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METHODS FOR THE DIRECT CALCULATION OF REDUCED

DENSITY MATRICES

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METHODS FOR THE DIRECT CALCULATION OF

REDUCED DENSITY MATRICES

by

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METHODS FOR THE DIRECT CALCULATION OF REDUCED

DENSITY MATRICES[*]

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Under the supervision of Associate Professor John E. Harriman

ABSTRACT

This thesis contains the results of four separate efforts
to overcome some of the mathematical difficulties involved in formulating
atomic and molecular quantum mechanics in terms of reduced density
matrices. First the problem of constructing approximately N-repre-
sentable density matrices which can be used in variational calculations
is studied in detail. The effects of approximate N-representability
on calculated properties are also analyzed.

Secondly use is made of field theoretical Green's functions
to directly determine the second-order density matrix of an N-fermion

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system. This method is applied to the ground state of the helium
atom as a test case. Thirdly a new technique for calculating, in a
self-consistent fashion, the first-and second-order density matrices
of atoms and molecules is put forth. This scheme makes use of a
generalized random-phase approximation to obtain equations for various
spin components of the density matrices. The results of applying this
new method to helium, lithium, and beryllium are presented. Finally,
the first-and second-order density matrices of symmetry-projected
single determinants are derived and analyzed.

In memory of my friend

David Guzaliak

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INTRODUCTION

For a quantum mechanical system composed of N identical, pairwise-interacting particles, the Hamiltonian operator can be written as follows:

$$H = \sum_{i=1}^{N} f(i) + \frac{1}{2} \sum_{i \neq j}^{N} g(i,j) \tag{1}$$

The one-particle operator $f(i)$ operates only on the space-spin variables of the ith particle, which are represented by the index i. Similarly the two-particle operator $g(i,j)$ operates on the space-spin variables of both the ith and j^{th} particles. The system wave function $\Psi(1,2,3,\ldots N)$ is the solution of the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(t) = H(t) \Psi(t) \tag{2}$$

with the initial condition

$$\Psi(t) = \psi, \quad \text{at} \quad t = t_o . \tag{3}$$

If the Hamiltonian does not depend explicitly on time, the time-dependent Schrödinger equation allows the separation of variables

$$\Psi(t) = \exp\left(-\frac{iE}{\hbar}(t-t_o)\right)\psi , \tag{4}$$

which leads to the time-independent Schrödinger equation

$$H \psi = E \psi \tag{5}$$

The solution ψ of Eqn. (5) describes a stationary state of the system whose energy is equal to the eigenvalue E.

The expectation value of any observable Q for a system described by the wave function ψ is given as

$$\langle Q \rangle = \int \psi^* \hat{Q} \psi \, d\tau \Big/ \int \psi^* \psi \, d\tau \quad , \tag{6}$$

where $\hat{Q}$ is the quantum mechanical operator corresponding to the observable Q, and $d\tau$ implies integration over the space-spin variables of all N particles. If the particles which comprise the system are fermions (bosons) then the wave function ψ (1,2,3,...N) must be antisymmetric (symmetric) under permutation of the space-spin variables of any two particles:

$$\psi(1,2,\cdots i,\cdots j,\cdots N) = (\bar{+}) \psi(1,2,\cdots,j,\cdots i,\cdots N) \, . \tag{7}$$

This fact allows the expectation value expressed in Eqn. (6) to be written in a more suggestive form. For example, if the operator $\hat{Q}$ is a one-particle operator

$$\hat{Q} = \sum_{i=1}^{N} \hat{Q}(i) \quad , \tag{8}$$

then Eqn. (6) can be written as follows:

$$\langle Q \rangle = N \; \frac{\int \psi^*(1,2,\cdots N) \; \hat{Q}(1) \; \psi(1,2,\cdots N) \, d\tau_1 \cdots d\tau_N}{\int \psi^*(1,2,\cdots N) \; \psi(1,2,\cdots N) \, d\tau_1 \cdots d\tau_N} \qquad (9)$$

