)} \otimes V_2 \rho_{(m\infty)} \otimes \Lambda_2 S_{(2\infty)}$
$\oplus \Lambda^2 \rho^{(m\infty)} \otimes V^2 S^{(2\infty)} \otimes V_2 \rho_{(m\infty)} \otimes \Lambda_2 S_{(2\infty)}.$

$$\oplus V^2\rho^{(m\infty)} \otimes \Lambda^2 S^{(2\infty)} \otimes \Lambda_2 P_{(m\infty)} \otimes V_2 S_{(2\infty)}$$

which in equivalent notation to that of before becomes

$$\begin{aligned}\Lambda_2^2 F^{(2m\infty)} \equiv{}& \Lambda_2^2 \rho^{(m\infty)}_{\alpha\alpha\alpha\alpha} \oplus \Lambda_2^2 \rho^{(m\infty)}_{\alpha\alpha\alpha\beta_t} \oplus \Lambda_2^2 \rho^{(m\infty)}_{\alpha\alpha\beta\beta} \\ &\oplus \Lambda_2^2 \rho^{(m\infty)}_{\alpha\beta_t\alpha\alpha} \oplus \Lambda_2^2 \rho^{(m\infty)}_{\alpha\beta_t\alpha\beta_t} \oplus \Lambda_2^2 \rho^{(m\infty)}_{\alpha\beta_t\beta\beta} \\ &\oplus \Lambda_2^2 \rho^{(m\infty)}_{\beta\beta\alpha\alpha} \oplus \Lambda_2^2 \rho^{(m\infty)}_{\beta\beta\alpha\beta_t} \oplus \Lambda_2^2 \rho^{(m\infty)}_{\beta\beta\beta\beta} \\ &\oplus \Lambda^2 V_2 \rho^{(m\infty)}_{\alpha\alpha\alpha\beta_s} \oplus \Lambda^2 V_2 \rho^{(m\infty)}_{\alpha\beta_t\alpha\beta_s} \oplus \Lambda^2 V_2 \rho^{(m\infty)}_{\beta\beta\alpha\beta_s} \\ &\oplus V^2\Lambda_2 \rho^{(m\infty)}_{\alpha\beta_s\alpha\alpha} \oplus V^2\Lambda_2 \rho^{(m\infty)}_{\alpha\beta_s\alpha\beta_t} \oplus V^2\Lambda_2 \rho^{(m\infty)}_{\alpha\beta_s\beta\beta} \\ &\oplus V_2^2 \rho^{(m\infty)}_{\alpha\beta_s\alpha\beta_s}\end{aligned}$$

Clarity will be restored in the following Direct product representation of an element of $\Lambda_2^2 F^{(2m\infty)}$ which is partitioned in the same way as the above decomposition

$$\Lambda_2 \rho^{\alpha\alpha}_{(m\infty)} \; V_2 \rho^{\alpha\beta_s}_{(m\infty)} \; \Lambda_2 \rho^{\alpha\beta_t}_{(m\infty)} \; \Lambda_2 \rho^{\beta\beta}_{(m\infty)}$$

$\Lambda^2 \rho^{(m\infty)}_{\alpha\alpha}$	$\alpha\alpha\alpha\alpha$	$\alpha\alpha\alpha\beta_s$	$\alpha\alpha\alpha\beta_t$	$\alpha\alpha\beta\beta$
$V^2 \rho^{(m\infty)}_{\alpha\beta_s}$	$\alpha\beta_s\alpha\alpha$	$\alpha\beta_s\alpha\beta_s$	$\alpha\beta_s\alpha\beta_t$	$\alpha\beta_s\beta\beta$
$\Lambda^2 \rho^{(m\infty)}_{\alpha\beta_t}$	$\alpha\beta_t\alpha\alpha$	$\alpha\beta_t\alpha\beta_s$	$\alpha\beta_t\alpha\beta_t$	$\alpha\beta_t\beta\beta$
$\Lambda^2 \rho^{(m\infty)}_{\beta\beta}$	$\beta\beta\alpha\alpha$	$\beta\beta\alpha\beta_s$	$\beta\beta\alpha\beta_t$	$\beta\beta\beta\beta$

Thus w.r.t. spin symmetry a Tensor $\in \Lambda_2^2 F^{(2m\infty)}$ has 16 components. These components are completely spin independent (within the qualification that each one is associated with a particular spin symmetry). The dimension of this representation is: -

$$({}^{m}C_n + {}^{m+n-1}C_n) \times ({}^{m}C_n + {}^{m+n-1}C_n)$$

(ii)

$$\Lambda_2^2 F^{(2m\infty)} \equiv \Pi_A \left[\otimes^2 \rho_{\alpha\alpha}^{(m\infty)} \oplus \otimes^2 \rho_{\alpha\beta}^{(m\infty)} \oplus \otimes^2 \rho_{\beta\alpha}^{(m\infty)} \oplus \otimes^2 \rho_{\beta\beta}^{(m\infty)} \right] \otimes \Pi_a$$

$$\left[\otimes_2 \rho_{(m\infty)}^{\alpha\alpha} \oplus \otimes_2 \rho_{(m\infty)}^{\alpha\beta} \oplus \otimes_2 \rho_{(m\infty)}^{\beta\alpha} \oplus \otimes_2 \rho_{(m\infty)}^{\beta\beta} \right]$$

$$\equiv \Pi^A \Big[\otimes_2^2 \rho_{\alpha\alpha\alpha\alpha}^{(m\infty)} \oplus \otimes_2^2 \rho_{\alpha\alpha\alpha\beta}^{(m\infty)} \oplus \otimes_2^2 \rho_{\alpha\alpha\beta\alpha}^{(m\infty)} \oplus \otimes_2^2 \rho_{\alpha\alpha\beta\beta}^{(m\infty)} \oplus \otimes_2^2 \rho_{\alpha\beta\alpha\alpha}^{(m\infty)}$$

$$\oplus \otimes_2^2 \rho_{\alpha\beta\alpha\beta}^{(m\infty)} \oplus \otimes_2^2 \rho_{\alpha\beta\beta\alpha}^{(m\infty)} \oplus \otimes_2^2 \rho_{\alpha\beta\beta\beta}^{(m\infty)} \oplus \otimes_2^2 \rho_{\beta\alpha\alpha\alpha}^{(m\infty)} \oplus \otimes_2^2 \rho_{\beta\alpha\alpha\beta}^{(m\infty)}$$

$$\oplus \otimes_2^2 \rho_{\beta\alpha\beta\alpha}^{(m\infty)} \oplus \otimes_2^2 \rho_{\beta\alpha\beta\beta}^{(m\infty)} \oplus \otimes_2^2 \rho_{\beta\beta\alpha\alpha}^{(m\infty)} \oplus \otimes_2^2 \rho_{\beta\beta\alpha\beta}^{(m\infty)} \oplus \otimes_2^2 \rho_{\beta\beta\beta\alpha}^{(m\infty)}$$

$$\oplus \otimes_2^2 \rho_{\beta\beta\beta\beta}^{(m\infty)} \Big]$$

In Direct Product Representation of $\Lambda_2^2 F^{(2m\infty)}$ the above decomposition is represented by the following partitioning: -

$$\Pi^A : \otimes_2 \rho_{(m\infty)}^{\alpha\alpha} \ldots\ldots\ldots\ldots\ldots$$

$\Pi^A : \otimes^2 \rho_{\alpha\alpha}^{(m\infty)}$	$\alpha\alpha\alpha\alpha$	$\alpha\alpha\alpha\beta$	$\alpha\alpha\beta\alpha$	$\alpha\alpha\beta\beta$
$\Pi^A : \otimes^2 \rho_{\alpha\beta}^{(m\infty)}$	$\alpha\beta\alpha\alpha$	$\alpha\beta\alpha\beta$	$\alpha\beta\beta\alpha$	$\alpha\beta\beta\beta$
$\Pi^A : \otimes^2 \rho_{\beta\alpha}^{(m\infty)}$	$\beta\alpha\alpha\alpha$	$\beta\alpha\alpha\beta$	$\beta\alpha\beta\alpha$	$\beta\alpha\beta\beta$
$\Pi^A : \otimes^2 \rho_{\beta\beta}^{(m\infty)}$	$\beta\beta\alpha\alpha$	$\beta\beta\alpha\beta$	$\beta\beta\beta\alpha$	$\beta\beta\beta\beta$

This decomposition is not a decomposition into a factored Tensor space of the form position functions x spin functions. Thus each component is dependent on spin and each block is in general a different subspace w.r.t. spin and position. The dimension of this representation is $4m^2 \times 4m^2$

In general $(4m)^2 > (3^m C_n + {}^{m+n-1}C_n)$

If the Tensors $\in \otimes_2^2 F^{(2m\infty)}$ are antisymmetric then

$$\Pi_A^A : \otimes_2^2 F^{(2m\omega)} = \otimes_2^2 F^{(2m\omega)} \equiv \Lambda_2^2 F^{(2m\omega)}$$

(ii)

	$\Lambda_2 \rho^{\alpha\alpha}_{(m\omega)}$	$\rho^{\alpha\beta}_{(m\omega)}$	$\Lambda_2 \rho^{\beta\beta}_{(m\omega)}$
$\Lambda^2 \rho^{(m\omega)}_{\alpha\alpha}$	$\alpha\alpha\alpha\alpha$	$\alpha\alpha\alpha\beta$	$\alpha\alpha\beta\beta$
$\rho^{\alpha\beta}_{(m\omega)}$	$\alpha\beta\alpha\alpha$	$\alpha\beta\alpha\beta$	$\alpha\beta\beta\beta$
$\Lambda^2 \rho^{(m\omega)}_{\beta\beta}$	$\beta\beta\alpha\alpha$	$\beta\beta\alpha\beta$	$\beta\beta\beta\beta$

This Direct Product representation corresponds to the decomposition

$$\Lambda_2^2 F^{(2m\omega)} \equiv \left[\Lambda^2 \rho^{(m\omega)}_{\alpha\alpha} \oplus \rho^{(m\omega)}_{\alpha\beta} \oplus \Lambda^2 \rho^{(m\omega)}_{\beta\beta}\right] \otimes \left[\Lambda_2 \rho^{\alpha\alpha}_{(m\omega)} \oplus \rho^{\alpha\beta}_{(m\omega)} \oplus \Lambda_2 \rho^{\beta\beta}_{(m\omega)}\right]$$

$$= \Lambda_2^2 \rho^{(m\omega)}_{\alpha\alpha\alpha\alpha} \oplus \Lambda_2^2 \rho^{(m\omega)}_{\alpha\alpha\beta\beta} \oplus \Lambda_2^2 \rho^{(m\omega)}_{\beta\beta\alpha\alpha} \oplus \Lambda_2^2 \rho^{(m\omega)}_{\beta\beta\beta\beta}$$

$$\oplus \Lambda^2 \rho^{(m\omega)}_{\alpha\alpha} \otimes \rho^{\alpha\beta}_{(m\omega)} \oplus \Lambda^2 \rho^{(m\omega)}_{\beta\beta} \otimes \rho^{\alpha\beta}_{(m\omega)}$$

$$\oplus \rho^{(m\omega)}_{\alpha\beta} \otimes \rho^{(m\omega)}_{\alpha\beta} \oplus \rho^{(m\omega)}_{\alpha\beta} \otimes \Lambda_2 \rho^{\alpha\alpha}_{(m\omega)}$$

$$\oplus \rho^{(m\omega)}_{\alpha\beta} \otimes \Lambda_2 \rho^{\beta\beta}_{(m\omega)}.$$

This decomposition is into a partially factored space, the components containing an $\alpha\beta$ subscript are not a product of position-space spin parts while the others are. Thus these latter subspaces are spin independent. The dimension of this representation is

$$(2 \cdot {}^m C_n + m^2) \times (2 \cdot {}^m C_n + m^2)$$

which is equal to the Dimension of representation (ii), though there are only 9 different components in the above decomposition.

The preceeding analysis of the structure of $\Lambda_2 F_{(2m\omega)}$ and $\Lambda_2^2 F^{(2m\omega)}$ shows the structure of $\chi_k(x_1 x_2) \in \Lambda_2 F_{(2m\omega)}$ and $\lambda(x_1' x_2' | x_1 x_2) \in \Lambda_2^2 F_{(2m\omega)}$ w.r.t. spin symmetry, and in certain decompositions we can separate spatial and spin parts of the functions, thus making it possible to work in position functions that have implicit spin properties

A set of orthonormal functions $\in \Lambda_2 F_{(2m\infty)}$ can form a basis for $\Lambda_2 F_{(2m)}$ (i.e. a discret functional space), thus a basis for $\Lambda_2^2 F_{(2m)}$ can be derived. As the spaces $\Lambda_2 F_{(2m\infty)}$ and $\Lambda_2 F_{(2m)}$ are isomorphous the spin decompositions in $\Lambda_2 F_{(2m\infty)}$ are exactly reflected in $\Lambda_2 F_{(2m)}$

Representation of π^A, π^S, U^A and U^S on $\otimes^2 \rho^{(m)}$

π^A is defined as $\frac{1}{2} \sum_{\substack{\underline{\sigma_\chi} \\ \underline{\sigma_\chi} \in \underline{S_{2,m}}}} \varepsilon_{\sigma_\chi} . \underline{\sigma_\chi}$ when it $\in \otimes^2 \rho^{(m)}$

$\pi^A : \otimes^2 \rho^{(m)} \rightarrow \pi^A [\otimes^2 \rho^{(m)}]$

π^S is defined as $\frac{1}{2} \sum_{\substack{\underline{\sigma_\chi} \\ \underline{\sigma_\chi} \in \underline{S_{2,m}}}} \underline{\sigma_\chi}$ when it $\in \otimes^2 \rho^{(m)}$

$\pi^S : \otimes^2 \rho^{(m)} \rightarrow \pi^S [\otimes^2 \rho^{(m)}]$

U^A and U^S have the following action

$U^A : \otimes^2 \rho^{(m)} \rightarrow \Lambda^2 \rho^{(m)}$

$U^S : \otimes^2 \rho^{(m)} \rightarrow V^2 \rho^{(m)}$

Thus $U^A \in L(M^2 \rightarrow {}^m C_n)$ and $U^S \in L(M^2 \rightarrow {}^{m+n-1} C_n)$

while $\pi^A \in L_\rho (M^2 \rightarrow M^2)$ and $\pi^S \in L_\rho (M^2 \rightarrow M^2)$

(L_ρ indicates subspace of L, the subspace of l.t.s that are projections)

In Dirac Notation the projection operators π^A and π^S are represented as:-

$$\pi^A {}^{\sigma_{\nu_1}, \sigma_{\nu_2}}_{\sigma_{\mu_1}, \sigma_{\mu_2}} = \langle \sigma^{\sigma_{\nu_1}}(r_1') \sigma^{\sigma_{\nu_2}}(r_2') | \frac{1}{2} \sum_{\substack{\underline{\sigma_\chi} \\ \underline{\sigma_\chi} \in \underline{S_{2,m}}}} \varepsilon_{\sigma_\chi} . \underline{\sigma_\chi} | \sigma_{\sigma_{\mu_1}}(r_1) \sigma_{\sigma_{\mu_2}}(r_2) \rangle$$

Now the action of $\underline{\sigma_\chi}$ is defined on m integers as $\underline{\sigma_\chi} . (i_1, \ldots i_m) = (\sigma_{\chi_1}, \sigma_{\chi_2})$ while its action on two integers is $\sigma_\chi . (i_1 i_2) = i_1 i_2$, $i_2 i_1$, or 0 depending whether $\sigma_{\chi_1}, \sigma_{\chi_2} = i_1$ or i_2

Thus

$$\pi^A {}^{\sigma_{\nu_1}, \sigma_{\nu_2}}_{\sigma_{\mu_1}, \sigma_{\mu_2}} = \frac{1}{2} \langle \sigma^{\sigma_{\nu_1}}(r_1') \sigma^{\sigma_{\nu_2}}(r_2') | \sigma_{\sigma_{\mu_1}}(r_1) \sigma_{\sigma_{\mu_2}}(r_2) - \sigma_{\sigma_{\mu_2}}(r_1) \sigma_{\sigma_{\mu_1}}(r_2) \rangle$$

$$= \frac{1}{2} \left\{ \delta^{\sigma_{\nu_1}, \sigma_{\nu_2}}_{\sigma_{\mu_1}, \sigma_{\mu_2}} - \delta^{\sigma_{\nu_1}, \sigma_{\nu_2}}_{\sigma_{\mu_2}, \sigma_{\mu_1}} \right\}$$

and

$$\Pi^{S}{}^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{\mu_1}\sigma_{\mu_2}} = \langle \sigma^{\sigma_{v_1}}(r_1')\sigma^{\sigma_{v_2}}(r_2') \,|\, \tfrac{1}{2}\sum_{\substack{\sigma_\chi \\ \sigma_\chi \in S_{2,m}}} \sigma_\chi \,|\, \sigma_{\sigma_{\mu_1}}(r_1)\,\sigma_{\sigma_{\mu_2}}(r_2)\rangle$$

$$= \tfrac{1}{2}\langle \sigma^{\sigma_{v_1}}(r_1')\,\sigma^{\sigma_{v_2}}(r_2') \,|\, \sigma_{\sigma_{\mu_1}}(r_1)\,\sigma_{\sigma_{\mu_2}}(r_2) + \sigma_{\sigma_{\mu_2}}(r_1)\,\sigma_{\sigma_{\mu_1}}(r_2)\rangle$$

$$= \tfrac{1}{2}\left\{ \delta^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{\mu_1}\sigma_{\mu_2}} + \delta^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{\mu_2}\sigma_{\mu_1}} \right\}$$

The projection matrices can be represented by a product of the form U^+U where U is a rectangular $(r \times s)$ matrix, and $UU^+ = I_s$, i.e. U has as its right inverse U^+, thus we can say that it is unitary to the right, and $U \in L(r \to s)$.

Thus we have

$\Pi^S = U^{S+}U^S$ where $U^S U^{S+} = I_{M^2}$, $U^S \in L(M^2 \to {}^{m+n-1}C_n)$ and

$\Pi^A = U^{A+}U^A$ " $U^A U^{A+} = I_{M^2}$, $U^A \in L(M^2 \to {}^{m}C_n)$

The elements of U^S and U^A are given by: -

$$U^{S}{}^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{\mu_1}\sigma_{\mu_2}} = \frac{1}{\sqrt{2M(\sigma_v)}}\left\{ \delta^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{\mu_1}\sigma_{\mu_2}} + \delta^{\sigma_{v_2}\sigma_{v_1}}_{\sigma_{\mu_1}\sigma_{\mu_2}} \right\} \text{ where } \begin{matrix} \sigma_v \in S_{2,m} \\ \sigma_\mu \in G_{2,m} \end{matrix}$$

$$U^{A}{}^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{\mu_1}\sigma_{\mu_2}} = \frac{1}{\sqrt{2M(\sigma_v)}}\left\{ \delta^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{\mu_1}\sigma_{\mu_2}} - \delta^{\sigma_{v_2}\sigma_{v_1}}_{\sigma_{\mu_1}\sigma_{\mu_2}} \right\} \begin{matrix} \sigma_v \in S_{2,m} \\ \sigma_\mu \in Q_{2,m} \end{matrix}$$

It can be shown quite easily that

$$\frac{1}{\sqrt{2}}\,\sigma^{\sigma_{v_1}}(r_1) \wedge \sigma^{\sigma_{v_2}}(r_2) = \sum_{\sigma_{\mu_n} \in S_{2,m}} U^{A}{}^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{\mu_1}\sigma_{\mu_2}}\,\sigma^{\sigma_{\mu_1}}(r_1)\sigma^{\sigma_{\mu_2}}(r_2) \qquad \sigma_v \in Q_{2,m}$$

and

$$\frac{1}{\sqrt{2M(\sigma_v)}}\,\sigma^{\sigma_{v_1}}(r_1) \vee \sigma^{\sigma_{v_2}}(r_2) = \sum_{\sigma_\mu \in S_{2,m}} U^{S}{}^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{\mu_1}\sigma_{\mu_2}}\,\sigma^{\sigma_{\mu_1}}(r_1)\sigma^{\sigma_{\mu_2}}(r_2)\ \sigma_v \in G_{2,m}$$

thus showing that U^A transforms a basis of $\otimes^2 p^{(m)}$ into a basis for $\wedge^2 p^{(m)}$ and that U^S transforms a basis of $\otimes^2 p^{(m)}$ into a basis for $\vee^2 p^{(m)}$ and it is also easily verified that

$\Pi^S = U^{S+}U^S$ and $\Pi^A = U^{A+}U^A$

So we have that if $X \in \otimes^2 p^{(m)}$ then

$$U^S X = X^S \in \vee^2 p^{(m)}$$

and

$U^A X = X^A \in \Lambda^2 \rho^{(m)}$

$\pi^A X = (\pi X)^A \in \otimes^2 \rho^{(m)} = U^{A+} U^A X = U^{A+} X^A$

$\pi^S X = (\pi X)^S \in \otimes^2 \rho^{(m)} = U^{S+} U^S X = U^{S+} X^S$

Thus the reverse transformations on X^A and X^S viz $U^{A+} X^A$ and $U^{S+} X^S$ give the antisymmetric and symmetric projections of X onto $\otimes^2 \rho^{(m)}$ not X itself, and in fact as $X = \pi^A X + \pi^S X$ then $X = U^{A+} X^A + U^{S+} X^S$.

Now,

$$\otimes_2^2 \rho^{(m)} = (\pi^A_A : \otimes_2^2 \rho^{(m)} \oplus \pi^A_S : \otimes_2^2 \rho^{(m)} \oplus \pi^S_A : \otimes_2^2 \rho^{(m)} \oplus \pi^S_S : \otimes_2^2 \rho^{(m)}$$

$$= (\pi^A : \otimes^2 \rho^{(m)} \oplus \pi^S : \otimes^2 \rho^{(m)}) \otimes (\pi_A : \otimes \rho_{(m)} \oplus \pi_S : \otimes \rho_{(m)})$$

$$= \otimes^2 \rho^{(m)} \otimes \otimes_2 \rho_{(m)}$$

and any element $\omega \in \otimes_2^2 \rho^{(m)}$ can be represented by the projections

$\pi^A \omega \pi_A$, $\pi^A \omega \pi_S$, $\pi^S \omega \pi_A$, $\pi^S \omega \pi_S$

onto the various subspaces of $\otimes_2^2 \rho^{(m)}$ and the associated l.t.s will give the reduced projections onto $\Lambda_2^2 \rho^{(m)}$, $\Lambda^2 V_2 \rho^{(m)}$, $V^2 \Lambda_2 \rho^{(m)}$ and $V_2^2 \rho^{(m)}$ viz $U^A \omega U_A$, $U^A \omega U_S$, $U^S \omega U_A$ and $U^S \omega U_S$.

Thus we can write in terms of $U^S, U^A \in L(M^2 \to {}^{m+n-1}C_n)$ and $L(M^2 \to {}^{m}C_n)$ that if $\omega \in \otimes_2^2 \rho^{(m)}$ then

$U^S \omega U^{S+} = \omega^{SS} \in V_2^2 \rho^{(m)}$

$U^S \omega U^{A+} = \omega^{SA} \in \Lambda^2 V_2 \rho^{(m)}$

$U^A \omega U^{S+} = \omega^{AS} \in V^2 \Lambda_2 \rho^{(m)}$

$U^A \omega U^{A+} = \omega^{AA} \in \Lambda_2^2 \rho^{(m)}$

and noting $\pi^+ = \pi$

$\pi^S \omega \pi^S = U^{S+} U^S \omega U^{S+} U^S = U^{S+} \omega^{SS} U^S \in \pi^S_S : \otimes_2^2 \rho^{(m)}$

$\pi^S \omega \pi^A = U^{S+} U^S \omega U^{A+} U^A = U^{S+} \omega^{SA} U^A \in \pi^S_A : \otimes_2^2 \rho^{(m)}$

$\pi^A \omega \pi^S = U^{A+} U^A \omega U^{S+} U^S = U^{A+} \omega^{AS} U^S \in \pi^A_S : \otimes_2^2 \rho^{(m)}$

$$\Pi^A W \Pi^A = U^{A+} U^A W U^{A+} U^A = U^{A+} W^{AA} U^A \in \Pi^A_A : \otimes^2_1 \rho^{(m)}$$

and hence the reverse transformations from the subspaces are only onto the associated projections of $\otimes^2_1 \rho^{(m)}$

Thus

$$W = \Pi^S W \Pi^S \oplus \Pi^S W \Pi^A \oplus \Pi^A W \Pi^S \oplus \Pi^A W \Pi^A$$
$$= U^{S+} W^{SS} U^S \oplus U^{S+} W^{SA} U^A \oplus U^{A+} W^{AS} U^S \oplus U^{A+} W^{AA} U^A$$

CHAPTER THREE.

Representations of 2nd Order Reduced Matrix

The central point of interest in this thesis is the 2nd Order Reduced Density Matrix. In this chapter we analyse its various forms of representation for Singlet Spin states, its symmetry properties (with respect to spin for this state) and its associated natural spin geminals (N.S.G's). Then in conclusion we study the relation of the natural spin-orbitals (N.S.O's) of the 1st Order Reduced Density Matrix with the N.S.O's associated with the N.S.G's, and thus infering in general the difficulty in relating Natural expansions of different orders of Reduction of the Density Matrix to each other.

The 2nd Order Reduced Density Operator $\hat{\Gamma}^{(2)}$ can be represented on $\Lambda_2^2 F^{(2m_\infty)}$ by $\Gamma^{(2)}(X_1' X_2' \mid X_1 X_2)$. This can be expanded over a basis for $\Lambda_2^2 F^{(2m)}$ in the form

$$\Gamma^{(2)}(X_1' X_2' | X_1 X_2) = \sum_{\sigma_\nu} \sum_{\sigma_\mu} \Gamma^{(2)\,\sigma_\nu}_{\sigma_\mu}\, \omega^{\sigma_{\mu_1}}(1') \wedge \omega^{\sigma_{\mu_2}}(2') \otimes \omega_{\sigma_{\nu_1}}(1) \wedge \omega_{\sigma_{\nu_2}}(2)$$
$$\sigma_\nu, \sigma_\mu \in Q_{2,2m}$$

Thus $\Gamma^{(2)}$ forms a representation of $\hat{\Gamma}^{(2)}$ over $\Lambda_2^2 F^{(2m)}$

When we consider the decomposition $(\Lambda^2 \rho^{(m)} \otimes V^2 S^{(2)} \oplus V^2 \rho^{(m)} \otimes \Lambda^2 S^{(2)})$
$$\otimes (\Lambda_2 \rho_{(m)} \otimes V_2 S_{(2)} \oplus V_2 \rho_{(m)} \otimes \Lambda_2 S_{(2)})$$
of $\Lambda_2^2 F^{(2m)}$ on which the representation of $S^{(2)^2}$ is diagonal(the scalar total spin angular momentum operator), $\Gamma^{(2)}(X_1' X_2' | X_1 X_2)$ can be expanded as

$$\Gamma^{(2)}(1'2'|12) = \sum_{\sigma_\nu} \sum_{\sigma_\mu} \Gamma^{(2)\,\sigma_\nu}_{\alpha\alpha\alpha\alpha\,\sigma_\mu} \prod_i^2 \wedge \sigma^{\sigma_{\mu_i}}(r'_i) \otimes \prod_j^2 \sigma_{\sigma_{\nu_j}}(r_j) \cdot \alpha(1)\alpha(2)\alpha(1)\alpha(2)$$
$$+ \sum_{\sigma_\nu} \sum_{\sigma_\mu} \Gamma^{(2)\,\sigma_\nu}_{\beta\beta\beta\beta\,\sigma_\mu} \prod_i^2 \wedge \sigma^{\sigma_{\mu_i}}(r'_i) \otimes \prod_j^2 \sigma_{\sigma_{\nu_j}}(r_j) \beta(1)\beta(2)\beta(1)\beta(2)$$
$$+ \sum_{\sigma_\nu} \sum_{\sigma_\mu} \Gamma^{(2)\,\sigma_\nu}_{\alpha\beta\alpha\beta\,\sigma_\mu} \prod_i^2 \wedge \sigma^{\sigma_{\mu_i}}(r'_i) \otimes \prod_i^2 \wedge \sigma_{\sigma_{\nu_j}}(r_j) \tfrac{1}{2}(\alpha(1)\beta(2)+\alpha(2)\beta(1)) \cdot (\alpha(1)\beta(2)+\alpha(2)\beta(1))$$
$$+ \sum_{\chi_\nu} \sum_{\chi_\mu} \Gamma^{(2)\,\chi_\nu}_{\alpha\beta_s\alpha\beta_s\,\chi_\mu} \prod_i^2 \vee \sigma^{\chi_{\mu_i}}(r'_i) \otimes \prod_j^2 \vee \sigma_{\chi_{\nu_j}}(r_j) \tfrac{1}{2}(\alpha(1)\beta(2)-\alpha(2)\beta(1)) \cdot (\alpha(1)\beta(2)-\alpha(2)\beta(1))$$

$$+\sum_{X}\sum_{Y}\sum_{\sigma_\nu}\sum_{\sigma_\mu} T^{(2)\sigma_\nu}_{XY\sigma_\mu}\prod_i^{2\wedge}\sigma^{\sigma_{\mu i}}(r'_i)\otimes\prod_j^{2\wedge}\sigma_{\sigma_{\nu j}}(r_j).\textcircled{H}_X(12)\textcircled{H}_Y(12)$$

$$+\sum_{X}\sum_{\sigma_\nu}\sum_{\chi_\mu}\Big\{T^{(2)\sigma_\nu}_{\chi_\mu}.\prod_i^{2\wedge}\sigma^{\chi_{\mu i}}(r'_i)\otimes\prod_j^{2\wedge}\sigma_{\sigma_{\mu j}}(r_j)\textcircled{H}_X(12).\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)-\alpha(2)\beta(1))$$

$$+T^{(2)\chi_\mu}_{\alpha\beta_S X\sigma_\nu}\prod_i^{2\wedge}\sigma^{\sigma_{\nu i}}(r'_i)\otimes\prod_i^{2\wedge}\sigma_{\chi_{\mu j}}(r_j)\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)-\alpha(2)\beta(1))\textcircled{H}_X(12)\Big\}$$

where $X,Y=\alpha\alpha,\beta\beta,\alpha\beta_t$

and $\textcircled{H}_{\alpha\alpha}(12)=\alpha(1)\alpha(2)$; $\textcircled{H}_{\beta\beta}(12)=\beta(1)\beta(2)$; $\textcircled{H}_{\alpha\beta_t}(12)=\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\alpha(2)\beta(1))$

where $\sigma_\nu,\sigma_\mu\in Q_{2,m}$ and $\chi_\nu,\chi_\mu\in G_{2,m}$

The terms involving mixed spin functions are zero if $T^{(2)}(1'2'|12)$ represents a pure Singlet Spin state.

The most succinct bilinear expansion of $T^{(2)}(1'2'12)$ in terms of a set of functions that form a basis for $\Lambda^2_2 F^{(2m)}$ is its Natural expansion i.e. its expansion in terms of its eigenfunctions, viz functions with the property

$$\int T(1'2'|12).\Omega^K(12)dT_{12}=N^K.\Omega^K(12)$$

where N^K is the eigenvalue associated with the eigenfunction $\Omega^K(12)$

In terms of such functions that form an orthonormal basis for $\Lambda^2_2 F^{(2m)}$

where $\int\Omega_K(12)\Omega^L(12)dT_{12}=\delta^L_K$,

$$T^{(2)}(1'2'|12)=\sum_K^{m(2m-1)}T_d{}^{(2)K}_{K}\,\Omega^K(1'2')\Omega_K(12)\ \text{where}\ T_d{}^{(2)K}_{K}=N^K.$$

Notice that the sub and superscripts associated with each function are no longer associated with sequences in $Q_{2,2m}$ This as will be shown is because exterior products formed from a common set of functions that form a basis for $F^{(2m)}$ cannot in general form the set of functions

$$\{\Omega_K(12)\}_{K=1,\ldots\ldots m(2m-1)}$$

We can connect the two bases of $\Lambda^2 F^{(2m)}$ viz $\{\Omega^K(12)\}$ and $\{\prod_i^{2\wedge}\omega^{\sigma_{\nu i}}(x_i)\}$ by a unitary transformation matrix V viz.

$$\Omega^K(12) = \sum_{\sigma_\nu \in Q_{2,2m}} V^K_{\sigma_\nu} \prod_i^2 \wedge \omega^{\sigma_{\nu i}}(x_i) \quad \text{s.t. } V^+V = VV^+ = I_{2m C_2}$$

If $T^{(2)}$ can be diagonalised on the spin symmetric basis of $\Lambda^2 F^{(2m)}$ we can consider the Natural expansion of $T^{(2)}(1'2'|12)$ over the spin symmetric decomposition of $\Lambda^2_2 F^{(2m)}$ and we see that

$$T^{(2)}(1'2'|12) = \sum_K^{m(m-1)/2} T^{(2)}_{d_{\alpha\alpha\alpha K}} {}^K\,{}^A\mu^K(1'2')\,{}^A\mu_K(12).\alpha(1)\alpha(2)\alpha(1)\alpha(2)$$
$$+ \sum_K^{m(m-1)/2} T^{(2)}_{d_{\beta\beta\beta\beta K}} {}^K\,{}^A\mu^K(1'2')\,{}^A\mu_K(12)\beta(1)\beta(2)\beta(1)\beta(2)$$
$$+ \sum_K^{m(m-1)/2} T^{(2)}_{d_{\alpha\beta t\alpha\beta t K}} {}^K\,{}^A\mu^K(1'2')\,{}^A\mu_K(12)\tfrac{1}{2}[\alpha(1)\beta(2)+\alpha(2)\beta(1)][\alpha(1)\beta(2)+\alpha(2)\beta(1)]$$
$$+ \sum_K^{m(m+1)/2} T^{(2)}_{d_{\alpha\beta_s\alpha\beta_s}} {}^S\mu^K(1'2')\,{}^S\mu_K(12)\tfrac{1}{2}[\alpha(1)\beta(2)-\alpha(2)\beta(1)][\alpha(1)\beta(2)-\alpha(2)\beta(1)]$$

all other terms being zero, which would not be the case if $T^{(2)}$ was not diagonalisable over the spin partitioned bases, but when it represents a pure Singlet spin state it is always possible to find a diagonal form over the spin symmetric decomposition of $\Lambda^2_2 F^{(2m)}$

${}^A\mu^K(12) \in \Lambda^2 \rho^{(m)}$, ${}^S\mu^K(12) \in V^2\rho^{(m)}$.

The two bases of $\Lambda^2\rho^{(m)}$ are linked by the unitary transformation

$${}^A\mu^K(12) = \sum_{\sigma_\nu \in Q_{2,m}} V_A{}^K_{\sigma_\nu} \prod_i^2 \wedge \sigma^{\sigma_{\nu i}}(r_i) \quad \text{s.t. } V_A^+ V_A = V_A V_A^+ = I_{m C_N}$$

and the two bases of $V^2\rho^{(m)}$ by

$${}^S\mu^K(12) = \sum_{\sigma_\nu \in G_{2,m}} V_S{}^K_{\sigma_\nu} \prod_i^2 V \sigma^{\sigma_{\nu i}}(r_i) \text{ where } V_S V_S^+ = V_S^+ V_S = I_{m+n-1 C_n}$$

These transformations between bases of $\Lambda^2 F^{(2m)}$, $\Lambda^2\rho^{(m)}$ and $V^2\rho^{(m)}$ on to bases of $\Lambda^2 F^{(2m)}$, $\Lambda^2\rho^{(m)}$ and $V^2\rho^{(m)}$ can be represented in the form

$\Omega(12) = V.\omega(12)$ where $\Omega(12)$ is the column vector with components $\Omega^K(12)$, and $\omega(12)$ is the column vector with components $\prod_i^2 V \omega^{\sigma_{\nu i}}(x_i)$.

Similarly

$^{A}\mu(12) = V_A \sigma^{\wedge}(12)$ where the components of the column vectors $^{A}\mu(12)$, $^{S}\mu(12)$, $\sigma^{\wedge}(12)$ and $\sigma^{\vee}(12)$ are defined in an analagous fashion to those of $\omega(12)$ and $\Omega^{K}(12)$.

and $^{S}\mu(12) = V_S \sigma^{\vee}(12)$

If a function $f(12)$ is represented by a vector f_1 on the $\Omega(12)$ basis of $\Lambda^2 F^{(2m)}$ and by f_2 on the $\omega(12)$ bases of $\Lambda^2 F^{(2m)}$ then f_1 and f_2 are related by

$$f_1 = V_\cdot f_2,$$

and if $D(1'2'|12)$ is represented by a matrix D_1 on the $\Omega(1'2') \otimes \Omega(12)$ basis of $\Lambda^2_2 F^{(2m)}$ and by D_2 on the $\omega(1'2') \otimes \omega(12)$ basis, then D_1 and D_2 are related by

$$D_1 = V D_2 V^{+}$$

Now the expansion of $T^{(2)}(1'2'|12)$ over the $\omega(1'2') \otimes \omega(12)$ basis of $\Lambda^2_2 F^{(2m)}$ can be written as

$$T^{(2)}(1'2'|12) = T_r W(1'2'|12) . T^{(2)}$$

where $W(1'2'|12)$ is the matrix defined as $W(1'2'|12) = W(1'2') \otimes W(12)$ and thus has elements $W(1'2'|12)^{\sigma\nu}_{\sigma\mu} = \overset{2}{\underset{i}{\Pi}}{}^{\wedge} W^{\sigma\nu_i}(X_i') \otimes \overset{2}{\underset{j}{\Pi}}{}^{\wedge} W_{\sigma\mu_j}(X_j)$

$T^{(2)}$ is the representation of $T^{(2)}(1'2'|12)$ on $\Lambda^2_2 F^{(2m)}$ w.r.t. the $\omega(1'2') \otimes \omega(12)$ basis.

Hence we can write the Natural expansion as

$$T^{(2)}(1'2'|12) = T_r \Omega(1'2'|12) . T_d^{(2)} \text{ where } \Omega(1'2'|12) = \Omega(1'2') \otimes \Omega(12)$$

and has elements $\Omega(1'2'|12)^{K}_{L} = \Omega^{K}(1'2') \otimes \Omega_L(1'2')$.

We can also write $\Omega(1'2'|12) = V\, \omega(1'2'|12)\, V^{+}$

$$T_d^{(2)} = V T^{(2)} V^{+}$$

i.e. $T^{(2)}(1'2'|12) = T_r V \omega(1'2'|12) V^{+} V T^{(2)} V^{+}$

Similarly we can apply this formalism to the spin symmetric decomposition

of $\Lambda_2^2 F^{(2m)}$ viz

$$^A\mu(1'2'|12) = V_A\, \sigma^\wedge(1'2'|12)\, V_A^+$$

$$^S\mu(1'2'|12) = V_S\, \sigma^\vee(1'2'|12)\, V_S^+$$

$$T^{(2)}_{d\alpha\alpha\alpha\alpha} = V_A\, T^{(2)}_{\alpha\alpha\alpha\alpha}\, V_A^+;\quad T^{(2)}_{d\beta\beta\beta\beta} = V_A\, T^{(2)}_{\beta\beta\beta\beta}\, V_A^+;\quad T^{(2)}_{d\alpha\beta_t\alpha\beta_t} = V_A\, T^{(2)}_{\alpha\beta_t\alpha\beta_t}\, V_A^+$$

$$\text{and } T^{(2)}_{d\alpha\beta_s\alpha\beta_s} = V_S\, T^{(2)}_{\alpha\beta_s\alpha\beta_s}\, V_S^+.$$

The matrices V_A and V_S are submatrices of the total matrix that transforms the basis $\left\{ \sigma^\wedge(12)\alpha(1)\alpha(2) \oplus \sigma^\wedge(12)\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)+\alpha(2)\beta(1)\} \oplus \sigma^\wedge(12)\beta(1)\beta(2) \oplus \sigma^\vee(12)\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\} \right\}$ onto the corresponding natural basis of $\Lambda_2^2 F^{(2m)}$ i.e. $V = V_A \oplus V_A \oplus V_A \oplus V_S$

$$\sigma(12) = \sigma^\wedge(12)_{\alpha\alpha} \oplus \sigma^\wedge(12)_{\alpha\beta_t} \oplus \sigma^\wedge(12)_{\beta\beta} \oplus \sigma^\vee(12)_{\alpha\beta_s}$$

and $V.\sigma(12) = \mu(12)$ and $VV^\dagger = V^\dagger V = \left[I_{mC_N} \oplus I_{mC_N} \oplus I_{mC_N} \oplus I_{m+n-1C_N} \right]$

where $\mu(12) = \mu^\wedge(12)_{\alpha\alpha} \oplus \mu^\wedge(12)_{\alpha\beta_t} \oplus \mu^\wedge(12)_{\beta\beta} \oplus \mu^\vee(12)_{\alpha\beta_s}$

and $T_d^{(2)} = \left[V_A \oplus V_A \oplus V_A \oplus V_S \right] . T^{(2)} . \left[V_A^+ \oplus V_A^+ \oplus V_A^+ \oplus V_S^+ \right]$

where $T^{(2)}$ is expressed on the spin symmetric $\sigma(12)$ basis, and is of block diagonal form on this basis i.e.

$$T^{(2)} = T^{(2)}_{\alpha\alpha\alpha\alpha} \oplus T^{(2)}_{\alpha\beta_t\alpha\beta_t} \oplus T^{(2)}_{\beta\beta\beta\beta} \oplus T^{(2)}_{\alpha\beta_s\alpha\beta_s}$$

(as we assume $T^{(2)}$ represents a pure spin state of the system)

Thus we can write when $T^{(2)}(1'2'|12)$ represents a pure spin state that

$$T^{(2)}(1'2'|12) \equiv T_r \left[\begin{bmatrix} V_A & 0 \\ 0 & V_A \end{bmatrix} \begin{bmatrix} T^{(2)}_{\alpha\alpha\alpha\alpha} & 0 \\ 0 & T^{(2)}_{\alpha\beta_t\alpha\beta_t} \end{bmatrix} \begin{bmatrix} V_A^+ & 0 \\ 0 & V_A^+ \end{bmatrix} \begin{bmatrix} V_A & 0 \\ 0 & V_S \end{bmatrix} \right] \sigma(12) \left[\begin{bmatrix} V_A^+ & 0 \\ 0 & V_A^+ \end{bmatrix} \begin{bmatrix} V_A^+ & 0 \\ 0 & V_S^+ \end{bmatrix} \right]$$

where $T^{(2)}_{\beta\beta\beta\beta}$ and $T^{(2)}_{\alpha\beta_s\alpha\beta_s}$ sit on the diagonal of the middle block matrix, and $\sigma(12)$ is the matrix

$$\left[\sigma^{\wedge}(12)_{\alpha\alpha}\oplus\sigma^{\hat{}}(12)_{\alpha\beta_t}\oplus\sigma^{\hat{}}(12)_{\beta\beta}\oplus\sigma^{V}(12)_{\alpha\beta_s}\right]\otimes\left[\sigma_{\wedge}(12)_{\alpha\alpha}\oplus\sigma_{\wedge}(12)_{\alpha\beta_t}\oplus\sigma_{\wedge}(12)_{\beta\beta}\oplus\sigma_{V}(12)_{\alpha\beta_s}\right]$$

and this is not of block diagonal form.

The eigenfunctions $\mu^j(r_1,r_2)\cdot\textcircled{H}_i(\eta_1,\eta_2)$ $i=\alpha\alpha,\alpha\beta_t,\beta\beta,\alpha\beta_s$.

are called Natural Spin Geminals (N.S.G.) and they form Natural representations of $\hat{\Gamma}^{(2)}$ on $\Lambda_2^2 F^{(2m)}$

The bases that form a diagonal representation of $\hat{\Gamma}^{(2)}$ can thus be constructed in two different ways

i.e. either from diagonalising $\hat{\Gamma}^{(2)}$ as represented on the $\{\omega(x_1,x_2)\}$ basis of $\Lambda^2 F^{(2m)}$ or by diagonalising $\hat{\Gamma}^{(2)}$ as represented on the

$\{\sigma^{\hat{}}_{\alpha\alpha}(r_1r_2)\oplus\sigma^{\hat{}}_{\beta\beta}(r_1r_2)\oplus\sigma^{\hat{}}_{\alpha\beta_t}(r_1r_2)\oplus\sigma^{V}_{\alpha\beta_s}(r_1r_2)\}$ basis of $\Lambda^2 F^{(2m)}$ and the new bases are

$\{\Omega(x_1,x_2)\}$ and $\{\sum^{\oplus}_{\text{over spinfunctions}}\mu(r_1r_2)\textcircled{H}_i(\eta_1,\eta_2)\}$ respectively

which are identical to each other or can be made so; thus there is a unique correspondence s.t.

$$\Omega^K(x_1,x_2)=\mu^j(r_1r_2)\textcircled{H}_i(\eta_1,\eta_2).$$

$K=1,\ldots\ldots m(2m-1)$ $\quad j=1,\ldots\ldots m(m-1)/2$ when $i=\alpha\alpha,\alpha\beta_t,\beta\beta$

and $j=1\ldots\ldots m(m+1)/2$ " $i=\alpha\beta_s$

As we see an N.S.G. can be constructed from a direct product of a pure position space function with a spin space function. The position space function $\mu^j(r_1r_2)$ is called a Natural Geminal and the set of Natural Geminals forms a basis for either $\Lambda^2\rho^{(m)}$ or $V^2\rho^{(m)}$

The elements of the diagonal representation of $\hat{\Gamma}^{(2)}$ on $\Lambda_2^2 F^{(m)}$ are called the occupation numbers of the associated N.S.G. (i.e. the N.S.G. they are associated with when $\Gamma^{(2)}(1'2'|12)$ is expanded over the set of N.S.G's).

When $\Gamma^{(2)}(1'2'|12)$ represents a pure spin state of the N

particle system then we have see that its N.G's are either anti-

symmetric or symmetric functions

i.e. either $\in \Lambda^2 \rho^{(m\infty)}$ or $V^2 \rho^{(m\infty)}$

viz $\mu_i^a(r_1 r_2) = -\mu_i^a(r_2 r_1)$ superscript a denoting $\in \Lambda^2 \rho^{(m\infty)}$

and $s \in V^2 \rho^{(m\infty)}$.

and $\mu_i^s(r_1 r_2) = \mu_i^s(r_2 r_1)$

Hence they can always be written as the symmetric or exterior product

of the functions $\in \rho^{(m\infty)}$

$$\mu^s(r_1 r_2) = \frac{1}{\nu}\left\{\phi(r_1)\chi(r_2) + \phi(r_2)\chi(r_1)\right\} \text{ if } \phi \neq \chi \quad \nu = \sqrt{2}$$

$$\phi = \chi \quad \nu = 2$$

and

$$\mu^a(r_1 r_2) = \frac{1}{\sqrt{2}}\left\{\phi(r_1)\chi(r_2) - \phi(r_2)\chi(r_1)\right\}$$

Orthonormality of Geminals and Overlap

A geminal k is spatially orthonormal to another geminal k' when the following relationship is satisfied.

$$\langle \lambda_k(12) \mid \lambda^{k'}(12) \rangle = \delta^k_{k'} = \int \lambda_k(r_1 r_2)\, \lambda^{k'}(r_1 r_2)\, dr_1\, dr_2$$

where λ^k and $\lambda_{k'}$ are purely spatial functions.