Eqn. (9) follows directly from Eqn. (6) by repeated application of the following identity:

$$\int \psi^*(1,2,\cdots i,\cdots N) \; \hat{Q}(i) \; \psi(1,2,\cdots i,\cdots N) \, d\tau$$

$$= \int \psi^*(i,2,\cdots 1,\cdots N) \; \hat{Q}(1) \; \psi(i,2,\cdots 1,\cdots N) \, d\tau$$

$$= \int \psi^*(1,2,\cdots i,\cdots N) \; \hat{Q}(1) \; \psi(1,2,\cdots i,\cdots N) \, d\tau \qquad (10)$$

The first equality in Eqn. (10) is obtained by relabeling dummy integration variables; the second equality is a consequence of Eqn. (7). Arguments similar to those employed above can be used to rewrite the expectation value of a two-particle operator in the form given below:

$$\langle P \rangle = \binom{N}{2} \; \frac{\int \psi^*(1,2,\cdots N) \; \hat{P}(1,2) \; \psi(1,2,\cdots N) \, d\tau_1 \cdots d\tau_N}{\int \psi^*(1,2,\cdots N) \; \psi(1,2,\cdots N) \, d\tau_1 \cdots d\tau_N} , \qquad (11)$$

where $\binom{N}{2}$ is the binomial coefficient.

It is clear from Eqns. (9) and (11) that knowledge of the N-particle

wave function is <u>not necessary</u> for the calculation of expectation values of one-and two-particle operators. All of the necessary information is contained in the first-and second-order reduced density matrices defined as follows:

$$\gamma(1;1') = N \frac{\int \psi^*(1',2,\cdots N)\, \psi(1,2,\cdots N)\, d\tau_2 \cdots d\tau_N}{\int \psi^*(1,2,\cdots N)\, \psi(1,2,\cdots N)\, d\tau_1 \cdots d\tau_N} \tag{12}$$

and

$$\Gamma(1,2;1',2') = \binom{N}{2}\frac{\int \psi^*(1',2',3,4\cdots N)\, \psi(1,2,3,\cdots N)\, d\tau_3 \cdots d\tau_N}{\int \psi^*(1,2,\cdots N)\, \psi(1,2,\cdots N)\, d\tau_1 \cdots d\tau_N} \tag{13}$$

Higher order density matrices are defined in an analogous fashion. In terms of these reduced quantities, the expectation values given in Eqns. (9) and (11) can be written as

$$\langle Q \rangle = \int \delta(1-1')\, \hat{Q}(1)\, \gamma(1;1')\, d\tau_1\, d\tau_{1'} \tag{14}$$

and

$$\langle P \rangle = \int \delta(1-1')\delta(2-2')\, \hat{P}(1,2)\, \Gamma(1,2;1',2')\, d\tau_1\, d\tau_{1'}\, d\tau_2\, d\tau_{2'} \tag{15}$$

For an N-particle system the wave function ψ depends on 3N continuous variables and N spin variables, whereas the second-order

density matrix Γ is a function of only twelve continuous variables
and 4 spin variables, <u>independent of the number of particles</u>. Moreover
the second-order density matrix contains all of the information needed
to calculate the properties of systems composed of pairwise-interacting
particles. These facts, together with the knowledge that accurate
wave functions are extremely difficult to obtain for any but the simplest
systems, lead naturally to investigating the possibility of determining
directly the first-and second-order density matrices.

By using the definitions of the reduced density matrices, e.g,
Eqns. (12) and (13), and the fact that the wave function obeys the
Schrödinger equation, a system of coupled integro-differential equations
involving the density matrices can be derived. In statistical mechanics
this hierarchy of equations is known as the BBGKY (Bogolubov, Born,
Green, Kirkwood, Yvon) equations. The main difficulty with such an
approach is that the equations are coupled; the equation which should
be used to determine the first-order density matrix contains the second-
order density matrix. Likewise the equation for the second-order
density matrix is coupled to the third-order density matrix, and so on.
There are many decoupling procedures which can be used to approximate
the solutions of the first few equations in the hierarchy, but they are
not based on sound theoretical foundations.

Another approach to the direct determination of first-anad second-
order density matrices would be to use trial density matrices in a
variational calculation. The difficulty with this approach is that the
trial density matrices <u>must</u> be restricted to the class of functions
which are derivable from an antisymmetric or symmetric wave function as

in Eqns. (12) or (13). Such density matrices are said to be N-representable. The problem of restricting trial density matrices to be N-representable is very difficult and has yet to be solved.

Presented in this thesis are the results of four separate efforts to develop techniques allowing the N-particle wave function to be by-passed in favor of reduced density matrices. In the first chapter the problem of constructing approximately N-representable density matrices which can be used in variational calculations is studied in detail. The effects of approximate N-representability on calculated properties are also analyzed.

In chapter two use is made of field-theoretical Green's functions to directly determine the second-order density matrices of N-fermion systems. As a test case the method is applied to the ground state of the helium atom.

Chapter three contains the derivation of a new technique for calculating, in a self-consistent fashion, the first-and second-order density matrices of atoms and molecules. This new method makes use of a generalized random-phase approximation to obtain equations for various spin components of the density matrices. These equations are solved by an iterative procedure. The results of applying this method to the helium, lithium, and beryllium atoms are also presented.

Finally, in chapter four the first-and second-order density matrices of symmetry-projected single determinants are derived. The totally symmetric components of the density matrices are also presented and discussed.

It is hoped that the research reported in this thesis will help

provide theoreticians with a useful set of tools for calculating the
properties of atomic and molecular systems. If this is too ambitious,
perhaps some thoughts for more productive research will arise in the
readers' minds.

CHAPTER ONE

CONSTRUCTION OF APPROXIMATELY

N-REPRESENTABLE DENSITY MATRICES

I. INTRODUCTION

The <u>pth</u> order reduced density matrix,[1-6] or p-matrix,[7] for a pure

state of an N-fermion system can be obtained from the wave function Ψ as

$$D^p(1\ldots p;1'\ldots p')= \int \Psi(1\ldots p,p+1\ldots N)\, \Psi^*(1'\ldots p',p+1\ldots N)\, d\tau_{p+1}\cdots d\tau_N \ . \quad (1)$$

It has certain properties as immediate consequences of this definition:

it is hermitian, and if Ψ is a normalized, antisymmetric function

$D^{(p)}$ is antisymmetric with respect to permutations of the primed or of

the unprimed variables, and is of trace 1. However, a proposed density

matrix having these properties is not necessarily derivable from an

antisymmetric, N-particle wave function. The problem of determining

conditions on a proposed density matrix such that there exists at least

one antisymmetric function Ψ from which the given $D^{(p)}$ can be obtained

according to Eqn. (1) is known as the (pure state) N-representability

problem.[7-17] It has received much attention in recent years but remains

unsolved.

One reason for interest in this problem is that it would be easier

to do a variational calculation with the 2-matrix directly than with a

many-electron wave function.[10,18,19] This is particularly true when

correlation effects are of interest, since they can be dealt with fairly

well in two electron systems. If a trial density matrix is not N-repre-

sentable, however, then the energy computed as the trace of the product

of the density matrix and an appropriate reduced hamiltonian matrix is

not in general an upper bound to the ground state energy of the system,

as is a variational energy calculated from the wavefunction. The energy

calculated from a non-N-representable density matrix is rigorously bounded below only by the lowest eigenvalue of the reduced hamiltonian. This eigenvalue is also a lower bound for the ground state energy of the system, and may be quite far below it. Unless N-representability constraints are imposed, a density matrix calculation is thus of doubtful value.[20-23]

Although N-representability conditions for the 1-matrix can be stated entirely in terms of its eigenvalues, those for the 2-matrix necessarily involve not only the matrix elements but also the geminals in terms of which the matrix is expanded. One of the many problems associated with direct attacks on the N-representability of the 2-matrix has been that the conditions on geminals seem to involve the very weakly occupied geminals to exactly the same extent as the most strongly occupied geminals.[13] This is unfortunate since the weakly occupied geminals have relatively little effect on calculated physical properties. It is a consequence of the statement of the N-representability question in "all or nothing" terms. We are thus led to consider the possibility of an approximately N-representable density matrix.