Now if $\lambda^k, \lambda_{k'} \in \Lambda^2 \rho^{(m\infty)}$ or $V_2 \rho^{(m\infty)}$ they can be expressed in terms of one variable function so

(a) $\in \Lambda^2 \rho^{(m)}$

$$\lambda^{k'}(12) = \frac{1}{\sqrt{2}} \left\{ \phi^i(1)\, \phi^j(2) - \phi^i(2)\, \phi^j(1) \right\} \qquad k = f_a(ij)$$

(b) $\in V^2 \rho^{(m)}$

$$\lambda^{k'}(12) = \frac{1}{\nu^{ij}} \left\{ \phi^i(1)\, \phi^j(2) + \phi^i(2)\, \phi^j(1) \right\} \qquad \nu^{ij} = 2 \text{ if } i = j, \quad = \sqrt{2} \text{ if } i \neq j$$

$$k = f_s(ij)$$

We make no assumption about the properties of the set of functions $\{\phi^i\}$ except they form a basis for $F^{(m)}$ (i.e. they are l.i.)

The orthonormality condition in terms of these 1 variable functions is thus

(a) $\in \Lambda^2 \rho^{(m)}$

$$\langle \lambda_k(12) \mid \lambda^{k'}(12) \rangle = \frac{1}{2} \left\{ \langle \phi^i(1)\phi^j(2) \mid \phi_r(1)\phi_s(2) \rangle - \langle \phi^i(1)\phi^j(2) \mid \phi_s(1)\phi_r(2) \rangle \right.$$
$$\left. - \langle \phi^j(1)\phi^i(2) \mid \phi_r(1)\phi_s(2) \rangle + \langle \phi^j(1)\phi^i(2) \mid \phi_s(1)\phi_r(2) \rangle \right\}$$
$$= \frac{1}{2} \left\{ S^i_r . S^j_s - S^i_s . S^j_r - S^j_r . S^i_s + S^j_s . S^i_r \right\}$$
$$= S^i_r . S^j_s - S^i_s . S^j_r .$$

where $S^n_m = \langle \phi_m(1) \mid \phi^n(1) \rangle$

Similarly (b) $\langle \lambda_k(12) \mid \lambda^{k'}(12) \rangle = \frac{1}{\nu^{ij}_{rs}} \left\{ S^i_r . S^j_s + S^i_s . S^j_r + S^j_r . S^i_s + S^j_s . S^i_r \right\}$

$$= \frac{2}{\nu^{ij}_{rs}} \left\{ S^i_r . S^j_s + S^i_s . S^j_r \right\}$$

$\nu^{ij}_{rs} = 4$ if $i=j$ and $r=s$

$= 2\sqrt{2}$ if $i=j$ and $r\neq s$ or $i\neq j$ and $r=s$

$= 2$ if $i\neq j$ and $r\neq s$

Thus for the geminal orthonormality relationships to hold

@ in $\Lambda^2 \rho^{(m\infty)}$ $S^i_r \cdot S^j_s = S^i_s \cdot S^j_r$ when $k \neq k'$

i.e. $f_a(ij) \neq f_a(rs)$

and $S^i_i \cdot S^j_j - S^i_j \cdot S^j_i = 1$ when $k = k'$

ⓑ in $V^2 \rho^{(m\infty)}$ $S^i_r \cdot S^j_s = -S^i_s S^j_r$ when $k \neq k'$

i.e. $f_s(ij) \neq f_s(rs)$

and $S^i_i \cdot S^j_j + S^i_j \cdot S^j_i = \frac{\nu^{ij}_{ij}}{2}$ when $k = k'$.

One possible solution in terms of the functions $\{\phi_i\}$ is when these functions form an orthonormal basis for $F^{(m)}$ i.e. $S^m_n = \delta^m_n$. However, this is only a particular solution not a general one, and generally the set $\{\phi_i\}$ would have to be l.d if it was to furnish a solution for all k.

{ i.e. for all the orthonormal geminals in $\Lambda^2 F^{(m)}$ and $V^2 F^{(m)}$ }

N.S.G's and their N.S.O's

We have seen that

$$\Gamma^{(2)}(1'2'|12) = \sum_k^{m(2m-1)} \Omega^k(1'2')\,\Omega_k(12)\,T^{(2)k}_{d\,k}$$

Now if we define a partial 2nd Order Reduced Density Matrix, or the 2nd Order Reduced Density Matrix associated with a particular N.S.G as

$$\Gamma^{(2)}_k(1'2'|12) = \Omega^k(1'2')\,\Omega_k(12)$$

Then

$$\Gamma^{(2)}(1'2'|12) = \sum_k^{m(2m-1)} \Gamma^{(2)}_k(1'2'|12)\,T^{(2)\,k}_{d\;k}.$$

$\Gamma^{(2)}_k(1'2'|12)$ is also the projection Matrix associated with the k^{th}

eigensubspace of $\Gamma^{(2)}(1'2'|12)$ and it projects elements of $\Lambda^2 F^{(m\infty)}$ onto this subspace, in common with all projection operators

$$\left[\Gamma_K^{(2)}(1'2'|12)\right]^2 = \Gamma_K^{(2)}(1'2'|12)$$

i.e. it is idempotent and it has one eigenvalue of 1 and the rest of zero. Thus $\mathrm{Tr}\,\Gamma_K^{(2)}(1'2'|12) = 1$, the eigenfunction associated with the non zero eigenvalue is $\Omega^K(12)$

With $\Gamma_K^{(2)}(1'2'|12)$ we can associate a 1st Order Reduced Density Matrix so

$$\int \Gamma_K^{(2)}(1'2'|12)\, d\tau_2 = \rho_K(1'|1)$$

The 1 variable eigenfunctions of $\rho_K(1'|1)$ form a basis for $F^{(m)}$ that gives a diagonal matrix representation of $\rho_K(1'|1)$ viz

$$\rho_K(1'|1) = \sum_\ell^m {}^K\phi_\ell(1')\,{}^K\phi^\ell(1)\,\rho_{K\ell}^{d\ell}$$

where $\int \rho_K(1'|1)\,{}^K\phi^\ell(1)\, d\tau_1 = \rho_{K\ell}^{d\ell}\,{}^K\phi^\ell(1)$.

In Matrix notation we can write

$$\rho_K(1'|1) = \mathrm{Tr}\,{}^K\Phi\,\rho_K^d \quad \text{where} \quad {}^K\Phi_j^i = {}^K\phi^i(1')\,{}^K\phi_j(1).$$

The elements of ρ_K^d are the statistical weights with which each ${}^K\phi^i(X_1)$ appears in $\rho_K(1'|1)$ known as the occupation number of that orbital.

ρ_K^d expressed in the orthonormal basis $\{\omega(1)\}$ of $F^{(m)}$ is a unitary transformation of ρ_K^d i.e.

$$\rho_K = {}^K U\,\rho_K^d\,{}^K U^+, \quad \text{where} \quad {}^K U\,{}^K U^+ = {}^K U^+\,{}^K U = I_m$$

and ${}^K\phi^i(1) = \sum_j^m {}^K U_j^i\,\omega^j(1)$.

${}^K\phi^i(1)$'s are known as the N.S.O's of $\Gamma_K^{(2)}(1'2'|12)$.

Each of the N.S.G'S gives rise to an associated 2nd Order Reduced Density Matrix $\Gamma_K^{(2)}(1'2'|12)$, labelled with a subscript α when the N.G

$\in \Lambda^2 \rho^{(m\omega)}$ and a subscript s when it $\in V^2 \rho^{(m\omega)}$ viz $T^{(2)}_{K_a}(1'2'|12)$ or $T^{(2)}_{K_s}(1'2'|12)$. The N.S.O's are a direct product of position space functions ${}^K\psi_i(r_1)$ and spin space functions $s_i(\eta)$. The spin functions are

$$S_\alpha(1) = \int \Theta_{\alpha\alpha}(\eta_1\eta_2)\,\Theta_{\alpha\alpha}(\eta_1\eta_2).d\eta_2 = \alpha(1)$$

$$S_\beta(1) = \int \Theta_{\beta\beta}(\eta_1\eta_2)\,\Theta_{\beta\beta}(\eta_1\eta_2).d\eta_2 = \beta(1)$$

$$S_{\alpha\beta_t}(1) = \int \Theta_{\alpha\beta_t}(\eta_1\eta_2)\,\Theta_{\alpha\beta_t}(\eta_1\eta_2).d\eta_2 = \frac{1}{\sqrt{2}}\left(\alpha(1)+i\beta(1)\right)$$

$$S_{\alpha\beta_s}(1) = \int \Theta_{\alpha\beta_s}(\eta_1\eta_2)\,\Theta_{\alpha\beta_s}(\eta_1\eta_2).d\eta_2 = \frac{1}{\sqrt{2}}\left(\alpha(1)+i\beta(1)\right).$$

where $i=\sqrt{-1}$.

Each set of N.S.O's associated with an N.S.G has m orthonormal members and forms a basis for $F^{(2m)}$ and only when the ρ_K's can be simultaneously diagonalised are the sets $\left\{{}^K\phi_i(1)\right\}$ the same.

Every Reduced 2nd Order Density Matrix can be represented as a direct product of a pure position space density matrix and a spin space density matrix, so

$$T^{(2)}_K(x_1'x_2'|x_1x_2) = T^{(2)}_K(r_1'r_2'|r_1r_2).\Theta(\eta_1'\eta_2'|\eta_1\eta_2) \quad \text{where } T^{(2)}_K(r_1'r_2'|r_1r_2) = \mu^K(r_1'r_2')\mu_K(r_1r_2)$$

Also every $\rho_K(x_1'|x_1)$ can be so factored

$$\rho_K(x_1'|x_1) = \rho_K(r_1'|r_1).\Theta(\eta'|\eta) \quad \text{where } \rho_K(r_1'|r_1) = {}^K\psi^i(r_1')\,{}^K\psi_i(r_1)$$

Where the context is clear 1 will still be used to denote r_1 and $2 \equiv r_2$ etc; and spin function $\Theta(\eta'|\eta) = \Theta_{\alpha\beta_t}(\eta'|\eta)$ for example is given by

$$\Theta_{\alpha\beta_t}(\eta'|\eta) = S_{\alpha\beta_t}(\eta')S_{\alpha\beta_t}(\eta) = \frac{1}{2}\left(\alpha(1)-i\beta(1)\right)\left(\alpha(1)+i\beta(1)\right) = \frac{1}{2}\left(\alpha(1)\alpha(2)+\beta(1)\beta(2)\right)$$

If an N.G can be expressed as a symmetric or antisymmetric product of two functions $\psi(1)$, $\chi(1)$, the type of product depending on whether $\mu^K(12) \in \Lambda^2\rho^{(m)}$ or $\mu^K(12) V^2\rho^{(m)}$ then we can say that

$$\mu^K(12) = \frac{1}{\nu}\{\psi(1)\chi(2) \pm \psi(2)\chi(1)\}$$

where ν is a normalisation factor satisfying

$$\int \mu_K(12)\mu^K(12)\,dr_{12} = 1 = \int \Gamma_K(r_1' r_2' | r_1 r_2)\,dr_{12}.$$

$$\Gamma_K(1'2'|12) = \frac{1}{\nu^2}\{|\psi(1)\chi(2)\rangle\langle\psi(1)\chi(2)| \mp |\psi(1)\chi(2)\rangle\langle\psi(2)\chi(1)| \mp |\psi(2)\chi(1)\rangle\langle\psi(1)\chi(2)| + |\psi(2)\chi(1)\rangle\langle\psi(2)\chi(1)|\}$$

$$\therefore \rho_K(r'|r) = \rho_K(1'|1) = \frac{1}{\nu^2}\{|\psi(1)\rangle\langle\psi(1)|N_\chi \mp |\psi(1)\rangle\langle\chi(1)|S_\psi^\chi \mp |\chi(1)\rangle\langle\psi(1)|S_\chi^\psi + |\chi(1)\rangle\langle\chi(1)|N_\psi\}$$

where $N_\chi = \langle\chi(1)|\chi(1)\rangle$; $N_\psi = \langle\psi(1)|\psi(1)\rangle$;

$$S_\psi^\chi = S_\chi^\psi = \langle\chi(1)|\psi(1)\rangle = \langle\psi(1)|\chi(1)\rangle$$

For the geminal to be normalised $\int \rho(1'|1)\,dr_1 = 1$, i.e. $\frac{2}{\nu^2}[N_\chi N_\psi \pm S_\psi^{\chi^2}] = 1$

Thus $\nu^2 = 2[N_\chi N_\psi \pm S_\psi^{\chi^2}]$

$\therefore \nu = 2^{\frac{1}{2}}[N_\chi N_\psi \pm S_\psi^{\chi^2}]^{1/2}$ top sign for $\mu^K \in V^2\rho(m)$

bottom " $\mu^K \in \Lambda^2\rho(m)$

The eigenfunctions of $\rho_K(r_1'|r_1)$ associated with non-zero eigenvalues must be of the form $c_1|\psi(1)\rangle + c_2|\chi(1)\rangle$, thus:-

$$\rho_K(1'|1)[c_1|\psi(1)\rangle + c_2|\chi(1)\rangle] = \frac{1}{\nu^2}\{N_\chi N_\psi c_1|\psi(1)\rangle + N_\chi S_\chi^\psi c_2|\psi(1)\rangle \mp S_\psi^{\chi^2} c_1|\psi(1)\rangle \mp S_\psi^\chi N_\chi c_2|\psi(1)\rangle \mp S_\chi^\psi N_\psi c_1|\chi(1)\rangle \mp S_\chi^{\psi^2} c_2|\chi(1)\rangle + N_\psi S_\psi^\chi c_1|\chi(1)\rangle + N_\psi N_\chi c_2|\chi(1)\rangle\}$$

$$= \frac{1}{\nu^2}\{[(N_\chi N_\psi \mp S_\psi^{\chi^2})c_1 + (N_\chi S_\chi^\psi \mp S_\chi^\psi N_\chi)c_2]|\psi(1)\rangle + [(N_\psi S_\psi^\chi \mp S_\psi^\chi N_\psi)c_1 + (N_\chi N_\psi \mp S_\psi^{\chi^2})c_2]|\chi(1)\rangle\}$$

Thus for $\Gamma_K(1'2'|12) \in \Lambda^2\rho(m)$ we have

$$\rho_K(1'|1)[c_{i_1}|\psi(1)\rangle + c_{i_2}|\chi(1)\rangle] = \frac{1}{\nu^2}\{(N_\chi N_\psi - S_\psi^{\chi^2})c_{i_1}|\psi(1)\rangle + (N_\chi N_\psi - S_\psi^{\chi^2})c_{i_2}|\chi(1)\rangle\}$$

$$= \frac{1}{\nu^2}(N_\chi N_\psi - S_\psi^{\chi^2})[c_{i_1}|\psi(1)\rangle + c_{i_2}|\chi(1)\rangle]$$

$$= \frac{1}{2}\left[c_{i1}|\psi(1)\rangle + c_{i2}|\chi(1)\rangle\right]$$

For the eigenvectors to be orthonormal

$$\left[\langle\psi(1)|c_{i1} + \langle\chi(1)|c_{i2}\right]\left[c_{i1}|\psi(1)\rangle + c_{i2}|\chi(1)\rangle\right] = 1$$

$$\left[\langle\psi(1)|c_{i1} + \langle\chi(1)|c_{i2}\right]\left[c_{j1}|\psi(1)\rangle + c_{j2}|\chi(1)\rangle\right] = 0$$

i.e. $N_\psi \cdot c_{i1}^2 + N_\chi c_{i2}^2 + 2c_{i1}\cdot c_{i2}\cdot S_\chi^\psi = 1$ ..... ①

$N_\psi \cdot c_{i1}c_{j1} + N_\chi c_{i2}c_{j2} + (c_{i1}c_{j2} + c_{i2}c_{j1})S_\chi^\psi = 0$ ..... ②

As all l.c's of $\psi(1)$ and $\chi(1)$ can be eigenvectors we can choose $c_{i1} = c_{i2}$,

then we have from ①, $c_{i1}^2(N_\psi + N_\chi + 2S_\chi^\psi) = 1$

$$\therefore\ c_{i1} = \pm(N_\psi + N_\chi + 2S_\chi^\psi)^{-1/2} = c_{i2}.$$

If we choose $c_{i1} = +(N_\psi + N_\chi + 2S_\chi^\psi)^{-1/2} = c_{i2}$

we have from ② $N_\psi c_{j1} + N_\chi c_{j2} + (c_{j2} + c_{j1})S_\chi^\psi = 0$

$$\text{i.e. } (N_\psi + S_\chi^\psi)c_{j1} = -(N_\chi + S_\chi^\psi)c_{j2}$$

If we let $X = \dfrac{(N_\psi + S_\chi^\psi)}{(N_\chi + S_\chi^\psi)}$, then $-Xc_{j1} = c_{j2}$

Then from the normalisation on the 2nd eigenfunction we have

$$N_\psi c_{j1}^2 + N_\chi X^2 c_{j1}^2 - 2X c_{j1}^2 S_\chi^\psi = 1$$

$$\therefore\ c_{j1} = \pm\left[X^2N_\chi + N_\psi - 2XS_\chi^\psi\right]^{-1/2}$$ we choose +ve sign

and

$$c_{j2} = -X\left[X^2N_\chi + N_\psi - 2XS_\chi^\psi\right]^{-1/2}$$

Thus we have

$$^K\phi^1(1) = \frac{1}{(N_\psi + N_\chi + 2S_\chi^\psi)^{1/2}}\left[|\psi(1)\rangle + |\chi(1)\rangle\right]$$

$$^K\phi^2(1) = \frac{1}{(X^2N_\chi + N_\psi - 2XS_\chi^\psi)^{1/2}}\left[|\psi(1)\rangle - X|\chi(1)\rangle\right]$$

where $X = \dfrac{(N_\psi + S_\chi^\psi)}{(N_\chi + S_\chi^\psi)}$

Both eigenfunctions have the eigenvalue $= \frac{1}{2}$.

When $\chi = 1$, $\mu^K(12)$ can be expressed an an antisymmetric product of its N.O's. This is the case when $N_\psi = N_\chi$, but we always scale the functions $\Psi(1)$ and $\chi(1)$ so that $N_\psi = N_\chi$ without altering their eigenvalues.

Then

$$^K\phi^1(1) = \frac{1}{[2(N+S_\chi^\psi)]^{1/2}} \left[|\psi(1)\rangle + |\chi(1)\rangle\right]$$

$$^K\phi^2(1) = \frac{1}{[2(N-S_\chi^\psi]^{1/2}} \left[|\psi(1)\rangle - |\chi(1)\rangle\right]$$

then we can form l.c's of $^K\phi^1(1)$ and $^K\phi^2(1)$ that are still eigenfunctions with eigenvalues $= \frac{1}{2}$.

i.e. $$\frac{1}{2N^{1/2}} \left[[2(N+S_\chi^\psi)]^{1/2}\ {}^K\phi^1(1) + [2(N-S_\chi^\psi)]^{1/2}\ {}^K\phi^2(1)\right] = \frac{1}{N^{1/2}} |\psi(1)\rangle$$

and $$\frac{1}{2N^{1/2}} \left[[2(N+S_\chi^\psi)]^{1/2}\ {}^K\phi^1(1) - [2(N-S_\chi^\psi)]^{1/2}\ {}^K\phi^2(1)\right] = \frac{1}{N^{1/2}} |\chi(1)\rangle$$

and we can always scale $|\psi(1)\rangle$ and $|\chi(1)\rangle$ to be normalised to 1 i.e. $N = 1$ and thus $\mu^K(12) \in \Lambda^2 \rho^{(m)}$ can always be expressed as an antisymmetric product of its N.O's viz

$$\mu^K(12) = \frac{1}{\sqrt{2}} \left\{\psi(1)\chi(12) - \psi(2)\chi(1)\right\} \quad (\nu = \sqrt{2})$$

This analysis can be generalised to functions $\in \Lambda_\rho^\rho F^{(2mco)}$ for any ρ and it can be shown that if $G^{(\rho)}(1'\ldots\rho'|1\ldots\rho) = \chi^*(1'\ldots\rho')\chi(1\ldots\rho)$ then the 1st Order Reduced Density Matrix associated $G^{(\rho)}(1'\ldots\rho'|1\ldots\rho)$ and defined as $G^{(1)}(1'|1) = \int G^{(\rho)}(1'\ldots\rho'|1\ldots\rho).dx_2\ldots x_\rho$ has N.S.O's $\{g^i(1)\}_{i=1,\ldots 2m}$ each associated with the eigenvalue $\frac{1}{\rho}$ or 0. There are ρ N.S.O's associated with the eigenvalue $\frac{1}{\rho}$ and $m-\rho$ with the eigenvalue 0.

$$G^{(1)}(1'|1) = \frac{1}{\rho} \sum_{i=1}^{i=m} g^i(1')g_i(1).$$

and $\chi(1....p)$ can be constructed from the exterior product of the N.S.O's associated with the non-zero eigenvalues i.e.

$$\chi(1....p) = g^1(x_1) \wedge .. \wedge g^p(x_p) \quad \text{where } g^1(1), ... g^p(1)$$

have eigenvalues $\frac{1}{p}$ and $g^{p+1}(1)....g^m(1)$ have eigenvalues of 0.

For symmetric N.G's i.e. $\mu^k(12) \in V^2p^{(m)}$ we have:-

$$\varrho_k(1'1)\left[c_{i1}|\psi(1)\rangle + c_{i2}|\chi(1)\rangle\right] = \frac{1}{\sqrt{2}}\left\{\left[(N_\chi N_\psi + S_\psi^{\chi^2})c_{i1} + 2N_\chi S_\chi^\psi c_{i2}\right]|\psi(1)\rangle + \left[2N_\psi S_\chi^\psi c_{i1} + (N_\chi N_\psi + S_\psi^{\chi^2})c_{i2}\right]|\chi(1)\rangle\right\}$$

For $c_{i1}|\psi(1)\rangle + c_{i2}|\chi(1)\rangle$ to be an eigenfunction we have the constraining condition

$$\underbrace{\left[(N_\chi N_\psi + S_\psi^{\chi 2})\, c_{i1} + 2N_\chi S_\chi^\psi\, c_{i2}\right]}_{c_{i1}} = \underbrace{\left[2N_\psi S_\chi^\psi\, c_{i1} + (N_\chi N_\psi + S_\psi^{\chi 2})c_{i2}\right]}_{c_{i2}}$$

i.e. $\frac{c_{i2}}{c_{i1}} = \pm\left[\frac{N_\psi}{N_\chi}\right]^{1/2}$

The eigenequation then becomes

$$\varrho_k(1'1)\left[c_{i1}|\psi(1)\rangle + c_{i2}|\chi(1)\rangle\right] = \frac{1}{\sqrt{2}}\left[N_\chi N_\psi + S_\psi^{\chi^2} \pm 2S_\psi^\chi (N_\psi N_\chi)^{1/2}\right]\left[c_{i1}|\psi(1)\rangle + c_{i2}|\chi(1)\rangle\right]$$

$$= \frac{1}{\sqrt{2}}\left[\left([N_\chi N_\psi]^{1/2} \pm S_\psi^\chi\right)^2\right]\left[c_{i1}|\psi(1)\rangle + c_{i2}|\chi(1)\rangle\right]$$

So the eigenfunctions are no longer degenerate except in the special case $S_\psi^\chi = 0$.

[This is a special case for $\mu^k(12) \in V^2p^{(m)}$ and not for $\mu^k(12) \in V^2p^{(m)}$ as in the latter case the eigenvalues are independent of S_ψ^χ while in the former they depend on S_ψ^χ]

For orthonormality of the eigenfunctions we have the same conditions as before viz

$$N_\psi c_{i1}^2 + N_\chi c_{i2}^2 + 2c_{i1}\cdot c_{i2}\cdot S_\psi^\chi = 1 \ldots\ldots\ldots \text{①}$$

$$N_\psi c_{i1}\cdot c_{j1} + N_\chi c_{i2}\cdot c_{j2} + (c_{i1}c_{j2} + c_{i2}c_{j1})S_\psi^\chi = 0 \ldots \text{②}$$

Using ① and the above condition on $\frac{C_{i2}}{C_{i1}}$ we have

$$N_\psi C_{i1}^2 + N_\psi C_{i1}^2 \pm 2 C_{i1}^2 S_\psi^\chi \left[\frac{N_\psi}{N_\chi}\right]^{1/2} = 1$$

$$\text{i.e. } 2 C_{i1}^2 \left[N_\psi \pm \left[\frac{N_\psi}{N_\chi}\right]^{1/2} S_\psi^\chi\right] = 1$$

which gives for $N_\psi \neq \left[\frac{N_\psi}{N_\chi}\right]^{1/2} S_\psi^\chi$ that

$$C_{i1} = \pm\frac{1}{\sqrt{2}}\left[N_\psi \pm \left[\frac{N_\psi}{N_\chi}\right]^{1/2} S_\psi^\chi\right]^{-1/2}$$

when $N_\psi = \left[\frac{N_\psi}{N_\chi}\right]^{1/2} S_\psi^\chi$ i.e. $\left[N_\chi N_\psi\right]^{1/2} = S_\psi^\chi$

We have only 1 non-zero eigenvalue of the value $\frac{1}{\sqrt{2}}\left(\left[2 N_\chi N_\psi\right]^{1/2}\right)^2$

$= \frac{4 N_\chi N_\psi}{\sqrt{2}} = \frac{4 N_\chi N_\psi}{4 N_\chi N_\psi} = 1$, and C_{i1} can only have the value

$$C_{i1} = \pm\frac{1}{\sqrt{2}}\left[N_\psi + \left[\frac{N_\psi}{N_\chi}\right]^{1/2}\left[N_\chi N_\psi\right]^{1/2}\right]^{-1/2} = \pm\frac{1}{\sqrt{2}}\left[2 N_\psi\right]^{-1/2} = \pm\frac{1}{2N_\psi}$$

Thus the eigenvector associated with the non-zero eigenvalue can only be of the form

$$^K\phi'(1) = \pm\frac{1}{2N_\psi}\left(|\psi(1)\rangle + |\psi(1)\rangle\right) = \pm\frac{1}{N_\psi}|\psi(1)\rangle .$$

For the more general case of 2 non-zero eigenvalues we take

$$C_{i1} = +\frac{1}{\sqrt{2}}\left[N_\psi + \left[\frac{N_\psi}{N_\chi}\right]^{1/2} S_\psi^\chi\right]^{-1/2} = \left(\frac{N_\chi}{2\left[N_\psi N_\chi^{1/2} + N_\psi^{1/2} S_\psi^\chi\right]}\right)^{1/2},$$

$$\text{then } C_{i2} = +\left[\frac{N_\psi}{N_\chi}\right]^{1/2}\left(\frac{1}{\sqrt{2}}\left[N_\psi + \left[\frac{N_\psi}{N_\chi}\right]^{1/2} S_\psi^\chi\right]^{-1/2}\right) = \left(\frac{N_\psi}{2(N_\psi N_\chi)^{1/2}\left[(N_\psi N_\chi)^{1/2} + S_\psi^\chi\right]}\right)^{1/2}.$$

$$\text{and } C_{j1} = \frac{1}{\sqrt{2}}\left[N_\psi - \left[\frac{N_\psi}{N_\chi}\right]^{1/2} S_\psi^\chi\right]^{-1/2} = \left(\frac{N_\chi}{2\left[N_\psi N_\chi^{1/2} - N_\psi^{1/2} S_\psi^\chi\right]}\right)^{1/2}$$

$$\text{then } C_{j2} = -\left[\frac{N_\psi}{N_\chi}\right]^{1/2}\left(\frac{1}{\sqrt{2}}\left[N_\psi - \left[\frac{N_\psi}{N_\chi}\right]^{1/2} S_\psi^\chi\right]^{-1/2}\right) = -\left(\frac{N_\psi}{2(N_\psi N_\chi)^{1/2}\left[(N_\psi N_\chi)^{1/2} - S_\psi^\chi\right]}\right)^{1/2}$$

The eigenfunction $^K\phi^i(1) = C_{i1}|\psi(1)\rangle + C_{i2}|\chi(1)\rangle$ is associated with the eigenvalue $\frac{1}{\sqrt{2}}\left[\left(\left[N_\chi N_\psi\right]^{1/2} + S_\psi^\chi\right)^2\right]$, and the eigenfunction $^K\phi^j(1) = C_{j1}|\psi(1)\rangle + C_{j2}|\chi(1)\rangle$ with the eigenvalue $\frac{1}{\sqrt{2}}\left[\left(\left[N_\chi N_\psi\right]^{1/2} - S_\psi^\chi\right)^2\right]$.

These two functions satisfy condition ② for orthoganility.

A $\mu^K(12) \in \wedge^2 \rho(m)$ can have 1 or 2 non-zero eigenvalues, and in general cannot be expressed as a symmetric product of its N.O's.

Thus we have the following expansions in terms of their eigenfunctions for $\rho_K(1'|1)$ associated with $\mu^K(12) \in \Lambda^2 \rho(m)$ and $\rho_K(1'|1)$ associated with $\mu^K(12) \in \vee^2 \rho(m)$

$$\rho_K(1'|1) = \sum_{i=1}^{i=m} \tfrac{1}{2}\, {}^K\phi^i(1')\, {}^K\phi_i(1) = \tfrac{1}{2}\left\{ {}^K\phi^i(1')\, {}^K\phi_i(1) + {}^K\phi^j(1')\, {}^K\phi_j(1)\right\}$$

$\mu^K(12) \in \Lambda^2 \rho(m)$ i and j being the eigenfunctions associated with the only 2 non-zero eigenvalues.

$$\rho_K(1'|1) = \sum_{i=1}^{i=m} \lambda_i^i\, {}^K\phi^i(1')\, {}^K\phi_i(1) \quad \text{where } {}^K\lambda_i^i \text{ is}$$

$\mu^K(12) \in \vee^2 \rho(m)$ the eigenvalue associated with the i^{th} eigenfunction

2 possible expansions exist for $\mu^K(12) \in \vee^2 \rho(m)$ viz: -

$\rho_K(1'|1) = {}^K\phi^i(1')\, {}^K\phi_i(1)$ i.e. only one non zero eigenvalue = 1.

$= {}^K\lambda_i^i\, {}^K\phi^i(1')\, {}^K\phi_i(1) + {}^K\lambda_j^j\, {}^K\phi^j(1')\, {}^K\phi_j(1)$ two non zero eigenvalues ${}^K\lambda_i^i$ and ${}^K\lambda_j^j$

Because of the normalisation condition on $\mu^K(12)$ the sum of the eigenvalues belonging to any one decomposition must be unity i.e. ${}^K\lambda_i^i + {}^K\lambda_j^j = 1$.

We can now write out two equivalent expansions of the 1st Order Reduced Density Matrix. These can be arrived at by considering the contraction of $\Gamma^{(2)}(1'2'|12)$ in two different ways.

The Natural expansion of the Reduced 2nd Order Density Matrix can be written as

$$\Gamma^{(2)}(1'2'|12) = \sum_i^{m(m-1)/2} {}^A\mu^i(1'2')\, {}^A\mu_i(12)\left\{ \Gamma^{(2)}_{d\alpha\alpha\alpha\alpha\,i}\, \alpha(1)\alpha(2)\alpha(1)\alpha(2) + \Gamma^{(2)}_{d\beta\beta\beta\beta\,i}\, \beta(1)\beta(2)\beta(1)\beta(2) \right.$$
$$\left. + \Gamma^{(2)}_{d\alpha\beta_t\alpha\beta_t} \tfrac{1}{2}\left(\alpha(1)\beta(2)+\alpha(2)\beta(1)\right)\left(\alpha(1)\beta(2)+\alpha(2)\beta(1)\right)\right\}$$
$$+ \sum_i^{n(n+1)/2} {}^S\mu^i(1'2')\, {}^S\mu_i(12)\, \Gamma^{(2)}_{d\alpha\beta_s\alpha\beta_s} \tfrac{1}{2}\left(\alpha(1)\beta(2)-\alpha(2)\beta(1)\right)\left(\alpha(1)\beta(2)-\alpha(2)\beta(1)\right)$$

Hence the 1st Order Reduced Density Matrix can be defined as

$$\rho(1'|1) = \frac{2}{N-1}\int \Gamma^{(2)}(1'2'|12)\,d\tau_2 = \frac{2}{N-1}\Big\{\sum_i^{n(m-1)/2} \rho_{i_A}(1'|1)\Big[\Gamma^{(2)}_{d\alpha\alpha\alpha\alpha_i^i}\alpha(1)\alpha(1) + \Gamma^{(2)}_{d\beta\beta\beta\beta_i^i}\beta(1)\beta(1)$$
$$+ \Gamma^{(2)}_{d\alpha\beta_t\alpha\beta_t}\tfrac{1}{2}\big(\alpha(1)\alpha(1)+\beta(1)\beta(1)\big)\Big] + \sum_i^{n(m+1)/2}\rho_{i_S}(1'|1)\,\Gamma^{(2)}_{d\alpha\beta_s\alpha\beta_s}\tfrac{1}{2}\big(\alpha(1)\alpha(1)+\beta(1)\beta(2)\big)\Big\}$$

Now if we expand each $\rho_{i_A}(1'|1)$ and $\rho_{i_S}(1'|1)$ in terms of their N.O's we can write

$$\rho(1'|1) = \frac{2}{N-1}\Big\{\sum_i^{n(m-1)/2}\sum_j^m {}^{i_A}\lambda_j\,{}^{i_A}\phi^j(1')\,{}^{i_A}\phi_j(1)\Big[\Gamma^{(2)}_{d\alpha\alpha\alpha\alpha_i^i}\alpha(1)\alpha(1) + \Gamma^{(2)}_{d\beta\beta\beta\beta_i^i}\beta(1)\beta(1)$$
$$+ \Gamma^{(2)}_{d\alpha\beta_t\alpha\beta_t}\tfrac{1}{2}\big(\alpha(1)\alpha(1)+\beta(1)\beta(1)\big)\Big] + \sum_i^{n(m+1)/2}\sum_j^m {}^{i_S}\phi^j(1')\,{}^{i_S}\phi_j(1)\cdot{}^{i_S}\lambda_j\,\Gamma^{(2)}_{d\alpha\beta_s\alpha\beta_s}$$
$$\cdot\tfrac{1}{2}\big(\alpha(1)\alpha(1)+\beta(1)\beta(1)\big)\Big\}$$

We can write this in matrix notation as

$$\rho(1'|1) = \frac{2}{N-1}\Big\{\sum_i^{n(m-1)/2}\Big[\Gamma_r\,{}^{i_A}\lambda\,{}^{i_A}\phi(1'|1)\Big]\cdot\big(\gamma_{t\,i}^{\alpha\,i} + \gamma_{t\,i}^{\beta\,i}\big) + \sum_i^{n(m+1)/2}\Big[\Gamma_r\,{}^{i_S}\lambda\,{}^{i_S}\phi(1'|1)\Big]$$
$$\cdot\big(\gamma_{s\,i}^{\alpha\,i} + \gamma_{s\,i}^{\beta\,i}\big)\Big\}$$

where $\gamma_{t\,i}^{\alpha\,i} = \Gamma^{(2)}_{d\alpha\alpha\alpha\alpha_i^i}\alpha(1)\alpha(1) + \Gamma^{(2)}_{d\alpha\beta_t\alpha\beta_t}\tfrac{1}{2}\alpha(1)\alpha(1)$

$\gamma_{t\,i}^{\beta\,i} = \Gamma^{(2)}_{d\beta\beta\beta\beta_i^i}\beta(1)\beta(1) + \Gamma^{(2)}_{d\alpha\beta_t\alpha\beta_t}\tfrac{1}{2}\beta(1)\beta(1)$.

$\gamma_{s\,i}^{\alpha\,i} = \Gamma^{(2)}_{d\alpha\beta_s\alpha\beta_s}\tfrac{1}{2}\alpha(1)\alpha(1)$

$\gamma_{s\,i}^{\beta\,i} = \Gamma^{(2)}_{d\alpha\beta_s\alpha\beta_s}\tfrac{1}{2}\beta(1)\beta(1)$

${}^{i_A}\lambda$ is the diagonal matrix with elements ${}^{i_A}\lambda^j_j = {}^{i_A}\lambda_j$.

${}^{i_S}\lambda$ " " " " " " ${}^{i_S}\lambda^j_j = {}^{i_S}\lambda_j$.

${}^{i_A}\phi(1'|1)$ is the matrix with elements ${}^{i_A}\phi(1'|1)^k_\ell = {}^{i_A}\phi^k(1')\cdot{}^{i_A}\phi_\ell(1)$

${}^{i_S}\phi(1'|1)$ " " " " " ${}^{i_S}\phi(1'|1)^k_\ell = {}^{i_S}\phi^k(1')\cdot{}^{i_S}\phi_\ell(1)$.

Now if we write each ${}^{i_A}\phi(1'|1)$, ${}^{i_S}(1'|1)$, ${}^{i_A}\lambda$ and ${}^{i_S}\lambda$ in terms of the $\{\sigma^i(1)\}$ basis of $\rho^{(m)}$ we can write

$$\rho(1'|1) = \frac{2}{N-1}\Big\{\sum_i^{n(m-1)/2}\Big[\Gamma_r\,{}^{i}V_A\cdot{}^{i_A}\lambda\cdot{}^{i}V_A^{+}\,{}^{i}V_A\cdot{}^{i_A}\phi(1'|1)\,{}^{i}V_A^{+}\Big]\big[\gamma_{t\,i}^{\alpha\,i} + \gamma_{t\,i}^{\beta\,i}\big]$$

$$+\sum_i^{m(m+1)/2}\left[\mathrm{Tr}\,{}^iV_s\,{}^{is}\lambda\,{}^iV_s^+\,{}^iV_s\,{}^{is}\phi(1'|1)V_s^+\right]\left[Y_{si}^{\alpha\,i}+Y_{si}^{\beta\,i}\right]\Big\}.$$

where the matrices ${}^iV_s$, ${}^iV_A$ transform from the basis $\{{}^{iA}\phi_j(1)\}$ and $\{{}^{is}\phi_j(1)\}$ onto the basis $\{\sigma_j(1)\}$

$$\therefore \rho(1'|1)=\frac{2}{N-1}\Big\{\sum_i^{m(m+1)/2}\left[\mathrm{Tr}\,{}^iV_A\,{}^{iA}\lambda\,{}^iV_A^+.\sigma(1'|1)\right]\left[Y_{ti}^{\alpha\,i}+Y_{ti}^{\beta\,i}\right]$$
$$+\sum_i^{m(m+1)/2}\left[\mathrm{Tr}\,{}^iV_s\,{}^{is}\lambda\,{}^iV_s^+\,\sigma(1'|1)\right]\left[Y_{si}^{\alpha\,i}+Y_{si}^{\beta\,i}\right]\Big\}$$

and we can define

$$\rho^\alpha(1'|1)=\frac{2}{N-1}\Big\{\sum_i^{m(m-1)/2}\left[\mathrm{Tr}\,{}^iV_A\,{}^{iA}\lambda\,{}^iV_A^+\,\sigma(1'|1)\right]Y_{ti}^{\alpha\,i}+\sum_i^{m(m+1)/2}\left[\mathrm{Tr}\,{}^iV_s\,{}^{is}\lambda\,{}^iV_s^+\,\sigma(1'|1)\right]$$
$$\cdot Y_{si}^{\alpha\,i}\Big\}$$

$$\text{and } \rho^\beta(1'|1)=\frac{2}{N-1}\Big\{\sum_i^{m(m+1)/2}\left[\mathrm{Tr}\,{}^iV_A\,{}^{iA}\lambda\,{}^iV_A^+\,\sigma(1'|1)\right]Y_{ti}^{\beta\,i}+\sum_i^{m(m+1)/2}\left[\mathrm{Tr}\,{}^iV_s\,{}^{is}\lambda\,{}^iV_s^+\,\sigma(1'|1)\right]Y_{si}^{\beta\,i}\Big\}$$

then $\rho(1'|1)=\rho^\alpha(1'|1)+\rho^\beta(1'|1)=\rho^\alpha(1'|1)\alpha(1')\alpha(1)+\rho^\beta(1'|1)\beta(1')\beta(1)$

where $\rho^\alpha(1'|1)$ and $\rho^\beta(1'|1)$ are the spinless 1st Order Reduced Density Matrices.

Now we can expand $\rho(1'|1)$ in terms of its own N.S.O's so

$$\rho(1'|1)=\sum_{i=1}^{m}{}^\alpha\chi^i(1')\,{}^\alpha\chi(1)\,\rho_{di}^{\alpha\,i}\,\alpha(1')\alpha(1)+\sum_{i=1}^{m}{}^\beta\chi^i(1')\,{}^\beta\chi(1)\,\rho_{di}^{\beta\,i}\,\beta(1')\beta(1)$$

where ρ_d^α and ρ_d^β are the representations of $\rho^\alpha(1'|1)$ and $\rho^\beta(1'|1)$ on $F^{(2m)}$ w.r.t. a basis of eigenfunctions of $\rho(1'|1)$

We can write this expansion of $\rho(1'|1)$ as

$$\rho(1'|1)=\mathrm{Tr}^\alpha\chi(1'|1)\rho_d^\alpha+\mathrm{Tr}^\beta\chi(1'|1)\rho_d^\beta$$

where ${}^\alpha\chi(1'|1)$ is the matrix with elements ${}^\alpha\chi(1'|1)_j^i={}^\alpha\chi^i(1')\,{}^\alpha\chi_j(1)$

and ${}^\beta\chi(1'|1)$ " " " " " ${}^\beta\chi(1'|1)_j^i={}^\beta\chi^i(1')\,{}^\beta\chi_j(1)$

Also

$$\rho(1'|1)=\mathrm{Tr}^\alpha V^\alpha\chi(1'|1)^\alpha V^{+\alpha}V\rho_d^\alpha\,{}^\alpha V^+ +\mathrm{Tr}^\beta V^\beta\chi(1'|1)^\beta V^{+\beta}V\rho_d^\beta\,{}^\beta V^+$$

where ${}^{\alpha}\chi_j(1) = \sum_k^m {}^{\alpha}V_j^k \sigma_k(1)$ and ${}^{\beta}\chi_j(1) = \sum_k^m {}^{\beta}V_j^k \sigma_k(1)$

and ${}^{\alpha}V\,{}^{\alpha}V^+ = {}^{\alpha}V^+\,{}^{\alpha}V = {}^{\beta}V\,{}^{\beta}V^+ = {}^{\beta}V^+\,{}^{\beta}V = I_m$

Thus $\rho(1'|1) = Tr\,\sigma(1'|1)\,{}^{\alpha}V\,\rho_d^{\alpha}\,{}^{\alpha}V^+ + Tr\,\sigma(1'|1)\,{}^{\beta}V\,\rho_d^{\beta}\,{}^{\beta}V^+$.

We can now compare the two expansions of $\rho(1'|1)$ which gives the equalities

$$\frac{2}{N-1}\left\{\sum_i^{m(m-1)/2} Tr\,{}^{i}V_A\left({}^{iA}\lambda \cdot \gamma_{ti}^{\alpha i}\right){}^{i}V_A^{+}\,\sigma(1'|1) + \sum_i^{m(m+1)/2} Tr\,{}^{i}V_S\left({}^{is}\lambda \cdot \gamma_{si}^{\alpha i}\right){}^{i}V_S^{+}\,\sigma(1'|1)\right.$$

$$= Tr\,{}^{\alpha}V\,\rho_d^{\alpha}\,{}^{\alpha}V^+\sigma(1'|1) - (1)$$

and

$$\frac{2}{N-1}\left\{\sum_i^{m(m-1)/2} Tr\,{}^{i}V_A\left({}^{iA}\lambda \cdot \gamma_{ti}^{\beta i}\right){}^{i}V_A^{+}\,\sigma(1'|1) + \sum_i^{m(m+1)/2} Tr\,{}^{i}V_S\left({}^{is}\lambda \cdot \gamma_{si}^{\beta i}\right)V_S^{+}\,\sigma(1'|1)\right\}$$

$$= Tr\,{}^{\beta}V\,\rho_d^{\beta}\,{}^{\beta}V^+\sigma(1'|1) - (2)$$

where we have multiplied the matrices ${}^{iA}\lambda$, ${}^{is}\lambda$ by the scalars

$$\gamma_{ti}^{\alpha i},\ \gamma_{si}^{\alpha i},\ \gamma_{ti}^{\beta i},\ \gamma_{si}^{\beta i}$$

If we make the hypothesis that for all i and i'

${}^{i}V_A = {}^{i'}V_A$, and ${}^{i}V_S = {}^{i'}V_S$

and ${}^{i}V_A = {}^{i}V_S$

and thus ${}^{iA}\lambda = \frac{1}{2}I_m$, for all relevent i

${}^{is}\lambda = \frac{1}{2}I_m$, " " " i

Then we can write the L.H.S of (1) as

$$\frac{2}{N-1}\left\{Tr\,V_1 C\left[T^{(2)}_{d\alpha\alpha\alpha\alpha} + \frac{1}{2}T^{(2)}_{d\alpha\beta_t\alpha\beta_t}\right]V_1^{+}\,\sigma(1'|1) + \frac{1}{2}Tr\,V_1 C\left[T^{(2)}_{d\alpha\beta_s\alpha\beta_s}\right]V_1^{+}\sigma(1'|1)\right\}$$

and L.H.S of (2) as

$$\frac{2}{N-1}\left\{Tr\,V_2 C\left[T^{(2)}_{d\beta\beta\beta\beta} + \frac{1}{2}T^{(2)}_{d\alpha\beta_t\alpha\beta_t}\right]V_2^{+}\sigma(1'|1) + \frac{1}{2}Tr\,V_2 C\left[T^{(2)}_{d\alpha\beta_s\alpha\beta_s}\right]V_2^{+}\sigma(1'|1)\right\}$$

and only when is the above hypothesis satisfied can we express

ρ^{α}_{d} and ρ^{β}_{d} as Contractions of $T^{(2)}_{d\alpha\alpha\alpha\alpha}$, $T^{(2)}_{d\alpha\beta_t\alpha\beta_t}$, $T^{(2)}_{d\beta\beta\beta\beta}$ and $T^{(2)}_{d\alpha\beta_s\alpha\beta_s}$

and only then can double subscripts be used to relate the elements of $T^{(2)}_{d}$ with a common set of functions $\in F^{(2m\omega)}$, viz only then do the N.S.G's have common N.S.O's, and these are the same as the N.S.O's of the 1st Order Reduced Density Matrix i.e.

$^{\alpha}V = V_1$, $^{\beta}V = V_2$

and $\rho^{\alpha}_{d} = \frac{1}{N-1} C\left[T^{(2)}_{d\alpha\alpha\alpha\alpha} + \frac{1}{2} T^{(2)}_{d\alpha\beta_t\alpha\beta_t} + \frac{1}{2} T^{(2)}_{d\alpha\beta_s\alpha\beta_s}\right]$.

and $\rho^{\beta}_{d} = \frac{1}{N-1} C\left[T^{(2)}_{d\beta\beta\beta\beta} + \frac{1}{2} T^{(2)}_{d\alpha\beta_t\alpha\beta_t} + \frac{1}{2} T^{(2)}_{d\alpha\beta_s\alpha\beta_s}\right]$.

The non-equality of the N.S.O's associated with N.S.G's and those of the 1st Order Reduced Density Matrix is true in general of all other orders of Natural functions, and we can say in general that the N.S.O's of the p^{th} Order Reduced Density Matrices associated with the p^{th} order Natural functions are not identical with the N.S.O's of the 1st Order Reduced Density Matrix formed by reduction of the p^{th} Order Reduced Density Matrix, which infers that the p^{th} natural functions are not exterior products of a common orthonormal set of functions

CHAPTER FOUR.

A general N-particle Operator can be expressed as a sum of 1, 2, ... N particle operators so

$$\hat{O}(1.....N) = \hat{O}_0 + \sum_i^N \hat{O}_1(i) + \frac{1}{2!} \sum_{ij}' \hat{O}_2(ij) + ... \hat{O}(1.....N)$$

where primed summation infers $i \neq j$ and the arguments of the Operator $O_k(i.....)$ refer to the particle i..... .

$\hat{O}(1.....N)$ can be represented in the co-ordinate representation over $\otimes_1' F^{(\infty)}, \Lambda_2^2 F^{(\infty)}, ... \Lambda_n^n F^{(\infty)}$

As we are only interested in at most two particle operators for the purpose of this thesis, we concern ourselves only with a truncated expansion of $\hat{O}(1....N)$ viz

$$\hat{O}(1.....N) \simeq \hat{O}_0 + \sum_i^n \hat{O}_1(i) + \frac{1}{2!} \sum_{ij}' \hat{O}_2(ij)$$

With a system of identical particles, operation on one particle must be the same as operation on another thus

$$\hat{O}(1.....N) \simeq \hat{O}_0 + N \hat{O}_1(1) + \frac{N(N-1)}{2} \hat{O}_2(12)$$

and we can write

$$\hat{O}(12) = \left[\hat{O}_0 + N \hat{O}_1(1) + \frac{N(N-1)}{2} \hat{O}_2(12)\right]_{\frac{2}{N(N-1)}}$$

over 2 particle sub-system of an N particle system

The operator $\hat{O}(12)$ can be wholly represented over $L(\Lambda^2 F^{(\infty)})$ as its eigenfunctions must belong to that space. If, however, we limit ourselves to $L(\Lambda^2 F^{(2m\infty)})$ we can approximately represent $\hat{O}(12)$, and thus we can construct approximate eigenfunctions of $\hat{O}(12)$

We note that all orders of operators are self conjugate i.e.

$$\hat{O}^+(1..... \rho) = \hat{O}(1..... \rho)$$

Thus the representation of $\hat{O}(1..... \rho) \in L(\Lambda^2 F^{(2m\infty)})$

= the representation of $\hat{O}(1..... \rho) \in L(\Lambda_2 F_{(2m\infty)})$

Representation of Operators in $\otimes^2 F^{(2m)}$ and $\wedge^2 F^{(2m)}$.

The basis of $\otimes^2 F^{(2m)}$ is defined as $\{\omega_{\sigma_\nu}(12)\}\ \sigma_\nu \in S_{2,2m}$

or $\{\sigma_{\sigma_\mu}(12) \otimes \textcircled{H}_{\sigma_\chi}(12)\}$ where $\sigma_\mu \in S_{2,m}$, $\sigma_{\sigma_\mu}(12) \in \otimes^2 \rho^{(m\infty)}$

and $\sigma_\chi \in S_{2,2}$ $\textcircled{H}_{\sigma_\chi}(12) \in \otimes^2 S^{(2)}$

where $\omega_{\sigma_{\nu_i}\sigma_{\nu_j}}(12) = \omega_{\sigma_{\nu_1}}(1)\,\omega_{\sigma_{\nu_2}}(2)$

$\sigma_{\sigma_{\mu_1},\sigma_{\mu_2}}(12) = \sigma_{\sigma_{\mu_1}}(1)\,\sigma_{\sigma_{\mu_2}}(2)$

$\textcircled{H}_{\sigma_\chi}(12) = S_{\sigma_{\chi_1}}(1)\,S_{\sigma_{\chi_2}}(2)$ $\quad S_{\sigma_{\chi_i}}(1) \in S^{(2)}$

The basis of $\wedge^2 F^{(2m)}$ as $\{\omega_{\sigma_\nu}(12)\}\ \sigma_\nu \in Q_{2,2m}$

where $\omega_{\sigma_\nu}(12) = \frac{1}{\sqrt{2}}\{\omega_{\sigma_{\nu_1}}(1)\,\omega_{\sigma_{\nu_2}}(2) - \omega_{\sigma_{\nu_1}}(2)\,\omega_{\sigma_{\nu_2}}(1)\}$

that of $\wedge^2 \rho^{(m)}$ as $\{\sigma^{\wedge}_{\sigma_\nu}(12)\}\ \sigma_\nu \in Q_{2,m}$

where $\sigma^{\wedge}_{\sigma_\nu}(12) = \frac{1}{\sqrt{2}}\{\sigma_{\sigma_{\nu_1}}(1)\,\sigma_{\sigma_{\nu_2}}(2) - \sigma_{\sigma_{\nu_1}}(2)\,\sigma_{\sigma_{\nu_2}}(1)\}$.

and that $V^2 \rho^{(m)}$ as $\{\sigma^{V}_{\sigma_\nu}(12)\}\ \sigma_\nu \in G_{2,m}$

where $\sigma^{V}_{\sigma_\nu}(12) = \frac{1}{\sqrt{M(\sigma_\nu)2}}\{\sigma_{\sigma_{\nu_1}}(1)\,\sigma_{\sigma_{\nu_2}}(2) + \sigma_{\sigma_{\nu_1}}(2)\,\sigma_{\sigma_{\nu_2}}(1)\}$

The bases of the spin spaces of rank 2 can be written explicitly

$\wedge^2 S^{(2)} \equiv \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\} \equiv \textcircled{H}_{\alpha\beta_S}(12)$ only 1 function as it is a 1 dimensional space

$V^2 S^{(2)} \equiv \{\alpha(1)\alpha(2), \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \alpha(2)\beta(1)), \beta(1)\beta(2)\} \equiv \{\textcircled{H}_{\alpha\alpha}(12), \textcircled{H}_{\alpha\beta_t}(12), \textcircled{H}_{\beta\beta}(12)\}$

SPIN FREE OPERATORS

These can be represented completely in $L(\wedge^2 \rho^{(m)})$, $L(V^2 \rho^{(m)})$ or $L(\otimes^2 \rho^{(m)})$ then assigned to a particular spin symmetry.

The bases of $L(\wedge^2 \rho^{(m)})$, $L(V^2 \rho^{(m)})$ and $L(\otimes^2 \rho^{(m)})$ are respectively

$\{\sigma^{\wedge\sigma_\nu}(1'2') \otimes \sigma^{\wedge}_{\sigma_\mu}(12)\}$, $\sigma_\nu, \sigma_\mu \in Q_{2,m}$

$\{\sigma^{V\sigma_\nu}(1'2') \otimes \sigma_{\sigma_\mu}(12)\}$, $\sigma_\nu, \sigma_\mu \in G_{2,m}$

and $\{\sigma^{\sigma_\nu}(1'2') \otimes \sigma_{\sigma_\mu}(12)\}$ $\sigma_\nu, \sigma_\mu \in S_{2,m}$.

and if $O(1'2'|12)$ is an operator representation in $\Lambda_2^2 \rho^{(m\infty)}$ its representations over $L(\otimes^2 \rho^{(m)})$, $L(\Lambda^2 \rho^{(m)})$ and $L(V^2 \rho^{(m)})$ can be written in Dirac Notation as

$$O^{\sigma_\nu}_{\sigma_\mu} = \langle \sigma^{\sigma_\nu}(1'2') | O(1'2'|12) | \sigma_{\sigma_\mu}(12) \rangle \in L(\otimes^2 \rho^{(m)}) \quad \sigma_\nu, \sigma_\mu \in S_{2,m}$$

$$O^{\sigma_\nu}_{\sigma_\mu} = \langle \sigma^{\wedge\sigma_\nu}(1'2') | O(1'2'|12) | \sigma^{\wedge}_{\sigma_\mu}(12) \rangle \in L(\Lambda^2 \rho^{(m)}) \quad \sigma_\nu, \sigma_\mu \in Q_{2,m}$$

$$O^{\sigma_\nu}_{\sigma_\mu} = \langle \sigma^{\vee\sigma_\nu}(1'2') | O(1'2'|12) | \sigma^{\vee}_{\sigma_\mu}(12) \rangle \in L(V^2 \rho^{(m)}) \quad \sigma_\nu, \sigma_\mu \in G_{2,m}$$

and each of these elements can be assigned to a following spin symmetry respectively viz

$\textcircled{H}_{\sigma_\chi}(1'2'|12)\sigma_\chi \in S_{4,4}$ (i.e. one such sequence is $\alpha(1')\beta(2')\beta(1)\alpha(2)$)

$\textcircled{H}_{\alpha\beta_s\,\alpha\beta_s}(1'2'|12)$

$\textcircled{H}_{\alpha\alpha\alpha\alpha}(1'2'|12)$, $\textcircled{H}_{\alpha\beta_t\alpha\beta_t}(1'2'|12)$ and $\textcircled{H}_{\beta\beta\beta\beta}(1'2'|12)$

The representation of the operators over $L(\Lambda^2 \rho^{(m)})$ and $L(V^2 \rho^{(m)})$ can be written solely in terms of the elements that represent the operator over $L(\otimes^2 \rho^{(m)})$

viz if

$$\left.\begin{array}{l} {}^{\wedge}O^{\sigma_\nu}_{\sigma_\mu} \in L(\Lambda^2 \rho^{(m)}) \text{ and } \sigma_\nu = (i_1 i_2) \\ \sigma_\mu = (j_1 j_2) \end{array}\right\} \in Q_{2,m}$$

then $${}^{\wedge}O^{i_1 i_2}_{j_1 j_2} = \frac{1}{2}\left\{O^{i_1 i_2}_{j_1 j_2} - O^{i_2 i_1}_{j_1 j_2} - O^{i_1 i_2}_{j_2 j_1} + O^{i_2 i_1}_{j_2 j_1}\right\}$$

where $O^{\sigma_\chi}_{\sigma_\ell} \in L(\otimes^2 \rho^{(m)})$, $\sigma_\chi, \sigma_\ell \in S_{2,m}$

and if $$\left.\begin{array}{l} {}^{\vee}O^{\sigma_\nu}_{\sigma_\mu} \in L(V^2 \rho^{(m)} \text{ and } \sigma_\nu = (i_1 i_2) \\ \sigma_\mu = (j_1 j_2) \end{array}\right\} \in G_{2,m}$$

then $${}^{\vee}O^{i_1 i_2}_{j_1 j_2} = \frac{1}{\sqrt{M(i_1 i_2) M(j_1 j_2)}\,2}\left\{O^{i_2 i_1}_{j_1 j_2} + O^{i_1 i_2}_{j_2 j_1} + O^{i_1 i_2}_{j_2 j_1} + O^{i_2 i_1}_{j_2 j_1}\right\}$$

<u>POSITION SPACE FREE OPERATORS - SPIN DEPENDENT</u>

These can be completely represented on $L(\Lambda^2 S^{(2)})$, $L(V^2 S^{(2)})$

or $L(\otimes^2 S^{(2)})$ then assigned to a representation of a particular position space function

Thus

$O^{\sigma_\chi}_{\sigma_\ell} = \langle \textcircled{H}^{\sigma_\chi}(1'2') | O(1'2'|12) | \textcircled{H}_{\sigma_\ell}(12) \rangle$ $\sigma_\chi, \sigma_\ell \in S_{2,2}$ and go over the sequences based on α, β

$\in L(\otimes^2 S^{(2)})$

$O^{\alpha\beta_S}_{\alpha\beta_S} = \langle \textcircled{H}^{\alpha\beta_S}(1'2') | O(1'2'|12) | \textcircled{H}_{\alpha\beta_S}(12) \rangle \in L(\Lambda^2 S^{(2)})$

$O^{\sigma_\chi}_{\sigma_\ell} = \langle \textcircled{H}^{\sigma_\chi}(1'2') | O(1'2'|12) | \textcircled{H}_{\sigma_\ell}(12) \rangle \in L(V^2 S^{(2)})$ $\sigma_\chi, \sigma_\ell = \alpha\beta_t, \alpha\alpha, \beta\beta$

The representations of the operators over $L(\Lambda^2 S^{(2)})$ and $L(V^2 S^{(2)})$ can be written solely in terms of the elements that represent the operators over $L(\otimes^2 S^{(2)})$

viz

$$O^{\alpha\beta_S}_{\alpha\beta_S} = \frac{1}{2}\left(O^{\alpha\beta}_{\alpha\beta} - O^{\alpha\beta}_{\beta\alpha} - O^{\beta\alpha}_{\alpha\beta} + O^{\beta\alpha}_{\beta\alpha}\right) \in L(\Lambda^2 S^{(2)})$$

and $$O^{\alpha\beta_t}_{\alpha\beta_t} = \frac{1}{2}\left(O^{\alpha\beta}_{\alpha\beta} + O^{\alpha\beta}_{\beta\alpha} + O^{\beta\alpha}_{\alpha\beta} + O^{\beta\alpha}_{\beta\alpha}\right) \in L(V^2 S^{(2)})$$

and each one of these elements can be assigned to a spatial representation

$$\langle \sigma^{V\sigma_\nu}(1'2') | \sigma^V_{\sigma_\mu}(12) \rangle = \delta^{\sigma_\nu}_{\sigma_\mu} \in V^2 P^{(m)} \quad \sigma_\nu, \sigma_\mu \in G_{2,m}$$

$$\langle \sigma^{\wedge\sigma_\nu}(1'2') | \sigma^\wedge_{\sigma_\mu}(12) \rangle = \delta^{\sigma_\nu}_{\sigma_\mu} \in \Lambda^2 P^{(m)} \quad \sigma_\nu, \sigma_\mu \in Q_{2,m}$$

$$\text{and } \langle \sigma^{\sigma_\nu}(1'2') | \sigma_{\sigma_\mu}(12) \rangle = \delta^{\sigma_\nu}_{\sigma_\mu} \in \otimes^2 P^{(m)} \quad \sigma_\nu, \sigma_\mu \in S_{2,m}$$

If the position space functions were not orthonormal the representations assigned to the spin functions would not be δ's

The general spin-position space dependent operator has to be represented over $L(\Lambda^n_n F^{(2m)})$ or $L(\otimes^n_n F^{(2m)})$ completely. This will be dealt with a little later as for the particular case of the 2nd Order Reduced Density Matrix.

PARTICULAR EXAMPLES

1. 2 particle Hamiltonian $\hat{H}(12)$

$\hat{H}(12)$ is defined in a two particle picture as

$\left(\frac{1}{N-1}\right)\left[\hat{h}(1)+\hat{h}(2)\right] + \hat{h}(12) + \frac{2}{N(N-1)}\cdot\hat{h}(0)$

where $\hat{h}(i)$ is a 1 electron operator, defined in the co-ordinate representation as

$\hat{h}(i) = \nabla_i^2 - \sum_{s=1}^{s=n_u} \frac{Z_s}{r_{is}}$ where the number of nucleii in the system = n_u

r_{is} = distance of i^{th} electron from s^{th} nucleus

Z_s = charge on s^{th} nucleus

$i = 1$ or 2

and $h(0)$ nuclear-nuclear repulsion term i.e.

$\hat{h}(0) = \sum_{sr}^{n_u} \frac{Z_s . Z_r}{R_{sr}}$ R_{sr} = inter nuclear distance

and $\hat{h}(12) = \frac{1}{r_{12}}$ where r_{12} is distance between electron 1 and electron 2.

We define $X_{ij}^{kl} \in L(\otimes^2 \rho(w))$ as

$$\left\langle \sigma_i(1)\,\sigma_j(2) \left| \frac{1}{(N-1)}\left[h(1'|1)+h(2'|2)\right] + h(1'2'|12) + \frac{2}{N(N-1)}h(0) \right| \sigma^k(1)\,\sigma^l(2) \right\rangle$$

$$= \frac{1}{(N-1)}\left[h_i^k\,\delta_j^l + h_j^l\,\delta_i^k\right] + G_{ij}^{kl} + \frac{2}{N(N-1)}\,\delta_i^k\,\delta_j^l . h(0)$$

where $h_i^k = \langle \sigma_i(1') \,|\, h(1'|1) \,|\, \sigma^k(1) \rangle$

$G_{ij}^{kl} = \langle \sigma_i(1)\,\sigma_j(2) \,|\, h(1'2'|12) \,|\, \sigma^k(1)\,\sigma^l(2) \rangle$

The term $\frac{2}{N(N-1)}\delta_i^k\,\delta_j^l\,h(0)$ is usually ignored as it is a constant and is independent of the functional form of $\{\sigma_i(1)\}$'s. Its effect is allowed for later in the evaluation of energies, but it is not pertinent in the discussion of the properties of Hamiltonian operators.

Thus we take

$$X_{ij}^{kl} \equiv \frac{1}{(N-1)}\left[h_i^k\,\delta_j^l + h_j^l\,\delta_i^k\right] + G_{ij}^{kl}$$

and we say that the representations of $H(12)$ in $L(\Lambda^2 p^{(m)})$ and $L(V^2 p^{(m)})$ are respectively: -

$$H2^{a}{}_{ij}^{kl} \equiv \tfrac{1}{2}\left\{X_{ij}^{kl} - X_{ij}^{lk} - X_{ji}^{kl} + X_{ji}^{lk}\right\}$$

$$= \frac{1}{(N-1)}\left[h_i^k \delta_j^l - h_i^l \delta_j^k - h_j^k \delta_i^l + h_j^l \delta_i^k\right]$$

$$+ \tfrac{1}{2}\left[G_{ij}^{kl} - G_{ij}^{lk} - G_{jk}^{kl} + G_{ji}^{lk}\right]$$

for $i < j$

$k < l$

$$H2^{s}{}_{ij}^{kl} \equiv \frac{1}{2\sqrt{M(ij)M(kl)}}\left\{X_{ij}^{kl} + X_{ij}^{lk} + X_{ji}^{kl} + X_{ji}^{lk}\right\}$$

$$= \frac{1}{2\sqrt{M(ij)M(kl)}}\left\{\frac{2}{(N-1)}\left[h_i^k \delta_j^l + h_i^l \delta_j^k + h_j^k \delta_i^l + h_j^l \delta_i^k\right] + G_{ij}^{kl} + G_{ij}^{lk} + G_{jk}^{kl} + G_{ji}^{lk}\right\}$$

for $i \leq j$

$k \leq l$

2. 2 particle S^2 operator $\hat{S}^2(12)$.

$\hat{S}^2(12)$ is a scalar operator defined as $\hat{S}(12) \circ \hat{S}(12)$ (scalar product)

where $\hat{S}(12)$ is a vector operator, defined as

$$\hat{S}(12) = \hat{S}(1) + \hat{S}(2)$$

Thus $\hat{S}^2(12) = [\hat{S}(1) + \hat{S}(2)] \circ [\hat{S}(1) + \hat{S}(2)] = \hat{S}(1)^2 + 2.\hat{S}(1) \circ \hat{S}(2) + \hat{S}^2(2)$

So $\hat{S}^2(12)$ is made up of 1 particle operators $\hat{S}(1)^2 + \hat{S}(2)^2$ and a two particle operator $2\hat{S}(1).\hat{S}(2)$. In order that $\hat{S}(1)^2 + \hat{S}(2)^2$ gives the correct expectation value in a 2 particle space it must be scaled by a factor of $\frac{1}{(N-1)}$.

Thus $\hat{S}^2(12) \equiv \frac{1}{(N-1)}\left[\hat{S}(1)^2 + \hat{S}(2)^2\right] + 2\,\hat{S}(1) \circ \hat{S}(2)$

Now

$$\hat{S}(1)^2 = \hat{S}_-(1)\,\hat{S}_+(1) + \hat{S}_z^2(1) + \hat{S}_z(1)$$

$$\hat{S}(2)^2 = \hat{S}_-(2)\,\hat{S}_+(2) + \hat{S}_z^2(2) + \hat{S}_z(2)$$

$$2\hat{S}(1) \circ \hat{S}(2) = 2\left[\hat{S}_x(1).\hat{S}_x(2) + \hat{S}_y(1).\hat{S}_y(2) + \hat{S}_z(1).\hat{S}_z(2)\right]$$

where $\hat{S}_x, \hat{S}_y$ and $\hat{S}_z$ are scalar operators defined as operating along the cartesian axes x, y, z respectively.

The action of S_x, S_y and S_z when represented in spin space are defined as

$$S_x(j)\alpha(j) = \tfrac{1}{2}\beta(j) \qquad S_z(j)\alpha(j) = \tfrac{1}{2}\alpha(j)$$

$$S_x(j)\beta(j) = \tfrac{1}{2}\alpha(j) \qquad S_z(j)\beta(j) = -\tfrac{1}{2}\beta(j)$$

$$S_y(j)\alpha(j) = \tfrac{1}{2}i\beta(j)$$

$$S_y(j)\beta(j) = -\tfrac{1}{2}i\alpha(j)$$

As the representation of $S(12)^2$ in $\Lambda_2^2 S^{(2)}$ and $V_2^2 S^{(2)}$ can be expressed in terms of the 16 elements representing $S(12)^2$ in $\otimes_2^2 S^{(2)}$ we find these elements thus:-

Firstly the effect of $S^2(12)$ on $\begin{cases}\alpha(1)\alpha(2)\\ \alpha(1)\beta(2)\\ \alpha(2)\beta(1)\\ \beta(1)\beta(2)\end{cases}$

$$S^2(12)\alpha(1)\alpha(2) = \frac{1}{(N-1)}\left[\frac{3}{2}\alpha(1)\alpha(2)\right] + \frac{1}{2}\alpha(1)\alpha(2)$$

$$S^2(12)\alpha(1)\beta(2) = \frac{1}{(N-1)}\left[\frac{3}{2}\alpha(1)\beta(2)\right] + \alpha(2)\beta(1) - \frac{1}{2}\alpha(1)\beta(2)$$

$$S^2(12)\alpha(2)\beta(1) = \frac{1}{(N-1)}\left[\frac{3}{2}\alpha(2)\beta(1)\right] + \alpha(1)\beta(2) - \frac{1}{2}\alpha(2)\beta(1)$$

$$S^2(12)\beta(1)\beta(2) = \frac{1}{(N-1)}\left[\frac{3}{2}\beta(1)\beta(2)\right] + \frac{1}{2}\beta(1)\beta(2)$$

Then

$$\langle\alpha(1)\alpha(2)|S^2(12)|\alpha(1)\alpha(2)\rangle = \frac{3}{2(N-1)} + \frac{1}{2}$$

$$\langle\alpha(1)\alpha(2)|S^2(12)|\alpha(1)\beta(2)\rangle = 0$$

$$\langle\alpha(1)\alpha(2)|S^2(12)|\alpha(2)\beta(1)\rangle = 0$$

$$\langle\alpha(1)\alpha(2)|S^2(12)|\beta(1)\beta(2)\rangle = 0$$

The representation of S^2 in $L(\otimes^2 S^{(2)})$ being symmetric the remaining elements are defined by the elements given.

$$\langle \alpha(1)\beta(2) \mid S^2(12) \mid \alpha(1)\beta(2)\rangle = \frac{3}{2(N-1)} - \frac{1}{2}$$

$$\langle \alpha(1)\beta(2) \mid S^2(12) \mid \alpha(2)\beta(1)\rangle = 1$$

$$\langle \alpha(1)\beta(2) \mid S^2(12) \mid \beta(1)\beta(2)\rangle = 0$$

$$\langle \alpha(2)\beta(1) \mid S^2(12) \mid \alpha(2)\beta(1)\rangle = \frac{3}{2(N-1)} - \frac{1}{2}$$

$$\langle \alpha(2)\beta(1) \mid S^2(12) \mid \beta(1)\beta(2)\rangle = 0$$

$$\langle \beta(1)\beta(2) \mid S^2(12) \mid \beta(1)\beta(2)\rangle = \frac{3}{2(N-1)} + \frac{1}{2}$$

Thus $S^2 \in L(\Lambda^2 S^{(2)})$ is given by

$$\langle \Theta^{\alpha\alpha}_{\beta\beta}(12) \mid S^2(12) \mid \Theta^{a}_{\alpha\beta}(12)\rangle = \frac{1}{2}\left[S^{2\alpha\beta}_{\alpha\beta} - S^{2\beta\alpha}_{\alpha\beta} - S^{2\alpha\beta}_{\beta\alpha} + S^{2\beta\alpha}_{\beta\alpha}\right]$$

$$= \frac{1}{2}\left[\frac{3}{2(N-1)} - \frac{1}{2} - 1 - 1 + \frac{3}{2(N-1)} - \frac{1}{2}\right] = \frac{3}{2(N-1)} - \frac{3}{2}$$

and $S^2 \in L(V^2 S^{(2)})$ are given by

$$\langle \Theta^{s}_{s_i s_j}(12) \mid S^2(12) \mid \Theta^{s}_{s_i s_j}(12)\rangle \quad i \le j \quad \{s_1 = \alpha,\ s_2 = \beta\}$$

viz

$$\frac{1}{4}\left[S^{2\alpha\alpha}_{\alpha\alpha} + S^{2\alpha\alpha}_{\alpha\alpha} + S^{2\alpha\alpha}_{\alpha\alpha} + S^{2\alpha\alpha}_{\alpha\alpha}\right] = \frac{3}{2(N-1)} + \frac{1}{2}$$

$$\frac{1}{2}\left[S^{2\alpha\beta}_{\alpha\beta} + S^{2\beta\alpha}_{\alpha\beta} + S^{2\alpha\beta}_{\beta\alpha} + S^{2\beta\alpha}_{\beta\alpha}\right] = \frac{1}{2}\left[\frac{3}{2(N-1)} - \frac{1}{2} + 1 + 1 + \frac{3}{2(N-1)} - \frac{1}{2}\right]$$

$$= \frac{3}{2(N-1)} + \frac{1}{2}$$

$$\frac{1}{4}\left[S^{2\beta\beta}_{\beta\beta} + S^{2\beta\beta}_{\beta\beta} + S^{2\beta\beta}_{\beta\beta} + S^{2\beta\beta}_{\beta\beta}\right] = \frac{3}{2(N-1)} + \frac{1}{2}$$

The matrix elements representing $S^2(12)$ in $L(\Lambda^2 S^{(2)})$ and $L(V^2 S^{(2)})$ are of the form

$$\langle \Theta_{\alpha\beta_s}(1'2') \mid S^2(1'2'|12) \mid \Theta^{\sigma_\chi}(12)\rangle \qquad \sigma_\chi \in G_{2,2}$$

and $\{\Theta^{\sigma_\chi}(12)\}$ form a basis for $V^2 S^{(2)}$

$$= \frac{1}{2\sqrt{M(\sigma_\chi)}}\left\{S^{2\sigma_{\chi_1}\sigma_{\chi_2}}_{\alpha\beta} - S^{2\sigma_{\chi_1}\sigma_{\chi_2}}_{\beta\alpha} - S^{2\sigma_{\chi_2}\sigma_{\chi_1}}_{\alpha\beta} + S^{2\sigma_{\chi_2}\sigma_{\chi_1}}_{\beta\alpha}\right\} - (1)$$

while $\langle \Theta_{\sigma_\chi}(1'2') \mid S^2(1'2'|12) \mid \Theta^{\alpha\beta_s}(12)\rangle$ is given by

$$= \frac{1}{2\sqrt{M(\sigma_\chi)}} \left\{ S^{2\alpha\beta}_{\sigma_{\chi_1}\sigma_{\chi_2}} - S^{2\beta\alpha}_{\sigma_{\chi_1}\sigma_{\chi_2}} - S^{2\alpha\beta}_{\sigma_{\chi_2}\sigma_{\chi_1}} + S^{2\beta\alpha}_{\sigma_{\chi_2}\sigma_{\chi_1}} \right\} - (2)$$

which is equivalent to (1). Substituting in the 3 possible sequences $\sigma_\chi \in G_{2,2}$ we have

$$\frac{1}{2\sqrt{2}} \left\{ S^{2\alpha\alpha}_{\alpha\beta} - S^{2\alpha\alpha}_{\beta\alpha} - S^{2\alpha\alpha}_{\beta\alpha} + S^{2\alpha\alpha}_{\alpha\beta} \right\} \text{ which } = 0$$

$$\frac{1}{2\sqrt{2}} \left\{ S^{2\beta\beta}_{\alpha\beta} - S^{2\beta\beta}_{\beta\alpha} - S^{2\beta\beta}_{\beta\alpha} + S^{2\beta\beta}_{\alpha\beta} \right\} \quad \text{which } = 0$$

$$\text{and } \frac{1}{2} \left\{ S^{2\alpha\beta}_{\alpha\beta} - S^{2\beta\alpha}_{\beta\alpha} - S^{2\beta\alpha}_{\alpha\beta} + S^{2\beta\alpha}_{\alpha\beta} \right\} = \frac{1}{2} \left\{ \frac{3}{2(N-1)} - \frac{3}{2(N-1)} - 1 + 1 \right\}$$

$$\text{which } = 0$$

Thus confirming the spin symmetric decomposition of $\Lambda^2 F^{(2m)}$ does indeed lead to a diagonal representation of $\hat{S}^2(12)$ over $L(\Lambda^2 F^{(2m)})$ when we are working in an orthonormal basis of $\Lambda^2 F^{(2m)}$

SPIN AND POSITION SPACE DEPENDENT OPERATOR i.e. 2nd Order Reduced Density Operator $\hat{T}^{(2)}(12)$ of a Singlet Spin State

which in the approximate co-ordinate representation is designated by the 2nd Order Reduced Density Matrix $T^{(2)}(1'2'|12) \in \Lambda^2_2 F^{(2m\omega)}$

If we consider the spin symmetric decomposition of $\Lambda^2 F^{(2m)}$ then $\Lambda^2_2 F^{(2m)}$ is defined as

$$\left[\Lambda^2 \rho^{(m)} \otimes V^2 S^{(2)} \oplus V^2 \rho^{(m)} \otimes \Lambda^2 S^{(2)} \right] \otimes$$
$$\left[\Lambda_2 \rho_{(m)} \otimes V_2 S_{(2)} \oplus V_2 \rho_{(m)} \otimes \Lambda_2 S_{(2)} \right]$$

over which we can represent $T^{(2)}(1'2'|12)$. We see then we have to consider representations over

$$\left[\Lambda^2 \rho^{(m)} \otimes V^2 S^{(2)} \right] \otimes \left[\Lambda_2 \rho_{(m)} \otimes V_2 S_{(2)} \right]$$
$$\left[V^2 \rho^{(m)} \otimes \Lambda^2 S^{(2)} \right] \otimes \left[V_2 \rho_{(m)} \otimes \Lambda_2 S_{(2)} \right]$$
$$\left[\Lambda^2 \rho^{(m)} \otimes V^2 S^{(2)} \right] \otimes \left[V_2 \rho_{(m)} \otimes \Lambda_2 S_{(2)} \right]$$

and $\left[V^2\rho^{(m)} \otimes \Lambda_2^2 S^{(2)}\right] \otimes \left[\Lambda_2 P_{(m)} \otimes V_2 S_{(2)}\right]$

Giving a matrix structure of the form

	$\alpha\alpha$	$\alpha\beta+\beta\alpha$	$\beta\beta$	$\alpha\beta-\beta\alpha$
$\alpha\alpha$	AA	A(A+B)	AB	A(A−B)
$\alpha\beta+\beta\alpha$	(A+B)A	(A+B)(A+B)	(A+B)B	(A+B)(A−B)
$\beta\beta$	BA	B(A+B)	BB	B(A−B)
$\alpha\beta-\beta\alpha$	(A−B)A	(A−B)(A+B)	(A−B)B	(A−B)(A−B)

(when $V_2^2 S^{(2)}$ and $\Lambda_2^2 S^{(2)}$ are explicitly expanded in terms of their basis functions)

which is quite general for any Operator $\in \Lambda_2^2 F^{(2m)}$ or $L(\Lambda^2 F^{(2m)})$

The matrix of structures of non-general operators in $\Lambda^2 F^{(2m)}$ i.e. $\hat{H}2$ and $\hat{S}^2$ are special forms of that just shown with certain null blocks.

For $\hat{H}2$ blocks $AA, (A+B)(A+B), BB, (A-B)(A-B)$ are the only non-zero ones - due to spin orthoganility.

And for $\hat{S}^2$ again only blocks $AA, (A+B)(A+B), BB, (A-B)(A-B)$ are non-zero and they are also diagonal when the bases of $\Lambda^2\rho^{(n)}$ and $V^2\rho^{(n)}$ are orthonormal and also for Singlet Spin States the blocks $AA, (A+B)(A+B), BB$ and $(A-B)(A-B)$ are the only non- zero blocks of $T^{(2)}$

Expectation Values

The 2nd Order reduced density matrix represents the system as expressed as particle pairs. If there are N particles in the system then the number of particle pairs is $N(N-1)/2$. Now the Quantum (and statistical) value of any observable (taking into account at most two particle properties) is defined as being

$\langle Ob \rangle = Tr\, Ob\, T^{(2)}$ where Ob and $T^{(2)}$ are representations of the

Operator associated with the observable and 2nd Order reduced density matrix respectively.

In a continuous representation T_r is an integral operation,

i.e. $T_r\, O_b\, T^{(2)} = \int\int O_b(x''_{12} | x'_{12})\, T^{(2)}(x'_{12} | x''_{12}).\, dx'_{12}\, dx''_{12}$

while in a discrete representation it has the usual matrix definition

$$T_r\, Ob\, T^{(2)} = \sum_i \sum_k Ob_i^k\, T_k^{(2)i}$$

As there are identically $N(N-1)/2$ particle pairs in the system we define

$$T_r\, I\, T^{(2)} = N(N-1)/2.$$

where I is the representation of the identity operator.

The expectation value of the hamiltonian operator, viz the energy is given by

$$E = T_r\, H2\, T^{(2)}$$

and if $H2$ is represented as an operator in $\Lambda^2 F^{(2m)}$ over the decomposition

$$\Lambda^2 F^{(2m)} \equiv \Lambda^2 p^{(m)} \otimes V^2 S^{(2)} \oplus V^2 p^{(m)} \otimes \Lambda^2 S^{(2)}$$

then it has the components w.r.t. spin symmetry

$$H2 \equiv H2_{\alpha\alpha\alpha\alpha} \oplus H2_{\alpha\beta_t\alpha\beta_t} \oplus H2_{\alpha\beta_s\alpha\beta_s} \oplus H2_{\beta\beta\beta\beta}$$

all others being zero (as $H2$ is a spinless operator)

Thus the only components of $T^{(2)}$ that are effective are

$$T^{(2)}_{\alpha\alpha\alpha\alpha},\ T^{(2)}_{\alpha\beta_t\alpha\beta_t},\ T^{(2)}_{\alpha\beta_s\alpha\beta_s},\ T^{(2)}_{\beta\beta\beta\beta}$$

and the energy is given by

$$\langle H \rangle = E = T_r\, H2_{\alpha\alpha\alpha\alpha}\, T^{(2)}_{\alpha\alpha\alpha\alpha} + T_r\, H2_{\alpha\beta_t\alpha\beta_t}\, T^{(2)}_{\alpha\beta_t\alpha\beta_t} + T_r\, H2_{\alpha\beta_s\alpha\beta_s}\, T^{(2)}_{\alpha\beta_s\alpha\beta_s} + T_r H2_{\beta\beta\beta\beta}\, T^{(2)}_{\beta\beta\beta\beta}$$

and the expectation value of the $S^{(2)}$ operator is given by

$$\langle S^2 \rangle = \mathrm{Tr}\, S^{(2)}_{\alpha\alpha\alpha\alpha} T^{(2)}_{\alpha\alpha\alpha\alpha} + \mathrm{Tr}\, S^{(2)}_{\alpha\beta_t\alpha\beta_t} T^{(2)}_{\alpha\beta_t\alpha\beta_t} + \mathrm{Tr}\, S^{(2)}_{\alpha\beta_s\alpha\beta_s} T^{(2)}_{\alpha\beta_s\alpha\beta_s} + \mathrm{Tr}\, S^{(2)}_{\beta\beta\beta\beta} T^{(2)}_{\beta\beta\beta\beta}$$

Now in an orthonormal basis for $\Lambda^2 \rho^{(m)}$ and $V^2\rho^{(m)}$, $S^2_{\alpha\alpha\alpha\alpha}$, $S^2_{\alpha\beta_t\alpha\beta_t}$ $S^2_{\alpha\beta_s\alpha\beta_s}$, $S^2_{\beta\beta\beta\beta}$ are scalar matrices i.e. multiples of the unit matrix.

Thus,

$$\langle S^2 \rangle = \mathrm{Tr}\, S^2 T^{(2)} = S_{\alpha\alpha\alpha\alpha} \mathrm{Tr}\, T^{(2)}_{\alpha\alpha\alpha\alpha} + S_{\alpha\beta_t\alpha\beta_t} \mathrm{Tr}\, T^{(2)}_{\alpha\beta_t\alpha\beta_t} + S_{\alpha\beta_s\alpha\beta_s} \mathrm{Tr}\, T^{(2)}_{\alpha\beta_s\alpha\beta_s} + S_{\beta_t} \mathrm{Tr}\, T^{(2)}_{\beta_t}$$

where $S_{\alpha\alpha\alpha\alpha} = S_{\alpha\beta_t\alpha\beta_t} = S_{\beta\beta\beta\beta} = \frac{3}{2(N-1)} + \frac{1}{2} = \frac{N+2}{2(N-1)} = \frac{\alpha+\beta+2}{2(\alpha+\beta-1)}$

and $S_{\alpha\beta_s\alpha\beta_s} = \frac{3}{2(N-1)} - \frac{3}{2} = \frac{6-3N}{2(N-1)} = \frac{6-3\alpha-3\beta}{2(\alpha+\beta-1)}$

If $T^{(2)}$ represents a pure spin state, the following trace relationships are satisfied by the components (w.r.t. spin subspaces) of $T^{(2)}$

$\mathrm{Tr}\, T^{(2)}_{\alpha\alpha\alpha\alpha}$ = Number of alpha electron pairs in the system = $\alpha(\alpha-1)/2$

$\mathrm{Tr}\, T^{(2)}_{\beta\beta\beta\beta}$ = " " beta " " " " " " = $\beta(\beta-1)/2$

$\mathrm{Tr}\, T^{(2)}_{\alpha\beta_t\alpha\beta_t}$ = " " spin symmetric alpha-beta electron pairs = $(\alpha-1)\beta/2$

$\mathrm{Tr}\, T^{(2)}_{\alpha\beta_s\alpha\beta_s}$ = " " " antisymmetric " " " " = $(\alpha+1)\beta/2$

$$\therefore \langle S^2 \rangle = \left[\alpha(\alpha-1)/2 + (\alpha-1)\beta/2 + \beta(\beta-1)/2\right]\left[\frac{\alpha+\beta+2}{2(\alpha+\beta-1)}\right]$$

$$+ \left[(\alpha+1)\beta/2\right]\left[\frac{6-3\alpha-3\beta}{2(\alpha+\beta-1)}\right]$$

$$= S(S+1)$$

where S is the total spin of the system

Representation in $F^{(2m)}$ ($\otimes^1 F^{(2m)} = \Lambda^1 F^{(2m)} = V^1 F^{(2m)}$)

Bases of $F^{(2m)}$ we let be $\{w^i(1)\} \equiv \{\sigma^k(1) \otimes s^l(1)\}$

$s^l = \alpha$ or β

$i = 1, \ldots\ldots 2m$

$k = 1 \ldots\ldots m$

$l = 1, 2.$

an operator in $F^{(2m)} \in L(F^{(2m)})$

If $X(1'|1)$ is a general operator in the continuous co-ordinate space representation, then its matrix elements over $\otimes'_1 F^{(2m)}$ are defined as

$$X_i^j = \langle \omega_i(1') \mid X(1'|1) \mid \omega^j(1) \rangle \left\{ \text{symbolising} \iint \omega_j(x_1') X(x_1'|x_1) \omega^i(x_1) dx_1 dx_1' \right\}$$

$$= \langle \sigma_l(1') s_k(1') \mid X(1'|1) \sigma^r(1) s^s(1) \rangle$$

$$= \langle \sigma_l(1') | X(1'|1) | \sigma^r(1) \rangle \langle s_k(1') | X(1'|1) | s^s(1) \rangle \text{ where } \begin{matrix} j \equiv (r,s) \\ i \equiv (l,k) \end{matrix}$$

If the operator is spin independent then it can be represented in $L(\rho^{(m)})$ then assigned a spin symmetry thus making it a representation in $L(F^{(2m)})$

viz

$$X_i^j = \langle \sigma_i(1') | X(1'|1) | \sigma^j(1) \rangle$$

then X_i^j can be assigned a spin symmetry $\alpha\alpha$ or $\beta\beta$ representation. If the operator is position independent and spin dependent, then it can be represented in $L(S^{(2)})$ then assigned a position space part.

<u>Representation of 1 electron hamiltonian and 1st Order Reduced Density Matrix</u>

$$\hat{h}(1) = \nabla_1^2 - \sum_{s=1}^{s=n_u} \frac{z_s}{r_{1s}}$$ in the co-ordinate representation

As the 1 electron hamiltonian is a spin independent operator we can write its representation in $L(F^{(2m)})$ as: -

$$h_j^i = \langle \sigma_j(1) | \nabla_1^2 - \sum_{s=1}^{s=n_u} \frac{z_s}{r_{1s}} | \sigma^i(1) \rangle \delta_j^{s_i}$$

$$= \left\{ \langle \sigma_j(1) | \nabla_1^2 | \sigma^i(1) \rangle - \sum_{s=1}^{s=n_u} \langle \sigma_j(1) | \frac{Z_s}{r_{1s}} | \sigma^i(1) \rangle \right\} \delta_{s_j}^{s_i}$$

$i, j = 1 \ldots\ldots m$

$s_i = \alpha$ or β

$s_j = \alpha$ or β

while ρ the 1st Order Reduced Density Matrix is both spin and position dependent thus we can only write its representation in $\otimes_1' F^{(2m)}$ which is a subspace of $L(F^{(2m)})$ as

$$\rho_j^i = \langle \omega_j(1) | \rho(1) | \omega^i(1) \rangle$$

$i, j = 1 \ldots\ldots 2m$

The general structure of an operator $\in L(F^{(2m)})$ w.r.t. spin symmetry (when $F^{(2m)}$ is expressed as a direct product of the form $F^{(2m)} = \rho^{(m)} \otimes S^{(2)}$)

	α	β
α	AA	AB
β	BA	BB

The basis of $S^{(2)}$ is given explicitly as $\{\alpha(1), \beta(1)\}$

For spin independent operators e.g. $\hat{h}(1)$ the only non-zero components are AA and BB , as they are for spatial independent operators $\hat{S_z}(1)$ and $\hat{S^2}(1)$, while for general 1 electron operators of the type $\hat{\rho}(1)$ all blocks are non-zero.

Expectation Values

The 1st Order reduced density matrix represents an $N \times 1$ particle subsystem of an N particle system. Thus we define

$$Tr\, I\rho = N = Tr\, \rho$$

The 1 particle energy is given by

$$\langle h(1) \rangle = \mathcal{E} = \mathrm{Tr}\, h \rho = \mathrm{Tr}\, h^{\alpha} \rho^{\alpha} + \mathrm{Tr}\, h^{\beta} \rho^{\beta}$$

where superscript α or β represents the component of that spin symmetry i.e.

$$\alpha \in \rho^{(m)}_{\alpha} \otimes \rho^{(m)}_{\alpha}$$

$$\alpha\beta \in \rho^{(m)}_{\alpha} \otimes \rho^{(m)}_{\beta}$$

$$\beta\alpha \in \rho^{(m)}_{\beta} \otimes \rho^{(m)}_{\alpha}$$

$$\beta \in \rho^{(m)}_{\beta} \otimes \rho^{(m)}_{\beta}$$

Component of angular momenta along the Z - direction of a 1 particle subsystem is (in atomic units of momenta)

$$\langle S_z(1) \rangle = \mathrm{Tr}\, S_z \rho = \mathrm{Tr}\, S_z^{\alpha} \rho^{\alpha} + \mathrm{Tr}\, S_z^{\beta} \rho^{\beta}$$

$$= \frac{1}{2} \mathrm{Tr} \left\{ \rho^{\alpha} - \rho^{\beta} \right\} = \frac{1}{2} \left[\alpha - \beta \right]$$

α = number of alpha electrons; β = number of beta electrons

Contraction

Contraction is a procedure by which one can average out the effect of one or more particles, i.e. we map from ρ particle representation onto a q particle representation where $\rho > q$

The 2nd Order Reduced Density Matrix is a contraction of the full N particle density matrix i.e.

$$\Gamma^{(2)}(1'2'|12) = \frac{N(N-1)}{2} C_{N-2} \left[\Gamma^{(n)}(1' \ldots N'|1 \ldots N) \right]$$

and the 1st Order Reduced Density Matrix can be considered to be a contraction of either the 2nd Order Reduced Density Matrix

$$\rho(1'|1) = \frac{2}{N-1} C \left[\Gamma^{(2)}(1'2'|12) \right]$$

or a contraction of the full N particle Density Matrix

$$\rho(1'|1) = N.\, C\left[T^{(n)}(1'\ldots N'|1\ldots N)\right]$$

where contraction of a continuous tensor (i.e. many variable function) is defined as

$$C_{N-p}\left[F(X'_1\ldots N|X_1\ldots N)\right] = \int F(X'_1\ldots N|X_1\ldots N)\,dX_{p+1\ldots N} = F(X'_1\ldots p|X_1\ldots p).$$

These contractions are from

$C'_{n-2}\Lambda^n_n F^{(2m\infty)} \to \Lambda^2_2 F^{(2m\infty)}$ where the exterior product spaces are represented over the Tensor product spaces

$C'_{n-1}\Lambda^n_n F^{(2m\infty)} \to \Lambda'_1 F^{(2m\infty)}$

$C'\Lambda^2_2 F^{(2m\infty)} \to \Lambda' F^{(2m\infty)}$ $(\equiv \otimes'_1 F^{(2m\infty)})$.