Some work has been done in which conditions which are known to be necessary, but not sufficient, for N-representability are imposed and a variational calculation carried out. The results have been encouraging.[10,24,25] Perhaps if enough necessary conditions are imposed the resultant density matrices will not be too far from being N-representable. It would clearly be more satisfactory, however, if some measure of deviation from N-representability could be introduced and the consequences for calculation of properties such as the energy

quantitatively estimated.

In this chapter we will consider the following question, which is closely related to that of the N-representability of a 2-matrix:

Given a set of M orthonormal, antisymmetric spin geminals $\{\phi_i(1,2), i + 1,\ldots,M\}$ in terms of which 2-matrices can be expressed as

$$D^{(2)}(1,2;1',2') = \sum_{\substack{i,j \\ =1}}^{M} d_{ij} \phi_i(1,2) \phi_j^*(1',2') \qquad (2)$$

what are the restrictions on the coefficients d_{ij} such that $D^{(2)}$ is as nearly N-representable as possible?

We find this problem to be somewhat more tractable than the N-representability problem itself. It will be of interest if we can establish a measure of the extent to which $D^{(2)}$ is N-representable, and an estimate of the maximum extent to which an energy calculated from $D^{(2)}$ can fall below the ground state energy of the system. Since we hope to do a variational calculation, we want to obtain a density matrix which has some free parameters in it. We will examine the way in which maximization of N-representability interacts with minimization of the approximate energy.

As a first step in investigating the question posed above, we introduce in Section II a continuous measure of the N-representability of a density matrix, and define a procedure which can in principle be used to obtain the density matrix or matrices of optimal N-representability for a given geminal basis set. The method could easily be extended to consider a general p-matrix, but we will confine our discussion to the

2-matrix, because of its physical interest for systems of pairwise interacting fermions. We find that the exact N-representability problem can be treated as a special case, but the solution which then results is not of great interest, leading in general to the equivalent of a complete CI calculation.

In Section III we consider the effects of approximate N-representability on variational energy calculations. We find that the maximum extent to which the calculated energy can go below the true ground state energy can be related to our measure of N-representability and to the eigenvalues of the reduced hamiltonian in a greatly restricted basis set.

In Section IV we expand on methods of calculation which could be used in practice and consider the effects of truncation of certain expansions on our results. We also show how the geminal set can be systematically expanded to improve N-representability and decrease maximum possible errors. We conclude with a discussion in Section V of the results which have been obtained, and a view to future efforts.

II. DEVELOPMENT OF FORMALISM

In this treatment we will assume that we have available a fixed set of orthonormal, antisymmetric spin geminals $\{\phi_i\}$. They may be explicitly correlated or given as CI expansions in Slater geminals. Any member of the family of N-particle functions whose 2-matrix is expressible in terms of these spin geminals can be written as

$$\Psi(1...N) = \sum_{i=1}^{M} \phi_i(1,2) \chi_i(3...N) \tag{3}$$

where the χ_i are arbitrary N-2 particle functions. Of course Ψ will not in general be antisymmetric in all particles. The 2-matrix of such a function is given by Eqn. (2) with the coefficients d_{ij} determined by

$$d_{ij} = \int \chi_i(3\ldots N)\chi_j^*(3\ldots N)d\tau_3\ldots d\tau_N \quad . \tag{4}$$

It is clear that the matrix of coefficients $\underset{\sim}{d}$ is hermitian, positive semi-definite, and that trace $\underset{\sim}{d} = 1$ if Ψ is normalized to unity. (This will be assumed to be the case throughout what follows.) These are well known necessary conditions for N-representability.