$\otimes^\wedge_n F^{(2m\infty)}, \otimes'_1 F^{(2m\infty)}, \otimes^2_2 F^{(2m\infty)}$.

When we consider the contractions of the representations of these contractions on the functional spaces we have the relationships: -

$$\rho = \frac{1}{N-1} C\left[T^{(2)}\right] \quad \rho \in \otimes'_1 F^{(2m)};\ T^{(2)} \in \Lambda^2_2 F^{(2m)}$$

$$T^{(2)} = C_{N-2}\left[T^{(n)}\right] \quad T^{(2)} \in \Lambda^2_2 F^{(2m)};\ T^{(n)} \in \Lambda^n_n F^{(2m)}$$

and

$$\rho = C\left[T^{(n)}\right] \quad \rho \in \otimes'_1 F^{(2m)}, T^{(n)} \in \Lambda^n_n F^{(2m)}$$

Contractions retain the symmetry of the Tensor space i.e. contractions of antisymmetric spaces are antisymmetric spaces.

Thus when we contract into the one particle space in which ρ exists we contract onto the basis of $\Lambda'_1 F^{(2m)}$ which although $\Lambda'_1 F^{(2m)} \equiv \otimes'_1 F^{(2m)}$, is different from the basis of $\otimes'_1 F^{(2m)}$ usually defined. This is particularly inconvenient as we refer ρ to the $\left\{\omega^i(1') \otimes \omega_j(1')\right\}$ basis. To overcome this problem we usually transform representations on $\Lambda^p_p F^{(2m)}$ to representations on $\otimes^p_p F^{(2m)}$ which does contract onto $\otimes'_1 F^{(2m)}$ with basis $\left\{\omega^i(1') \otimes \omega_j(1)\right\}$

The transformation $U^A_A : \otimes^p_p F^{(2m)} \to \Lambda^p_p F^{(2m)}$ (and thus the reverse

one) has been defined.

The contractions in terms of the Direct product spaces are

$$\rho = \frac{2}{N-1} C\left[T^{(2)}\right] \quad T^{(2)} \in \otimes_2^2 F^{(2m)}, \ \rho \in \otimes_1^1 F^{(2m)}$$

$$T^{(2)} = \frac{N(N-1)}{2} C_{n-2}\left[T^{(n)}\right] \quad T^{(n)} \in \otimes_n^n F^{(2m)}, \ T^{(2)} \in \otimes_2^2 F^{(2m)}$$

$$\rho = N C_{N-1}\left[T^{(n)}\right] \quad T^{(n)} \in \otimes_n^n F^{(2m)}, \ \rho \in \otimes_1^1 F^{(2m)}$$

In particular we will now consider the relationship between the 1st and 2nd Order Reduced Density Matrices.

When the spin symmetric decomposition of $\Lambda_2^2 F^{(2m)}$ is considered and $T^{(2)} \in \Lambda_2^2 F^{(2m)}$ represents a pure spin state it can be thought of as a product of a position space representations $\in \Lambda_2^2 \rho^{(m)}$ and $V_2^2 \rho^{(m)}$ times spin space representation $V_2^2 S^{(2)}$ and $\Lambda_2^2 S^{(2)}$ respectively.

(It is shown elsewhere that $T^{(2)}$ when representing a pure spin state is of block diagonal form on the spin symmetric decomposition of $\Lambda_2^2 F^{(2m)}$).[1]

Contractions of Direct product spaces satisfy the condition

$$C\left[S_1 \otimes S_2\right] = C\left[S_1\right] \otimes C\left[S_2\right]$$

where S_1 and S_2 are 2 tensor product spaces.

When $T^{(2)}$ is a pure singlet spin state it is represented over

$$\Lambda_2^2 \rho^{(m)} \otimes V_2^2 S^{(2)} \oplus V_2^2 \rho^{(m)} \otimes \Lambda_2^2 S^{(2)}$$

Then we can write the relationships between the 1 and 2 particle spaces as

$$C\left[\Lambda_2^2 \rho^{(m)} \otimes V_2^2 S^{(2)} \oplus V_2^2 \rho^{(m)} \otimes \Lambda_2^2 S^{(2)}\right] = \Lambda_1^1 \rho^{(m)} \otimes V_1^1 S^{(2)} \oplus V_1^1 \rho^{(m)} \otimes \Lambda_1^1 S^{(2)}$$

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and

$$C\left[\left[U_A^{A+};\Lambda_2^2 P^{(m)}\right]\otimes\left[U_S^{S+};V_2^2 S^{(2)}\right]\oplus\left[U_S^{S+};V_2^2 P^{(m)}\right]\otimes\left[U_A^{A+};\Lambda_2^2 S^{(2)}\right]\right]$$
$$=\otimes_1' P^{(m)}\otimes\otimes_1' S^{(2)}\oplus\otimes_1' P^{(m)}\otimes\otimes_1' S^{(2)}$$

when we contract onto the $\{\omega^i(1)\otimes\omega_j(1)\}$ basis of $\otimes_1' F^{(2m)}$.

Let us consider the spin space contractions first.

(1) $C\left[V_2^2 S^{(2)}\right] = V_1' S^{(2)}$

The only elements of interest in $V_2^2 S^{(2)}$ are the bases elements viz

$$\alpha(1')\alpha(2')\otimes\alpha(1)\alpha(2);\ \tfrac{1}{2}(\alpha(1')\beta(2')+\alpha(2')\beta(1')(\alpha(1)\beta(2)+\alpha(2)\beta(1));\ \beta(1')\beta(2')\beta(1)\beta(2)$$

these contract to basis elements of $V_1' S^{(2)}$ which are

$$\alpha(1')\alpha(1),\ \tfrac{1}{2}(\alpha(1')\alpha(1)+\beta(1')\beta(1)),\ \text{and}\ \beta(1')\beta(1)$$

the contraction being defined as

$$\Theta_i(1'|1) = \int \Theta_i(1'2'|12)\, d^3b_2.$$

(2) $C\left[\Lambda_2^2 S^{(2)}\right] = \Lambda_1' S^{(2)}$

Here there is only 1 basis element

$$\tfrac{1}{2}\left(\alpha(1')\beta(2')-\alpha(2')\beta(1')\right)\left(\alpha(1)\beta(2)-\alpha(2)\beta(1)\right)$$

which contracts to the basis element of

$$\Lambda_1' S^{(2)},\ \tfrac{1}{2}(\alpha(1')\alpha(1)+\beta(1')\beta(1)).$$

(3) $C\left[\otimes_2^2 S^{(2)}\right] = \otimes_1' S^{(2)}$

The bases elements of $\otimes_1' S^{(2)}$ are $\alpha(1')\beta(1)$, $\alpha(1')\alpha(1)$, $\beta(1')\beta(1)$ and $\beta(1')\alpha(1)$ which are formed from the contraction of the bases elements $\{\alpha(1')\beta(2')\alpha(1)\beta(2)$, $\alpha(1')\beta(2')\alpha(2)\beta(1), \alpha(2')\beta(1')\alpha(1)\beta(2)\ \alpha(2)\beta(1)\alpha(2)\beta(1), \alpha(1')\alpha(2')\alpha(1)\alpha(2), \ldots\ldots\text{etc}\}$

of $\otimes_2^2 S^{(2)}$

POSITION SPACE CONTRACTIONS

(i) $C\left[\otimes_2^2 \rho^{(m)}\right] = \otimes_1^1 \rho^{(m)}$.

The basis elements of $\otimes_2^2 \rho^{(m)}$, $\left\{\sigma^{\sigma_\nu}(1'2') \otimes \sigma_{\sigma_\mu}(12)\right\}\ \sigma_\nu, \sigma_\mu \in S_{2,m}$

contract so $\int \sigma^{\sigma_{\nu_1}}(1')\sigma^{\sigma_{\nu_2}}(2)\sigma_{\sigma_{\mu_1}}(1)\sigma_{\sigma_{\mu_2}}(2)\,dr_2 = \sigma^{\sigma_{\nu_1}}(1').\sigma_{\sigma_{\mu_1}}(1)\delta^{\sigma_{\nu_2}}_{\sigma_{\mu_2}} \in \otimes_1^1 \rho^{(m)}$

as $\sigma_{\nu_2} = \sigma_{\mu_2}$ m times; M basis Tensors of $\otimes_2^2 \rho^{(m)}$ maps onto

1 basis tensor of $\otimes_1^1 \rho^{(m)}$ and the mapping is $M:1$.

Tensors $\in \otimes_2^2 \rho^{(m)}$ i.e. $x = x' \otimes x^2 \otimes x_3 \otimes x_4$ contract to

Tensors $\in \otimes_1^1 \rho^{(m)}$ in the following way

$$C\left[x' \otimes x^2 \otimes x_3 \otimes x_4\right]_i^k = \sum_j x'_i . x_3^k . x_j^2\, x_4^j = y_i^k \in \otimes_1^1 \rho^{(m)}$$

or more generally if $X \in \otimes_2^2 \rho^{(m)}$

then

$$C\left[X\right]_i^k = \sum_j^m X_i^{k\ j}_{\ j} = Y_i^k \in \otimes_1^1 \rho^{(m)}.$$

(ii) $C\left[\Lambda_2^2 \rho^{(m)}\right] = \Lambda_1^1 \rho^{(m)}$

The basis elements of $\Lambda_2^2 \rho^{(m)}$, $\left\{\prod_i^{2\wedge} \sigma^{\sigma_{\nu_i}}(x'_i) \otimes \prod_j^{2\wedge} \sigma_{\sigma_{\mu_j}}(x_i)\right\}\ \sigma_\nu\ \sigma_\mu \in Q_{2,m}$

contract so $\frac{1}{2}\int \left(\sigma^{\sigma_{\nu_1}}(1')\sigma^{\sigma_{\nu_2}}(2) - \sigma^{\sigma_{\nu_1}}(2)\sigma^{\sigma_{\nu_2}}(1')\right)\left(\sigma_{\sigma_{\mu_1}}(1)\sigma_{\sigma_{\mu_2}}(2) - \sigma_{\sigma_{\mu_1}}(2)\sigma_{\sigma_{\mu_2}}(1)\right) dr_2$

$$= \frac{1}{2}\left\{\sigma^{\sigma_{\nu_1}}(1')\sigma_{\sigma_{\mu_1}}(1')\delta^{\sigma_{\nu_2}}_{\sigma_{\mu_2}} - \sigma^{\sigma_{\nu_1}}(1')\sigma_{\sigma_{\mu_2}}(1)\delta^{\sigma_{\nu_2}}_{\sigma_{\mu_1}} - \sigma^{\sigma_{\nu_2}}(1')\sigma_{\sigma_{\mu_1}}(1)\delta^{\sigma_{\nu_1}}_{\sigma_{\mu_2}} + \sigma^{\sigma_{\nu_2}}(1')\sigma_{\sigma_{\mu_2}}(1).\delta^{\sigma_{\nu_1}}_{\sigma_{\mu_1}}\right\} \in \Lambda_1^1 \rho^{(m)}$$

and Tensors $\in \Lambda_2^2 \rho^{(m)}$ i.e. $x = x' \wedge x^2 \otimes x_3 \wedge x_4$ contract to

Tensors $\in \Lambda_1^1 \rho^{(m)}$ in the following way: -

$$C\left[x' \wedge x^2 \otimes x_3 \wedge x_4\right]_i^k = \sum_{j>k,i}^m x_i^{k\ j}_{\ j} + \sum_{j<k,i}^m x_j^{j\ k}_{\ i} = y_i^k \in \Lambda_1^1 \rho^{(m)}$$

(iii) $C\left[V_2^2 \rho^{(m)}\right] = V_1^1 \rho^{(m)}$

The basis elements of $V_2^2 \rho^{(m)}$, $\left\{\prod_i^{2\vee} \sigma^{\sigma_{\nu_i}}(x'_i) \otimes \prod_j^{2\vee} \sigma_{\sigma_{\mu_j}}(x_j)\right\}\ \sigma_\nu, \sigma_\mu \in G_{2,m}$

contract so $\frac{1}{2\sqrt{M(\sigma_\nu)M(\sigma_\mu)}}\int \left(\sigma^{\sigma_{\nu_1}}(1')\sigma^{\sigma_{\nu_2}}(2) + \sigma^{\sigma_{\nu_1}}(2)\sigma^{\sigma_{\nu_2}}(1)\right)\left(\sigma_{\sigma_{\mu_1}}(1)\sigma_{\sigma_{\mu_2}}(2) + \sigma_{\sigma_{\mu_1}}(2)\sigma_{\sigma_{\mu_2}}(1)\right) dr_2.$

$$= \frac{1}{2\sqrt{M(\sigma_\nu)M(\sigma_\mu)}} \Big\{ \sigma^{\sigma_{\nu_1}}(1')\sigma_{\sigma_{\mu_1}}(1')\delta^{\sigma_{\nu_2}}_{\sigma_{\mu_2}} + \sigma^{\sigma_{\nu_1}}(1')\sigma_{\sigma_{\mu_2}}(1)\delta^{\sigma_{\nu_2}}_{\sigma_{\mu_1}} + \sigma^{\sigma_{\nu_2}}(1')\sigma_{\sigma_{\mu_1}}(1)\delta^{\sigma_{\nu_1}}_{\sigma_{\mu_2}}$$
$$+ \sigma^{\sigma_{\nu_2}}(1')\sigma_{\sigma_{\mu_2}}(1)\delta^{\sigma_{\nu_1}}_{\sigma_{\mu_1}} \Big\} \in V_1' \rho^{(m)}$$

and Tensors $\in V_2^2 \rho^{(m)}$ i.e. $x = x' \vee x^2 \otimes x_3 \vee x_4$

contract to Tensors $\in V_1' \rho^{(m)}$ in the following way

$$C\left[x' \vee x^2 \otimes x_3 \vee x_4\right]^k_i = \sum_{j \geq k,i} x^{kj}_{ij} + \sum_{j \leq k,i} x^{jk}_{ji} = Y^k_i \in V_1' \rho^{(m)}$$

Any Tensor $\in \Lambda_2^2 \rho^{(m)}$ or $V_2^2 \rho^{(m)}$ can be expressed in terms of its components $\in \otimes_2^2 \rho^{(m)}$ viz: -

$$X^{\sigma_\nu}_{\sigma_\mu} = \frac{1}{2}\left\{ x^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\mu_1},\sigma_{\mu_2}} - x^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\mu_2}\sigma_{\mu_1}} - x^{\sigma_{\nu_2}\sigma_{\nu_1}}_{\sigma_{\mu_1},\sigma_{\mu_2}} + x^{\sigma_{\nu_2}\sigma_{\nu_1}}_{\sigma_{\mu_1},\sigma_{\mu_2}} \right\} \sigma_\nu, \sigma_\mu \in Q_{2,m}$$

where $X \in \Lambda_2^2 \rho^{(m)}$, $x \in \otimes_2^2 \rho^{(m)}$

and

$$Y^{\sigma_\nu}_{\sigma_\mu} = \frac{1}{2\sqrt{M(\sigma_\nu)M(\sigma_\mu)}} \left\{ y^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\mu_1},\sigma_{\mu_2}} + y^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\mu_2}\sigma_{\mu_1}} + y^{\sigma_{\nu_2}\sigma_{\nu_1}}_{\sigma_{\mu_1},\sigma_{\mu_2}} + y^{\sigma_{\nu_2}\sigma_{\nu_1}}_{\sigma_{\mu_1},\sigma_{\mu_2}} \right\} \sigma_\nu, \sigma_\mu \in G_{2,m}$$

$Y \in V_2^2 \rho^{(m)}$, $y \in \otimes_2^2 \rho^{(m)}$

If we now write the contractions of X and Y in terms of x and y and consider only the diagonal elements of the contracted Tensors we see that

$$C\left[X\right]^{\sigma_{\nu_1}}_{\sigma_{\nu_1}} = \sum_{\sigma_{\nu_2} > \sigma_{\nu_1}} X^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\nu_1}\sigma_{\nu_2}} + \sum_{\sigma_{\nu_2} < \sigma_{\nu_1}} X^{\sigma_{\nu_2}\sigma_{\nu_1}}_{\sigma_{\nu_2}\sigma_{\nu_1}} -$$

$$= \frac{1}{2}\Big\{ \sum_{\sigma_{\nu_2} > \sigma_{\nu_1}} \left(x^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\nu_1}\sigma_{\nu_2}} - x^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\nu_2}\sigma_{\nu_1}} - x^{\sigma_{\nu_2}\sigma_{\nu_1}}_{\sigma_{\nu_1}\sigma_{\nu_2}} + x^{\sigma_{\nu_2}\sigma_{\nu_1}}_{\sigma_{\nu_2}\sigma_{\nu_1}} \right)$$
$$+ \sum_{\sigma_{\nu_2} < \sigma_{\nu_1}} \left(x^{\sigma_{\nu_2}\sigma_{\nu_1}}_{\sigma_{\nu_2}\sigma_{\nu_1}} - x^{\sigma_{\nu_2}\sigma_{\nu_1}}_{\sigma_{\nu_1}\sigma_{\nu_2}} - x^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\nu_2}\sigma_{\nu_1}} + x^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\nu_1}\sigma_{\nu_2}} \right) \Big\}$$
$$+ \frac{1}{2}\Big\{ \sum_{\sigma_{\nu_2}\sigma_{\nu_1}} 4\left(x^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\nu_1}\sigma_{\nu_2}} \right) = 2\,C\left[X\right]^{\sigma_{\nu_1}}_{\sigma_{\nu_1}}$$

As $x^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\nu_1}\sigma_{\nu_2}}$ are the components of X as represented in $\otimes_2^2 \rho^{(m)}$

$$x^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\nu_1}\sigma_{\nu_2}} = x^{\sigma_{\nu_2}\sigma_{\nu_1}}_{\sigma_{\nu_2}\sigma_{\nu}} \; ; \; -x^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\nu_2}\sigma_{\nu_1}} = x^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\nu_1}\sigma_{\nu_2}} \text{ and } -x^{\sigma_{\nu_2}\sigma_{\nu_1}}_{\sigma_{\nu_1}\sigma_{\nu_2}} = x^{\sigma_{\nu_1}\sigma_{\nu_2}}_{\sigma_{\nu_1}\sigma_{\nu_2}}$$

and that

$$C[Y]^{\sigma_{v_1}}_{\sigma_{v_1}} = \sum_{\sigma_{v_2} \geq \sigma_{v_1}} Y^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{v_1}\sigma_{v_2}} + \sum_{\sigma_{v_2} \leq \sigma_{v_1}} Y^{\sigma_{v_2}\sigma_{v_1}}_{\sigma_{v_2}\sigma_{v_1}}$$

$$= \sum_{\sigma_{v_2} \geq \sigma_{v_1}} \frac{1}{2\sqrt{M(\sigma_v)M(\sigma_v)}} \left(Y^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{v_1}\sigma_{v_2}} + Y^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{v_2}\sigma_{v_1}} + Y^{\sigma_{v_2}\sigma_{v_1}}_{\sigma_{v_1}\sigma_{v_2}} + Y^{\sigma_{v_2}\sigma_{v_1}}_{\sigma_{v_2}\sigma_{v_1}} \right)$$

$$+ \sum_{\sigma_{v_2} \leq \sigma_{v_1}} \frac{1}{2\sqrt{M(\sigma_v)M(\sigma_v)}} \left(Y^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{v_1}\sigma_{v_2}} + Y^{\sigma_{v_1}\sigma_{v_2}}_{\sigma_{v_2}\sigma_{v_1}} + Y^{\sigma_{v_2}\sigma_{v_1}}_{\sigma_{v_1}\sigma_{v_2}} + Y^{\sigma_{v_2}\sigma_{v_1}}_{\sigma_{v_2}\sigma_{v_1}} \right)$$

$$= 2\, C[Y]^{\sigma_{v_1}}_{\sigma_{v_1}}$$

i.e. the contractions that give rise to diagonal elements in $\Lambda'_1 \rho^{(m)}$ and $V'_1 \rho^{(m)}$ are just twice those that give rise to diagonal elements in $\otimes'_1 \rho^{(m)}$.

Now we can write the contraction of $T^{(2)} \in \Lambda^2_2 F^{(2m)}$ as

$$T^{(2)} = T^{(2)}_{\alpha\alpha\alpha\alpha} + T^{(2)}_{\alpha\beta_t\alpha\beta_t} + T^{(2)}_{\beta\beta\beta\beta} + T^{(2)}_{\alpha\beta_s\alpha\beta_s}$$

The spin space parts of the density matrices contract to give

$$\alpha(1')\alpha(1),\ \tfrac{1}{2}\left(\alpha(1')\alpha(1)+\beta(1')\beta(1)\right),\ \beta(1')\beta(1),\ \text{and}\ \tfrac{1}{2}\left(\alpha(1')\alpha(1)+\beta(1')\beta(1)\right)$$

respectively.

If we then express the position space parts of the density matrices into the Tensor product space $\otimes^2_2 \rho^{(m)}$ i.e.

$$U^+_A T^{(2)}_{\alpha\alpha\alpha\alpha} U_A,\ U^+_A T^{(2)}_{\alpha\beta_t\alpha\beta_t} U_A,\ U^+_A T^{(2)}_{\beta\beta\beta\beta} U_A \text{ and } U^+_S T^{(2)}_{\alpha\beta_s\alpha\beta_s} U_S$$

we can then contract as described i.e. from $\otimes^2_2 \rho^{(m)} \rightarrow \otimes'_1 \rho^{(m)}$.

If we then collect together parts of the same spin symmetry we can then define the 1st Order Reduced Density Matrix of $\alpha\alpha$ or $\beta\beta$ spin symmetry as

$$\rho_\alpha = \frac{2}{N-1}\left\{C\cdot\left[U^+_A T^{(2)}_{\alpha\alpha\alpha\alpha} U_A + \tfrac{1}{2} U^+_A T^{(2)}_{\alpha\beta_t\alpha\beta_t} U_A + \tfrac{1}{2} U^+_S T^{(2)}_{\alpha\beta_s\alpha\beta_s} U_S\right]\right\}\alpha(1')\alpha(1)$$

$$\rho_\beta = \frac{2}{N-1}\left\{C\left[U^+_A T^{(2)}_{\beta\beta\beta\beta} U_A + \tfrac{1}{2} U^+_A T^{(2)}_{\alpha\beta_t\alpha\beta_t} U_A + \tfrac{1}{2} U^+_S T^{(2)}_{\alpha\beta_s\alpha\beta_s} U_S\right]\right\}\beta(1')\beta(1)$$

We also note that the diagonal elements of ρ_α and ρ_β could be defined as: -

$$\rho^{i}_{\alpha i} = \frac{1}{N-1}\left\{ C\left[T^{(2)}_{\alpha\alpha\alpha\alpha} + \frac{1}{2} T^{(2)}_{\alpha\beta_t\alpha\beta_t} + \frac{1}{2} T^{(2)}_{\alpha\beta_s\alpha\beta_s} \right]^{ij}_{ij} \right\} \alpha(1')\alpha(1).$$

$$\rho^{i}_{\beta i} = \frac{1}{N-1}\left\{ C\left[T^{(2)}_{\beta\beta\beta\beta} + \frac{1}{2} T^{(2)}_{\alpha\beta_t\alpha\beta_t} + \frac{1}{2} T^{(2)}_{\alpha\beta_s\alpha\beta_s} \right]^{ij}_{ij} \right\} \beta(1')\beta(1).$$

i.e the diagonal elements of the reduced first order density matrix represented on the $\{\omega^i(1') \otimes \omega_j(1)\}$ basis of $\otimes^1_1 F^{(2M)}$ are directly linked to the contractions of the diagonal elements of the reduced second order density matrix represented on $\wedge^2_2 F^{(2M)}$.

CHAPTER FIVE.

Probability and Physical Interpretation

Having a mathematical recipe that, given certain input data, enables an output to be manifested, which can be tested against an experimental 'fact' is all any theoretical formalism would want to acheive. However, certain qualifications are desirable. For if the output is just a set of parameters like pressure, volume, energy, temperature and the mathematical recipe has no physical interpretation then the end result is a characterisation of a system without any reference to its structure. 'Feel' for the output parameters in terms of structure is lost, thus prediction (non-mathematical) about future values of the parameters given new circumstances becomes virtually impossible. If, on the other hand, information about the structure is output like spatial densities (of varying kinds), then a picture, schematic as it may be, can be built up in one's mind and the system can become an envisaged dynamic entity with many conjectured possibilities. The optimum theoretical description is when each stage of the mathematical recipe is open to physical interpretation, in contrast with a set of mathematical abstractions leading - 'as if by magic' - to a physical picture. When this is the case, inferential logic can begin to play an important part in the analysis of the problem one is studying and thus leads more quickly to useful results than if one had worked through all the deductive possibilities.

Given that a physical interpretation (at the maximum possible times) is the desired state, one has to be careful of the many dangers that may trap the unwary, viz. a Non-realistic interpretation of the mathematical forms - giving them a meaning when they have no such meaning - is worse than giving them no meaning at all, for this will lead to misguided inferences about the possibilities of the

system, and a fallacious understanding of the mechanism by which the parameters characterising the system come to have their values.

The problem of mathematical/physical description is of particular importance in chemistry, where multitudes of qualitative theoriies are based upon a physical interpretation of quantitative work. Unfortunately, not always is this done in a realistic way (in the above sense) and inherent faults thus become a part of the qualitative theory. The incorporation of such faults is thus made easier by the physical uninterruptible path through which the mathematics meanders before reappearing in a physical tangible form. For this reason, the Density Matrix picture, in terms of Natural expansions is of particular benefit, for this leads directly at all stages of the mathematical treatment to physically meaningful interpretation in terms of probability distribution functions, but care must be taken in understanding what these PDFs are of.

A short section will follow on the probability notation and some properties of probability measures. Then will follow a probalistic discussion of Density and Reduced Density Matrices, with relation to their expansion over a basis set of matrices.

Axioms of Probability Measure

1. For any event A, $P(A) \geq 0$ where $P(A)$ is the probability measure associated with the event A.

2. $P(u) = 1$ where u is the universal event for that set of events to which the probability measure refers (to a particular sample space).

3. If $A_1 \cap A_2 = \phi$ then
$P(A_1 \cup A_2) = P(A_1) + P(A_2)$ where ϕ is the null event.

(3) is when the events A and B are mutually exclusive.

$\cup \equiv$ set Theoretical Union.

$\cap \equiv$ " " Intersection.

4. If $A_1, \ldots\ldots A_m, \ldots\ldots$ are pairwise mutually exclusive events then
$$P(\cup_{i=1}^{\infty} A_i) = \sum_i^{\infty} P(A_i)$$
and for finite m
$$P(\cup_{i=1}^{m} A_i) = \sum_i^{m} P(A_i).$$

The following Theorems also hold:-

1. $P(\phi) = 0$

2. $P(A) = 1 - P(\bar{A})$ where $\bar{A}$ is the complement of the event A s.t. $u = A \cup \bar{A}$.

3. If A and B are any two events then
$$P(A \cup B) = P(A) + P(B) - P(A \cap B)$$
when the probability measures refer to the same sample space.

4. A generalisation of (3).

If $A_1, \ldots\ldots A_m$ are any m events then

$$P(\bigcup_{i=1}^{i=M} A_i) = \sum_{i}^{m} P(A_i) - \sum_{i<j}^{m} P(A_i \cap A_j) + \sum_{i<j<k}^{m} P(A_i \cap A_j \cap A_k)$$
$$+ \ldots\ldots (-1)^{m-1} P(\bigcap_{i=1}^{i=m} A_i).$$

5. If $A \subset B$ then $P(A) \leq P(B)$

i.e. if the event A contains the event B then the probability of B occurring is less than or equal to the probability of A occurring.

Sample Space: - i.e. a set of events

Set of Elementary Events: - a set of events that are pairwise mutually exclusive that define the sample space. (This set is not unique).

i.e. $S \equiv \{a_1, \ldots a_m\}$ where a_i are elementary events. Such events can be described by experiments or questions that have a Yes/No answer (i.e. obey a binary logic). If the space is infinite, $m = \infty$

As the universal event is the union of all such events $\bigcup_{i=1}^{i=m} a_i$

Then $P(\bigcup_{i=1}^{i=m} a_i) = 1$, as $a_i \cap a_j = \phi$ we have from (4) above

$$P(\bigcup_{i=1}^{i=m} a_i) = \sum_{i=1}^{i=m} P(a_i) = 1.$$

A sample space does not need to have discrete elementary events i.e. a continuous sample space.

$S \equiv \{a(x)\}$ x-continuous parameter.

Then the union is written as $\bigcup_{x=x_0}^{x=x_m} a(x)$ if finite, if infinite

$x_m = \infty$ and $P(\bigcup_{x=x_0}^{x=x_m} a(x)) = \int_{x_0}^{x_m} P(a(x))\,dx = 1.$

The functions $P(a)$ defined over a set of events are called probability distribution functions PDF. These are discontinuous discrete functions when defined over a discrete sample space (i.e. a space with discrete elementary events) and are continuous when defined over a sample space with continuous elementary events.

The values of the function $\left[P(a)\right]_{a=a_i}$ is the probability associated with the occurrence of a_i.

As the probability associated with the universal event is 1, the value of the functions $P_i(b)$ (any PDF) must lie between 0 and 1, otherwise it is not a probability measure. (b is any type of event, compound or elementary).

Only when the function is defined over a complete set of elementary events does

$\int_{x_0}^{x_m} P(a(x))\,dx$ (for continuous sample space) = 1.

or $\sum_{i=1}^{i=m} P(a_i)$ (for discrete sample space) = 1.

If the functions are defined over compound events $b(x)\,(x=(x_0,x_m))$ or $(x = x_1, \ldots\ldots x_m)$ then

$$\int_{x_0}^{x_m} P(b(x))\,dx \qquad \sum_{i=1}^{i=m} P(b(x_i)) \qquad \left\{\begin{array}{l}\text{can have any}\\ \text{positive value}\end{array}\right.$$

For clarity we here interpret into English the concept of Union and intersection of Events.

Union:- $A \cup B$ (A and B any two events), this is the event that occurs when the event A occurs or the event B occurs.

Intersection:- $A \cap B$, this is the event that occurs only when A and B occur.

Thus $P(A \cup B)$ is the probability that A or B will occur, and

$P(A \cap B)$ " " " " A and B " " .

Conditional Probability:- This is the probability that given B has occurred then A will occur, which is written as $P(A/B)$.

This is a renormalised measure of the probability of A occurring, i.e. instead of it being a measure w.r.t. the sample space $S \supset A$ and B , it is a relative measure w.r.t. the probability of B occurring, i.e. the probability of A and B occurring simultaneously is scaled up by a factor of $1/P(B)$ which makes the probability of B occurring in this new relative measure = 1, and thus define a new sample

space in which B is the universal event.

Thus $$P(A|B) = \frac{P(A \cap B)}{P(B)}$$

If $P(A|B)=0$ then the events A and B are exclusive (as then $P(A \cap B) = 0$) and if $P(A|B)=1$ then $B \supset A$ (as $A \cup B = B$).

Now if two events A and B are independent then the occurrence of one will not effect the occurrence of the other.

Thus $$P(A|B) . P(B) = P(A) . P(B) = P(B) . P(A)$$

↳ this factor scales the relative measure s.t. it can be directly cf to the absolute measure, and

$$P(B|A) . P(A) = P(B) . P(A) . = P(A) . P(B)$$

Thus $$P(A \cap B) = P(B \cap A) = P(A) . P(B)$$

So we can say that the events A and B are independent if and only if $P(A \cap B) = P(A) . P(B)$

Thus exclusive events are not independent.

This generalised to k events is:- $A_1, \ldots\ldots A_k$ are mutually independent if and only if we have for $j = 2, \ldots\ldots k$

$$P(A_i \cap A_{i_2} \ldots\ldots \cap A_{i_k}) = P(A_{i_1}) . P(A_{i_2}) \ldots\ldots P(A_{i_k}).$$

For all $k!$ permutations $\{i_1, \ldots\ldots i_k\}$ of k integers.

Probabilistic Interpretation of Density Matrices

We will consider a system of N identical Fermions i.e. obeying Fermi-Dirac Statistics and thus the system is antisymmetric w.r.t. particle interchange.

Any state of a micro-system is fully characterised by its full N particle Density Matrix associated with that state in the co-ordinate representation

$$T^{(N)}(1' \ldots\ldots N' | 1 \ldots\ldots N) = \underline{\Phi}^*(1' \ldots\ldots N') \, \underline{\Phi}(1 \ldots\ldots N)$$

$\underline{\Phi}$ being the wave function of that state.

The co-ordinate and spin space properties of the system are fully determined by the diagonal elements of the density Matrix

$$T'^{(n)}(1'.....N'/1.....N) \equiv T^{(n)}(1.....N)$$

The off diagonals only being pertinent for momentum properties (such as KE.) of the system. Even though it will not be very informative about momentum properties, it is very instructive and useful to study the properties of the diagonal elements of $T^{(n)}(1'.....N'/1.....N)$ i.e. the position and spin space structure of the system.

The diagonal elements of the full N particle Density Matrix form a continuous PDF over a sample space $S^{[N]}$ based on the elementary events.

"Is there a particle at point X_1, at the same time as there being a particle at X_2,..... etc.....?", where these are co-ordinates or position vectors in position-spin space.

These elementary events i.e. the simultaneity of particles at the points $X_1,.....X_n$ or in the configuration $(X_1,.....X_n)$ are denoted by $E(X_1.....X_n)$. Such a sample space is infinite as well as being continuous.

Thus $T^{(n)}(X_1.....X_n)$ is the probability that there are N particles in the configuration $(X_1.....X_n)$

$T^{(N)}(1.....N)$ at once fulfils the normalisation condition of PDF over a complete set of elementary events viz. $\int T^{(n)}(1.....N)\,d\tau_1.....d\tau_n = 1$

The universal event $U_{x=-\infty}^{x=+\infty} E(1.....N)$ is the occurrence of N particles in space, and as the events are exclusive they can be expressed as

$$U_{x=-\infty}^{x=+\infty} = \int E(1.....N)\,d\tau_1.....n.$$

Now let us consider the following union of events

$E(X) = \bigcup_{(1.....N) \supset X} E(1.....N)$ i.e. the union over all events associated with the configurations that contain the position vector X in them.

Thus the event $E(x')$ is:-

$$E(x') = \bigcup_{2.....N=-\infty}^{2.....N=+\infty} E(x'2.....N) + \bigcup_{1,3.....N=-\infty}^{1,3.....N=+\infty} E(1,x'3....N) + ...$$

$$..... + \bigcup_{1.....N-1=-\infty}^{1.....N-1=+\infty} E(1..... N-1, x').$$

$$= \int E(x'_2.....N)\, d\tau_{2...N} + \int E(1,x'3,.....N)\, d\tau_{3.....N} + ...$$

$$..... + \int E(1.....N-1\, x')\, d\tau_{1.....n-1}.$$

due to the pairwise exclusiveness of the events

where the integrations are over the sample space $\int^{[N]}$

$$\therefore P(E(x')) = \sum_{\sigma_i \in G_{N-1,N}} \int P(E(x_{i_1}.....x_{i_{n-1}}\, x')\, d\tau_{i_1.....i_{n-1}}$$

where $\sigma_i \equiv \{i_1, ... i_{n-1}\}$ the set of N ordered sequences of $n-1$ different integers chosen from n integers.

And we have used $P\left(\int E(x_{i_1}..... x_{i_{n-1}}, x')\, d\tau_{i_1.....i_{n-1}}\right) = \int P(E(x_{i_1}....i_{n-1}\, x')\, d\tau_{i_1}....\tau_{n-1}$

i.e. we have replaced the integration in sample by the integration in probability measure space.

As we are dealing with indistinguishable particles

$$P(E(x_{j_1}..... x_{j_{n-1}}\, x')) = P(E(x_{i_1}..... x_{i_{n-1}}\, x')$$

where σ_i and σ_j are two different sequences in $G_{n-1,n}$.

Thus

$$P(E(x')) = N \int P(E(x'_2.....N))\, d\tau_{2.....N}$$

$$= N \int T^{(n)}(x'_2.....N)\, d\tau_{2.....N}$$

which is just the definition of the diagonal elements of the 1st. Order Reduced Density Matrix $\rho(1'|1)$.

Thus $\varrho(1|1) = \varrho(1) = P(E(1))$, and $\varrho(1)$ is a PDF defined over the compound events "IS THERE A PARTICLE AT POINT X'?" $\equiv E(x')$.

That the PDF $\varrho(1)$ is defined over a compound set of events is obvious as $\int \varrho(1) dT_1 = N$.

Similarly the union of events defined as

$E(x'X'') = \bigcup_{(1.....N) \supset X' \text{ and } X''} E(1.....N)$ i.e. the union of all events associated with the configurations that contain the position vectors X' and X'' in them.

$$= \sum_{\sigma_i \in G_{n-2,N}} \int P(E(x_{i_1} \ldots x_{i_{n-2}} x'x'')) dT_{i_1 \ldots i_{n-1}}$$

where $\sigma_i \equiv \{i_1 \ldots i_{n-2}\}$ the set of $N(N-1)/2$ ordered sequences of $n-2$ different integers chosen from n integers.

$$P(E(x'x'')) = \frac{N.(N-1)}{2} \int P(E(x'x''3.....N)) dT_{3.....N}$$

$$= \frac{N(N-1)}{2} \int T^{(n)}(x'x''3.....N) dT_{3.....N}$$

which is the definition of the diagonal elements of the 2nd Order Reduced Density Matrix $T^{(2)}(1'2'|12)$.

Thus $T^{(2)}(12|12) \equiv T^{(2)}(12) = P(E(12))$ and $T^{(2)}(12)$ is a PDF defined over the compound events in $\zeta^{[n]}$

"IS THERE A PARTICLE AT X' AND A PARTICLE AT X'' ? $\equiv E(x'x'')$.

The sum of all such probabilities is given by $\int T^{(2)}(12) dT_{12}$ which has the value $\int T^{(12)}(12) dT_2 = N(N-1)/2$.

$T^{(n)}(1.....N)$ represents N identical Fermions $\in \Lambda^n_n F^{(\infty)}$ and thus can be decomposed over the basis

$$\{ w^{\sigma_{\nu_1}}(x') \wedge w^{\sigma_{\nu_2}}(x_2) \wedge \ldots . w^{\sigma_{\nu_n}}(x_n) \otimes w_{\sigma_{\mu_1}}(x_1) \ldots . w_{\sigma_{\mu_n}}(x_n) \}$$

of $\Lambda^n_n F^{(2m)}$ $\qquad \sigma_\nu, \sigma_\mu \in Q_{n,2m}$

So

$$T^{(n)}(1.....N) = \sum_{\substack{\sigma_\nu, \sigma_\mu \in Q_{n,2m}}} \sum_{\sigma_\mu} T^{(n)\sigma_\mu}_{\sigma_\nu} \omega^{\sigma_\nu}(1.....N)\, \omega_{\sigma_\mu}(1.....N)$$

where $\omega^{\sigma_\nu} = \omega^{\sigma_{\nu_1}}(x') \wedge ..... \wedge \omega^{\sigma_{\nu_n}}(x_n)$.

The functions $\omega^{\sigma_\nu}(1'.....N')\, \omega_{\sigma_\mu}(1.....N) \in \Lambda^n_n F^{(2m\alpha\alpha)}$ can be thought of as Transition Density Matrices $\sigma_\nu \neq \sigma_\mu$ and Density Matrices $\sigma_\nu = \sigma_\mu$ i.e.

$$T^{(n)}_{\sigma_\nu \sigma_\mu}(1'.....N'|1.....N) \equiv \omega^{*}_{\sigma_\nu}(1'.....N')\, \omega_{\sigma_\mu}(1.....N)\,; \sigma_\nu \neq \sigma_\mu$$

and $T^{(n)}_{\sigma_\nu \sigma_\mu}(1'.....N'|1.....N) \equiv \omega^{*}_{\sigma_\nu}(1'.....N')\, \omega_{\sigma_\nu}(1.....N)\,; \sigma_\nu = \sigma_\mu$

and the diagonal elements can be thought of as PDFs when $\sigma_\nu = \sigma_\mu$ and Transition Distribution functions (TDF) when $\sigma_\nu \neq \sigma_\mu$

They have the normalisation properties

$$\int T^{(n)}_{\sigma_\nu}(1.....N)\, d\tau_{1.....N} = 1$$

$$\int T^{(n)}_{\sigma_\nu \sigma_\mu}(1.....N)\, d\tau_{1.....N} = 0$$

The decomposition of $T^{(n)}(1.....N)$ over the above basis of $\Lambda^n_n F^{(2m)}$ can thus be written as

$$T^{(n)}(1.....N) = \sum_{\sigma_\nu} T^{(n)\sigma_\nu}_{\sigma_\nu} T^{(n)}_{\sigma_\nu}(1.....N) + \sum_{\substack{\sigma_\nu, \sigma_\mu \\ \sigma_\nu \neq \sigma_\mu}} T^{(n)\sigma_\mu}_{\sigma_\nu} T^{(n)}_{\sigma_\nu \sigma_\mu}(1.....N)$$

Unfortunately, TDFs are different in character to PDFs and do not comply with the laws of probability measure, and in fact the values of TDFs lie in the interval $(-1, +1)$

However when we consider the Natural expansion of $T^{(n)}_i(1'....N|1.....N)$ i.e.

$$T^{(n)}(1'.....N'|1.....N) = \sum_i^{2m C_n} c_i\, \chi^i(1'.....N')\, \chi_i(1.....N)$$

we see that if we define $\chi^i(1'.....N')\, \chi_i(1.....N) \equiv T^{(n)}_i(1'....N'|1.....N)$ then $T^{(n)}(1.....N)$ can be expanded completely in terms of PDFs $T^{(n)}_i(1.....N)$ i.e.

$$T^{(n)}(1.....N) = \sum_i^{2m C_n} c_i\, T^{(n)}_i(1.....N)$$

c_i is the eigenvalue associated with the i^{th} eigenfunction of $\Gamma^{(n)}(1'.....N'|1.....N)$ i.e.

$$\int \Gamma^{(n)}(1'.....N'|1.....N)\ \chi^i(1.....N)\, d\tau_{1.....N} = c_i\, \chi^i(1'.....N').$$

The PDFs $\Gamma_i^{(n)}(1.....N)$ have the normalisation property

$$\int \Gamma_i^{(n)}(1.....N)\, d\tau_{1.....N} = 1\ ,\ \left\{\Gamma_i^{(n)}(1.....N)\right\}$$ are PDFs over $S^{[n]}$, and $\Gamma^{(n)}(1.....N)$ can be completely described in terms of this set of PDFs.

An interesting point about the Natural expansion above is that we can define a new PDF on a new sample space with elementary event "Are the N particles described by the PDF $\Gamma_i^{(n)}(1.....N)$?" $\equiv E(\Gamma_i^{(n)})$ The new PDF over this new sample space is the diagonal elements of the Density Matrix represented in a basis of its natural orbitals, i.e. the $\left\{\chi^i(1'....N') \otimes \chi_i(1....N)\right\}$ basis of $\Lambda_n^n F^{(2m\infty)}$ viz the PDF is

$$\Gamma_d^{(n)} = \Gamma^{(n)}{}_i^i = c_i$$

where $\Gamma_d^{(n)}{}_j^i = \langle \chi^i(1'.....N') | \Gamma^{(n)}(1'.....N'|1....N) | \chi_j(1.....N) \rangle$;

(which = 0 unless $i = j$).

This new sample space $SF^{[n]}$ is usually finite (if m is) and is discrete thus the PDF $\Gamma^{(n)}$ is discontinuous.

The events $E(\Gamma_i^{(n)})$ form a complete elementary basis for $SF^{[n]}$ and

$$\Gamma_r \Gamma_d^{(n)} = \sum_i \Gamma_d^{(n)i}{}_i = 1$$

The values of the PDF $\Gamma_d^{(n)}$ i.e. $\Gamma_d^{(n)i}{}_i$ are the probabilities that the PDFs (based on $S^{[n]}$) describe the N particles, or equivalently $\Gamma_d^{(n)}{}_i^i$ is the statistical weight of the PDF $\Gamma_i^{(n)}(1....N)$ in the decomposition of the PDF $\Gamma^{(n)}(1....N)$ over the set of PDFs $\left\{\Gamma_i^{(n)}(1....N)\right\}_{i=1....}^{2m}{}_{....C_N}$.

These probabilities or weights are known as the occupancy of the functions $\chi^i(1.....N)$

The probability that N particles are in the particular configuration

$(X_1 \ldots X_n)$ is now given by

$$\sum_{i=1}^{2m_{C_n}} T_d^{(n)\,i}{}_i \, T_i^{(n)}(X_1 \ldots X_n) = T^{(n)}(X_1 \ldots X_n)$$

Now let us consider the event $E(x')$ expressed in terms of the Natural Expansion of $T^{(n)}(1 \ldots N)$ viz

$$E(x') = N \sum_{i=1}^{2m_{C_n}} T_d^{(n)\,i}{}_i \bigcup_{(x'2 \ldots N) \supset (2 \ldots N)} E_i(x'2 \ldots N) = \sum_{i=1}^{2m_{C_n}} T_d^{(n)\,i}{}_i \, E_i(x')$$

where

$$E_i(x') = N \bigcup_{(x'2 \ldots N) \supset (2 \ldots N)} E_i(x'2 \ldots N)$$

and the events $E_i(1 \ldots N)$ have associated PDFs $T_i^{(n)}(1 \ldots N)$

The probability associated with the event $E(x')$ is then given by

$$P(E(x')) = \mathcal{P}(x') = N \sum_{i=1}^{2m_{C_n}} T_d^{(n)\,i}{}_i \int T_i^{(n)}(x'2 \ldots N)\, dT_{2 \ldots N}$$

$$= \sum_{i=1}^{2m_{C_n}} T_d^{(n)\,i}{}_i \, P(E_i(x'))$$

If we define $\lambda_i(x') = P(E_i(x'))$

then $\lambda_i(1) = N \int T_i^{(n)}(1\,2 \ldots N)\, dT_{2 \ldots N}$ and thus $\int \lambda_i(1)\, dT_1 = N$

and $\mathcal{P}(1) = \sum_{i=1}^{2m_{C_n}} T_d^{(n)\,i}{}_i \, \lambda_i(1)$

Now, $\lambda_i(1)$ is the diagonal elements of $\lambda_i(1'|1)$ where $\lambda_i(1'|1)$ is the Reduced 1st Order Density Matrix associated with the Natural Full N particle Density Matrix $T_i^{(n)}(1' \ldots N' | 1 \ldots N)$, and $\lambda_i(1'|1)$ can be written in terms of its natural 1st Order Density Matrices so:-

$$\lambda_i(1'|1) = \sum_{j=1}^{j=N} {}^i\eta_j(1'|1) \quad \text{where} \quad {}^i\eta_j(1'|1) = {}^i\psi_j(1')\ {}^i\psi_j(1)$$

$\{{}^i\psi_j(1)\}$ are the N.S.O.s of $\lambda_i(1'|1)$, each N.S.O. has the eigenvalue 1.

Thus $T_i^{(n)}(1' \ldots N' | 1 \ldots N)$ can be expressed as $\chi_i^*(1' \ldots N')\chi_i(1 \ldots N)$

where $\chi_i(1 \ldots N) = {}^i\psi_1(1) \wedge \ldots \ldots \wedge {}^i\psi_N(N)$.

The PDF $\lambda_i(1) \in S^{[n]}$ can thus be expanded as

$$\lambda_i(1) = \sum_{j=1}^{N} {}^i\eta_j(1)$$

$$\lambda_i(1) = \sum_{j=1}^{N} {}^{i}\eta_j(1)$$

$\lambda_i(1)$ gives the probability of finding 1 particle of a N particle system at a given point in spin-position space, but it is only a partial PDF for the whole system (as $T_i^{(N)}(1....N)$)is only a partial description). The weight with which it describes a 1 particle sub-system is given by $T_d^{(N)}{}_i^i$. The PDFs ${}^{i}\eta_j(1) \in S^{[1]}$ - referring to events "IS THERE A PARTICLE AT POINT X ?" which are 1 particle events and not associated with an N particle system. This is also expressed by the normalisation of $\lambda_i(1)$ and $\{{}^{i}\eta_j(1)\}$ i.e.

$$\int_{i=1.....}{}_{2m}C_n \lambda_i(1)\,d\tau_1 = N \qquad \text{and} \qquad \int {}^{i}\eta_j(1)\,d\tau_1 = 1$$
$$\text{for } \begin{matrix} i = 1..... {}_{2m}C_n \\ j = 1..... N \end{matrix}$$

The discrete PDF $T_d^{(N)} \in SF^{[N]}$ as well as referring to the events $E(T_i^{(N)})$ can be seen to refer also to the events $E(\lambda_i)$, and a link between $SF^{[N]}$ and $SF^{[1]}$ can be seen to be in the form $E(\lambda_i) = \bigcup_{j=1}^{j=N} E({}^{i}\eta_j)$ and in general only this form.

If we now consider the Natural expansion of $\varrho(1'|1)$ i.e.

$$\varrho(1'|1) = \sum_{i=1}^{2m} \varrho_d{}_i^i \eta_i(1'|1) \quad \text{where } \eta_i(1'|1) = \psi_i^*(1')\psi_i(1)$$

and thus the Natural decomposition of $\varrho(1)$

$$\varrho(1) = \sum_{i=1}^{2m} \varrho_d{}_i^i \eta_i(1)$$

we see that $\eta_i(1) \in S^{[1]}$, as $\int \eta_i(1)\,d\tau_1 = 1$ and thus $\varrho_d \in SF^{[1]}$

Now unless $E(\eta_i) = \bigcup_{\text{over Same } j} E(\lambda_j)$ $\quad \text{for } \begin{matrix} i = 1..... {}_{2m}C_N \\ j = 1..... {}_{2m}C_N \end{matrix}$

$\varrho_d \in SF^{[n]}$ if the above relationship is to be satisfied

$$\eta_i(1) = \sum_j \lambda_j(1)_{\text{over same } j}$$

i.e. $\eta_i(1'|1) = \sum_j \lambda_j(1'|1)$ if this is so the eigenfunctions of are also eigenfunctions of each $\lambda_j(1'|1)$ but we know in general that this is not so, and in fact is only the case when $\{\lambda_j(1'|1)\}_{j=1....{}_{2m}C_N}$

All have simultaneous eigenfunctions that are equal to the eigenfunctions of $\rho(1'|1)$.

Thus, in general, ρ_d is not a PDF over $SF^{[N]}$ which is based on the events $E(\tau_i^{(N)})$ and is not related in a probabilistic way to $\Gamma_d^{(N)}$. But ρ_d is a discrete representation of $\rho(1)$ - that represents the 1 particle subsystem of an N particle system, and thus $Tr\,\rho_d = N$, but the arguments of ρ_d refer to the events $E(\eta_i)$ i.e. "Does the PDF $\eta_i(1)$ describe 1 particle ?", and the 1 particle can belong to an N particle system.

It is in fact unfortunate that there is no direct link between ρ_d and $\Gamma_d^{(N)}$ for this would simplify the problem of N - Representability considerably.

If we consider the Natural Expansion of the 2nd Order Reduced Density Matrix viz

$$\Gamma^{(2)}(1'2'|12) = \sum_i^{2nC_2} \Gamma_d^{(2)}{}_i^i \, \Omega^i(1'2')\Omega_i(12)$$

and then the PDFs $\Gamma^{(2)}(12)$, $\Gamma_d^{(2)}$ and $\Gamma_i^{(2)}(12)$ where

$$\Gamma_i^{(2)}(1'2'|12) = \Omega^i(1'2')\Omega_i(12)$$

can be an analagous analysis to that presented previously for the 1st Order Reduced Density Matrix. We see that $\Gamma_d^{(2)}$ is a PDF $\in SF^{[2]}$ and not in general $\in SF^{[N]}$ but it does represent $\Gamma^{(2)}(12)$ which $\in S^{[N]}$, and thus

$$Tr\,\Gamma_d^{(2)} = N(N-1)/2, \text{ while } \int \Gamma_i^{(2)}(12)\,d\tau_{12} = 1.$$

The events $E(\Gamma_i^{(2)})$ can be interpreted as "Are 2 particles simultaneously described by $\Gamma_i^{(2)}$?" and the 2 particles could be a subsystem of an N particle system.

A similar problem arises in relating $\Gamma_d^{(2)}$ to ρ_d and analagous reasoning would show that $\rho_d \notin SF^{[2]}$ in general; in fact, not unless

$\rho_i(1'|1)$ the 1st Order Reduced Density Matrix associated with $\Gamma_i^{(2)}(1'2'|12)$ has the same eigenfunctions for all $i = 1 \ldots {}^{2m}C_2$ which are identical to the eigenfunctions of $\rho(1'|1)$, will $\rho d \in SF^{[2]}$

However, it is possible to link the PDFs $\Gamma^{(n)}(1\ldots N)$, $\Gamma^{(2)}(12)$ and $\rho(1)$ in a partial manner by considering the discrete PDFs

$\Gamma^{(n)} = \Gamma^{(n)\sigma_\nu}_{\sigma_\nu, \sigma_\nu \in Q_{N,2m}}$, $\Gamma^{(2)} = \Gamma^{(2)\sigma_\nu}_{\sigma_\nu, \sigma_\nu \in Q_{2,2m}}$

and $\rho = \rho^i_i$ i.e. the diagonals of the non-diagonal representation of $\Gamma^{(N)}(1' \ldots N'|1 \ldots N)$, $\Gamma^{(2)}(1'2'|12)$ and $\rho(1'|1)$ in $\Lambda^n_n F^{(2m)}$, $\Lambda^2_2 F^{(2m)}$ and $F^{(2m)}$

on the bases

$$\left\{ \prod_i^{N\wedge} \omega^{\sigma_{\nu_i}}(x'_i) \otimes \prod_j^{N\wedge} \omega_{\sigma_{\mu_j}}(x_j) \right\} \sigma_\nu, \sigma_\mu \in Q_{n,2m}$$

$$\left\{ \prod_i^{2\wedge} \omega^{\sigma_{\nu_i}}(x'_i) \otimes \prod_j^{2\wedge} \omega_{\sigma_{\mu_i}}(x_i) \right\} \text{ and } \{\omega^i(1)\}$$

$\sigma_\nu, \sigma_\mu \in Q_{2,2M}$

i.e. if we make the approximations

$$\Gamma^{(n)}(1 \ldots N) \triangleq \sum_{\sigma_\nu \in Q_{n,2m}} \Gamma^{(n)\sigma_\nu}_{\sigma_\nu} \Gamma^{(n)}_{\sigma_\nu}(1 \ldots N)$$

$$\Gamma^{(2)}(12) \triangleq \sum_{\sigma_\nu \in Q_{2,2m}} \Gamma^{(2)\sigma_\nu}_{\sigma_\nu} \Gamma^{(2)}_{\sigma_\nu}(12) \text{ where } \Gamma^{(2)}_{\sigma_\nu}(2) = \omega^{\sigma_{\nu_1}}(1) \wedge \omega^{\sigma_{\nu_2}}(2) \otimes \omega_{\sigma_{\nu_1}}(1) \wedge \omega_{\sigma_{\nu_2}}(2)$$

and $\rho(1) \triangleq \sum_i^{2m} \rho^i_i \rho_i(1)$ where $\rho_i(1) = \omega^i(1) \otimes \omega_i(1)$

If we define $\lambda_{\sigma_\nu}(1) = N \int \Gamma^{(n)}_{\sigma_\nu}(1 \ldots N) d\tau_{2 \ldots N}$, so $\int \lambda_{\sigma_\nu}(1) d\tau_1 = N$

$\lambda_{\sigma_\nu}(1)$ is given by

$$\lambda_{\sigma_\nu}(1) = N \int \omega_{\sigma_{\nu_1}}(1) \wedge \ldots \wedge \omega_{\sigma_{\nu_n}} \otimes \omega^{\sigma_{\nu_1}}(1) \wedge \ldots \omega^{\sigma_{\nu_n}}(n) d\tau_{2 \ldots N}$$

$$= N \sum_{i \in \sigma_\nu}^{N} \omega_i(1) \omega^i(1) \text{ where } \sigma_\nu \in Q_{N,2m}$$

Thus the eigenfunctions of $\lambda_{\sigma_\nu}(1)$ are $\{\omega^i(1)\}_{i \in \sigma_\nu}$

We have defined $\rho(1)$ to have eigenfunctions $\{\omega^i(1)\}_{i=1 \ldots 2m}$

Thus $\lambda_{\sigma_\nu}(1)$ and $\rho(1)$ have the same eigenfunctions when all values of σ_ν are considered.

Similarly the eigenfunctions of $\chi_{\sigma_\nu}(1'|1) = \left(2 \int \Gamma^{(2)}_{\sigma_\nu}(12) d\tau_2\right)_{\sigma_\nu \in Q_{2,2}}$

are also the set $\{\omega^i(1)\}$ when all values of σ_ν are considered.

Thus the N.S.O.s associated with $\{T^{(2)}_{\sigma_\nu}(12)\}_{\sigma_\nu \in Q_{2,2m}}$ and $\{T^{(N)}_{\sigma_\nu}(1.....N)\}_{\sigma_\nu \in Q_{N,2}}$ and $\varrho(1)$ are identical.

The relationships between t iscrete PDFs $T^{(N)}_{\sigma_\nu}(1.....N)\ \sigma_\nu \in Q_{N,2m}$, $T^{(2)}_{\sigma_\mu}(12)_{\sigma_\mu \in Q_{2,2m}}$ and ϱ re given by the contraction relationships, viz

$$\varrho^i_i = C_{n-1}\left[T^{(n)}\right]^i_i$$

$$T^{(2)ij}_{ij} = C_{n-2}\left[T^{(n)}\right]^{ij}_{ij}$$

$$\varrho^i_i = \frac{1}{N-1} C\left[T^{(2)}\right]^i_i$$

and

$$E(\rho_i) = N \bigcup_{\sigma_\nu \supset i} E(T^{(N)}_{\sigma_\nu})\ \sigma_\nu \in Q_{N,2m}$$

$$E(T^{(2)}_{(i,j)}) = \frac{N(N-1)}{2} \bigcup_{\sigma_\nu \supset i,j} E(T^{(N)}_{\sigma_\nu})\ \sigma_\nu \in Q_{N,2m}$$

$$E(\varrho_i) = \frac{1}{(N-1)} \bigcup_{\sigma_\nu \supset i} E(T^{(2)}_{\sigma_\nu})\ \sigma_\nu \in Q_{2,2m}$$

The discrete PDFs $T^{(n)}$, ϱ and $T^{(2)}$ all $\in SF^{1[N]}$ a sample based on the elementary event $E[T^{(N)}_i]$ where $T^{(N)}_i \equiv T^{(N)i}_i(1.....N|1.....N)$ and thus can be analysed in terms of each other which enables us to apply the probability measure relationships to them i.e. we can assign $T^{(2)}$ to be a PDF over discrete events E_{ij} that have Probability $P_{i\wedge j}$ of occurring, $T^{(n)}$ to be a PDF over discrete events $E_{i,.....i_n}$ with Probability $P_{i,n.....\wedge i_n}$ of occurring and ϱ a PDF over discrete events E_i with Probability P_i of occurring.

For an N particle system $T^{(N)}(1.....N)$ determines all lower order PDFs i.e. PDFs referring to subsystems of the N particle system, $T^{(N)}(1.....N)$ is found by determining a solution to

$$[H, J^2] = [H, T^{(N)}] = [T^{(N)}, J^2] = 0$$

and s.t. $T^{(N)}(1'.....N'|1.....N) \in \Lambda^n_n F^{(\infty)}$.

However, we usually determine approximate solutions over the subspace $\Lambda^{n}_{n} F^{(2mcc)}$ and only take into account 1 and 2 particle operators i.e. $H \equiv H^{(2)}$, $J^{2} \equiv J^{(2)^{2}}$, thus we find a solution w.r.t. a 2 particle subsystem of the N particle system. Hence, $\Gamma^{(2)}(1'2'|12)$ determines all the properties of the system (as fully as possible within a Quantum Mechanical description) w.r.t. the operators we are interested in (viz 1 and 2 particle ones) and $\Gamma^{(2)}(12)$ will then completely describe the positon-spin space structure. As $\Gamma^{(2)}_{d}$ represents both $\Gamma^{(2)}(1'2'|12)$ and $\Gamma^{(2)}(12)$ completely we can formulate the problem of determining $\Gamma^{(2)}(1'2'|12)$ in terms of $\Gamma^{(2)}_{d}$.

$\Gamma^{(2)}_{d}$ as well as being a discrete PDF representing $\Gamma^{(2)}(12)$ also gives a complete description of the momentum space properties of the system, a characteristic not shared by the diagonal elements of the non-diagonal 2nd Order Reduced Density Matrix.

Unfortunately, we cannot be sure that a $\Gamma^{(2)}_{d}$ that satisfies the above commutation relationships does in fact represent a 2 particle subsystem of an N particle system of identical Fermions (N Representability Problem).

One way round this is to determine the full N particle Density Matrix $\Gamma^{(n)}(1'.....N'|1.....N)$ w.r.t. all 2 particle operators, then construct $\Gamma^{(2)}(1'2'|12)$ and hence $\Gamma^{(2)}_{d}$ from it. This is often achieved by the method of full Configuration Interaction, but although sometimes practical, is laborious and lacks an aesthetic succinctness for we "oversolve" our system.

As we have noted before, there is no direct probabilistic link between the various orders of discrete PDFs $\Gamma^{(n)}_{d}, \Gamma^{(n-1)}_{d} .... \Gamma^{(1)}_{d} (\equiv \rho_{d})$ As in general they cannot all be expressed in terms of events forming $SF^{(N)}$

If this was not so we could constrain $T_d^{(2)}$ to comply with sufficient of the probability measure relationships manifested by an N particle system of Fermions, so that it is indeed a PDF describing a 2 particle subsystem of an N particle system. However, we do know that the PDFs $T^{(n)}, \ldots\ldots T^{(1)}$ (i.e. the diagonal elements of the non-diagonal Density Matrices of various orders of reduction) do all $\in SF^{[N]}$ Thus in theory we can characterise $T^{(2)}$ sufficiently to be a 2 particle description of an N particle system; unfortunately, even if we achieve this completely $T_d^{(2)}$ is only partially characterised.

In practice the probability relationship that $T^{(2)}$ has to comply with are numerous, and many are non-linear. We select the following events and associated probabilities for their simplicity and linear nature in terms of $T^{(2)}$ viz

$$E(e_i) = \frac{1}{N-1} \bigcup_{\sigma_\nu \supset i} E(T^{(2)}_{\sigma_\nu}) \quad \sigma_\nu \in Q_{2,2m}$$

$$\bigcup_{i \in \sigma_\nu} E(e_i) = \sum_{i \in \sigma_\nu} E(e_i) - \bigcap_{i \in \sigma_\nu} E(e_i)$$

and we note that

$$\bigcap_{i \in \sigma_\nu} E(e_i) = E(T^{(2)}_{\sigma_\nu})$$

also $E(e_i) \supset E(T^{(2)}_{\sigma_\nu})$ for $i \in \sigma_\nu$

The associated Probability relationships with these events gives:-

(i) $e^i_i = \frac{1}{N-1} \sum_{\sigma_\nu \supset i} T^{(2)\sigma_\nu}_{\sigma_\nu}$

(ii) $P(\bigcup_{i \in \sigma_\nu} E(e_i)) = \sum_{i \in \sigma_\nu} e^i_i - T^{(2)\sigma_\nu}_{\sigma_\nu}$

(iii) $e_i \geq T^{(2)\sigma_\nu}_{\sigma_\nu}$ for $i \in \sigma_\nu$

As e^i_i is a probability measure we know that it lies in the interval $(0,1)$ as does $P(\bigcup_{i \in \sigma_\nu} E(e_i))$, thus the constraints that can be held on $T^{(2)}_{\sigma_\nu}$ can be formulated as:-

(i) $N-1 \geq \sum_{\sigma_\nu \supset i} T^{(2)\sigma_\nu}_{\sigma_\nu}$

(ii) $1 \geqslant \sum_{i \in \sigma_v} \varrho_i^i - T^{(2)\sigma_v}_{\sigma_v} \geqslant 0$

(iii) $\varrho_i^a - T^{(2)\sigma_v}_{\sigma_v} \geqslant 0$

Coupled with these we have

(iv) $T^{(2)\sigma_v}_{\sigma_v} \geqslant 0$

Many more constraints linking $T^{(2)}_{\sigma_v}$ with $T^{(\rho)}_{\sigma_\chi}$ $(\sigma_\chi \in Q_{\rho,2m})$ for $\rho = 3 \ldots\ldots N$ give rise to non-linear constraints that if held would indeed completely characterise $T^{(2)}_{\sigma_v}$.

CHAPTER SIX.

An Attempt at Solution

As pointed out in the introduction, the central problem to solve in Quantum Mechanics is to determine the allowable density operators for a given system characterised by a Hamiltonian operator within certain symmetry constraints, which are usually due to angular momenta, and statistical requirements. The system is completely described by a maximal set of commuting operators, these embodying the above requirements, so we seek allowable D_i's (i can be discrete or continuous) such that

$$[H, D_i] = [J^2, D_i] = [H, J^2] = 0$$

and $[\pi^A_A, D_i] = 0$ for Fermions

$[\pi^S_S, D_i] = 0$ for Bosons

each D_i characterises a state of the system, and H is spin independent. Except for atomic problems we usually take the less stringent angular momentum requirement that of $[H, S^2] = [D_i, S^2] = 0$

where $J^2 = (L+S).(L+S) = L^2 + S^2 + 2L.S$

thus commutation with J^2 infers $[L^2, H] = [L^2, D_i] = [S^2, H] = [S^2, D_i]$

$= [L.S, H] = [L.S, D_i] = 0$

We have seen that we can characterise a n particle system completely w.r.t. two particle operators by $T_i^{(2)}$ where this is the 2nd Order Reduced Density operator. Thus we can write the characterisation of a system n particle w.r.t. two particle operations as the solution of the following commutation requirements when the system is in a Singlet spin state.

$$[H^{(2)}, T_i^{(2)}] = [H^{(2)}, J^{(2)^2}] = [T_i^{(2)}, J^{(2)^2}] = 0$$

$$\text{or } [H^{(2)}, T_i^{(2)}] = [H^{(2)}, S^{(2)^2}] = [T_i^{(2)}, S^{(2)^2}] = 0$$

and that $\Gamma_i^{(2)} = C_{n-2}\left[\Gamma_i^{(n)}\right]$ i.e. $\Gamma_i^{(2)}$ is a $(n-2)^{th}$ contraction of $\Gamma_i^{(n)}$, where $\left[\pi_A^A, \Gamma_i^{(n)}\right] = 0$ for Fermions.

This last condition is in fact the N-Representability problem which has enthused many attempts at solution.

No naive claims of complete solution are contemplated in this work, but the hope is for a practical method that leads to a partial solution, not solely in the form of mathematical equations but also of numerical results that can be analysed in terms of probability requirements that are introduced by a system of linear constraints.

The space we choose to represent the operators in is $L(\otimes^2 F^{(2m)})$ where $F^{(2m)}$ is a 2 m dimensional space spanned by the set of orthonormal space spin functions $\{\omega^i(x)\} \in F^{(m\infty)}$ which form a basis for $F^{(m)}$.

These functions are formed by determining a basis for $\rho^{(m)}$ then forming the direct product space $\rho^{(m)} \otimes S^{(2)}$. The orthonormal basis for $\rho^{(m)}$ is signified by $\{\sigma^i(r)\}$. These functions are generated from a set of l.i. atomic orbitals (spatial) based on each atomic centre. These orbitals are each formed by an expansion of gaussian functions. The atomic orbitals are signified by

$$1s_i(r), 2s_i(r), 2p_{x_i}(r), 2p_{y_i}(r), 2p_{z_i}(r), \ldots \text{ etc.}$$

The letter and number indicating spatial symmetry properties and i the atomic centre.

Each type of atomic orbital is expressed as a l.c. of gaussian functions i.e. $1s(r) = \sum_j^{\rho} c_j e^{-\alpha_j r^2}$ ρ - the number of gaussian functions used in the approximations

c_j and α_j are parameters that define $1s(r)$.

Atomic orbitals of the same symmetry type but based on a different

centre are l.i, thus only one expansion for each type is necessary. Hence $\sigma^i(r)$ is an l.c of atomic orbitals (the atomic orbitals are now written for simplicity as $a^j(r)$), and $P^{(m)}$ is defined by these orthonormal functions. However, it is easier to first compute representations of operators using the non-orthogonal functions $\{a^j(r)\}$ then transforming into a basis defined by the orthogonal functions $\{\sigma^i(r)\}$; the properties and relationships between representations on these two bases are discussed in Appendix 3, where transformations are given that enable us to work equivalently in either representation.

For molecular systems in a Singlet spin state, (i.e. $S = 0$) we must find, in the representation space, matrices that represent $\hat{S}^{(2)^2}$, $\hat{H}^{(2)}$ and $\hat{T}^{(2)}$ that commute.
The matrices that represent $\hat{S}^{(2)^2}$ and $\hat{H}^{(2)}$ such that they commute are easily computed, leaving the representation of $\hat{T}^{(2)}$ the only unknown that has to be determined, within the constraint that it must represent the two particle behaviour of an n particle Fermion system.

It is a well-known fact that commutating matrices have simultaneous eigenvectors†, thus we first find simultaneous eigenvectors of $\hat{S}^{(2)^2}$ and $H^{(2)}$ which have the property of being a basis in which representations $\hat{S}^{(2)^2}$ and $\hat{H}^{(2)}$ are diagonal. Then we assume that $T^{(2)}$ is also diagonal in this representation (as it represents a state with $S = 0$).

Production of Simultaneous Eigenvectors $\in \Lambda^2 F^{(2m)}$ of $H^{(2)}$, $S^{(2)^2}$ and $T^{(2)}$.‡

‡ See Chapters 2 and 3 for fuller discussion of structure of decomposition

† If the eigenvectors of a particular matrix are degenerate then we can construct an l.c of them that corresponds to the eigenvectors of the other matrices that it commutes with.

Now as $\Lambda^2 F^{(2m)} = \Lambda^2 \rho^{(m)} \otimes V^2 S^{(2)} \oplus V^2 \rho^{(m)} \otimes \Lambda^2 S^{(2)}$

and $\Lambda_2^2 F^{(2m)} = \left[\Lambda^2 \rho^{(m)} \otimes V^2 S^{(2)} \oplus V^2 \rho^{(m)} \otimes \Lambda^2 S^{(2)}\right]$

$$\otimes \left[\Lambda_2 \rho_{(m)} \otimes V_2 S_{(2)} \oplus V_2 \rho_{(m)} \otimes \Lambda_2 S_{(2)}\right]$$

We first set up the representations of the operator $\hat{S}^{(2)^2}$ in the 16 subspaces of $\left[V^2 S^{(2)} \oplus \Lambda^2 S^{(2)}\right] \otimes \left[V_2 S_{(2)} \oplus \Lambda_2 S_{(2)}\right]$

viz

$$\Lambda_2^2 S^{(1)}_{\alpha\alpha\alpha\alpha}, \Lambda_2^2 S^{(1)}_{\alpha\alpha\alpha\beta_t}, \Lambda_2^2 S^{(1)}_{\alpha\alpha\beta\beta}, \Lambda_2^2 S^{(1)}_{\alpha\beta_t\alpha\alpha}, \Lambda_2^2 S^{(1)}_{\alpha\beta_t\alpha\beta_t}, \Lambda_2^2 S^{(1)}_{\alpha\beta_t\beta\beta},$$

$$\Lambda_2^2 S^{(1)}_{\beta\beta\alpha\alpha}, \Lambda_2^2 S^{(1)}_{\beta\beta\alpha\beta_t}, \Lambda_2^2 S^{(1)}_{\beta\beta\beta\beta}, \Lambda^2 V_2 S^{(1)}_{\alpha\alpha\alpha\beta_s}, \Lambda^2 V_2 S^{(1)}_{\alpha\beta_t\alpha\beta_s},$$

$$\Lambda^2 V_2 S^{(1)}_{\beta\beta\alpha\beta_s}, V^2 \Lambda_2 S^{(1)}_{\alpha\beta_s\alpha\alpha}, V^2 \Lambda_2 S^{(1)}_{\alpha\beta_s\alpha\beta_s}, V^2 \Lambda_2 S^{(1)}_{\alpha\beta_s\beta\beta} \text{ and } V_2^2 S^{(1)}_{\alpha\beta_s\alpha\beta_s}.$$

To each component of the representation we multiply a vector from $\Lambda_2^2 \rho^{(m)}$, $V_2^2 \rho^{(m)}$, $\Lambda^2 V_2 \rho^{(m)}$ or $V^2 \Lambda_2 \rho^{(m)}$ and then we have a representation of $S^{(2)^2}$ on $\Lambda_2^2 F^{(2m)}$ ‡. The only non zero components of the spin space representation are the "diagonal" ones $\Lambda_2^2 S^{(1)}_{\alpha\alpha\alpha\alpha}, \Lambda_2^2 S^{(1)}_{\alpha\beta_t\alpha\beta_t}, \Lambda_2^2 S^{(1)}_{\beta\beta\beta\beta}$ and $V_2^2 S^{(1)}_{\alpha\beta_s\alpha\beta_s}$.

Thus if we multiply each vector of an orthonormal set of vectors $\in \Lambda^2 \rho^{(m)}$ and $V^2 \rho^{(m)}$ by the bases vectors of $\Lambda^2 S^{(1)}_{\alpha\alpha}$, $\Lambda^2 S^{(1)}_{\alpha\beta_t}$, $\Lambda^2 S^{(1)}_{\beta\beta}$, and $V^2 S^{(1)}_{\alpha\beta_s}$ such that we produce an anti-symmetric vector, then we have a diagonal representation of $\hat{S}^{(2)^2}$ on $\Lambda_2^2 F^{(2m)}$. The nature of the orthonormal set is quite arbitrary, and thus can be chosen as desired.

The basis on which $\hat{S}^{(2)^2}$ is represented as a diagonal matrix is hence a basis formed from its eigenvectors.

The arbitrary orthonormal set can be chosen such that the representation of $\hat{H}^{(2)}$ on $\Lambda_2^2 F^{(m)}$ is also diagonal. This is

‡ See Chapters 2 and 3 for fuller discussion of structure of decomposition

achieved by the diagonalising of the representation of $\hat{H}^{(2)}$ on $\Lambda^2_2 \rho^{(m)}$ and $V^2_2 \rho^{(m)}$, thus producing the position space eigenvectors of $H^{(2)}$, from which simultaneous eigenvectors of $H^{(2)}$ and $S^{(2)^2} \in \Lambda^2 F^{(2m)}$ are computed - viz the direct product of the respective eigenvectors such that a symmetric eigenvector is always multiplied by an antisymmetric eigenvector.

For Singlet states of molecular systems, we know that $T^{(2)}$ commutes with $H^{(2)}$ and $S^{(2)^2}$, thus the eigenvectors computed are also the eigenvectors of $T^{(2)}$, i.e. they are the N.S.G's. The only unknown is now the allowable sets of diagonal elements of $T^{(2)}$, on the basis of its eigenvectors (i.e. N.S.G's).

Practical Procedure to determine Simultaneous Eigenvectors

1. The representation of $H^{(2)}$ is set up in $\otimes_2^2 \rho^{(m)}$; this is accomplished by evaluating the integrals.

$$\langle \sigma_i(1) | \sigma^j(1) \rangle = \int \sigma^{i*}(1)\, \sigma^j(1)\, d\tau_1$$

$$\langle \sigma_i(1) | h(1) | \sigma^j(1) \rangle = \int \sigma^{i*}(1) \left[\nabla_i^2 - \sum_{s=1}^{s=n^e} \frac{Z_s}{r_{is}} \right] \sigma^j(1)\, d\tau_1$$

n^e = number of atomic centres.

$$\langle \sigma_i(1)\sigma_j(2) | \tfrac{1}{r_{12}} | \sigma^k(1)\sigma^l(12) \rangle = \iint \sigma^{i*}(1)\, \sigma^{*j}(2)\, \frac{1}{|r_1 - r_2|}\, \sigma^k(1)\sigma^l(2)\, d\tau_1 d\tau_2$$

which are best evaluated by expanding the $\sigma^i(r)$'s in terms of their constituent $a^j(r)$'s which are in turn expanded in terms of their constituent gaussians (for the evaluation of each "atomic" integral)

The representation of the Hamiltonian on the non-orthogonal basis of $\otimes_2^2 \rho^{(m)}$ is then given by:-

$$H^{(2)\,kl}_{n.o\;ij} = (h_i^k S_j^l + h_j^l S_i^k)/(N-1) + g_{ij}^{kl}$$

where $h_i^k = \langle \sigma_i(1) | h(1) | \sigma^k(1) \rangle$

$$S_i^k = \langle \sigma_i(1) | \sigma^k(1) \rangle$$

and $$g_{ij}^{kl} = \langle \sigma_i(1)\sigma_j(2) | \tfrac{1}{r_{12}} | \sigma^k(1)\sigma^l(2) \rangle$$

Hence the resultant matrix representation of $H^{(2)}$ is on the $\{a_i(r_1') \otimes a_j(r_2') \otimes a^k(r_1) \otimes a^l(r_2)\}$ basis of $\otimes_2^2 \rho^{(m)}$ and is converted to the orthonormal basis $\{\sigma_i(r_1') \otimes \sigma_j(r_2') \otimes \sigma^k(r_1) \otimes \sigma^l(r_2)\}$ by the transformation which also corrects for the metric of the non-orthogonal basis †.

$$H^{(2)} = (S^{-1/2} \otimes S^{-1/2}) \cdot H^{(2)}_{n.o} (S^{-1/2} \otimes S^{-1/2})$$

subscript $n.o$ = non-orthogonal

$H^{(2)}$, $H^{(2)}_{n.o}$, and $[S^{-1/2} \otimes S^{-1/2}]$ are $m^2 \times m^2$ matrices, where m is the

† APPENDIX 3

size of the basis set of atomic functions.

2. From $H^{(2)}$ we construct the representation of $H^{(2)}_{on} \Lambda^2_2 \rho^{(m)}$ and $V^2_2 \rho^{(m)}$. This is achieved by the following transformations† .

$H^{(2)}_S = U^S H^{(2)} U^{S\dagger} \in V^2_2 \rho^{(m)}$ $\left(\therefore H^{(2)} = U^{S\dagger} H^{(2)}_S U^S + U^{A\dagger} H^{(2)}_A U^A\right)$.

$H^{(2)}_A = U^A H^{(2)} U^{A\dagger} \in \Lambda^2_2 \rho^{(m)}$.

U^S is a $^{m+n-1}C_n \times M^2$ matrix.

U^A " " $^{m}C_n \times M^2$ " .

$H^{(2)}_S$ " " $^{m+n-1}C_n \times {}^{m+n-1}C_n$ matrix.

$H^{(2)}_A$ " " $^{m}C_n \times {}^{m}C_n$ " .

3. We find the eigenvectors of $H^{(2)}_S$ and $H^{(2)}_A$, thus we solve the eigenvalue equations

$H^{(2)}_A V_A = V_A H^{(2)}_{Ad}$ $\quad \therefore V^+_A H^{(2)}_A V_A = H^{(2)}_{Ad}$

$H^{(2)}_S V_S = V_S H^{(2)}_{Sd}$ $\quad \therefore V^+_S H^{(2)}_S V_S = H^{(2)}_{Sd}$

The eigenvectors are orthonormal s.t. $V_A V^+_A = V^+_A V_A = I_{{}^{m}C_n}$

and $V_S V^+_S = V^+_S V_S = I_{{}^{m+n-1}C_n}$

The eigenvectors are stored in columns of V_A and V_S .

These eigenvectors times the relevent spin vector thus form a basis for $\Lambda^2_2 F^{(2m)}$ in which $H^{(2)}$ and $S^{(2)^2}$ are simultaneously diagonal.

The Energy of the system is given by $E = T_r T^{(2)} H^{(2)}; \{T^{(2)}, H^{(2)} \in \Lambda^2_2 F^{(2m)}\}$

If we do not know $T^{(2)}$ we can treat $T^{(2)}$ as a variable matrix; we know that the stationary points of the equation

$\mathcal{E}(T^{(2)}) = T_r T^{(2)} H^{(2)}$ (fixed $H^{(2)}$, variable $T^{(2)}$).

† CHAPTER 2

give matrices $T^{(2)}$ that commute with $H^{(2)}$. However, not all solutions are allowable (N-representability), thus the variation must be a constrained variation of the function

$$\mathcal{E}(T^{(2)}) = \mathrm{Tr}\, T^{(2)} H^{(2)}$$ subjection to constraints $g_i(T^{(2)}) \leq G_i$.

$i:-1, \ldots\ldots$ any number

If, however, we use the diagonal representations of $H^{(2)}$, thus assuming $T^{(2)}$ to also be diagonal, we automatically have a stationary point of the above variational equation, one of the infinite solutions $T^{(2)}$ for $\delta \mathcal{E} = 0$ when $\mathcal{E}$ is unconstrained. These solutions can be written in the linear variational form

$$L(T_d^{(2)}) = \mathrm{Tr}\, T_d^{(2)} H_d^{(2)} = \sum_i^{m(2m-1)} T_{d\,i}^{(2)\,i} H_{d\,i}^{\,i}$$

All values of $L(T_d^{(2)})$ correspond to stationary values of $\mathcal{E}$. As we noted above only some of these solutions are admissible. The constraints $g_i(T^{(2)}) \leq G_i$, $i:-1, \ldots\ldots$ now have to be applied to $T_d^{(2)}$, i.e. $g_i(T_d^{(2)}) \leq G_i$.

As we usually are mainly interested in the Lowest Energy state, we look for the lowest stationary point of $\mathcal{E}(T^{(2)})$ that has an allowable $T^{(2)}$. When this is so $T^{(2)}$ corresponds to a reduced second order Density Matrix for the lowest energy state of our n particle system. In the diagonal form we thus look for the lowest value of $L(T_d^{(2)})$ that corresponds to an allowable $T_d^{(2)}$, i.e. a $T_d^{(2)}$ that satisfies the constraints $g_i(T_d^{(2)}) \leq G_i$.

As $T_d^{(2)}$ is to be expressed on the same bases that diagonalise $H^{(2)}$ and $S^{(2)2}$ for the particular spin state that we are interested in. We see that $T^{(2)}$ can be represented on the same subspaces as $H^{(2)}$ and $S^{(2)2}$ viz $T^{(2)}$ can be expressed as

$$T^{(2)} \equiv T^{(2)}_{\alpha\alpha\alpha\alpha} + T^{(2)}_{\alpha\alpha\alpha\beta_t} + T^{(2)}_{\alpha\alpha\beta\beta} + T^{(2)}_{\alpha\beta_t\alpha\alpha} + T^{(2)}_{\alpha\beta_t\alpha\beta_t} + T^{(2)}_{\alpha\beta_t\beta\beta}$$

$$+\Gamma^{(2)}_{\beta\beta\alpha\alpha}+\Gamma^{(2)}_{\beta\beta\alpha\beta_t}+\Gamma^{(2)}_{\beta\beta\beta\beta}+\Gamma^{(2)}_{\alpha\beta_s\alpha\alpha}+\Gamma^{(2)}_{\alpha\beta_s\alpha\beta_t}+\Gamma^{(2)}_{\alpha\beta_s\beta\beta}$$

$$+\Gamma^{(2)}_{\alpha\alpha\alpha\beta_s}+\Gamma^{(2)}_{\alpha\beta_t\alpha\beta_s}+\Gamma^{(2)}_{\beta\beta\alpha\beta_s}+\Gamma^{(2)}_{\alpha\beta_s\alpha\beta_s}$$

where the subscripts imply $\in$ to that subspace of $\Lambda_2^2 F^{(2m)}$ that has been defined by those subscripts previously, viz

$$\Gamma^{(2)}_{\alpha\beta_t\alpha\beta_s} \in \Lambda_2 \rho^{\alpha\beta_t}_{(m)} \otimes V^2 \rho^{(m)}_{\alpha\beta_s} \equiv V^2\left(\rho^{(m)} \otimes S^{(1)}_{\alpha\beta_s}\right) \otimes \Lambda_2\left(\rho_{(m)} \otimes S^{\alpha\beta_t}_{(1)}\right)$$

The diagonal matrix $\Gamma^{(2)}_d$ can thus be represented as

$$\Gamma^{(2)}_d = \Gamma^{(2)}_{d\alpha\alpha\alpha\alpha} + \Gamma^{(2)}_{d\alpha\beta_t\alpha\beta_t} + \Gamma^{(2)}_{d\beta\beta\beta\beta} + \Gamma^{(2)}_{d\alpha\beta_s\alpha\beta_s} .$$

It is these diagonal submatrices we wish to constrain. We know the following conditions that they have to fulfil due to normalisation of the subspaces: -

(i) $Tr\ \Gamma^{(2)}_{d\alpha\alpha\alpha\alpha} = \alpha(\alpha-1)/2$

(ii) $Tr\ \Gamma^{(2)}_{d\alpha\beta_t\alpha\beta_t} = (\alpha-1)\beta/2$

(iii) $Tr\ \Gamma^{(2)}_{d\beta\beta\beta\beta} = (\beta-1)\beta/2$

(iv) $Tr\ \Gamma^{(2)}_{d\alpha\beta_s\alpha\beta_s} = (\alpha+1)\beta/2$

where α is the number of alpha (spin symmetric) and β the number of Beta (spin antisymmetric) electons in the system.

When the normalisation conditions (i) - (iv) are fulfilled then the total normalisation of $\Gamma^{(2)}_d$ is indeed $Tr\ \Gamma^{(2)}_d = N(N-1)/2$.

We also know that $\Gamma^{(2)}_d$ should represent a discrete PDF over a given set of events and any value of a PDF must lie in the interval (0,1), hence we have the conditions

(v) $1 \geqslant \Gamma^{(2)}_{d\alpha\alpha\alpha\alpha} \geqslant 0$

(vi) $1 \geqslant \Gamma^{(2)}_{d\alpha\beta_t\alpha\beta_t} \geqslant 0$

(vii) $1 \geqslant \Gamma^{(2)}_{\alpha\beta\beta\beta\beta} \geqslant 0$

(viii) $1 \geqslant \Gamma^{(2)}_{\alpha\beta_s\alpha\beta_s} \geqslant 0$

Now, due to the non-equivalent nature of the pair probability space described by the N.S.G's and the individual probability space described by the N.S.O's we have been unable to formulate explicitly any constraints between the pair probability function $\Gamma^{(2)}_d$ and the individual probability function ρ_d. However, we see that a relationship between the pair PDF represented by the diagonal of $\Gamma^{(2)}$ and the individual PDF represented by the diagonal of ρ does exist, explicitly. Thus to each diagonal element of $\Gamma^{(2)} \in \Lambda^2_2 \rho^{(m)}_{\alpha\alpha\alpha\alpha}$, i.e. $\Gamma^{(2)\ ij}_{\alpha\alpha\alpha\alpha\ ij}$.

we can associate the event

"Simultaneous occupation of orbitals $\sigma_i(r)$ and $\sigma_j(r)$ which both have alpha spin symmetry", ;

to $\Gamma^{(2)\ ij}_{\beta\beta\beta\beta\ ij}$ the event

"Simultaneous occupation of orbitals $\sigma_i(r)$ and $\sigma_j(r)$ which both have beta spin symmetry";

to $\Gamma^{(2)\ ij}_{\alpha\beta t\alpha\beta_t\ ij}$ the event

"Simultaneous occupation of the orbitals $\sigma_i(r)$ and $\sigma_j(r)$ where they have alpha and beta spin symmetry, resulting in an alpha-beta triplet spin symmetry". ;

and to $\Gamma^{(2)\ ij}_{\alpha\beta_s\alpha\beta_s\ ij}$ the event

"Simultaneous occupation of the orbitals $\sigma_i(r)$ and $\sigma_j(r)$ where they have alpha and beta spin symmetry, resulting in an alpha-beta singlet spin symmetry".

We can then apply the probability relationships : -

(a) $\rho_i + \rho_j - \rho_{i \cap j} = \rho_{i \cup j}$

(b) $p_i \geq p_{i \cap j}$

(c) $p_j \geq p_{i \cap j}$

(d) $p_i = \frac{1}{N-1} \sum_j p_{i \cap j}$ (remembering that $p_{i \cap j} = p_{j \cap i}$).

where we associate ϱ_i with p_i and $T^{(2)}{}^{ij}_{ij}$ with $p_{i \cap j}$ and $p_{j \cap i}$.

As $p_{i \cup j}$ and p_i are probability measures they lie in the interval (0,1)

Thus we can write (a) and (d) as

(a) $1 \geq p_i + p_j - p_{i \cap j} \geq 0$

(d) $N-1 \geq \sum_j p_{i \cap j} \geq 0$

However, (b) and (c) ensure the lower limits of the constraints (a) and (d). Thus we can write our system of constraints as : -

(a) $p_i + p_j - p_{i \cap j} \leq 1$

(b) $p_{i \cap j} - p_i \leq 0$

(c) $p_{i \cap j} - p_j \leq 0$

(d) $\sum_j p_{i \cap j} \leq N-1.$

We also know from the contraction relatioships between the 1st and 2nd order reduced density matrices that the full equality expression for (d) is in fact the contraction of $T^{(2)}$ over $\Pi_A : \otimes^2_2 F^{(2m)}$ that gives the diagonal elements of ϱ over $\otimes^1 F^{(2m)}$.

Hence if we express the elements of $T^{(2)}_d$ over the orthonormal atomic geminal basis of $\Lambda^2 F^{(2m)}$ we can formulate indirect probability constraints on these elements (of $T^{(2)}_d$) by using (a), (b), (c) and (d).

All these constraints are linear in the elements of $T^{(2)}_d$, thus we have a linear programming problem, viz

$$\mathrm{Min}\left(L(T^{(2)}_d)\right) = \mathrm{Min}\left(\sum_i^{m(2m-1)} T^{(2)}_d{}^{i}_{i} H^{(2)}_d{}^{i}_{i}\right)$$

$$= \text{Min} \left(\sum_{i}^{m(m-1)/2} T^{(2)}_{d\alpha\alpha\alpha\alpha\, i} H^{(2)}_{d\alpha\alpha\alpha\alpha\, i} + \sum_{i}^{m(m-1)/2} T^{(2)}_{d\alpha\beta_t\alpha\beta_t\, i} H^{(2)}_{d\alpha\beta_t\alpha\beta_t\, i} \right.$$
$$\left. + \sum_{i}^{m(m+1)/2} T^{(2)}_{d\alpha\beta_s\alpha\beta_s} H^{(2)}_{d\alpha\beta_s\alpha\beta_s} + \sum_{i}^{m(m-1)/2} T^{(2)}_{d\beta\beta\beta\beta\, i} H^{(2)}_{\beta\beta\beta\beta\, i} \right)$$

subject to constraints (i) - (viii), (a), (b), (c), (d) formulated in terms of $T^{(2)}_{d\alpha\alpha\alpha\alpha}$, $T^{(2)}_{d\alpha\beta_t\alpha\beta_t}$, $T^{(2)}_{d\beta\beta\beta\beta}$ and $T^{(2)}_{d\alpha\beta_s\alpha\beta_s}$

Procedure to Construct Constraining Equations For Linear Programming

We use as our basis variables $\left\{ T^{(2)}_{d\alpha\alpha\alpha\alpha\, i}, T^{(2)}_{d\alpha\beta_t\alpha\beta_t\, i}, T^{(2)}_{d\beta\beta\beta\beta\, i} \right\}_{i=1,\ldots m(m-1)/2}$

and $\left\{ T^{(2)}_{d\alpha\beta_s\alpha\beta_s\, i} \right\}_{i=1,\ldots m(m+1)/2}$

If we define the constraints so as to be able to be expressed in the form $A.X \leq Y$

where X is a column vector containing the basic variables, thus has dimension $R \times 1$, where $R = m(2m-1)$.

A $a(S \times R)$ matrix containing the coefficients of the constraining equations, and Y a $S \times 1$ column vector containing the constraining values. S is the total number of constraints (excluding the non-negative constraints on the basic variables).

Any equality constraint i.e. $a_{(i)} X = y_i$ $\quad a_{(i)} = i^{th}$ row of A

is replaced by 2 constraints $a_{(i)}.X \leq y_i$ $\quad y_i = i^{th}$ component of Y

and $a_{(i)}.X \geq y_i$

The latter constaint is then replaced by

$$-a_{(i)}.X \leq -y_i$$

So we can always have the constraint equations in form $A.X \leq Y$.

There is no need to hold the non-negativity constraint on the basic variables, as these are automatically held by the linear programming method.