We now introduce as a measure of the antisymmetry of Ψ the norm of its antisymmetric component:

$$\mu[\Psi] = \int |\mathcal{O}_{1\ldots N}\Psi|^2 d\tau \tag{5}$$

$$= \int \Psi^*(1\ldots N)\mathcal{O}_{1\ldots N}\Psi(1\ldots N)d\tau_1\ldots d\tau_N \quad ,$$

where $\mathcal{O}_{1\ldots N}$ is the N particle antisymmetric projection operator

$$\mathcal{O}_{1\ldots N} = (N!)^{-1} \sum_{P \in S_N} (-1)^P P \quad . \tag{6}$$

The summation on P extends over all N! permutations of the N space-spin variables, and p is the parity of P. Because $\mathcal{O}_{1\ldots N}$ is a projection operator and Ψ is normalized we know that $0 \leq \mu[\Psi] \leq 1$ and that $\mu = 0$ implies that $\mathcal{O}_{1\ldots N}\Psi = 0$ while $\mu = 1$ implies that $\mathcal{O}_{1\ldots N}\Psi = \Psi$. Substituting from Eqn. (3) into Eqn. (5), we obtain an

expression for the measure of antisymmetry for any member of the desired class of functions:

$$\mu[\Psi] = \sum_{\substack{i,j \\ =1}}^{M} \int \phi_i^*(1,2)\chi_i^*(3\ldots N) \mathcal{O}_{1\ldots N} \phi_j(1,2)\chi_j(3\ldots N) d\tau_1 \ldots d\tau_N . \tag{7}$$

This expression can be simplified somewhat when we realize that $\mathcal{O}_{1\ldots N}$ can be decomposed as

$$\mathcal{O}_{1\ldots N} = \binom{N}{2}^{-1} \mathcal{T} \mathcal{O}_{1,2} \mathcal{O}_{3\ldots N} . \tag{8}$$

Here $\mathcal{O}_{1,2}$ and $\mathcal{O}_{3\ldots N}$ are the 2 particle and N-2 particle antisymmetric projection operators, respectively, and $\mathcal{T}$ is the sum of all signed transpositions between particles 1 and 2 and particles 3...N:[26]

$$\mathcal{T} = 1 - \sum_{j=3}^{N}(P_{1j} + P_{2j}) + \sum_{\substack{j<k \\ =3}}^{N} P_{1j} P_{2k} . \tag{9}$$

Our method of obtaining the density matrices which can be expanded in terms of the given set of spin geminals and which are as nearly N-representable as possible will be to choose the functions $\{\chi_i\}$ so as to maximize $\mu[\Psi]$ and then to take d_{NN} to be given by Eqn. (4). In general we will not be able to attain the result $\mu = 1$, which would imply exact N-representability. We can, however, interpret the maximum attainable value of μ as a measure of the N-representability of the density matrix we have obtained.

The form of $\mathcal{O}_{1...N}$ introduced in Eqn. (8) makes it clear that in seeking a maximum value of μ for normalized Ψ we need consider only those functions $\chi_i(3...N)$ which are antisymmetric in the N-2 particles. The spin geminals ϕ_i are also antisymmetric, by assumption, so that our expression for μ can be written as

$$\mu[\Psi] = \binom{N}{2}^{-1} \sum_{i,j=1}^{M} \int \phi_i^* \chi_i^* \, \mathcal{J} \, \phi_j \, \chi_j \, d\tau_1 ... d\tau_N \quad . \tag{10}$$

If the antisymmetric functions χ_i are varied so as to make μ stationary subject to the normalization constraint

$$\int \Psi^* \Psi \, d\tau = \sum_{i=1}^{M} \int \chi_i^* \chi_i d\tau_3 ... d\tau_N = 1 \quad , \tag{11}$$

a set of equations satisfied by the optimum $\{\chi_i\}$ is obtained:

$$\sum_{j=1}^{M} \binom{N}{2}^{-1} \int \phi_i^*(1,2) \, \mathcal{J} \, \phi_j(1,2) \chi_j(3...N) d\tau_1 d\tau_2 = \lambda \, \chi_i(3...N), i = 1...M \tag{12}$$

where λ is a lagrange multiplier introduced to assure that Eqn. (11) will be satisfied.