Constraint (i) then gives

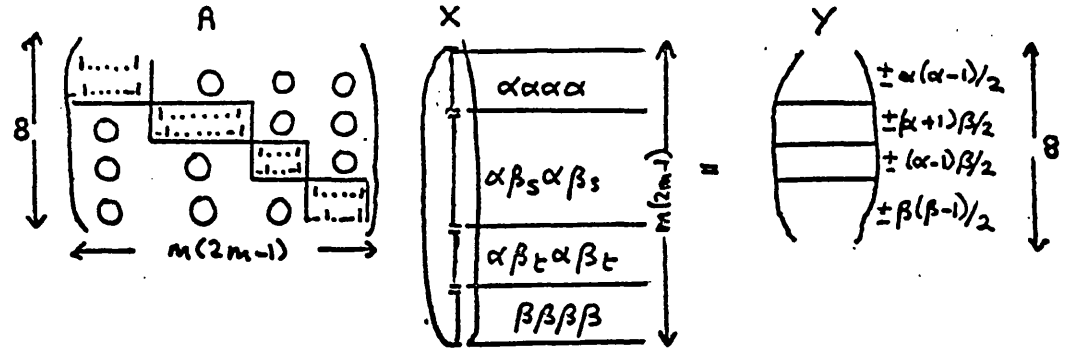
$$\left.\begin{aligned}\sum_{i=1}^{m(m-1)/2} T^{(2)\ i}_{d\alpha\alpha\alpha\alpha\ i} &\leq \alpha(\alpha-1)/2 \\ \sum_{i}^{m(m-1)/2} -T^{(2)\ i}_{d\alpha\alpha\alpha\alpha\ i} &\leq -\alpha(\alpha-1)/2\end{aligned}\right\}$$

$$\text{(ii)}\left.\begin{aligned}\sum_{i}^{m(m-1)/2} T^{(2)}_{d\alpha\beta_t\alpha\beta_t} &\leq (\alpha-1)\beta/2 \\ \sum_{i}^{m(m-1)/2} -T^{(2)}_{d\alpha\beta_t\alpha\beta_t} &\leq -(\alpha-1)\beta/2\end{aligned}\right\}$$

$$\text{(iii)}\left.\begin{aligned}\sum_{i}^{m(m-1)/2} T^{(2)\ i}_{d\beta\beta\beta\beta\ i} &\leq \beta(\beta+1)/2 \\ \sum_{i}^{m(m-1)/2} -T^{(2)\ i}_{d\beta\beta\beta\beta\ i} &\leq -\beta(\beta+1)/2\end{aligned}\right\}$$

$$\text{(iv)}\left.\begin{aligned}\sum_{i}^{m(m+1)/2} T^{(2)\ i}_{d\alpha\beta_s\alpha\beta_s\ i} &\leq (\alpha+1)\beta/2 \\ \sum_{i}^{m(m+1)/2} -T^{(2)\ i}_{d\alpha\beta_s\alpha\beta_s\ i} &\leq -(\alpha+1)\beta/2\end{aligned}\right\}$$

This gives rise to the block of A and Y matrices as shown : -



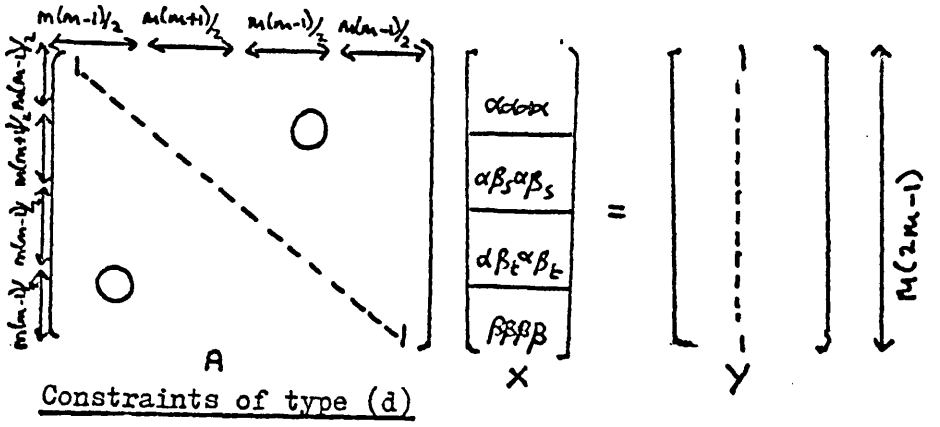
(v) $T^{(2)\ i}_{d\alpha\alpha\alpha\alpha\ i} \leq 1$ for $i = 1, \ldots m(m-1)/2$

(vi) $T^{(2)\ i}_{d\alpha\beta_t\alpha\beta_t\ i} \leq 1$ for $i = 1, \ldots m(m-1)/2$

(vii) $T^{(2)\ i}_{d\beta\beta\beta\beta\ i} \leq 1$ for $i = 1, \ldots m(m-1)/2$

(viii) $T^{(2)\ i}_{d\alpha\beta_s\alpha\beta_s\ i} \leq 1$ for $i = 1, \ldots m(m+1)/2$

These constraints give the block



Constraints of type (d)

$$(N-1)\rho_{\alpha\ i}^{\ i} = (N-1)C\left[T^{(2)}_{\alpha\alpha\alpha\alpha} + \tfrac{1}{2}T^{(2)}_{\alpha\beta_t\alpha\beta_t} + \tfrac{1}{2}T^{(2)}_{\alpha\beta_s\alpha\beta_s}\right]_i^i$$

$$\text{and } (N-1)\rho_{\beta\ i}^{\ i} = (N-1)C\left[T^{(2)}_{\beta\beta\beta\beta} + \tfrac{1}{2}T^{(2)}_{\alpha\beta_t\alpha\beta_t} + \tfrac{1}{2}T^{(2)}_{\alpha\beta_s\alpha\beta_s}\right]_i^i$$

$$\text{Now } T^{(2)}_{\alpha\alpha\alpha\alpha} = V_A\, T^{(2)}_{d\alpha\alpha\alpha\alpha}\, V_A^{+} \therefore T^{(2)\ ij}_{d\alpha\alpha\alpha\alpha\ ij} = \sum_k^{m(m-1)/2} V_{A\ ij}^{\ k}\, T^{(2)\ \ k}_{d\alpha\alpha\alpha\alpha\ k}\, V_{A\ ij}^{\ k}$$

$$T^{(2)}_{\alpha\beta_t\alpha\beta_t} = V_A\, T^{(2)}_{d\alpha\beta_t\alpha\beta_t}\, V_A^{+} \therefore T^{(2)\ ij}_{\alpha\beta_t\alpha\beta_t\ ij} = \sum_k^{m(m-1)/2} V_{A\ ij}^{\ k}\, T^{(2)\ \ k}_{d\alpha\beta_t\alpha\beta_t\ k}\, V_{A\ ij}^{\ k}$$

$$T^{(2)}_{\beta\beta\beta\beta} = V_A\, T^{(2)}_{d\beta\beta\beta\beta}\, V_A^{+} \therefore T^{(2)\ ij}_{\beta\beta\beta\beta\ ij} = \sum_k^{m(m-1)/2} V_{A\ ij}^{\ k}\, T^{(2)\ \ k}_{d\beta\beta\beta\beta\ k}\, V_{A\ ij}^{\ k}$$

$$\text{and } T^{(2)}_{\alpha\beta_s\alpha\beta_s} = V_s\, T^{(2)}_{d\alpha\beta_s\alpha\beta_s}\, V_s^{+} \therefore T^{(2)\ ij}_{\alpha\beta_s\alpha\beta_s\ ij} = \sum_k^{m(m+1)/2} V_{s\ ij}^{\ k}\, T^{(2)\ \ k}_{d\alpha\beta_s\alpha\beta_s\ k}\, V_{s\ ij}^{\ k}$$

$$C\left[T^{(2)}_{\alpha\alpha\alpha\alpha}\right]_i^i = \sum_{j>i}^{m} T^{(2)\ ij}_{d\alpha\alpha\alpha\alpha\ ij} + \sum_{j<i}^{m} T^{(2)\ ji}_{\alpha\alpha\alpha\alpha\ ji}$$

Analogues relationships hold true for $C\left[T^{(2)}_{\alpha\beta_t\alpha\beta_t}\right]_i^i$ and $C\left[T^{(2)}_{\beta\beta\beta\beta}\right]_i^i$

while $C\left[T^{(2)}_{\alpha\beta_s\alpha\beta_s}\right]_i^i = \sum_{j\gtrless i}^{m} T^{(2)\ ij}_{\alpha\beta_s\alpha\beta_s\ ij} + \sum_{j\lessgtr i}^{m} T^{(2)\ ji}_{\alpha\beta_s\alpha\beta_s\ ji}$

Thus

$$\begin{aligned}(N-1)\rho_{\alpha\ i}^{\ i} = &\sum_{j>i}^{m}\sum_{k}^{m(m-1)/2} V_{A\ ij}^{\ k^2}\left\{T^{(2)\ \ k}_{d\alpha\alpha\alpha\alpha\ k} + \tfrac{1}{2}T^{(2)\ \ k}_{d\alpha\beta_t\alpha\beta_t\ k}\right\}\\ &+\sum_{j<i}^{m}\sum_{k}^{m(m-1)/2} V_{A\ ji}^{\ k^2}\left\{T^{(2)\ \ k}_{d\alpha\alpha\alpha\alpha\ k} + \tfrac{1}{2}T^{(2)\ \ k}_{d\alpha\beta_t\alpha\beta_t\ k}\right\}\\ &+\tfrac{1}{2}\sum_{j\gtrless i}^{m}\sum_{k}^{m(m+1)/2} V_{s\ ij}^{\ k^2}\, T^{(2)\ \ k}_{\alpha\beta_s\alpha\beta_s\ k} + \tfrac{1}{2}\sum_{j\lessgtr i}^{m}\sum_{k}^{m(m+1)/2} V_{s\ ji}^{\ k^2}\, T^{(2)\ \ k}_{d\alpha\beta_s\alpha\beta_s\ k}.\end{aligned}$$

which can be written as

$$(N-1)\rho_{\alpha\ i}^{\ i} = \sum_k^{m(m-1)/2}\left\{\sum_{j>i}^{m} V_{A\ ij}^{\ k^2}\left(T^{(2)\ \ k}_{d\alpha\alpha\alpha\alpha\ k} + \tfrac{1}{2}T^{(2)\ \ k}_{d\alpha\beta_t\alpha\beta_t\ k}\right) + \sum_{j<i}^{m} V_{A\ ji}^{\ k^2}\left(T^{(2)\ \ k}_{d\alpha\alpha\alpha\alpha\ k} + \tfrac{1}{2}T^{(2)\ \ k}_{\alpha\beta_t\alpha\beta_t\ k}\right)\right\}$$

$$+\tfrac{1}{2}\sum_{k}^{m(m+1)/2}\left\{\sum_{j\geq i}^{m} V_{s\,ij}^{k^2}\,\Gamma^{(2)}_{d\alpha\beta_s\alpha\beta_s\,k}{}^{k} + \sum_{j\leq i}^{m} V_{s\,ji}^{k^2}\,\Gamma^{(2)}_{d\alpha\beta_s\alpha\beta_s}\right\}$$

and similarly

$$(N-1)\rho_{\beta i}^{\ i} = \sum_{k}^{m(m-1)/2}\left\{\sum_{j>i}^{m} V_{A\,ij}^{k^2}\left(\Gamma^{(2)}_{d\beta\beta\beta\beta\,k}{}^{k} + \tfrac{1}{2}\,\Gamma^{(2)}_{d\alpha\beta_t\alpha\beta_t\,k}{}^{k}\right) + \sum_{j<i}^{m} V_{A\,ji}^{k^2}\left(\Gamma^{(2)}_{d\beta\beta\beta\beta\,k}{}^{k} + \tfrac{1}{2}\,\Gamma^{(2)}_{d\alpha\beta_t\alpha\beta_t\,k}{}^{k}\right)\right\}$$

$$+\tfrac{1}{2}\sum_{k}^{m(m+1)/2}\left\{\sum_{j\geq i}^{m}\left(V_{s\,ij}^{k}\right)^2\Gamma^{(2)}_{d\alpha\beta_s\alpha\beta_s\,k}{}^{k} + \sum_{j\leq i}^{m}\left(V_{s\,ji}^{k}\right)^2\Gamma^{(2)}_{d\alpha\beta_s\alpha\beta_s\,k}{}^{k}\right\}$$

Thus for any particular constraining equation of this type

$$a_{(i)}^{k} = \sum_{j>i}^{m}\left(V_{A\,ij}^{k}\right)^2 + \sum_{j<i}^{m}\left(V_{A\,ji}^{k}\right)^2 \qquad \text{for } k \in \alpha\alpha\alpha\alpha \text{ set of basic variables}$$

or $\beta\beta\beta\beta$ depending on value of i.

$$a_{(i)}^{k} = \tfrac{1}{2}\left\{\sum_{j>i}^{m}\left(V_{A\,ij}^{k}\right)^2 + \sum_{j<i}^{m}\left(V_{A\,ji}^{k}\right)^2\right\} \qquad \text{for } k \in \alpha\beta_t\alpha\beta_t$$

$$a_{(i)}^{k} = \tfrac{1}{2}\left\{\sum_{j\geq i}^{m}\left(V_{s\,ij}^{k}\right)^2 + \sum_{j\leq i}^{m}\left(V_{s\,ji}^{k}\right)^2\right\}$$

for $k \in \alpha\beta_s\alpha\beta_s$ subspace of $\Lambda_2^2 F^{(2m)}$

and $y^k = N-1$ for all values of $k \in \alpha\alpha\alpha\alpha, \beta\beta\beta\beta, \alpha\beta_t\alpha\beta_t$ and $\alpha\beta_s\alpha\beta_s$.

Then these constraints can be written in the form for this block ${}^{d}A$ of A and the section ${}^{d}y$ of y.

$${}^{d}A.X \leq {}^{d}y.$$

The constraining coefficients of type (d) constraints are signified by ${}^{d}a_{(i)}$ which are the rows of ${}^{d}A$.

Constraints of Type (a) i.e. $\rho_i + \rho_j - \rho_{i\wedge j} \leq 1$.

From type (d) above we have the coefficients of $(N-1)\rho_{i}^{\ i}$ and $(N-1)\rho_{j}^{\ j}$ viz ${}^{d}a_{(i)}$ and ${}^{d}a_{(j)}$ thus the constraining equation of type (a) becomes

$${}^{d}a_{(i)} + {}^{d}a_{(j)} + (1-N)\,\Gamma^{(2)}{}_{ij}^{\ ij} \leq N-1$$

where $\Gamma^{(2)}{}_{ij}^{\ ij} \equiv \left\{\Gamma^{(2)}_{\alpha\alpha\alpha\alpha\,ij}{}^{ij}, \Gamma^{(2)}_{\alpha\beta_t\alpha\beta_t\,ij}{}^{ij}, \Gamma^{(2)}_{\alpha\beta_s\alpha\beta_s\,ij}{}^{ij} \text{ or } \Gamma^{(2)}_{\beta\beta\beta\beta\,ij}{}^{ij}\right\}$

depending on i and j , referring to $\rho_{\alpha}{}^{i}_{i}$, $\rho_{\beta}{}^{i}_{i}$, $\rho_{\alpha}{}^{j}_{j}$ or ρ^{j}_{j}.

For the cases

(i) $\rho_{\alpha}{}^{i}_{i}$ and $\rho_{\alpha}{}^{j}_{j}$ i.e. union of two alpha individual events $\equiv T^{(2)}_{\alpha\alpha\alpha\alpha}{}^{ij}_{ij}$

(ii) $\rho_{\beta}{}^{i}_{i}$ and $\rho_{\beta}{}^{j}_{j}$ i.e. " " " beta " " $\equiv T^{(2)}_{\beta\beta\beta\beta}{}^{ij}_{ij}$

and

(iii) $\rho_{\alpha}{}^{i}_{i}$ and $\rho_{\beta}{}^{j}_{j}$ i.e. union of a beta and alpha individual event resulting in a triplet pair situation. $\equiv T^{(2)}_{\alpha\beta t\alpha\beta_t}{}^{ij}_{ij}$

Thus the coefficient of ℓ^{th} basic variable $\in \alpha\alpha\alpha\alpha$, $\beta\beta\beta\beta$ or $\alpha\beta_t\alpha\beta_t = \left(V_A{}^{\ell}_{ij}\right)^2$ so we can write the ℓ^{th} constraining coefficient for constraints of type (a) where i and j refer to orbitals of the type described as

$$^{a}a^{\ell}_{(ij)} = {}^{d}a^{\ell}_{(i)} + {}^{d}a^{\ell}_{(j)} + (1-N)\left(V_A{}^{\ell}_{ij}\right)^2$$

For the case

(iv) $\rho_{\alpha}{}^{i}_{i}$ and $\rho_{\beta}{}^{j}_{j}$ i.e. union of a beta and alpha individual event resulting in a singlet pair situation . $\equiv T^{(2)}_{\alpha\beta_s\alpha\beta_s}{}^{ij}_{ij}$

The coefficient of the ℓ^{th} basic variable $\in \alpha\beta_s\alpha\beta_s = \left(V_s{}^{\ell}_{ij}\right)^2$

so we can write the ℓ^{th} constraining coefficients of type (a) where orbitals i and j form a singlet pair events as

$$^{a}a^{\ell}_{(ij)} = {}^{d}a^{\ell}_{(i)} + {}^{d}a^{\ell}_{(ij)} + (1-N)\left(V_s{}^{\ell}_{ij}\right)^2 .$$

y^{ij} for constraints of type (a) always $= N-1$ for all ij .

<u>Constraints of type (b) and (c)</u> i.e. $\rho_{i\wedge j} - \rho_i \leq 0$ and $\rho_{i\wedge j} - \rho_j \leq 0$.

The coefficients of this type of constraint can be completely determined from the coefficients of the previous types of constraint. Thus the ℓ^{th} coefficient is then given by

$$^{b}a^{\ell}_{(ij)} = {}^{d}a^{\ell}_{(i)} - {}^{a}a^{\ell}_{(ij)}$$

and

${}^{c}a^{\ell}_{(ij)} = {}^{d}a^{\ell}_{(ij)} - {}^{a}a^{\ell}_{(ij)}$ and y^{ij} for constraints of the type (b) and (c) is equal to 0 for all ij.

In the case of a second order reduced density matrix that describes a system in a singlet spin state

$$\Gamma^{(2)}_{\alpha\alpha\alpha\alpha} = \Gamma^{(2)}_{\alpha\beta_t\alpha\beta_t} = \Gamma^{(2)}_{\beta\beta\beta\beta}$$

thus we only need to determine the optimum feasible values for $\Gamma^{(2)}_{\alpha\alpha\alpha\alpha}$ and $\Gamma^{(2)}_{\alpha\beta_s\alpha\beta_s}$.

The constrained Linear Minimization is carried out by the SIMPLEX† method. The matrix A and the vector Y are constructed by the methods just described and are used by the Simplex method in a prescribed manner which divulges (quite quickly) optimum values for $T^{(2)}_{d\alpha\alpha\alpha\alpha\, i\, i}\left(=T^{(2)}_{d\alpha\beta t\alpha\beta t\, i\, i}=T^{(2)}_{d\beta\beta\beta\beta\, i\, i}\right)$ and $T^{(2)}_{d\alpha\beta s\alpha\beta s\, i\, i}$ that give the lowest value for $L\left(T^{(n)}_{d}\right)$ within the given constraints. Obviously the method is only as good as its constraints, which we know are not complete, but we hope will give some insight into the structure of further constraints that may be required.

From these values of $T^{(2)}_{d}$ we may then construct $T^{(2)}_{\alpha\alpha\alpha\alpha}$ $\left(=T^{(2)}_{\alpha\beta t\alpha\beta t}=T^{(2)}_{\beta\beta\beta\beta}\right)$ and $T^{(2)}_{\alpha\beta s\alpha\beta s}$ from which we can derive the α and β spin symmetric reduced 1st Order Density Matrices. However, Tensors $\in \Lambda^2_2 \rho^{(m)}$ and $V^2_2 \rho^{(m)}$ contract to vectors expressed on a 'symmetrised' or 'antisymmetrised' bases of $\otimes^1 \rho^{(m)}$ not on the $\left\{\sigma_i(r_1')\otimes\sigma^j(r_1)\right\}$ bases. So before we apply the contraction operation it is beneficial to work with the representations of $T^{(2)}_{\alpha\alpha\alpha\alpha}$ $T^{(2)}_{\alpha\beta t\alpha\beta t}$, $T^{(2)}_{\alpha\beta s\alpha\beta s}$ and $T^{(2)}_{\beta\beta\beta\beta}\in\otimes^2_2\rho^{(m)}$ expressed on the $\left\{\sigma_i(r_1')\sigma_j(r_2')\otimes\sigma^k(r_1)\sigma^\ell(r_2)\right\}$ bases, which does contract to the bases $\left\{\sigma_i(r_1')\otimes\sigma^j(r_1)\right\}$. From ρ_α and ρ_β we evaluate the alpha and beta N.S.O's and their associated occupation numbers,

$\rho_\alpha+\rho_\beta$ = charge Density Matrix over orthonormal basis orbitals $\sigma_i(r)$

From these matrices we can construct the distribution of charge and spin over the non-orthogonal atomic orbitals.

The 1st Order Reduced Density Matrices associated with each N.S.G are also computed, and thus the N.S.O's and their occupation numbers, associated with a particular N.S.G. These can be expressed on both bases of $\rho^{(m)}$ which is linked by the transformations given in APPENDIX 3.

† APPENDIX 2

Computation of ρ^{α} , ρ^{β} and associated vectors and matrices

$$\Gamma^{(2)}_{\alpha\alpha\alpha\alpha} = V_A \Gamma^{(2)}_{d\alpha\alpha\alpha\alpha} V_A^{+}, \text{ then } U^{A+} \Gamma^{(2)}_{\alpha\alpha\alpha\alpha} U^{A} = {}^{\alpha}\Gamma^{(2)} \in \pi^{A}_{A} : \otimes^{2}_{2\alpha\alpha\alpha\alpha} \rho^{(m)}$$

$$\Gamma^{(2)}_{\alpha\beta_t\alpha\beta_t} = V_A \Gamma^{(2)}_{d\alpha\alpha\alpha\alpha} V_A^{+}, \quad " \quad U^{A+} \Gamma^{(2)}_{\alpha\beta_t\alpha\beta_t} U^{A} = {}^{\alpha\beta_t}\Gamma^{(2)} \in \pi^{A}_{A} : \otimes^{2}_{2} \rho^{(m)}_{\alpha\beta_t\alpha\beta_t}$$

$$\Gamma^{(2)}_{\beta\beta\beta\beta} = V_A \Gamma^{(2)}_{d\beta\beta\beta\beta} V_A^{+}, \quad " \quad U^{A+} \Gamma^{(2)}_{\beta\beta\beta\beta} U^{A} = {}^{\beta}\Gamma^{(2)} \in \pi^{A}_{A} : \otimes \rho^{(m)}_{\beta\beta\beta\beta}$$

$$\Gamma^{(2)}_{\alpha\beta_s\alpha\beta_s} = V_s \Gamma^{(2)}_{d\alpha\beta_s\alpha\beta_s} V_s^{+}, \quad " \quad U^{s+} \Gamma^{(2)}_{\alpha\beta_s\alpha\beta_s} U^{s} = {}^{\alpha\beta_s}\Gamma^{(2)} \in \pi^{s}_{s} : \otimes^{2}_{2} \rho^{(m)}_{\alpha\beta_s\alpha\beta_s}$$

$$\rho_{\alpha} = \left[C\left[{}^{\alpha}\Gamma^{(2)} \right] + \tfrac{1}{2} \left\{ C\left[{}^{\alpha\beta_t}\Gamma^{(2)} \right] + C\left[{}^{\alpha\beta_s}\Gamma^{(2)} \right] \right\} \right] * \frac{2}{N-1}$$

$$\rho_{\beta} = \left[C\left[{}^{\beta}\Gamma^{(2)} \right] + \tfrac{1}{2} \left\{ C\left[{}^{\alpha\beta_t}\Gamma^{(2)} \right] + C\left[{}^{\alpha\beta_s}\Gamma^{(2)} \right] \right\} \right] * \frac{2}{N-1}$$

Contractions of Tensors $\omega \in \otimes^{2}_{2} \rho^{(m)}$ are defined as

$$C[\omega]^{i}_{i} = \sum_{j}^{m} \omega^{ij}_{ij}$$

thus all the above contractions are performed in this manner.

The α - N.S.O's are found as solution to the eigenvalue equation

$$\rho_{\alpha} K_{\alpha} = K_{\alpha} D_{\alpha}$$

where D_{α} is a diagonal matrix containing the occupation numbers of the α - N.S.O's.

The columns of K_{α} i.e. $K_{\alpha}^{\,i}$ are the α - N.S.O's vector represented.

Similarly, solution of

$$\rho_{\beta} K_{\beta} = K_{\beta} D_{\beta}$$ gives the β N.S.O's.

Each 2nd Order Density Matrix associated with an N.S.G is constructed

so

$$\Gamma^{(2)(i)}_{A} = V_A^{(i)} \otimes V_A^{(i)}$$

$i = 1, \ldots m(m-1)/2$

for N.S.G's of $\alpha\alpha$, $\alpha\beta_t$ or $\beta\beta$ spin symmetric type.

$V_A^{(i)}$ - i^{th} column of the matrix

and $\Gamma^{(2)(i)}_{s} = V_s^{(i)} \otimes V_s^{(i)}$

$i = 1, \ldots m(m+1)/2$

for N.S.G's of $\alpha\beta_s$ spin symmetry

From which we obtain the representations in $\Pi^A_A : \otimes^2_2 \rho^{(m)}$ and $\Pi^S_S : \otimes^2_2 \rho^{(m)}$ so

$${}^A T^{(2)(i)} = U^{A+} T_A^{(2)(i)} U^A \quad \text{and} \quad {}^S T^{(2)(i)} = U^{S+} T_S^{(2)(i)} U^S.$$

Thence

$$\rho_A^{(i)} = C\left[{}^A T^{(2)(i)}\right] \quad \text{and} \quad \rho_S^{(i)} = C\left[{}^S T^{(2)(i)}\right]$$

The solutions of the eigenvalue equations

$$\rho_A^{(i)} . K_A^{(i)} = K_A^{(i)} D_A^{(i)} \quad \text{and} \quad \rho_S^{(i)} K_S^{(i)} = K_S^{(i)} \rho_S^{(i)}$$

then give the N.S.O's associated with an N.S.G as columns of $K_A^{(i)}$ or $K_S^{(i)}$ with the associated eigenvalues as the diagonal elements of $D_A^{(i)}$ or $D_S^{(i)}$.

The results are listed in the following format : -

Calculations within the 1 Determinent R.H.F. method are compared to results obtained by the application of

(1) Contraints (i), (ii), (iii), (iv), (v), (vi), (vii) and (viii).

(2) The contraints of (1) + constraints of type (d).

(3) " " " (1) + (2) + type (a).

(4) " " " (1) + (2) + (3) + type (b) and (c).

Table I: N.S.O's referred to Non-orthogonal atomic orbital basis $\{a_i(1)\}$ with Associated Occupation Numbers.

Table II: CHARGE DENSITY MATRICES

(a) referred to non orthogonal basis $\{a_i(1)\}$

(b) " " orthogonal basis $\{\sigma_i(1)\}$

Table III: N.S.G's (on orthogonal basis) and associated occupation numbers for Methods 1,2,3 and 4, and Energies.

Table IV: N.S.O's of the N.S.G's and associated occupation numbers (on non-orthogonal basis).

Table V: 2nd ORDER REDUCED DENSITY MATRICES (on orthogonal basis).

Table VI: MOLECULAR ENERGIES FOR THE DIFFERENT METHODS.

As the molecular system under consideration is of Singlet spin symmetry, obviously no distinction exists between alpha and beta electrons.

Hence, $\rho_\alpha = \rho_\beta$

(alpha and beta 1st Order Reduced Density Matrices)

Thus the alpha and beta N.S.O's are identical.

$$\Gamma^{(2)}_{\alpha\alpha\alpha\alpha} = \Gamma^{(2)}_{\alpha\beta_t\alpha\beta_t} = \Gamma^{(2)}_{\beta\beta\beta\beta}$$

and thus the triplet N.S.G's belonging to the spin components

$\alpha(1)\alpha(2)$, $\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2)+\alpha(2)\beta(1)\right)$ and $\beta(1)\beta(2)$

are also identical.

Table I

$1s_{Li}$	$2s_{Li}$	$1s_{H}$	OCCUPATION NUMBERS	
.999794	-.000451	.001910	1.000000	
.091854	-.351899	-.787912	1.000000	R.H.F.
-.096639	-1.084105	.834866	0.000000	

$1s_{Li}$	$2s_{Li}$	$1s_{H}$		
.999345	-.035421	.000666	1.166648	
-.066756	-.025107	1.014005	.666671	METHOD 1.
-.069875	-1.114432	.472876	.166681	

$1s_{Li}$	$2s_{Li}$	$1s_{H}$		
.992869	.055864	.044096	1.003392	
.149116	-.058709	-.973185	.779186	METHOD 2.
.002303	-1.112329	.550258	.217422	

$1s_{Li}$	$2s_{Li}$	$1s_{H}$		
.988540	-.151303	-.003319	.982151	
-.175131	-1.104797	.482818	.918897	METHOD 3.
-.012118	-.019376	1.009304	.098952	

$1s_{Li}$	$2s_{Li}$	$1s_{H}$		
.974934	-.223226	.032064	.982301	
-.239517	-1.09269	.494752	.946215	METHOD 4.
-.012789	-.004682	1.003000	.071484	

Table II

(a) ORTHOGONAL BASIS				(b) NON-ORTHOGONAL BASIS			
				$1s_{Li}$	$2s_{Li}$	$1s_{H}$	
			$1s_{Li}$	2.016052	-.06550.	-.140926	
			$2s_{Li}$		.247667	.554530	R.H.F.
			$1s_{H}$			1.241620	
2.328599	-.083139	.042852		2.337809	-.054399	-.099717	
	.378768	.198702			.417789	-.206677	METHOD 1
		1.292632				1.445495	
2.000000	.059077	.033335		2.012918	.096552	-.137734	
	.527639	.307683			.549657	-.172174	METHOD 2
		1.472362				1.611483	
1.959927	-.029242	-.046800		1.975935	.061830	-.164262	
	1.768388	-.336703			2.288209	-.983192	METHOD 3
		.271670				.630039	
1.959828	-.026227	-.047037		1.975938	.067738	-.164677	
	1.808799	-.380381			2.357446	-1.037811	METHOD 4
		.231373				.609076	

Table III N.S.G's.

TRIPLET GEMINALS.

$\sigma_1 \wedge \sigma_2$	$\sigma_1 \wedge \sigma_3$	$\sigma_2 \wedge \sigma_3$	OCCUPATION NUMBERS METHOD 1/1	2/1	3	4
-.204544	-.977815	.045166			.081238	.059126
.978244	-.205831	-.025915	0	0	.899444	.921475
.034637	.038882	.998643	0	0	.019319	.019399

SINGLET GEMINALS.

$\sigma_1 \vee \sigma_1$	$\sigma_1 \vee \sigma_2$	$\sigma_1 \vee \sigma_3$	$\sigma_2 \vee \sigma_2$	$\sigma_2 \vee \sigma_3$	$\sigma_3 \vee \sigma_3$	METHOD 1/1	2/1	3/0	4/0
-.185137	-.290251	-.937321	.017374	.027231	-.043177				
.556041	.754704	-.342424	-.045668	.040101	-.017083	1	1	.981322	.980987
.810228	-.584789	.020879	.025061	-.022071	-.000069	1	.403967	1	1
-.003353	.016139	-.033792	-.318081	.943617	-.033648	0	.596035	.144369	.025477
-.007551	-.062359	.008416	-.944979	.309756	.083960	0	0	.841019	.941962
.001929	.006962	-.050261	.053138	-.103925	-.103925	0	0	.033389	.051574

ENERGIES Ev

TRIPLET	SINGLET
-1.749875	-1.755404
-1.608652	-1.656530
- .583034	-1.433450
	- .593380
	-. 422240
	- .241622

Table IV

SINGLET N.S.G's

	N.S.O's			OCCUPATION NUMBERS
	$1s_{Li}$	$2s_{Li}$	$1s_{H}$	
	.720633	.033789	.623770	.648014
N.S.G 1.	.694822	-.094706	-.726811	.351986
	.077069	1.110735	-.578337	.000001
	-.875675	.579189	-.387037	.827205
N.S.G. 2.	.488855	-.924881	.573744	.172794
	-.047352	.230167	.879112	.000000
	.914141	-.419386	.079653	.976586
N.S.G 3.	.405972	.988630	-.190286	.023414
	.086964	.300947	-1.09966	.000000
	-.010048	.668464	.505556	.771535
N.S.G 4.	-.098482	-.891981	.998108	.228443
	.999114	-.037010	.003311	.000022
	-.069590	-1.114288	.467705	.983402
N.S.G 5.	.064123	.030889	-1.016401	.016567
	.999537	-.035391	-.002346	.000032

	-.082999	-.337623	1.106082	.997742
N.S.G 6	-.057760	-1.06198	.168519	.002258
	.998901	-.045263	.001471	.000000

TRIPLET N.S.G's

N.S.O's				OCCUPATION NUMBERS
		$1s_{Li}$	$2s_{Li}$	$1s_{H}$	
	1.001049	-.034568	-.034201	0.5
N.S.G 1	-.032342	-.026328	1.01344	0.5
	-.0699031	-1.114431	.472861	0
	.996921	.151085	-.077291	0.5
N.S.G 2	.097916	-1.104712	.466504	0.5
	-.067744	-.025088	1.014011	0
	.052601	1.079316	-.229009	0.5
N.S.G 3	.081907	.278717	-1.09516	0.5
	.999276	-.035478	.001681	0

Table V

TRIPLET SECOND ORDER REDUCED DENSITY MATRICES

	.041838	.200006	-.009238	
		.956122	-.044164	METHOD 1
			.002039	

	$\sigma_1\wedge\sigma_2$	$\sigma_1\wedge\sigma_3$	$\sigma_2\wedge\sigma_3$	
$\sigma_1\wedge\sigma_2$	.041838	.200006	-.009238	
$\sigma_1\wedge\sigma_3$		.956122	-.044163	METHOD 2
$\sigma_2\wedge\sigma_3$			.002039	

	$\sigma_1\wedge\sigma_2$	$\sigma_1\wedge\sigma_3$	$\sigma_2\wedge\sigma_3$	
$\sigma_1\wedge\sigma_2$	.864155	-.164831	-.022884	
$\sigma_1\wedge\sigma_3$		.115808	.001960	METHOD 3
$\sigma_2\wedge\sigma_3$			.020036	

	$\sigma_1\wedge\sigma_2$	$\sigma_1\wedge\sigma_3$	$\sigma_2\wedge\sigma_3$	
$\sigma_1\wedge\sigma_2$	.884313	-.173689	-.023258	
$\sigma_1\wedge\sigma_3$		.095601	.003057	METHOD 4
$\sigma_2\wedge\sigma_3$			.020086	

SINGLET SECOND ORDER REDUCED DENSITY MATRICES

	$\sigma_1\vee\sigma_1$	$\sigma_1\vee\sigma_2$	$\sigma_1\vee\sigma_3$	$\sigma_2\vee\sigma_2$	$\sigma_2\vee\sigma_3$	$\sigma_3\vee\sigma_3$	
$\sigma_1\vee\sigma_1$	.999928	-.000430	.000047	-.008304	-.000626	-.001561	
$\sigma_1\vee\sigma_2$		.995803	.001420	-.054164	.035268	-.000319	
$\sigma_1\vee\sigma_3$			.996261	-.000124	-.039716	.046319	METHOD 1
$\sigma_2\vee\sigma_2$				.003015	-.001911	.000028	
$\sigma_2\vee\sigma_3$					.002837	-.001859	
$\sigma_3\vee\sigma_3$						.002156	

	$\sigma_1\vee\sigma_1$	$\sigma_1\vee\sigma_2$	$\sigma_1\vee\sigma_3$	$\sigma_2\vee\sigma_2$	$\sigma_2\vee\sigma_3$	$\sigma_3\vee\sigma_3$	
$\sigma_1\vee\sigma_1$	.608656	.281947	-.009968	-.019771	.011919	-.001360	
$\sigma_1\vee\sigma_2$		.792127	.008372	-.048488	.018498	-.001149	
$\sigma_1\vee\sigma_3$			.996682	.005971	-.020437	.048048	METHOD 2
$\sigma_2\vee\sigma_2$				.062945	.177316	.015887	
$\sigma_2\vee\sigma_3$					.533264	.045186	
$\sigma_3\vee\sigma_3$						.006327	

	$\sigma_1\vee\sigma_1$	$\sigma_1\vee\sigma_2$	$\sigma_1\vee\sigma_3$	$\sigma_2\vee\sigma_2$	$\sigma_2\vee\sigma_3$	$\sigma_3\vee\sigma_3$	
$\sigma_1\vee\sigma_1$	.959927	-.061616	-.169969	.001545	.002482	-.009806	
$\sigma_1\vee\sigma_2$		.904228	-.266343	.003534	.024140	-.016979	
$\sigma_1\vee\sigma_3$			.115808	.010641	-.006969	.005076	METHOD 3
$\sigma_2\vee\sigma_2$				.768383	-.205409	-.060365	
$\sigma_2\vee\sigma_3$					.211580	.029148	
$\sigma_3\vee\sigma_3$						.040072	

	$\sigma_1\vee\sigma_1$	$\sigma_1\vee\sigma_2$	$\sigma_1\vee\sigma_3$	$\sigma_2\vee\sigma_2$	$\sigma_2\vee\sigma_3$	$\sigma_3\vee\sigma_3$	
$\sigma_1\vee\sigma_1$	.959828	-.061702	-.169927	.002148	.001859	-.009865	
$\sigma_1\vee\sigma_2$		.904399	-.266251	.006930	.023976	-.017217	
$\sigma_1\vee\sigma_3$			.115687	.008508	-.010394	.003903	METHOD 4
$\sigma_2\vee\sigma_2$				.846556	-.270712	-.070577	
$\sigma_2\vee\sigma_3$					.115687	.020522	
$\sigma_3\vee\sigma_3$						.057843	

TABLE VI

	R.H.F	METHOD 1	METHOD 2	METHOD 3	METHOD 4
ENERGY Ev.	-7.778464	-9.057825	-8.557116	-7.274157	-7.240477

Discussion

Application of constraints formulated in Method 1 lead to an energy which is very much lower than the R.H.F. energy. This, as has been observed before, is due to the non N representable nature of the 'optimised' second order reduced density matrix. Application of further constraints (Method 2) increases the energy to some extent, but still seem to lead to a description that is not physically viable. The charge density matrices associated with Methods 1 and 2 although similar to each other, are somewhat different from the charge distribution predicted by the R.H.F. method, and in fact predict far more charge on the atomic centres than the R.H.F method. Unfortunately, Methods 3 and 4 (i.e. application of further constraints as described) increase the energy above the R.H.F level, which suggests that the constraints are now too 'tight'. However, the reason for this is not clear, although the manifestations are, viz, the 2s orbital on the lithium atomic centre becomes very much more populated with charge, and the transition density between the 2S orbital on Lithium and the 1S orbital on Hydrogen becomes very negative.

Further investigation is thus called for concerning the interpretation of the connection between the elements of the 1st and 2nd order reduced density matrices with respect to constraints associated with the probability relationships

$$P_i \geq P_{i \wedge j} \quad \text{and} \quad P_j \geq P_{i \wedge j} .$$

At the present time it does not seem too productive to follow the probabilistic approach discussed in this thesis if practical approximations are sought. However, further study of the reduced density matrices reported might suggest new types of physically representive constraints.

The gaussian expansion coefficients used where those published by S.HUZINAGA J.Chem. Phys. 1965,42,1293.

PART TWO

CHAPTER ONE

The Multi Configuration Self Consistent Field Approach

Introduction

The elctron spin resonance spectra of many radical systems have been successfully explained using any one of a number of methods[1-8] which have been proposed to calculate spin density distributions. Agreement between these methods is generally only qualitative but this reflects the unusual sensitivity of spin density distributions to small details in the electron density which are insensitive to the energy. Electron correlation is normally introduced into calculations using either self-consistent field method with configuration interaction (SCFCI)or the unrestricted Hartree-Fock method (UHF) with annihilation of the largest contaminating spin component (AUHF). Both of these methods have one characteristic in common; the resultant wave functions have not been completely minimised with respect to all the variational parameters.

In the SCF-CI method the orbitals are obtained by minimising the restricted Hartree-Fock energy. The same orbitals are used for the configuration interaction wave function. In the AUHF method the orbitals are obtained by minimising the UHF energy. The same orbitals are used to construct the AUHF wave function. A practical attempt has been made[7] to obtain orbitals which lower the AUHF energy, producing significant differences in the spin density distributions (this is referred to as the IAUHF method in this paper,i.e. the Iterated AUHF method). The orbitals which lower the SCFCI energy can be obtained by the application of the partial multi-configurational self consistent field (PMCSCF) method. The complete variational minimisation procedure is called the MCSCF method[9].

Method of Calculation

(i) The SCF-CI method.

The solution of the SCF equations of Roothaan[10] gives the complete set of molecular orbitals, $\underset{\sim}{\Phi}$, in terms of basis orbitals, $\underset{\sim}{\phi}$,

$$\underset{\sim}{\Phi} = \underset{\sim}{\phi}\,\underset{\sim}{c} \quad ; \quad \underset{\sim}{c}\,\underset{\sim}{c}^{+} = \underset{\sim}{c}^{+}\underset{\sim}{c} = \mathrm{I}$$

where $\underset{\sim}{\Phi}$ and $\underset{\sim}{\phi}$ are 1 x n row matrices and $\underset{\sim}{c}$ is a n x n matrix, the columns containing the coefficients of each LCAO-MO.

The terminology used is in common with the rest of this thesis where $(\underset{\sim}{c})_{\mu A} = C_{\mu}^{A}$ where A refers to atomic orbital (i.e. basis orbital) and μ to molecular orbital.

The interaction of any two configurational states, χ_r and χ_s defined in terms of the molecular orbitals $\underset{\sim}{\Phi}$ is given by

$$\langle \chi_R | \hat{H} | \chi^S \rangle = \sum_{m_1 m_2} {}^{RS}\rho 1^{m_1}_{m_2} \langle m_1 | h | m_2 \rangle + \tfrac{1}{2} \sum_{m_1 m_2 m_3 m_4} {}^{RS}\rho 2^{m_1 m_2}_{m_3 m_4} \langle m_1 m_2 | g | m_3 m_4 \rangle .$$

The term state infering that the function (configuration of molecular orbitals) is an eigenfunction of the $\hat{S}^2$ operator.

${}^{RS}\underset{\sim}{\rho 1}$ and ${}^{RS}\underset{\sim}{\rho 2}$ are representations in molecular orbital space of basic first and second order reduced density matrices, i.e.

$${}^{RS}\rho 1 \equiv \int \chi^R(1' \ldots\ldots N')\, \chi_S(1 \ldots\ldots N)\, d\tau_{2 \ldots\ldots N}$$

$${}^{RS}\rho 2 \equiv \int \chi^R(1' \ldots\ldots N')\, \chi_S(1 \ldots\ldots N)\, d\tau_{3 \ldots\ldots N}.$$

where the basis of $\Lambda^N F^{(2m)}$ is defined as $\left\{\chi^R(1 \ldots\ldots N)\right\}_{R=1 \ldots\ldots {}^{2m}C_N}$ and $\chi^R(1 \ldots\ldots N) = \Phi^{\sigma_{R_1}}(1) \wedge \ldots\ldots \wedge \Phi^{\sigma_{R_N}}(N)$; $\sigma_R \in Q_{N,2m}$

$\left\{\Phi^i(1)\right\}_{i=1 \ldots\ldots 2m}$ being a basis for $F^{(2m)}$.

The functions $\left\{\Phi^i(1)\right\}$ are simultaneous eigenfunctions of the 1st order reduced Density Matrix (determined within the independent particle approximation) and the 1st Order Reduced Density Matrices

corresponding to the basic Density Matrices of $\Lambda^n_n F^{(2m)}$ defined as

$$^{RR}T^{(n)}(1'.....N'|1.....N) = \chi^R(1'.....N')\chi_R(1.....N)$$

The functions $\{\Phi^i(1)\}$ also form a natural basis for $T^{(2)}(1'2'|12)$ over $\Pi^A_A : \otimes^2_2 F^{(2m)}$, the basis being defined as

$$\{\overset{k}{\underset{i}{\Pi}}\otimes \Phi^{A\,\sigma_{Ri}}(x_i)\otimes \overset{2}{\underset{j}{\Pi}}\otimes \Phi_{\sigma_{Sj}}(x_j)\} \quad \sigma_R, \sigma_S \in S_{2,2m}$$

In the independent particle approximation $T^{(2)}(1'2'|12)$ is determined by $\rho(1'|1)$ completely.

The elements of the matrices $^{RS}\underset{\sim}{\rho 1} \in \otimes'_1 F^{(2m)}$ and $^{RS}\underset{\sim}{\rho 2} \in \Pi^A_A : \otimes^2_2 F^{(2m)}$ are given then on the Natural bases of $\rho(1'|1)$ and $T^{(2)}(1'2'|12)$ as

$$(^{RS}\underset{\sim}{\rho 1})^i_j = \delta^{\sigma_{Ri}}_{\sigma_{Sj}}\,,\quad (^{RS}\underset{\sim}{\rho 2})^{ik}_{jl} = \delta^{\sigma_{Ri}\sigma_{Rk}}_{\sigma_{Sj}\sigma_{Sl}}$$

where $\sigma_R, \sigma_S \in Q_{N,2m}$

For a given choice of molecular orbitals, $\underset{\sim}{\Phi}$, selected electron configurations χ_R corresponding to the spin symmetry of the molecule are constructed to form the configuration Interaction Matrix over a subspace of $\Lambda^n_n F^{(2m)}$ determined by the choice of χ_R.

$\underset{\sim}{\hat{H}}$ with elements

$$(\underset{\sim}{\hat{H}})^S_R = \langle \chi_R | \hat{H} | \chi^S \rangle$$

The Natural configurations (functions) of $\hat{H}$ over this subspace are then determined by the solution of the eigenvalue problem,

$$\underset{\sim}{\hat{H}} \cdot \underset{\sim}{d} = \underset{\sim}{d}\, E$$

which gives $\underset{\sim}{T}^{(n)}$ that commutes with $\underset{\sim}{\hat{H}}$ where $\underset{\sim}{T}^{(n)} = |\underset{\sim}{d}\rangle\langle\underset{\sim}{d}|$

$\underset{\sim}{T}^{(n)}$ corresponds to the energy state E, which is choosen to be the lowest (i.e. ground state)

The representation of the 2nd Order Reduced Density Matrix over $\Pi^A_A : \otimes^2_2 F^{(2m)}$ is then given by

$$\underset{\sim}{\rho 2} = \sum_{RS} T^{(n)R}_S \cdot {}^{RS}\underset{\sim}{\rho 2}$$

where $T^{(n)R}_{S} = d^{R}.d_{S}$

and the 1st Order Reduced Density Matrix over $\otimes; F^{(2m)}$ as

$$\underset{\sim}{P1} = \sum_{RS} T^{(n)R}_{S} \; {}^{RS}\underset{\sim}{P1}$$

The energy E can then be expressed as

$$E = Tr\left(\underset{\sim}{P1}.\underset{\sim}{H}\right) + \tfrac{1}{2}\, Tr\left(\underset{\sim}{P2}.\underset{\sim}{G}\right)$$

where $\left(\underset{\sim}{H}\right)^{m2}_{m1} = \langle m1|h|m2\rangle$

$$\left(\underset{\sim}{G}\right)^{m3m4}_{m1m2} = \langle m1\,m2|g|m3\,m4\rangle$$

(ii) The partial MCSCF method.

The configuration interaction wave function

$$\psi = \sum_{R} d_{R}\,\chi_{R}$$

does not necessarily use the optimum molecular orbitals $\underset{\sim}{\Phi}$. The purpose of the PMCSCF method is to vary the orbitals $\underset{\sim}{\Phi}$, for a given $\underset{\sim}{d}$, such that the energy, E, is minimised. In terms of the basiis orbitals, $\underset{\sim}{\phi}$, the energy E of the wave function ψ can be written

$$E = Tr\left(\underset{\sim}{C}^{+}\underset{\sim}{h}\,\underset{\sim}{C}\,\underset{\sim}{P1} + \tfrac{1}{2}\,\underset{\sim}{C}^{+}\underset{\sim}{g}\,\underset{\sim}{C}\,P2\right)$$

where $\underset{\sim}{C} = \underset{\sim}{C} \otimes \underset{\sim}{C}$, hence $C^{A1\,A2}_{M1\,M2} = C^{A1}_{M1}.\,C^{A2}_{M2}$

$$\left(\underset{\sim}{h}\right)^{A2}_{A1} = \langle A1|h|A2\rangle$$

$$\left(\underset{\sim}{g}\right)^{A3\,A4}_{A1\,A2} = \langle A1\,A2|g|A3\,A4\rangle$$

such that $\left(\underset{\sim}{G}\right)^{m3\,m4}_{m1\,m2} = \sum_{\substack{A1\,A2\\A3\,A4}} C^{A1\,A2}_{m1\,m2}\, g^{A3\,A4}_{A1\,A2}\, C^{m3\,m4}_{A3\,A4}$

Following McWeeny[9] $\underset{\sim}{C}$ is allowed to vary, within an orthonormality constraint, such that E is minimised,

i.e. $\underset{\sim}{C} + \underset{\sim}{\delta C} = \left(\underset{\sim}{I} + \underset{\sim}{V}\right)\underset{\sim}{C}$

such that $\underset{\sim}{I}+\underset{\sim}{V}$ is unitary. This implies that

$$\underset{\sim}{V}\,\underset{\sim}{V}^{+} + V + \underset{\sim}{V}^{+} = 0$$

The corresponding first order change in the energy is

$$E = 2\,Tr\left(\underset{\sim}{V}\left[\underset{\sim}{h}\;\underset{\sim}{c}\;\underset{\sim}{P1}\;\underset{\sim}{c}^{+} + Q\right]\right)$$

where $\left(\underset{\sim}{Q}\right)_{A1}^{A2} = \sum_{A3}\left(\underset{\sim}{z}\right)_{A1\;A4}^{A2\;A3}$ and $\underset{\sim}{z} = \underset{\sim}{g}\;\underset{\sim}{C}^{+}\underset{\sim}{P2}\;\underset{\sim}{C}$

i.e. $Q = C[z]$ viz Q is a contraction of z .

The direction of steepest descent is thus

$$\underset{\sim}{V}_{o} = -\left[\underset{\sim}{h}\;\underset{\sim}{c}\;\underset{\sim}{P1}\;\underset{\sim}{c}^{+} + \underset{\sim}{Q}\right]^{+}$$

the actual magnitude of the change which takes the energy, E , to its most negative value for the given direction V_o is

$\underset{\sim}{V} = \lambda \underset{\sim}{V}_{o}$ (λ is a scalar).

such that $\underset{\sim}{V}+\underset{\sim}{V}^{+}+\underset{\sim}{V}\,\underset{\sim}{V}^{+} = 0$ for an energy descent that would retain the orthonormality of the orbitals. In principle λ can be found by solving the equation $\partial E/\partial\lambda = 0$ but since $\underset{\sim}{V} = f(\underset{\sim}{V}_{o},\lambda)$, this necessitates solving a high order polynomial in λ . This should be clear since the $\underset{\sim}{V}$ that satisfies $\underset{\sim}{V} + \underset{\sim}{V}^{+} + \underset{\sim}{V}\,\underset{\sim}{V}^{+} = 0$ is found by finding that V_o which makes the function $Tr(\lambda \underset{\sim}{V}_{o}\underset{\sim}{V}_{o}^{+} + \underset{\sim}{V}_{o} + \underset{\sim}{V}_{o}^{+})^{2}$ a minimum, viz. the suitability of $\underset{\sim}{V}$ is a function of its length.

As an alternative the energy, E, is calculated for various selected values of λ from which that value of λ which minimises the energy is estimated numerically. (λ is generally found to be very small, the values selected being multiples of $\pm$ 0.015). Each value selected for λ gives only a first estimate of $\underset{\sim}{V}$, hence a first estimation of a trial $\underset{\sim}{C}$ [as $\underset{\sim}{I}+\underset{\sim}{V}$ will not in general be unitary as required]. So that the correct energies for each λ can be calculated $\underset{\sim}{V}$ is corrected such that $\underset{\sim}{V}\,\underset{\sim}{V}^{+}+\underset{\sim}{V}+\underset{\sim}{V}^{+} = 0$ as follows;

The function

$$U = Tr\left[(\underset{\sim}{V}+\underset{\sim}{V}^{+}+\underset{\sim}{V}\,\underset{\sim}{V}^{+})(\underset{\sim}{V}+\underset{\sim}{V}^{+}+\underset{\sim}{V}\,\underset{\sim}{V}^{+})\right]$$

is minimised, for which one obtains the descent direction

$$\underset{\sim}{D} = \left[\underset{\sim}{V}+\underset{\sim}{V}^{+}+2\underset{\sim}{V}^{+}\underset{\sim}{V}+\underset{\sim}{V}\,\underset{\sim}{V}+\underset{\sim}{V}\,\underset{\sim}{V}^{+}\underset{\sim}{V}\right]$$

and a step length along this direction to a second order

$$L = Tr(\underset{\sim}{D}\,\underset{\sim}{D}^{+})/Tr(\underset{\sim}{D}\,\underset{\sim}{D}+\underset{\sim}{D}\,\underset{\sim}{D}^{+}+4\underset{\sim}{D}\,\underset{\sim}{V}\,\underset{\sim}{D}^{+}+2\underset{\sim}{D}\,\underset{\sim}{D}\,\underset{\sim}{V}^{+}+$$

$$+2\underset{\sim}{D}\,\underset{\sim}{D}^{+}\underset{\sim}{V}\underset{\sim}{V}^{+}+\underset{\sim}{D}\,\underset{\sim}{V}\,\underset{\sim}{D}^{+}\underset{\sim}{V}^{+})$$

The process is repeated with a new $\underset{\sim}{V}_{n+1}=\underset{\sim}{V}_{n}-L\underset{\sim}{D}$. This produces a new set of molecular orbitals, $\underset{\sim}{C}_{n+1}$,

$$\underset{\sim}{C}_{n+1} = (\underset{\sim}{I}+\underset{\sim}{V})\underset{\sim}{C}_{n}$$

Although the new orbitals should be orthonormal this depends on how closely $\underset{\sim}{I}+\underset{\sim}{V}$ is unitary. Any non-orthonormality can be rectified by minimising the function,

$$U = Tr\left[(\underset{\sim}{I}-\underset{\sim}{C}^{+}\underset{\sim}{C})(\underset{\sim}{I}-\underset{\sim}{C}^{+}\underset{\sim}{C})\right]$$

with a descent direction

$$\underset{\sim}{D} = \underset{\sim}{C}^{+}\underset{\sim}{C}\,\underset{\sim}{C}^{+}-\underset{\sim}{C}^{+}$$

and step length along this direction

$$L = Tr(\underset{\sim}{D}\,\underset{\sim}{D}^{+})/Tr(2\underset{\sim}{D}\,\underset{\sim}{D}^{+}\underset{\sim}{C}^{+}\underset{\sim}{C}+\underset{\sim}{D}\,\underset{\sim}{C}\,\underset{\sim}{D}\,\underset{\sim}{C}-\underset{\sim}{D}\,\underset{\sim}{D}^{+})$$

which gives a new set of orbitals $\underset{\sim}{C}_{n+1}$ which are at least as orthonormal as the previous $\underset{\sim}{C}_{n}$

$$\underset{\sim}{C}_{n+1} = \underset{\sim}{C}_{n}-L\underset{\sim}{D}$$

and the process is repeated until the desired accuracy is obtained. The whole PMCSCF process is now repeated using the new matrix $\underset{\sim}{C}_{n+1}$ until self-consistency.

(iii) The MCSCF method.

Since $E = f(\underset{\sim}{c}, \underset{\sim}{d})$

where $\underset{\sim}{d}$ is obtained by the SCFCI method for a given $\underset{\sim}{c}$, and $\underset{\sim}{c}$ is then modified by the PMCSCF method for that $\underset{\sim}{d}$, it is logical to use the matrix $\underset{\sim}{c}$ resulting from the PMCSCF method as a new starting point in the SCFCI method to obtain a new $\underset{\sim}{d}$, and so on, until further iterations do not change $\underset{\sim}{c}$ or $\underset{\sim}{d}$.

Results

The MCSCF method has been applied to the molecules described in figure 1. The calculations were carried out within the framework of the Pariser-Parr-Pople approximation scheme for π - electrons systems using the integrals and bond lengths of Amos and Snyder[3] in order to facilitate comparison with results from references 3,4 and 7.

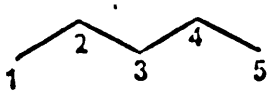
The doublet spin eigenfunctions used were , e.g., for pentadienyl

$$\Theta_0 = (2)^{-1}(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)\alpha$$

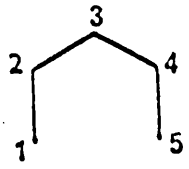
$$\Theta_1 = (12)^{-1/2}(\alpha\beta - \beta\alpha)(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$$

where Θ_0 is the ground state spin eigenfunction
and Θ_1 is the excited doublet state spin eigenfunction.
All possible excited states with spin eigenfunctions of the type Θ_1 are included in the calculations.

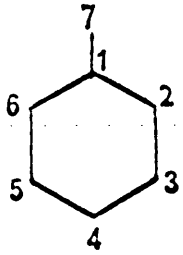
All the results are collected in Table 1.



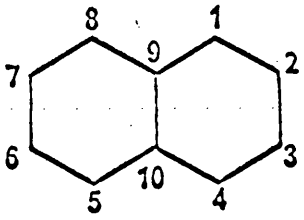
PENTADIENYL (a)



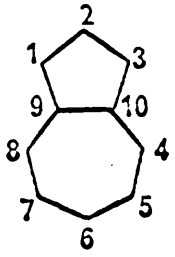
PENTADIENYL (b)



BENZYL



NAPHTHALENE



AZULENE

TABLE 1.—COMPARISON OF THEORETICAL RESULTS

system	atom	Hückel [4]	SCF	McLachlan [1]	SESCF [4]	UHF [7]	AUHF [7]	IAUHF [7]	SCFCI	PMCSF	MCSCF	UHFF [8]
pentadienyl	1	0.333	0.253	(0.413)	0.451	0.553	0.387	0.430	0.354	0.372	0.378	0.428
(*a*)	2	0	0	(−0.140)	−0.161	−0.314	−0.096	−0.109	−0.112	−0.111	−0.113	−0.151
	3	0.333	0.494	(0.452)	0.418	0.523	0.418	0.358	0.515	0.478	0.471	0.444
pentadienyl	1	0.333	0.297			0.540	0.392	0.430	0.388	0.388	0.389	0.429
(*b*)	2	0	0			−0.289	−0.089	−0.101	−0.109	−0.109	−0.110	−0.139
	3	0.333	0.406			0.497	0.395	0.341	0.443	0.442	0.441	0.420
benzyl	1	0	0	−0.102	−0.134	−0.197	−0.062	−0.103	−0.081	−0.081	−0.085	−0.096
	2	0.143	0.081	0.161	0.279	0.268	0.163	0.155	0.141	0.148	0.157	0.189
	3	0	0	−0.063	−0.143	−0.172	−0.054	−0.041	−0.048	−0.048	−0.051	−0.083
	4	0.143	0.046	0.137	0.260	0.238	0.134	0.174	0.104	0.105	0.106	0.160
	7	0.571	0.791	0.770	0.602	0.768	0.711	0.701	0.790	0.775	0.767	0.725
naphthalene±	1	0.181	0.190	0.222	0.252	0.262	0.215	0.213	0.230	0.231	0.231	0.227
	2	0.069	0.060	0.047	0.027	0.026	0.048	0.054	0.043	0.042	0.042	0.045
	9	0	0	−0.037	−0.059	−0.076	−0.024	−0.034	−0.046	−0.046	−0.046	−0.037
azulene	1	0.005	0.002	−0.027	0.001	0.005	0.004	−0.001	−0.021	−0.021	−0.021	0.004
	2	0.107	0.062	0.120	0.102	0.107	0.074	0.069	0.100	0.100	0.100	0.082
	4	0.213	0.186	0.292	0.317	0.328	0.244	0.251	0.232	0.232	0.232	0.265
	5	0.011	0.019	−0.081	−0.135	−0.197	−0.052	−0.053	−0.060	−0.060	−0.060	−0.088
	6	0.374	0.324	0.368	0.387	0.439	0.358	0.353	0.378	0.378	0.378	0.378
	9	0.089	0.100	0.071	0.072	0.090	0.089	0.092	0.110	0.110	0.110	0.089

Numbers in brackets correspond to complete CI calculations.

$\mathrm{UHFF} \equiv \frac{1}{4}(p_{\mathrm{UHF}} + 3p_{\mathrm{AUHF}})$

DISCUSSION

Since both the UHF and SCFCI methods are practical for large molecules it is of some interest to investigate if one is more reliable than the other in the calculation of spin density distributions. The SCFCI methods are normally limited to including only singly excited configurations. Since the wave function in the SCFCI method is also a spin eigenstate this would seem to be more appropriate than the UHF wave function to calculate spin density distributions, even though the AUHF method attempts to remove the major unwanted spin eigenstate from the UHF wave function. However, whereas electron correlation in the CI wavefunction is introduced after the orbitals have been optimised, in the UHF method the electron correlation is introduced before optimisation. It is possible that this dichotomy can only be resolved by comparison with an analagous complete CI calculation. Only a very few complete CI calculations exist and for these radicals only pentadienyl (a) has been studied[8]. For this radical (see table 1) the SCFCI and AUHF calculations are only in qualitative agreement. The agreement with the AUHF method is progressively improved for the PMCSCF and MCSCF methods. It has been suggested[3,8] that it is better to use the UHF formula $(\rho_{UHF} + 3\rho_{AUHF})/4$ to give a better estimate of the spin density distribution. This in fact[8] gives an excellent correlation with the complete CI results (those given in brackets in the column labelled McLachlan in table 1) for pentadienyl (a).

If we use the SCF calculations as a standard for comparison (because this method introduces no electron correlation between electrons of different spins), we can compare the relative magnitudes

of the spin densities due to the other methods. One of the most important aspects of π - electron calculations for aromatic radicals is to assign the observed hyperfine coupling constants to the various atomic centres. There are some significant discrepancies with the relative order of the spin densities as calculated by the SCF method:-

Pentadienyl: SESCF, UHF and IAUHF give opposite assignments for atoms 1 and 3.

Benzyl: SESCF gives the opposite assignment for atoms 1 and 3;
IAUHF gives the opposite assignment for atoms 2 and 4.

Azulene: Huckel, McLachlan, SESCF, UHF give opposite assignments for atoms 2 and 9.

Most of these discrepancies correspond to those positions, which are not related by symmetry, but have the same spin density when calculated by the Huckel method.

It is significant that the AUHF, UHFF, SCFCI and MCSCF methods are always in qualitative agreement. In view of this observation, the fact that UHF calculations are much quicker to perform for large molecular systems than SCFCI or MCSCF calculations, and the excellent agreement between the complete CI calculation and the UHF method for pentadienyl (a), it is concluded that the UHF methods have distinct advantages and are at least as reliable as other approximate practical methods.

THE AB - INITIO UNRESTRICTED HARTREE FOCK METHODS

A reasonable extension of the independent particle model, i.e. Restricted Hartree Fock (RHF), but still within the framework of a 1 determinant approximation is the Unrestricted Hartree Fock method (UHF). However the N particle wavefunction that is produced by optimizing the single determinent is not generally an eigenfunction of the total spin angular momenta operator S^2. This approximate wavefunction can though be expressed as a linear sum of wavefunctions corresponding to pure spin states,

$$\chi_{approx}(1 \ldots N) = \sum_{M=0}^{q} C_{s+M}\, \chi_{s+M}(1 \ldots N)$$

where s= p-q; p = number of electrons with alpha spin, and q = number of electrons with beta spin,

and $S^2 . \chi_{s+m} = (s+m)(s+m+1)\chi_{s+m}$

and hence it is possible to project out the pure spin wavefunction of interest, by the use of an annihilation operator[1]. It has been shown however that it is sufficient to annihilate only the major unwanted spin component[2] to obtain a wavefunction that represents a pure spin state to a fairly good degree of approximation. This procedure is known as the Unrestricted Hartree Fock Method After Annihilation (UHFAA).

Theoretical results can be calculated which are reasonable when compared to experimental values, these can be computed by an Ab - Initio method when the above UHFAA procedure is followed[3-7] provided that

(i) The atomic orbitals $a_i(r)$ (based on atomic centre i) are expressed as an optimised linear combinations of gaussian functions, i.e.

$$a_i(r) = \sum_j^m C_{ij} e^{-\alpha_i r^2}$$ where the coefficients Cij are optimised

(ii) When $a_i(r)$ refers to a hydrogen atom the exponent α_i is optimised,

and

(iii) The geometry of the system is optimised, i.e. bond angles and bond lengths are varied to give the energetically lowest molecular configuration.

These provisions are not arbitary since if isotropic hyperfine coupling constants are to be calculated from spin densities at the nuclei the wavefunction should describe the electron densities of the nuclei adequately. The obvious choice is to use SCF atomic orbitals, which are expressed for convenience as a linear combination of gaussian functions to facilitate the evaluation of the multicentre two electron repulsion integrals. Since the hydrogen 1s orbital contains electrons which are both valence and inner shell electrons this orbital requires optimising. In turn the geometry will effect the hydrogen 1s orbital, hence the hydrogen isotopic coupling constant, considerably and so this requires optimising. The variation of the SCF atomic orbitals for heavy atoms is much more difficult and thus this sort of optimisation is not attempted, nor is the bond length varied between heavy atoms.

Instead of representing each SCF atomic orbital of the minimal basis set by a linear combination of gaussian functions,

more flexibility is obtained by "uncontracting" these representations, i.e. each SCF atomic orbital is replaced by a number of orbitals each one being a simple gaussian function. Alternatively partially contracted gaussian expansions can be used.[8] The object of these modifications is to introduce flexibility into the calculation by allowing the orbitals to distort on molecular formation. Unfortunately this greater flexibility gives rise to an increase in spin contamination in certain cases. In order to restrict spin contamination it has been suggested elsewhere[9] that, at least for semi-emipirical calculations, it is feasible to minimise a function of the type

$$\alpha E + (1-\alpha) \langle \hat{S}^2 \rangle$$

where E can be E_{UHF} or E_{AA} $(AA \equiv UHFAA)$
and $\langle \hat{S}^2 \rangle$ can be $\langle \hat{S}^2 \rangle_{UHF}$ or $\langle \hat{S}^2 \rangle_{UHFAA}$

For Ab Initio calculations the use of E_{AA} is unrealistic regarding computer time and so the function

$\mathcal{E} = \alpha E_{UHF} + (1-\alpha) \langle \hat{S}^2 \rangle_{UHF}$ was minimised.

This function can be written as

$$\mathcal{E} = \alpha \{ \mathrm{Tr}\, P (h + \tfrac{1}{2} G^{S_\alpha}) + \mathrm{Tr}\, Q (h + \tfrac{1}{2} G^{S_\beta}) \}$$
$$+ (1-\alpha) \{ \tfrac{1}{4}(p-q)^2 + \tfrac{1}{2}(p+q) - \mathrm{Tr}\, PSQS \}$$

where
$$G^{S_\alpha}{}^{u}_{r} = \sum_{vt}' \{ (P^t_v + Q^t_v) g^{uv}_{rt} - P^t_v g^{uv}_{rt} \}$$
$$G^{S_\beta}{}^{u}_{r} = \sum_{vt}' \{ (P^t_v + Q^t_v) g^{uv}_{rt} - Q^t_v g^{uv}_{rt} \}$$
$$g^{uv}_{rt} = \int a^u(r_1) a^v(r_2) \cdot 1/r_{12} \cdot a_r(r_1) a_t(r_2)\, dr_1 dr_2$$

h is the representation of the one electron hamiltonian on the non-orthogonal atomic orbital basis $\{ a_i(r) \}$,
P and Q are the respective representations of the first order density matrices of the p alpha and q beta spin electrons, and S is the overlap matrix associated with the basis of atomic

orbitals $\{a_i(r)\}$.

The first order change in $\mathcal{E}$ is

$$\delta\mathcal{E} = \alpha \{ \mathrm{Tr}\ \delta P.\ (h + G^{S\alpha}) + \mathrm{Tr}\,\delta Q\ \ (h + G^{S\beta})\}$$
$$- (1-\alpha)\{ \mathrm{Tr}\ \ (\delta P\ SQS) - \mathrm{Tr}\ (\delta Q\ SPS\ )$$

from which the 'best' changes in the matrices P and Q i.e. those that cause $\mathcal{E}$ to decrease most, are given by the diagonalisation of

$$V^{S\alpha} = \alpha(h + G^{S\alpha}) - (1-\alpha)\ S\ Q\ S$$

and $V^{S\beta} = \alpha(h + G^{S\beta}) - (1-\alpha)\ S\ P\ S$ respectively.

This minimisation scheme shows some similarities to the elegant method of Segal[10].

Calculations were carried out on the hydroxyl and cyanide radicals as described in the following section. The major contaminating spin component in the UHF wave functions for these radicals is the quartet state, hence in the application of UHFAA method it is this component which is annihilated.

Results

1. HYDROXYL RADICAL

(a) using contracted set of gaussian functions

(b) using uncontracted set of gaussian functions

The calculation was carried out using various bond lengths and orbital exponents for the hydrogenlike wavefunction in order that an optimised description of the atomic orbitals be deduced. The variation of the oxygen atomic orbitals (w.r.t. orbital exponent and bond length) was not attempted.

In figure I, E_{AA} (of the radical) is plotted as a function of the bond distance r_{OH} for various values of the orbital exponent on the hydrogen atomic orbital. The results are also shown in table I.

The value of $\langle S^2 \rangle_{AA}$ for this calculation was found to be very near 0.75 (to 1 place in 10^7) and thus no limitation on the spin contamination was necessary, however in the calculation using an uncontracted set of gaussians for the hydrogen atomic orbital spin contamination was found, and hence the constraining procedure was used, i.e. minimisation of the function ξ for various values of δ, the results of which are shown in Table II, figures II, and III.

2. CYANIDE RADICAL

with (a) contracted set of gaussian functions

(b) uncontracted set of gaussian functions

Both of these cases showed considerable spin contamination and thus the constraining procedure was applied to try and reduce the amount of contaminating spin component in the computed wave functions; the results of these calculations are presented in Tables III and IV; and figures IV, V, VI and VII.

Discussion

Even though the molecular wave-function computed from the contracted set of gaussians for the hydroxyl radical showed little sign of spin contamination, the oxygen hyperfine constant, a_o is low in magnitude compared with the experimental value. No doubt the origin of this discrepancy is inherent in the UHFAA method and this view is substantiated by the more elaborate

Table 1. Experimental and Theoretical Results for the OH Radical. Only those calculations near the bond lehgth that minimises the energy for a given hydrogen orbital exponent are listed.

Method	Hydrogen orbital exponent	Bond length (a.u.)	Energy (a.u.) after annihilation	Hyperfine Coupling Constant (gauss) a_O	a_H
Expt. gas phase		1.8342[14]	-75.780 [21]	-30.75[13]	-26.7[15]
Expt. in ice					-23.3±4[16]
Expt. in ice					-23.2±4.5[17]
Expt. in $CaSO_4$					-25.2±1.1[18]
Expt. in $LiSO_4$					-23.3±1.3[19]
UHFAA	1.2	2.0	-75.36592	-8.49	-18.72
UHFAA	1.3	1.9	-75.37180	-9.44	-17.79
UHFAA	1.3	2.0	-75.37072	-8.53	-21.31
UHFAA	1.4	1.85	-75.37417	-9.52	-18.49
UHFAA	1.4	1.9	-75.37453	-9.16	-19.88
UHFAA	1.45	1.85	-75.37469	-9.31	-19.40
UHFAA	1.45	1.9	-75.37443	-8.98	-20.78
UHFAA	1.5	1.85	-75.37433	-9.07	-20.22
UHFAA	1.45*	1.85	-75.37474	-9.32	-20.51

* using 10 s-type gaussian expansion[20].

Table 2. Hydroxyl Radical Uncontracted Gaussian Basis

	$-E$	$-E_{aa}$	$\langle S^2 \rangle$	$\langle S^2 \rangle_{aa}$	$A_{o\ aa}$	$A_{H\ aa}$	A_o	A_H
1	75.39321	75.39417	.75360	.75000	-16.56	-14.46	-48.94	-44.18
0.95	75.39318	75.39390	.75241	.75000	-14.86	-11.88	-43.96	-36.20
0.90	75.39313	75.39369	.75173	.75000	-13.18	-10.02	-39.02	-30.46
0.85	75.39307	75.39351	.75131	.75000	-11.57	-8.61	-34.27	-26.14
0.80	75.39301	75.39337	.75101	.75000	-10.03	-7.49	-29.72	-22.69
0.75	75.39294	75.39324	.75079	.75000	-8.56	-6.55	-25.40	-19.84
0.70	75.39288	75.39288	.75063	.75000	-7.18	-5.76	-21.30	-17.41

FIGURE 1.

Summary of the calculations on the OH radical.

_____ Variatin of total energy after annihilation with bond length for the values of the hydrogen atom orbital exponent ,α,indicated.

-------- Estimated minimum total energy after annihilation as a function of bond length.

-.-.-.-. Estimated variation of the hydrogen isotropic hyperfine coupling constant with bond length.

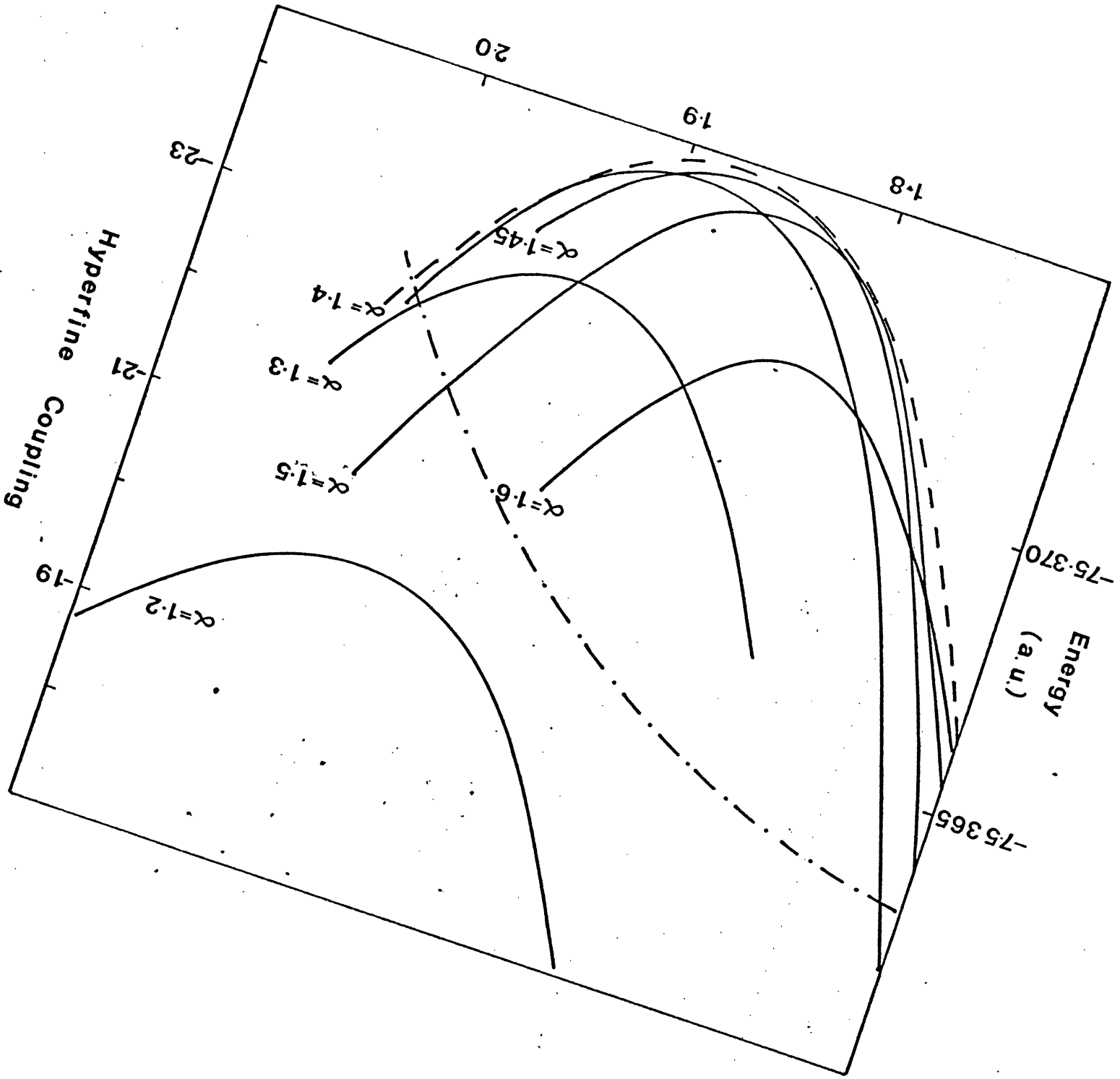
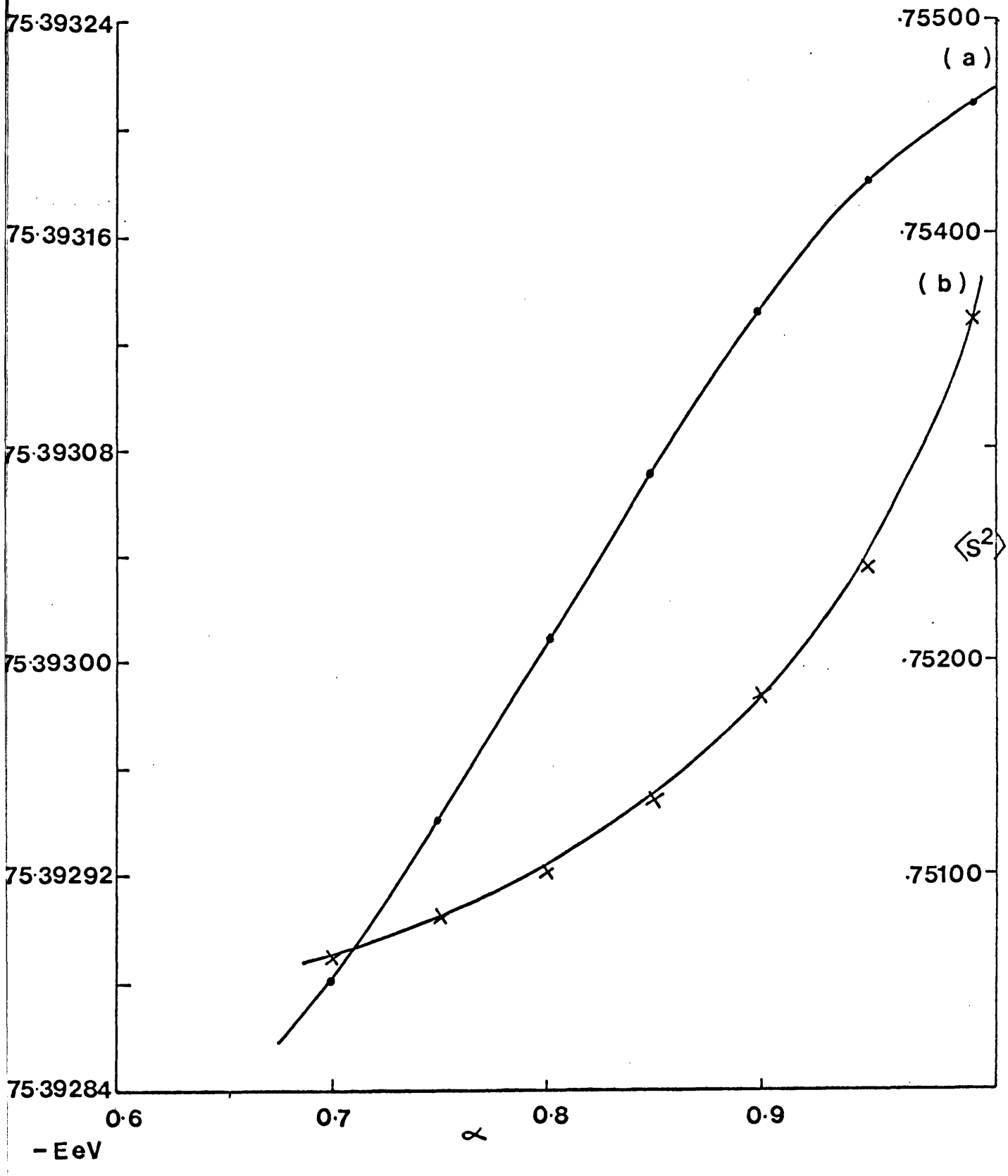

Hyperfine Coupling
-19
-21
-23
2·0
1·9
1·8
α=1·2
α=1·3
α=1·4
α=1·45
α=1·5
α=1·6
-75·370
-75 365
Energy (a.u.)

FIGURE TWO.

a) Variation of minimum energy with change of α.

b) Variation of $\langle S^2 \rangle$ value with change of α.

HYDROXYL RADICAL UNCONTRACTED BASIS.


75·39324
75·39316
75·39308
75·39300
75·39292
75·39284
- E eV
·75500
·75400
·75200
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(a)
(b)
0·6
0·7
0·8
0·9
α

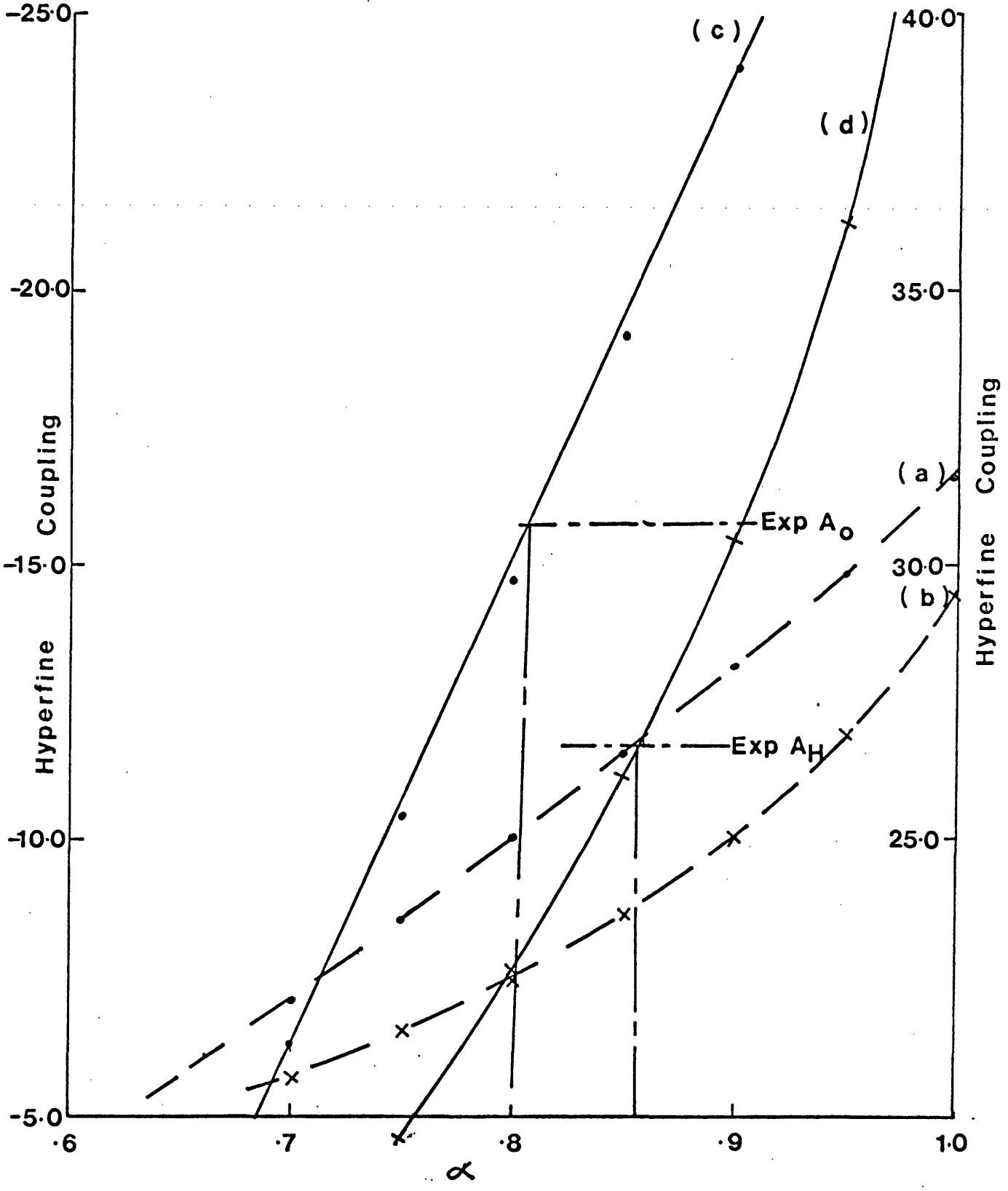

-25·0
-20·0
-15·0
-10·0
-5·0
Hyperfine Coupling
40·0
35·0
30·0
25·0
Hyperfine Coupling
(c)
(d)
(a)
(b)
Exp A_o
Exp A_H
·6
·7
·8
·9
1·0
α

Table 3. Cyanide Radical, Contracted Gaussian Basis

	$-E$	$-E_{aa}$	A_c	A_N	$A_{c\ aa}$	$A_{N\ aa}$	$\langle S^2 \rangle$	$\langle S^2 \rangle_{aa}$
1.0	92.06131	92.08598	377.4	-20.83	339.2	-6.18	1.11825	0.83559
0.975	92.05897	92.06954	342.0	-16.29	331.7	-4.67	0.91809	0.76687
0.95	92.05542	92.06001	315.3	-13.26	318.7	-3.83	0.82197	0.75305
0.90	92.05169	92.05329	292.7	-10.24	303.6	-3.01	0.77104	0.75028
0.85	92.05011	92.05101	285.8	-8.52	297.9	-2.50	0.75951	0.75006
0.80	92.04924	92.04985	283.8	-7.26	295.6	-2.11	0.75531	0.75002
0.75	92.04868	92.04911	283.8	-6.23	294.8	-1.79	0.75333	0.75001
0.70	92.04826	92.04859	284.6	-5.35	294.7	-1.51	0.75223	0.75000
0.60	92.04767	92.04786	287.4	-3.92	295.4	-1.04	0.75110	0.75000
0.50	92.04724	92.04735	290.3	-2.81	296.5	-0.67	0.75057	0.75000
0.30	92.04662	92.04665	296.0	-1.18	299.0	-0.12	0.75013	0.75000
0.10	92.04615	92.04615	300.5	-0.05	301.2	0.27	0.75001	0.75000

FIGURE FOUR.

a) change of minimum energy with variation of α.

b) Change of $\langle S^2 \rangle$ with variation of α.

CYANIDE RADICAL UNCONTRACTED BASIS.

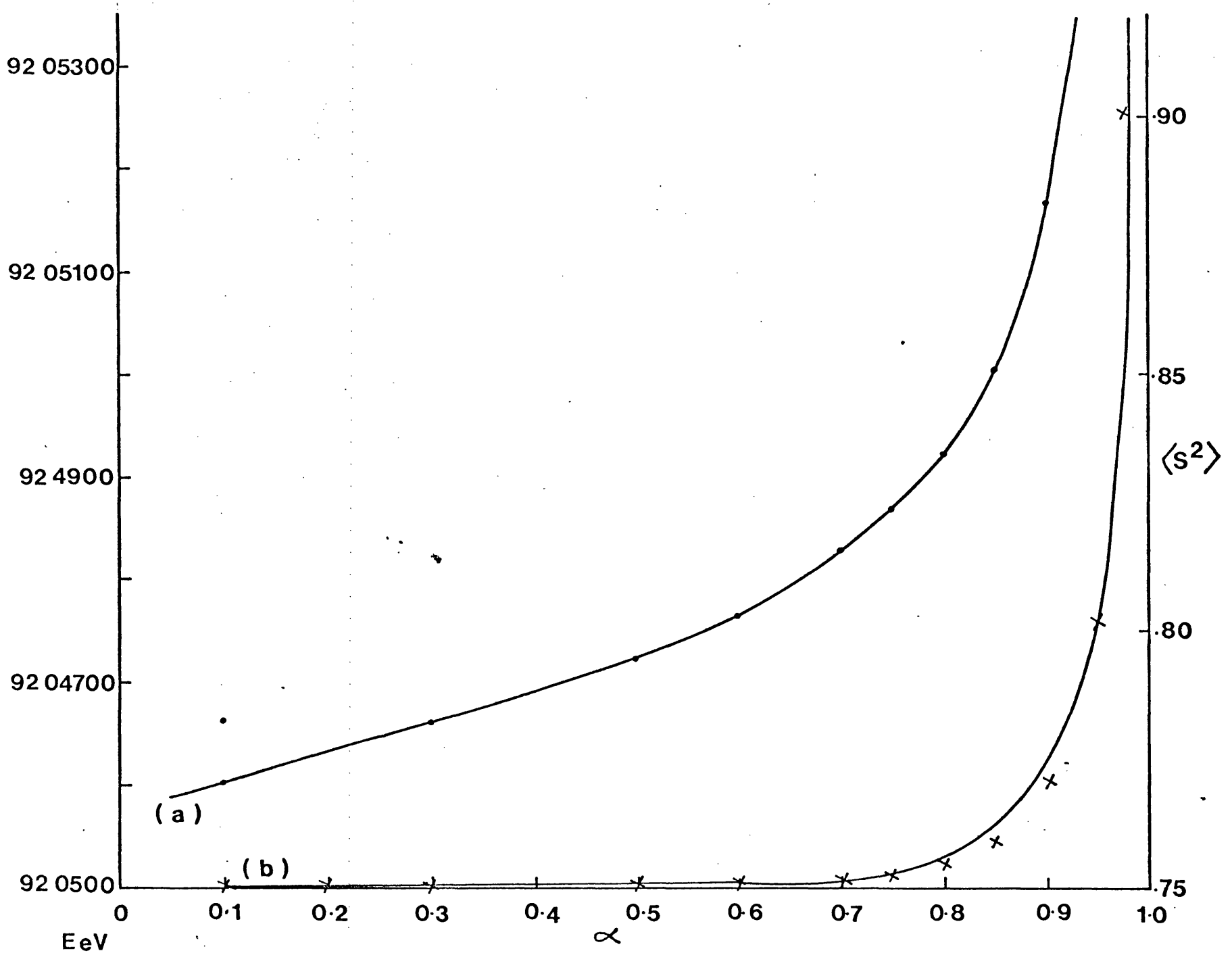

92 05300
92 05100
92 4900
92 04700
92 0500
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
EeV
∝
·90
·85
·80
·75
⟨S²⟩
(a)
(b)

FIGURE FIVE.

Curve (a) and (c) are related to higher valued axes.

Curves (b) and (d) to lowered valued axes.

Curve a):- α_c

Curve b):- α_N

Curve c):- $\alpha_{c\,aa}$

Curve d):- $\alpha_{N\,aa}$

CYANIDE RADICAL CONTRACTED BASIS.

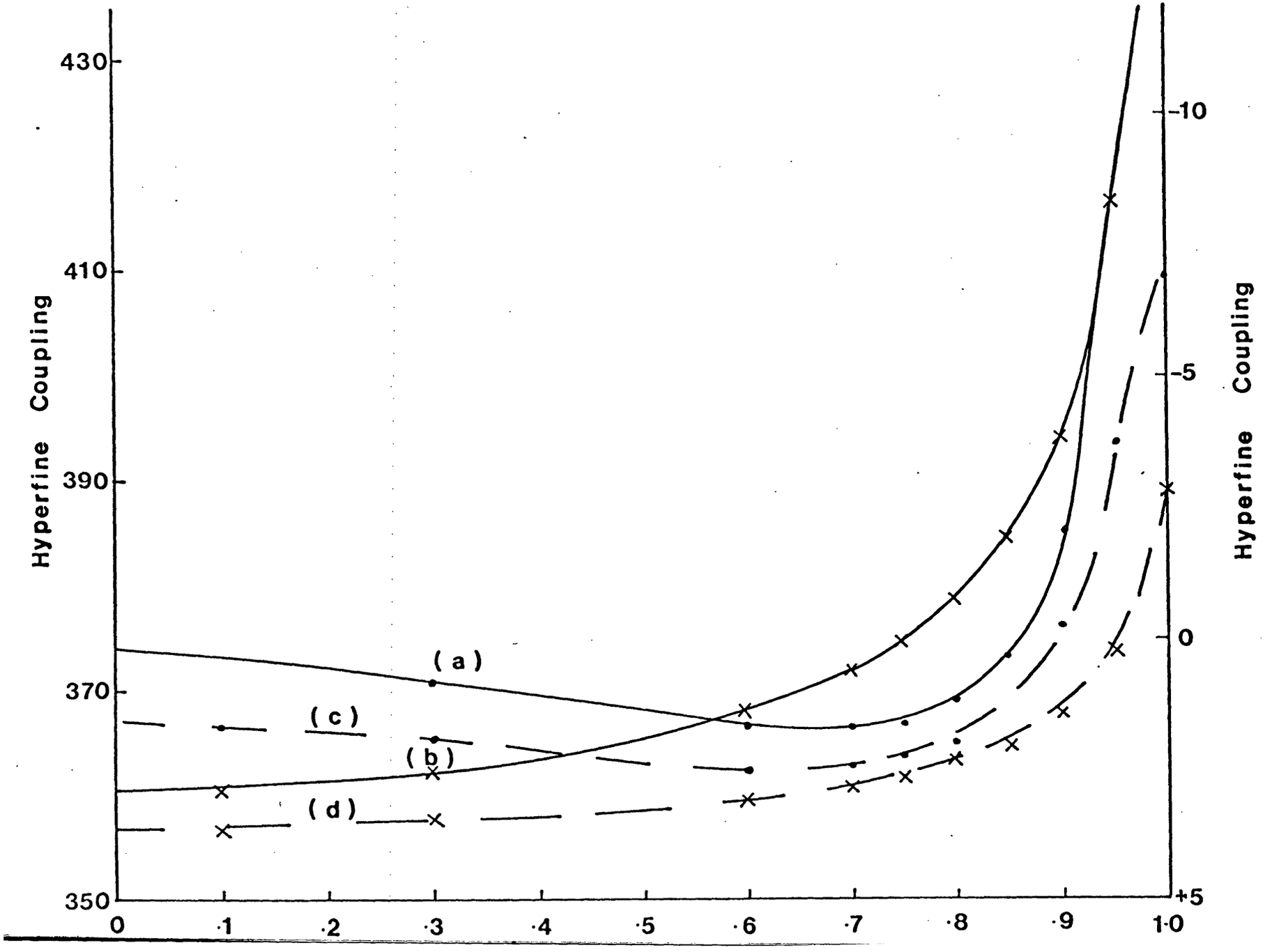

430
410
390
370
350
Hyperfine Coupling
-10
-5
0
+5
Hyperfine Coupling
0
·1
·2
·3
·4
·5
·6
·7
·8
·9
1·0
(a)
(b)
(c)
(d)

FIGURE SIX.

a) Change of minimum energy with variation of α.

b) Change of $\langle S^2 \rangle$ with variation of α.