In order to make progress in using Eqn. (12) to determine the optimum $\{\chi_i\}$ we introduce in Appendix 1 a set of R (perhaps infinite) orthonormal spin orbitals labeled by $\{\alpha_1, \alpha_2 ... \alpha_R\}$ in terms of which all the $\{\phi_i\}$ can be expressed. For convenience we denote the spin orbitals themselves by the indices α_i. Then

$$\phi_i(1,2) = \sum_{\substack{\alpha_1 < \alpha_2 \\ =1}}^{R} (i|\alpha_1\alpha_2) \, [\alpha_1\alpha_2] \tag{13}$$

Here $(i|\alpha_1\alpha_2)$ is an expansion coefficient and brackets denote a normalized Slater determinant

$$[\alpha_1\alpha_2] = 2^{-1/2} \{\alpha_1(1)\alpha_2(2) - \alpha_2(1)\alpha_1(2)\} \ . \tag{14}$$

In general there will be $\binom{R}{2}$ Slater determinants $[\alpha_i\alpha_j]$, but the number M of spin geminals used in the density matrix will be smaller, possibly much smaller, especially if the spin geminals are correlated.

It can also be shown that the optimum $\{\chi_i\}$ can be expressed exactly in terms of the $\binom{R}{N-2}$ $N-2$ particle Slater determinants which can be formed from the α_i.

$$\chi_i(3\ldots N) = \sum_{\alpha_3 < \ldots < \alpha_N}^{R} C_{i\alpha_3\ldots\alpha_N} [\alpha_3\ldots\alpha_N]$$

$$= \sum_{\alpha=1}^{\binom{R}{N-2}} C_{i\alpha} [\alpha] \tag{15}$$

where the set $\alpha_3\ldots\alpha_N$ has been replaced by α for brevity. That this expansion is possible for the optimum $\{\chi_i\}$ can most readily be verified by examining the dependence of the terms in Eqn. (12) on one particle, say particle 3, and making use of the antisymmetry of the functions.

Substitution of Eqn. (15) into Eqn. (10) gives

$$\mu[\Psi] = \binom{N}{2}^{-1} \sum_{i,j=1}^{M} \sum_{\alpha,\beta}^{\binom{R}{N-2}} C_{i\alpha}^{*} \int \phi_i^{*}[\alpha]^{*} \mathcal{O} \phi_j[\beta] d\tau\ C_{j\beta} \tag{16}$$

which is a hermitian form in the coefficients $\{C_{i\alpha}\}$. In Appendix 2 we show that the integral appearing in Eqn. (16) can be further reduced by use of the identity

$$\binom{N-1}{2}^{-1} \int \phi_i^*[\alpha]^* \mathcal{J} \; \phi_j[\beta] d\tau = \int \phi_i^*[\alpha]^* \; \hat{T} \; \phi_j[\beta] d\tau \; = \; \hat{T}_{i\alpha,j\beta} \tag{17}$$

with[27,28]

$$\hat{T} = \binom{N-1}{2}^{-1} [1 - 2(N-2)P_{13} + \frac{(N-2)(N-3)}{2} P_{13} P_{24}] \; . \tag{18}$$

Eqn. (16) can then be replaced by

$$\mu[\Psi] = \sum_{i,j=1}^{M} \sum_{\alpha,\beta=1}^{\binom{R}{N-2}} C_{i\alpha}^* \; \hat{T}_{i\alpha,j\beta} \; C_{j\beta} \tag{19}$$

The functional $\mu[\Psi]$ is thus a weighted average of the eigenvalues of the matrix $\hat{T}$ whose elements are given in Eqn. (17). The maximum value of $\mu[\Psi]$ is equal to the largest eigenvalue of $\hat{T}$, and occurs when the $\{C_{i\alpha}\}$ are the elements of an eigenvector of $\hat{T}$ associated with this largest eigenvalue. Thus we are led to consider the eigenvalue equation

$$\sum_{j=1}^{M} \sum_{\beta=1}^{\binom{R}{N-2}} \hat{T}_{i\alpha,j\beta} \; C_{j\beta} = \lambda \; C_{i\alpha}. \tag{20}$$

The normalization condition on Ψ takes the form

$$\sum_{i=1}^{M} \int \chi_i^* \chi_i \, d\tau_3 \ldots d\tau_N = \sum_{i=1}^{M} \sum_{\alpha=1}^{\binom{R}{N-2}} |c_{i\alpha}|^2 = 1 , \qquad (21)$$

so the eigenvector should be taken to be normalized. We will denote the largest eigenvalue of $\hat{\underset{\sim}{T}}$ by λ_0, and recall that it may be degenerate. Eqn. (20) is an eigenvalue equation which can in principle be solved directly, without requiring an iterative process. This reason alone may place the present method closer to being computationally useful than some previous schemes.[29] However, we must remember that the dimension of $\hat{\underset{\sim}{T}}$ is $M\binom{R}{N-2}$, which can be an extremely large number, or even infinite if R is infinite. In practice it would probably be necessary to choose some truncated set of spin orbitals $\{\alpha_i, i = 1, \ldots R'\}$ in terms of which to express the N-2 particle Slater determinants. Also, we have in mind a situation in which the number M of spin geminals ϕ_i is much less than $\binom{R}{2}$ and probably much less than $\binom{R'}{2}$. These approximations will be discussed in more detail in Sect. IV.

We assume that the degeneracy of the largest eigenvalue λ_0 is δ and denote the set of orthonormal eigenvectors associated with it by $\{c_{i\alpha}^{(a)} , a = 1, \ldots \delta\}$. Any linear combination of these will provide a set of coefficients optimizing $\mu[\Psi]$:

$$c_{i\alpha} = \sum_{a=1}^{\delta} Y_a \, c_{i\alpha}^{(a)} , \qquad (22)$$

in which the Y_a are arbitrary except for the normalization condition

$$\sum_{a=1}^{\delta} |Y_a|^2 = 1 , \tag{23}$$

will be an eigenvector of $\hat{\underset{\sim}{T}}$ with eigenvalue λ_o and thus with $\mu = \lambda_o$. The coefficients Y_a can be considered as variational parameters in the density matrix, which is given by Eqn. (2) with

$$d_{ij} = \sum_{\alpha=1}^{\binom{R}{N-2}} C_{i\alpha} C_{j\alpha}^* = \sum_{a,b=1}^{\delta} Y_a Y_b^* \sum_{\alpha=1}^{\binom{R}{N-2}} C_{i\alpha}^{(a)} C_{j\alpha}^{(b)*} . \tag{24}$$

This provides a solution in principle to the problem of constructing optimally N-representable 2-matrices. In practice there would remain problems associated with the construction of $\hat{\underset{\sim}{T}}$ and the determination of the $\{ C_{i\alpha}^{(a)} \}$. Except in simple cases, the large dimension of $\hat{\underset{\sim}{T}}$ would probably make the time and effort required to carry out these steps prohibitively large. For this reason we will examine later the possibility of decreasing the dimension of $\hat{\underset{\sim}{T}}$ by truncation of the set of determinants $[\alpha_3 \ldots \alpha_N]$ used in the expansion of the optimum $\{ \chi_i \}$.

If the $\{ \phi_i \}$ were equivalent to the set of all Slater geminals $[\alpha_i \alpha_j]$, which requires that $M = \binom{R}{2}$, then the largest eigenvalue λ_o would be equal to 1 and its degeneracy δ would be $\binom{R}{N}$. This is just a restatement of the fact that $\binom{R}{N}$ independent N particle Slater determinants can be formed from N spin orbitals.[30,31] The present approach then reduces (or expands!) to the equivalent of a conventional full configuration interaction calculation. In practice we hope to use a number, M, of spin geminals which is much smaller.

The question of how this reduction will affect the value of λ_o and its degeneracy is difficult to answer in general.

For such smaller sets of spin orbitals, λ_o may be nondegenerate or the degeneracy may be low. There may, however, be other eigenvalues of $\hat{T}$ nearly as large as λ_o. We can then gain more flexibility in the density matrix by including in the expansion of Eqn. (22) eigenvectors associated with these slightly smaller eigenvalues. The result will of course be to decrease slightly the value of $\mu[\Psi]$, i.e. the N-representability of the density matrix. The effects of such a decrease will be considered below, when we consider the error bounds which can be placed on energies calculated from the density matrix. It may be that a small loss of N-representability is tolerable in order to gain variational flexibility.