CYANIDE RADICAL UNCONTRACTED BASIS.

FIGURE SEVEN.

Curves (a) and (c) relate to the higher valued axis.

Curves (b) and (c) to the lowered valued axis.

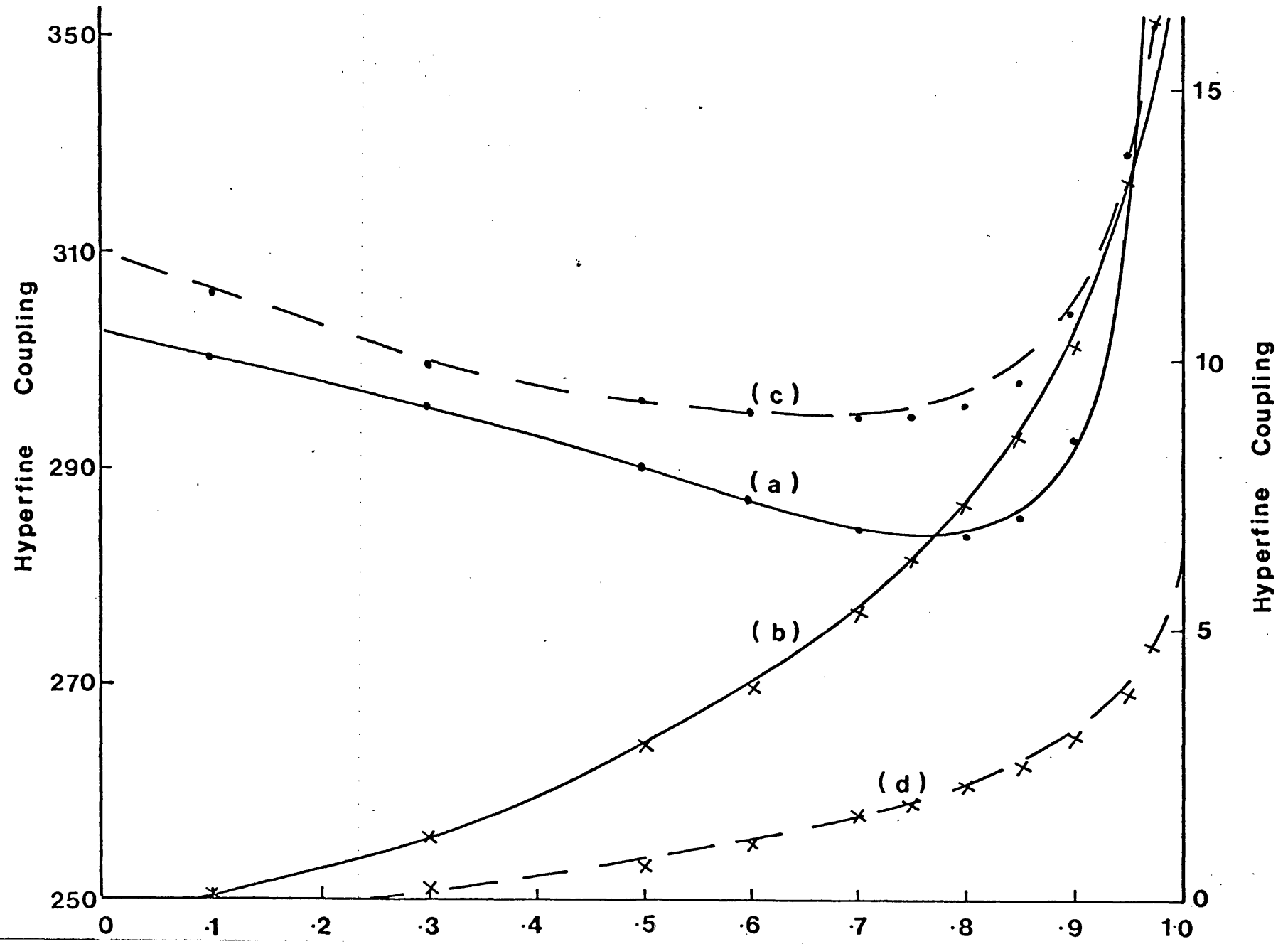
a):- a_c

b):- a_N

c):- $a_{c_{aa}}$

d):- $a_{N_{aa}}$

CYANIDE RADICAL UNCONTRACTED BASIS.


350
310
290
270
250
Hyperfine Coupling
15
10
5
0
Hyperfine Coupling
0
·1
·2
·3
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·6
·7
·8
·9
1·0
(a)
(b)
(c)
(d)

Table 4. Cyanide Radical, Uncontracted Gaussian Basis

	$-E$	$-E_{aa}$	A_C	A_N	$A_{C\ aa}$	$A_{N\ aa}$	$\langle S^2 \rangle$	$\langle S^2 \rangle_{aa}$
1.00	92.17162	92.20144	491.1	-20.20	409.6	-3.90	1.19518	.87855
0.95	92.16436	92.17038	417.4	-8.38	394.4	0.24	0.84852	.75575
0.90	92.15921	92.16118	385.3	-3.87	376.2	1.46	0.77815	.75049
0.85	92.15706	92.15811	373.8	-1.88	368.5	2.00	0.76239	.75010
0.80	92.15589	92.15658	369.0	-0.70	365.0	2.34	0.75677	.75003
0.75	92.15514	92.15564	366.9	0.10	363.3	2.58	0.75420	.75001
0.70	92.15461	92.15498	366.2	0.68	362.6	2.77	0.75274	.75001
0.60	92.15387	92.15409	366.5	1.46	362.4	3.04	0.75132	.75000
0.30	92.15261	92.15264	371.6	2.53	365.3	3.47	0.75016	.75000
0.10	92.15204	92.15204	373.3	2.96	366.2	3.62	0.75001	.75000

References

1. P.O. Lowdin, Phys. Rev. 1955, 97, 1474.

2. A.T. Amos and G.G. Hall, Proc. Roy Soc. A., 1961, 263, 483.

3. AB-INITIO UHF CALCULATIONS, Part I, T.A. Claxton and D. McWilliams Trans Faraday Soc. 1970, 66, 513.

4. - ditto - Part 2, T.A. Claxton Trans Faraday Soc. 1970, 66, 1537.

5. - ditto - Part 3, T.A. Claxton Trans Faraday Soc. 1970, 66, 1540.

6. - ditto - Part 4, T.A. Claxton and N.A. Smith Trans Faraday Soc. 1970, 66, 1825.

7. T.A. Claxton and D. McWilliams, Int. J. Quantum Chem, 4, 337, (1970).

8. {Hunzinago J. Chem. Physics, 1965, 42, 1293, for O and H atoms.
{Hunzinago J. Chem. Physics, 1969, 50, 1371, for C and N atoms.

9. T.A. Claxton and D. McWilliams, Theoret Chim Acta (BERL). 16, 346, 1970.

10. Segal, J. Chem. Physics, 1970, 52, 3530.

11. T.A. Claxton, Chem Phys. letters, 4, 469.

12. W. Easley and W. Weltner Jr., J. Chem Physics, 1970, 52, 197.

13. A. Carrington and N.J.D. Lucas, Proc. Roy Soc. (Lond) A314, 567, (1970).

14. Table of Interatomic Distances and Molecular Configurations (The Chemical Society, London, 1958; supplement 1965).

15. H.E. Radford, Phys. Rev., 1962, 126, 1035.

16. J.A. Brivati, M.C.R. Symons, D.J.A. Tinling, H.W. Wardale and D.O. Williams, Trans Faraday Soc. 1967, 63, 2112.

17. G.H. Dibdin, Trans Faraday Soc., 1967, 63, 210.

18. T.E. Gunter and C.D. Jeffries, U.C.R.L. 1964, 11387, 8.

19. T.E. Gunter, U.C.R.L., 1965, 16613, 82.

20. K O - OHATA, H. Taketh and S. Huzinaga,
J. Phys. Soc. Japan, 1966, 21, 2306.

21. P.E.Cade and W.M.Huo,J.Chem Physics 1967,47,614.

APPENDIX ONE

The stationary points of the equation

$$f(x) = (x^+ . A . x)/(x^+ . x) \qquad \text{A1-1}$$

where A is a fixed pxp matrix , X a variable column vector and $f(x)$ is a scalar function,

are s.t. the vectors X at these points are orthonormal eigenvectors of A .

The above equation A1-1 could be written in Dirac notation as $f(x) = \langle x|A|x\rangle / \langle x|x\rangle$

If the projection matrix P is defined as $\dfrac{|x\rangle\langle x|}{\langle x|x\rangle} \equiv \dfrac{xx^+}{x^+x}$

s.t. $P^2 = P$ i.e. $\dfrac{|x\rangle\langle x|}{\langle x|x\rangle}\cdot\dfrac{|x\rangle\langle x|}{\langle x|x\rangle} = \dfrac{|x\rangle\langle x|}{\langle x|x\rangle}$

then it projects vectors onto the vector X .

The function $f(x)$ can be written in terms of P as

$$f(P) = Tr\,PA = Tr\left\{\frac{xx^+A}{x^+x}\right\} = \frac{x^+Ax}{x^+x} = f(x).$$

Then the value of P at the stationary point of $f(P)$ are projection matrices that project onto orthonormal eigenvectors of A.

If we then define a fixed l.c. of projection matrices associated with the orthonormal eigenvectors of A i.e.

$$P_1 = \sum_i^p c_i\, y_i y_i^+ = \sum_i^p c_i\, P_{E_i} \quad ; \quad P_{E_i} = y_i y_i^+$$

where the set $\{y_i\}$ are the orthonormal eigenvectors of A.

P_1 is only a projection matrix if all c_i either $=1$ or 0.

The $Tr\,P_1 = p$,and the eigenvectors of P_1 are the orthonormal vectors $\{y_i\}_{i=1\ldots p}$ where the eigenvalue associated with y_i is c_i i.e. $P_1 . y_i = c_i . y_i$ for $i = 1 \ldots p$

Then $f(P_1)$ is also a stationary point of the function $f(P)$

with value $\sum_i^m f(P_{E_i})$.

If we apply the constraints $P=P^2$ and $\mathrm{Tr}P=1$ to the variation of the function $f(\rho)$ only p stationary points are found which are the projection matrices associated with the eigenvectors A ,however if we do not enforce these constraints enumerable stationary points are found. The matrices corresponding to these stationary points all have the the same eigenvectors as A .Thus all matrices P_K that are stationary points of f commute with A (as matrices with the same eigenvectors commute). As commuting matrices are simultaneously diagonisable all such solutions P_K are simultaneously diagonal with A .

APPENDIX TWO

SIMPLEX METHOD OF LINEAR PROGRAMMING.

As many text books on the general theory exist (as given in the references in the introduction) this appendix only describes the Linear Program written by myself.

The general problem is to maximise the function

$$\mathcal{E} = c^{+}.X \qquad \text{A2-1}$$

where C^{+} is a 1xN row vector containing the OBJECT FUNCTION coefficients $\{c_i\}_{i=1...N}$ of the BASIC VARIABLES $\{X_i\}_{i=1,...N}$ expressed as the variable Nx1 column vector X,

subject to the constraints

$$A.X \leq Y \qquad \text{A2-2}$$

$$X \geq O \qquad \text{A2-3}$$

(X being the Nx1 null vector).

Where A is a MxN matrix containing the constraining coefficients, and Y is a Mx1 column vector containing the constraint limits.

If any constraints are of the form

$$A_1.X \geq Y_1 \qquad \text{A2-4}$$

(A_1 is a RxN block of the constraining matrix A and Y_1 a 1xR block of Y)

they are replaced by

$$-A_1.X \leq Y_1 \qquad \text{A2-5}$$

so as to bring them into standerd form.

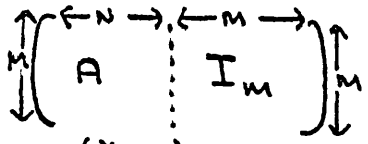
If the minimum of the function $\mathcal{E}$ is required, minus the maximum of the function $-c^{+}.X$ is found.

i.e if $\mathcal{E} = c^{+}.X$

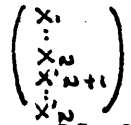
then min $\mathcal{E}$ = -max(-$\mathcal{E}$). A2-6

The SIMPLEX method implicitly expresses the problem in the form $[A \vdots I_m].[X \vdots X'_m] = Y$

where $[A \vdots I_m]$ is the matrix



and $[X \vdots X'_m]$ the vector



the variables $\{X'_{n+1} \ldots\ldots X'_{n+M}\}$ are called SLACK VARIABLES and X'_{n+i} gives a measure of the violation, or near violation of the i^{th} constraint $A^{j}_{(i)}.X \leq y_i$

if the constraint is violated $X'_{n+i} < 0$ (as $A^{j}_{(i)}.X + X'_{n+i} = y_i$).

If the i^{th} constraining limit is negative, ARTIFICIAL VARIABLES are added to the problem and the i^{th} constraining equation is redefined as

$$-A^{j}_{(i)}.X - X^{a} \leq y_i \qquad \text{A2-7}$$

and the object function as

$$\mathcal{E} = c^{+}.X - M\sum_{i}^{p}\{A_{(i)}.X + X_{a_i} - y_i\} \qquad \text{A2-8}$$

where M is an arbitrary large positive number and X_{a_i} are the p artificial variables corresponding to the constraining limits y_i that are negative.

The initial FEASIBLE solution is

$$\begin{pmatrix} X \\ \cdots \\ X_a \end{pmatrix} = \underline{0} \qquad \text{(null vector [N+P]x1)} \qquad \text{A2-9}$$

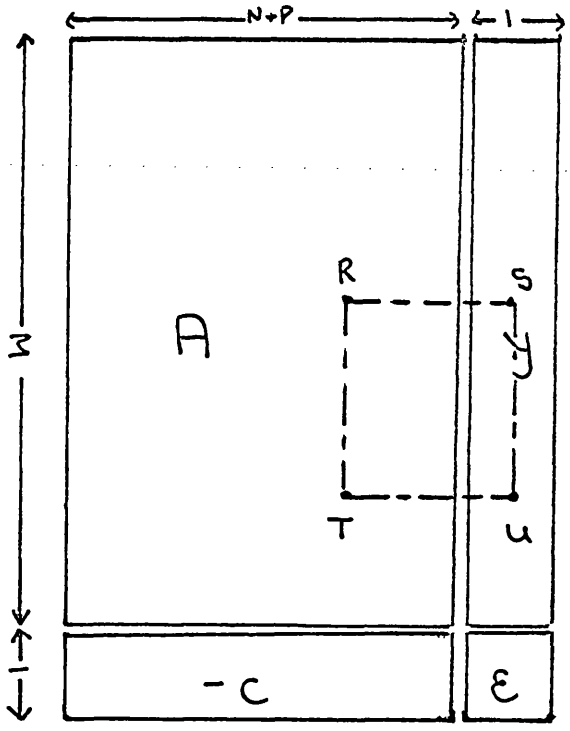
i.e. $\mathcal{E} = 0 + M\sum_{i}^{p} y_i$ A2-10

with slack variables

$$\begin{bmatrix} X' \end{bmatrix} = \begin{bmatrix} y \end{bmatrix} \qquad \text{A2-11}$$

The non zero variables are called BASIC , the zero variables NON BASIC .

The simplex tableaux starts at this solution implicitly and is of the form:-



PIVOTING ABOUT R

For all members of the tableaux.

$U_N := (RU_o - TS)/R$

Except for elements in the column or row of R.

U_n -new element in U position.

U_o -old element in U position.

(Initially $\varepsilon = M\sum_i^P y_i$).

The next feasible solution that is more positive than the initial is arrived at (if it exists) by choosing the most negative value in the $-C$ row, say the Lth column, then forming the ratios $y_i/A_i^{(u)}$ and finding

$\text{Min}\left(y_i/A_i^{(u)}\right)$ for $i = 1, \ldots\ldots M$

when $A_i^{(u)} \geq 0$

The value of i for which this is so , say K, then defines the element of A on which we PIVOT i.e. the element A_K^L

The elements of $-C$ (denoted by C^i) then become

$$C^i := C^i - C^L\left(\frac{A_K^i}{A_K^L}\right) \quad \text{where } i \neq L \qquad \text{A2-12}$$

and

$$C^L := -C^L/A_L^K \qquad \text{A2-13}$$

the elements of y become

$$y_i := y_i - y_k \left(A^l_i / A^l_k \right) \quad i \neq k \qquad \text{A2-14}$$

and $$y_k := y_k / A^l_k \qquad \text{A2-15}$$

the elements of A become

$$A^j_i := A^j_i - A^l_i \cdot (A^j_k / A^l_k) \text{ for } i \neq k, j \neq l \qquad \text{A2-16}$$

$$A^j_k := A^j_k / A^l_k \quad \text{for } j \neq l \qquad \text{A2-17}$$

$$A^l_i := - A^l_i / A^l_k \quad \text{for } i \neq k \qquad \text{A2-18}$$

$$A^l_k := 1 / A^l_k \qquad \text{A2-19}$$

The value of the object function becomes (where the values of A, y and C are the ones before transformation)

$$\varepsilon := \varepsilon - (y_k . C^l) / A^l_k \qquad \text{A2-20}$$

which never decreases the value of

Iterations continue until one of the following three conditions are satisfied:-

1. All C^i s are ≥ 0, and no artificial variables are non zero basic variables.
   Solution has then been reached and the maximum value of the object function is the current value of ε .

2. If all $C^i_s \geq 0$ and there is a non zero artificial basic variable then the constraints of the problem are inconsistent and there is no solution.

3. There is no $A^\omega_i \geq 0$, the value of ε is then unlimited, and the solution is UNBOUNDED .

Initially the function ε is expressed entirely in terms of non basic variables and the slack variables, that have values given by the column y (i.e. $x_{n+i} = y_i$)

form a basic solution. By pivoting about A^{L}_{K} the slack variable X_{n+K} becomes non basic and the variable X_L (which might be artificial) becomes basic with a value of y_K (after pivoting). If $k \neq i$ (say) throughout the iterative process the variable X_i never becomes basic and in the final solution has the value zero.

By recording the nature of the basic and non basic variables throughout the final values in the y column can be assigned to object function variables, artificial variables, or slack variables.

If there is no unique $\text{Min}\left(y_i / A^{\omega}_{i}\right)$ for $i=1 \ldots m$ at some stage of the process, i.e. say that

$\left(y_{i_k} / A^{\omega}_{i_k}\right)$ are all equal for $k = 1 \ldots r$

and $\{i_k\}_{k=1-r}$ = set of integers between $1 \ldots m$

then $\text{Min}\left(A^{j}_{i_k} / A^{L}_{i_k}\right)$ $\quad i_k \in \{i_k\}$ $k = 1 \ldots r$

(where j=1, then 2, then 3 ...etc, until a unique minimal ratio has been obtained)

determines i_k and thus which ratio $\frac{y_{i_k}}{A^{\omega}_{i_k}}$ to choose and hence the pivot row .

This method ensures that cycling will not occur in the iterative process.

Following is a listing of the Simplex procedure and the associated procedure for the addition of artificial variables (viz. Procedure NEG), which was designed for parametric linear programming, i.e. after the object function has been maximised new values of the constrianing coefficients can be calculated

(using the optimum values of the variables) and the artificial variables redefined, taking into account the initial transformations associated with the first up of the artificial variables.

```
          "PROCEDURE" NEG(NG,S,A,C,Y,EE,MM,NC);
"COMMENT" DESIGNED FOR RECURSIVE uSE,FOR 1 ST ITERATION S=1 THEN
AFTER S=2;
"COMMENT" NG IS THE NUMBER OF NEGATIVE CONSTRAINING VALUES;
"REAL" EE;
"INTEGER" NG,S,MM;
"ARRAY" A,C,Y;
"INTEGER" "ARRAY" NC;
"BEGIN"
"IF" NG "NE" 0 "THEN"
"BEGIN"
"REAL" Y1,Y2;
"INTEGER" I,J,K,K1,N1
"SWITCH" CLOUDY:=X1,X2;
"GO TO" CLOUDY[S];
X2:
N1:=N-NG;
"FOR" I:=1 "STEP" 1 "uNTIL" N1 "DO"
"BEGIN"
Y1:=0
"FOR" J:=1 "STEP" 1 "uNTIL" NG "DO"
"BEGIN"
K:=NC[J];
Y1:=-A[K,I]+Y1;
"END";
C[I]:=C[I]-10000*Y1;
"END";
Y2:=0;
"FOR" J:=1 "STEP" 1 "uNTIL" NG "DO"
"BEGIN"
K:=NC[J];
Y2:=Y2-Y[K];
"END";
EE:=EE+10000*Y2;
"GO TO" X3
X1:
J:=0;
"FOR" I:=1 "STEP" 1 "uNTIL" M "DO"
"IF" Y[I]<-1*10-6 "THEN"
"BEGIN"
J:=J+1
NC[J]:=I;
"END";
"FOR" I:=1 "STEP" 1 "UNTIL" M "DO"
"FOR" J:=N-NG+1 "STEP" 1 "UNTIL" N "DO"
A[I,J]:=0
N1:=N-NG;
"FOR" I:=1 "STEP" 1 "UNTIL" N1 "DO"
"BEGIN"
Y1:=0
"FOR" J:=1 "STEP" 1 "uNTIL" NG "DO"
"BEGIN"
K:=NC[J];
Y1:=A[K,I]+Y1;
"END";
```

```
C[I]:=C[I]-10000*Y1;
"END";
Y2:=0;
"FOR" J:=1 "STEP" 1 "UNTIL" NG "DO"
"BEGIN"
K:=NC[J];
Y2:=Y2+Y[K];
"END";
EE:=EE+10000*Y2;
"FOR" I:=1 "STEP" 1 "uNTIL" NG "DO"
"BEGIN"
J:=NC[I];
Y[J]:=-Y[J];
K1:=0;
"FOR" K:=N-NG+1 "STEP" 1 "UNTIL" N "DO"
"BEGIN"
K1:=K1+1;
"IF" K1=I "THEN" A[J,K]:=-1;
"END";
"FOR" K:=1 "STEP" 1 "UNTIL" N1 "DO"
A[J,K]:=-A[J,K];
"END";
"FOR" I:=N-NG+1 "STEP" 1 "UNTIL" N "DO"
C[I]:=-10000;
"END";
X3:"END" OF NEG;
```

```
"PROCEDURE" SIMPLEX(A,Y,C,EE,M,N,NG,X,MM);
"COMMENT"
SIMPLEX MAXIMIZES EE=C*X  (C[1XN],X[NX1]) SUBJECT TO THE CONSTRAINTS A*X 'LE' Y
(A[MXN],Y[MX1]),AND THE NON-NEGATIVE CONDITIONS X "GE" 0 .....
(IN THE TABLEAU  C IS REPLACED BY -C),
IF A SUB CONSTRAINT MATRIX SATISFIES B*X "GE" Y THEN IT BECOMES -B*X "LE"-Y
FOR A MINIMIZATION PROBLEM EE=C*X....-MAX[-C*X] IS FOUND
A- IS THE ARRAY OF CONSTRAINT COEFFICIENTS.
Y-THE CONSTRAINING VALUES.
C- THE OBJECT FUNCTION.
X-FINAL VALUES OF THE VARIABLES.
EE-THE VALUE OF THE OBJECT FUNCTION.
MM=1 FOR  MAXIMISATION  ,-1 FOR MINIMISATION.
(MM=-1 IF -MAX[-C*X] IS REQUIRED,  MM=1 IF MAX[C*X] IS REQUIRED).
M-THE NO. OF CONSTRAINTS.
N-THE TOTAL NO. OF VARIABLES (ARTIFICIAL +BASIC).
NG-THE NO. OF ARTIFICIAL VARIABLES;
"VALUE" A,Y;
"REAL" EE;
"INTEGER" M,N,NG,MM
"ARRAY" A,Y,C,X;
"BEGIN"
"INTEGER" I,J,K,L,IT,N1;
"INTEGER" I1,J1;
"REAL" BL,AL;
"ARRAY" B[1:M];
"INTEGER" "ARRAY" XI[1:N],YI[1:M];
"INTEGER" "ARRAY" P[6:7];
P[6]:=0
P[7]:=N;
"FOR" I:=1 "STEP" 1 "uNTIL" N "DO" C[I]:=-C[I];
N1:=N-NG;
"FOR" I:=1 "STEP" 1 "uNTIL" N "DO" XI[I]:=0;
"FOR" I:=1 "STEP" 1 "uNTIL" M "DO" YI[I]:=0;
IT:=0;
SPROUT(M,N,A,P,6);
PVOUT(N,C);
PVOUT(M,Y);
XL1:AL:=0;
"FOR" I:=1 "STEP" 1 "uNTIL" M "DO"
Y[I]:="IF" Y[I]=0 "THEN" 1*10-10 "ELSE" Y[I];
IT:=IT+1;
"FOR" I:=1 "STEP" 1 "UNTIL" N "DO"
"IF" C[I]<AL "THEN"
"BEGIN"
AL:=C[I];
L:=I;
"END";
"IF" AL=0 "THEN" "GO TO" XL2;
"FOR" I:=1 "STEP" 1 "uNTIL" M "DO"
"IF" A[I,L]>1*10-9 "THEN" B[I]:=Y[I]/A[I,L] "ELSE" B[I]:=-1
BL:=100000;
I1:=0
"FOR" I:=1 "STEP" 1 "UNTIL" M "DO"
"IF" B[I] "GE" 0 "AND" B[I] "LE" BL "THEN"
"BEGIN"
```

```
I1:=I1+1
"IF" I1=1 "OR" B[I]<BL "THEN"
"BEGIN"
K:=I;
BL:=B[I];
"END"
"ELSE"
"FOR" J1:=1 "STEP" 1 "UNTIL" N "DO"
"IF" A[I,J1]/A[I,L]<A[K,J1]/A[K,L] "THEN" "GO TO" XL5
"ELSE" "IF" A[I,J1]/A[I,L]>A[K,J1]/A[K,L] "THEN" "GO TO" XL6;
"GO TO" XL6;
XL5:K:=I;
XL6:"END";
"IF" BL=100000 "THEN" "GO TO" XL3
"IF" YI[K]=0 "THEN"
"BEGIN"
"IF" XI[L]=0 "THEN"
"BEGIN"
YI[K]:=L;
XI[L]:=-1;
"END"
"ELSE" "IF" XI[L] "NE" -1 "THEN"
"BEGIN"
YI[K]:=XI[L];
XI[L]:=-1;
"END"
"END"
"ELSE"
"BEGIN"
"IF" XI[L]=0 "THEN"
"BEGIN"
XI[L]:=YI[K];
YI[K]:=L;
"END"
"ELSE" "IF" XI[L]=-1 "THEN"
"BEGIN"
XI[L]:=YI[K];
YI[K]:=0;
"END"
"ELSE"
"BEGIN"
J:=YI[K];
YI[K]:=XI[L];
XI[L]:=J;
"END";
"END";
EE:=EE-Y[K]*C[L]/A[K,L];
"FOR" I:=1 "STEP" 1 "UNTIL" M "DO"
"IF" I "NE" K "THEN"
Y[I]:=Y[I]-A[I,L]*Y[K]/A[K,L];
Y[K]:=Y[K]/A[K,L];
"FOR" J:=1 "STEP" 1 "UNTIL" N "DO"
"IF" J "NE" L "THEN"
C[J]:=C[J]-C[L]*A[K,J]/A[K,L];
C[L]:=-C[L]/A[K,L];
"FOR" I:=1 "STEP" 1 "UNTIL" M "DO"
"FOR" J:=1 "STEP" 1 "UNTIL" N "DO"
"IF" I "NE" K "AND" J "NE" L "THEN"
A[I,J]:=A[I,J]-A[I,L]*A[K,J]/A[K,L];
"FOR" I:=1 "STEP" 1 "UNTIL" N "DO"
"IF" I "NE" L "THEN"
A[K,I]:=A[K,I]/A[K,L];
```

```
"FOR" I:=1 "STEP" 1 "UNTIL" M "DO"
"IF" I "NE" K "THEN"
A[I,L]:=-A[I,L]/A[K,L];
A[K,L]:=1/A[K,L];
"PRINT" ``L2``,SAMELINE,EE,K,L;
"GO TO" XL1;
XL2:N1:=N-NG
"FOR" I:=1 "STEP" 1 "uNTIL" N1 "DO" X[I]:=0;
"FOR" I:=1 "STEP" 1 "uNTIL" M "DO"
"IF" YI[I] "NE" 0 "THEN"
"BEGIN"
"IF" YI[I] "LE" N1 "THEN" X[YI[I]]:=Y[I] "ELSE"
"BEGIN"
"IF" Y[I]>1*10-9 "THEN" "GO TO" ALARM;
"END";
"END";
EE:=MM*EE:
"PRINT" ``L2``,`SOLUTION FOUND`;
"PRINT" ``L2``,SAMELINE,`ITERATION=`,IT;
"PRINT" ``L2``,SAMELINE,`VALUE OF FUNCTION=`,EE;
"PRINT" ``L5``;
"FOR" I:=1 "STEP" 1 "uNTIL" N1 "DO"
"PRINT" ``L2`` ,SAMELINE,`VARIABLE`,I,`=`,FREEPOINT(10),X[I];
PVOUT(M,Y);
"GO TO" XL4;
XL3:"PRINT" ``L2`,SOLUTION uNBOUNDED`;
"GO TO" XL10;
ALARM:"PRINT" ``L2``,`CONSTRAINTS ARE INCONSISTENT THUS
THERE IS NO SOLUTION`;
STOP;
XL10:
XL4:"END" OF SIMPLEX;
```

Procedures SPROUT and PVOUT are print out routines for a MxN matrix A and M or N dimensional vectors respectively.

APPENDIX THREE

SPACES WITH NON UNIT METRIC.

All the vector, functional and tensor spaces discussed elsewhere in this thesis apply to spaces whose metric is uniform and equal to unity. However if we to generalise to spaces where this is not the case we must explicitly take into account the metric of the space.

The metric of a space can be expressed as the matrix S where the elements of S are defined as $S^j_i = \langle a_i(1) | a^j(1) \rangle$ for $F^{(M)}$, $F_{(M)}$.
The inner product of any element of the dual spaces $F^{(M)}$ and $F_{(M)}$ w.r.t. the non orthogonal basis $\{a_i(1)\}$ of $F_{(M)}$ and $\{a^i(1)\}$ of $F^{(M)}$ is given by

$$[X_K | X^L] = \langle X_K | S | X^L \rangle = X_K . S . X^L \text{ or } X^{K+} . S . X^L$$

where $X_K \in F_{(M)}$; $X^L, X^{K+} \in F^{(M)}$
and $[\quad]$ denotes scalar product in a space with non unit metric.

Obviously in the case $S = I_M$

$$[X_K | X^L] = \langle X_K | I_M | X^L \rangle = \langle X_K | X^L \rangle$$

i.e. it becomes the scalar product as defined before for spaces defined on a orthonormal basis.

When $\langle X_K | S | X^L \rangle = \delta^L_K$ for a set of vectors $K, L = 1 \ldots\ldots M$. we say that the vectors X_K and X^L are orthonormal w.r.t. the non orthogonal basis i.e. the set of vectors are S orthonormal.

The eigenvalue problem expressed in terms of matrices belonging to such a non orthogonal space, constrained s.t. the eigenvectors be S orthonormal is written as

$$M.V = SVD$$

where M is the matrix we wish to obtain the eigenvalues of, V the eigenvectors of M arranged as columns, and D the diagonal matrix of eigenvalues.

i.e. $(S^{-1}M)V = VD$

viz. the eigenvalues and eigenvectors of $(S^{-1}M)$ are found and $(S^{-1}M)$ is diagonal in the basis of these vectors.

Also we can write for any particular eigenvalue

$$D^i_i = Tr\ V^{(i)+}.V^{(i)}(S^{-1}M)$$

where $V^{(i)}$ is the i th column of V.

CHANGE OF BASIS.

If we transform the non orthonormal basis $\{a^i(1)\}$ of $F^{(M)}$ to a orthonormal basis $\{\sigma^i(1)\}$ of $F^{(M)}$ we see that the transformation is given by $\sigma^i(1) = \sum_j^M a^j(1).S^{-1/2}{}^i_j$ where $S^{-1/2}$ is the matrix s.t. $S^{-1/2}.S^{-1/2} = S^{-1}$ and S the metric of the $\{a^i(1)\}$ basis. We can write the transformation in a super vector notation

where $\underline{\sigma}(1) \equiv (\sigma^1(1) \ldots\ldots \sigma^M(1))$ i.e. row vector

$\underline{a}(1) \equiv (a^1(1) \ldots . a^M(1))$ with components $\sigma^i(1), a^i(1)$.

thus $\underline{\sigma}(1) = \underline{a}(1).S^{-1/2}$

The relationship between any function $\in F^{(M\infty)}$ and its representative vector $\in F^{(M)}$ on the $\{a^i(1)\}$ basis can be written in this notation as $X(1) = \underline{a}(1).X_a$

and on the $\{\sigma^i(1)\}$ basis as $X(1) = \underline{\sigma}(1).X_\sigma$

The metric matrix of the $\underline{\sigma}(1)$ basis can be written as $\int \underline{\sigma}^+(1).\underline{\sigma}(1)dr_1$ and the metric matrix of the $\underline{a}(1)$ basis as $\int \underline{a}^+(1).\underline{a}(1).dr_1 = S$

As $\underline{\sigma}(i) = \underline{a}(i).S^{-1/2}$ we can write $\int \underline{\sigma}^{+}(i).\underline{\sigma}(i)\,d\tau_i = \int S^{-1/2}\underline{a}^{+}(i).\underline{a}(i)S^{-1/2}\,d\tau_i = S^{-1/2}.S.S^{-1/2} = I_M$.
which indeed shows that $\underline{\sigma}(i)$ is a orthonormal basis for $F^{(M)}$. The relationship between the representations of functions on the two different bases is then given by

$$\underline{a}(i).X_a = \underline{\sigma}(i).X_\sigma = \underline{a}(i).S^{-1/2}.X_\sigma$$

$$\therefore X_a = S^{-1/2}X_\sigma \quad \text{and} \quad X_\sigma = S^{1/2}X_a$$

The relationship between matrices on the two different bases is given by $M_a.X_a = Y_a$ ($X_a, Y_a \in F^{(M)}$ on $\underline{a}(i)$ bases)

$$\therefore M_a.S^{-1/2}X_\sigma = S^{-1/2}Y_\sigma \;,\; \therefore S^{1/2}M_aS^{-1/2}.X_\sigma = Y_\sigma$$

$$\therefore M_\sigma = S^{1/2}M_aS^{-1/2} \text{ and } M_a = S^{-1/2}M_\sigma S^{1/2}$$

Now if we wish to solve the eigenvalue problem

(w.r.t. $\underline{a}(i)$ basis of $F^{(M)}$) $S^{-1}H_aC_a = C_aE_a$

we can either find the eigenvectors of $S^{-1}H_a$ directly and thus find C_a w.r.t. the $\underline{a}(i)$ basis of $F^{(M)}$, s.t. $C_a^{+}.S.C_a = I_M$ where C_a contains the eigenvectors of $S^{-1}H_a$ in columns, or transform the equation to the orthonormal basis $\underline{\sigma}(i)$ viz. finding the eigenvectors of

$$S^{1/2}(S^{-1}H_a)S^{-1/2} = S^{-1/2}H_aS^{-1/2} \equiv H_\sigma$$

an equivalence we note with care as H_σ is not the representation of H_a on the $\underline{\sigma}(i)$ basis.

Thus we obtain the solutions of $H_\sigma C_\sigma = C_\sigma E_\sigma$

and to transform C_σ to the $\underline{a}(i)$ basis we have

$C_a = S^{-1/2}C_\sigma$ and $E_a = S^{-1/2}E_\sigma S^{-1/2} = E_\sigma$

(thus we drop the subscript for E)

C_a is then the matrix of eigenvectors of $S^{-1}H_a$.

Now if we define $P_\sigma^i = C_\sigma^{(i)}.C_\sigma^{(i)+}$ we can write $E_i^i = \mathrm{Tr}\,P_\sigma^i.H_\sigma$

and thus P^i_σ is a density matrix of the i th state on the $\underline{\sigma(i)}$ basis.

Now $S^{-1/2} P^i_\sigma S^{1/2} = S^{-1/2} C^{(i)}_\sigma C^{(i)+}_\sigma . S^{1/2} = S^{-1/2} S^{1/2} C^{(i)}_a . C^{(i)+}_a S^{1/2} S^{1/2} \equiv C^{(i)}_a C^{(i)+}_a S$

if we define $P^i_a = C^{(i)}_a C^{(i)+}_a$ then the representation of the density matrix P^i_σ on the $\underline{a(i)}$ basis is $P^i_a . S$

and $E^i_i = Tr\, P^i_a S S^{-1} H_a = Tr\, P^i_a H_a$

We can think of $S^{-1} H_a$ and $P^i_a S$ as the metric corrected representations of the Hamiltonian and the density operator of the i th state on the $\underline{a(i)}$ basis of $F^{(M)}$. The actual representations being P^i_a and H_a but due to the non unit metric are only relative representations.

We note that $S^{-1/2} . P^i_\sigma . S^{1/2} = P^i_a S \;\therefore\; S^{-1/2} P^i_\sigma S^{-1/2} = P^i_a$

and also that $S^{1/2} H_\sigma S^{1/2} = H_a$.

TRANSFORMATIONS IN TENSOR PRODUCT SPACES.

The relationship between the bases $\{ a^i_{(1)} \otimes a^j_{(2)} \}_{i,j=1,\ldots,M}$, which can be written as $\underline{a(1)} \otimes \underline{a(2)}$, and $\underline{\sigma(1)} \otimes \underline{\sigma(2)}$ of $\otimes^2 F^{(M)}$ is given by $\underline{\sigma(1)} \otimes \underline{\sigma(2)} = (\underline{a(1)} \otimes \underline{a(2)}) . S^{-1/2} \otimes S^{-1/2}$

Also the relationship between the bases of the exterior and symmetric product spaces are of the form

$(\underline{\sigma(1)} \wedge \underline{\sigma(2)}) = (\underline{a(1)} \wedge \underline{a(2)})(S^{-1/2} \wedge S^{-1/2})$ bases of $\wedge^2 F^{(M)}$

$(\underline{\sigma(1)} \vee \underline{\sigma(2)}) = (\underline{a(1)} \vee \underline{a(2)})(S^{-1/2} \vee S^{-1/2})$ bases of $V^2 F^{(M)}$

and hence the corresponding transformations for tensors $\in \otimes^2_2 F^{(M)}$, $\wedge^2_2 F^{(M)}$ and $V^2_2 F^{(M)}$.

APPENDIX FOUR.

General mathematical notation tends to be a bit meaningless unless concrete examples, of a simple nature, can be visualized when one meets many dimensional usage of the notation. In this appendix we explicitly deal with tensor, symmetric and external products of functions and functional representations that form second rank tensors and their relationship to each other.

1. TENSOR PRODUCT.

of basis of $F_{(2M)}$ to form a basis of $\otimes_2 F_{(2M)}$

Any function $\in F_{(2M\infty)}$ can be represented in $F_{(2M)}$ as a vector with components $\{a^i_k\}$ $i = 1 \ldots 2M$ s.t.

$$f(1) = \sum_i^{2M} a^i_k \omega_i(1)$$

where $\{\omega_i(1)\}_{i=1\ldots 2M}$ forms a basis for $F_{(2M)}$.

This can be represented as a scalar product of a_k with the 'super column vector' defined with elements $\omega_i(1)$.

i.e. $$f(1) = (\ldots\ldots a^i_k \ldots\ldots)\begin{pmatrix}\vdots\\ \omega_i(1)\\ \vdots\end{pmatrix} \equiv a_k . \underline{\omega}(1).$$

Similarly any two variable function $\in \otimes_2 F_{(2M\infty)}$ can be represented as the scalar product of a tensor $\in \otimes_2 F_{(2M)}$ and a basis 'super tensor' $\underline{\omega}(1) \otimes \underline{\omega}(2)$

i.e. $$f(12) = (\ldots\ldots a^i_k a^j_l \ldots\ldots)\begin{pmatrix}\vdots\\ \omega_i(1).\omega_j(2)\\ \vdots\end{pmatrix} \equiv (a_k \otimes a_l) \cdot (\underline{\omega}(1) \otimes \underline{\omega}(2)).$$

2. EXTERIOR PRODUCT.

The exterior product of two basis functions is (retaining normalisation)

$$\omega_i(1) \wedge \omega_j(2) = \frac{1}{\sqrt{2}} \{\omega_i(1)\omega_j(2) - \omega_i(2)\omega_j(1)\} \quad i<j$$

and any antisymmetric two variable function $\in \Lambda_2 F_{(2M,0)}$

can be expressed as a scalar product of a tensor $\in \Lambda_2 F_{(2M)}$

and the basis 'super tensor' so

$$f_a(12) = (\cdots a_k \wedge a_l \cdots)\begin{pmatrix} \omega(1) \wedge \omega(2) \\ \vdots \end{pmatrix}$$

elements of $a_k \wedge a_l$ are $\frac{1}{\sqrt{2}}(a_k \wedge a_l)^{ij} = \frac{1}{\sqrt{2}}(a_k^i a_l^j - a_k^j a_l^i)$

and of $\omega(1)\wedge\omega(2)$ " $\frac{1}{\sqrt{2}}(\omega(1)\wedge\omega(2))_{ij} = \frac{1}{\sqrt{2}}(\omega_i(1)\omega_j(2) - \omega_j^{i<j}(1)\omega_i^{i<j}(2))$

thus $f_a(12) = \frac{1}{2}\sum_{i<j}^{M}(a_k^i a_l^j - a_k^j a_l^i)(\omega_i(1)\omega_j(2) - \omega_j(1)\omega_i(2))$

$= \frac{1}{2}\{\sum_{i<j}^{M} a_k^i a_l^j \omega_i(1)\omega_j(2) - \sum_{j<i}^{M} a_k^j a_l^i \omega_j(2)\omega_i(1) - \sum_{i<j}^{M} a_k^j a_l^i \omega_i(1)\omega_j(2) + \sum_{j<i}^{M} a_k^i a_l^j \omega_j(2)\omega_i(1)\}$

(note the changes in some of the summation subscripts)

$= \frac{1}{2}\{\sum_{ij}^{M} a_k^i a_l^j \omega_i(1)\omega_j(2) - \sum_{ij}^{M} a_k^j a_l^i \omega_i(1)\omega_j(2)\}.$

$= \frac{1}{2}\sum_{ij}^{M}(a_k^i a_l^j - a_k^j a_l^i)\omega_i(1)\omega_j(2).$

3. SYMMETRIC PRODUCT.

Similarly to before $f_s(12) = (\cdots a_k \vee a_l \cdots)\begin{pmatrix} \omega(1) \vee \omega(2) \\ \vdots \end{pmatrix}$

where the elements are $(a_k \vee a_l)^{ij} = \frac{1}{\sqrt{2M(ij)}}(a_k^i a_l^j + a_k^j a_l^i)$

and $\frac{1}{\sqrt{2M(ij)}}(\omega_i(1)\omega_j(2) + \omega_i(2)\omega_j(1))$

$M(ij)$ is the multiplicitly of the sequence ij,

viz. if i=j then $M(ij)=2$ while if i=j $M(ij)=1$.

Thus $f_s(12) = \sum_{i\leq j}^{M} \frac{1}{2M(ij)}(a_k^i a_l^j + a_k^j a_l^i)(\omega_i(1)\omega_j(2) + \omega_i(2)\omega_j(1))$

$= \sum_{i<j}^{M} \frac{1}{2M(ij)} a_k^i a_l^j \omega_i(1)\omega_j(2) + \sum_{j<i}^{M} \frac{1}{2M(ij)} a_k^j a_l^i \omega_i(1)\omega_j(2) + \sum_{i\leq j}^{M} \frac{1}{2M(ij)} a_k^j a_l^i \omega_i(1)\omega_j(2)$

$+ \sum_{j\leq i}^{M} \frac{1}{2M(ij)} a_k^i a_l^j \omega_i(1)\omega_j(2).$

$= \frac{1}{2}\{\sum_{ij}^{M} a_k^i a_l^j \omega_i(1)\omega_j(2) + \sum_{ij}^{M} a_k^j a_l^i \omega_i(1)\omega_j(2)\}$ after taking into account $M(ii) = 2$.

$= \frac{1}{2}\sum_{ij}^{M}\{a_k^i a_l^j + a_k^j a_l^i\}\omega_i(1)\omega_j(2).$

If we then add $f_a(12)$ and $f_s(12)$ i.e.

$$f_a(12) + f_s(12) = \frac{1}{2}\Big\{\sum_{ij}{}' \left[a^i_k a^j_l - a^j_k a^i_l + a^i_k a^j_l + a^j_k a^i_l\right] \omega_i(1)\omega_j(2)\Big\}.$$

$$= \frac{1}{2}\sum_{ij}{}' 2\, a^i_k a^j_l\, \omega_i(1)\omega_j(2)$$

$$= \sum_{ij}{}' a^i_k a^j_l\, \omega_i(1)\omega_j(2)$$

$$= (a_k \otimes a_l).(\underline{\omega}(1) \otimes \underline{\omega}(2))$$

$$= f(12)$$