To make more explicit this possibility, let us suppose that we have decided that there are $q+1$ different eigenvalues of $\hat{T}$, $\lambda_o, \lambda_1 \ldots \lambda_q$, with degeneracies $\delta_o, \delta_1 \ldots \delta_q$, respectively, that are large enough to be included. The eigenvectors associated with them are added to the expansion, and Eqn. (22) is replaced by

$$C_{i\alpha} = \sum_{t=0}^{q} \sum_{a=1}^{\delta_t} Y_{at} C_{i\alpha}^{(t,a)} \tag{25}$$

where $C_{i\alpha}^{(t,a)}$ is the ath eigenvector of $\hat{T}$ associated with eigenvalue λ_t. The normalization condition then becomes

$$\sum_{t=0}^{q} \sum_{a=1}^{\delta_t} |Y_{at}|^2 = 1 \tag{26}$$

and the N-representability is measured by

$$\mu[\Psi] = \sum_{t=o}^{q} \sum_{a=1}^{\delta_t} |Y_{at}|^2 \lambda_t .$$ (27)

Before turning to a discussion of errors, methods and approximations, we find it of interest to relate this treatment to the exact N-representability problem for a given density matrix. We note that the $\{C_{i\alpha}\}$ are not the only coefficients which will lead to the matrix $\underset{\sim}{d}$. From the properties of $\underset{\sim}{d}$ we know that there exists a square, hermitian matrix $\underset{\sim}{d}^{1/2}$ such that

$$\sum_{k=1}^{M} d^{1/2}_{ik} d^{1/2}_{kj} = d_{ij} .$$ (28)

To relate $\underset{\sim}{d}^{1/2}$ to $\underset{\sim}{C} = \{C_{i\alpha}\}$ we define the rectangular matrix $\underset{\sim}{V}$ by

$$C_{i\alpha} = \sum_{j=1}^{M} d^{1/2}_{ij} V_{j\alpha} .$$ (29)

It then follows from Eqn. (28) and

$$d_{ij} = \sum_{\alpha=1}^{\binom{R}{N-2}} C_{i\alpha} C^*_{j\alpha} = \sum_{k,\ell=1}^{M} \sum_{\alpha=1}^{\binom{R}{N-2}} d^{1/2}_{ik} V_{k\alpha} V^*_{\ell\alpha} d^{1/2*}_{j\ell}$$ (30)

that

$$\sum_{\alpha=1}^{\binom{R}{N-2}} V_{i\alpha} V^*_{j\alpha} = \delta_{ij} .$$ (31)

However, it is not necessarily true that

$$\sum_{j=1}^{M} V_{j\alpha}^{*} V_{j\beta} = \delta_{\alpha\beta} \quad .$$

Matrices such as $\underset{\sim}{V}$ are referred to as partial isometries.

To relate these partial isometries to the exact N-representability problem, let us suppose that we are given a hermitian, non-negative matrix $\underset{\sim}{d}$ of unit trace, and a set of orthonormal, antisymmetric spin geminals $\{\phi_i\}$. We can then use Eqn. (29) to define a set of coefficients $\{C_{i\alpha}\}$ and thus a wave function Ψ, for $\underline{any}$ partial isometry $\underset{\sim}{V}$. We substitute this expression for the coefficients into Eqn. (19) and obtain

$$\mu[\Psi] = \sum_{k,\ell=1}^{M} \sum_{\alpha,\beta=1}^{\binom{R}{N-2}} V_{k\alpha}^{*} \, (\underset{\sim}{d}^{1/2} \, \hat{\underset{\sim}{T}} \, \underset{\sim}{d}^{1/2})_{k\alpha,\ell\beta} \, V_{\ell\beta} \tag{32}$$

where

$$(\underset{\sim}{d}^{1/2} \, \hat{\underset{\sim}{T}} \, \underset{\sim}{d}^{1/2})_{k\alpha,\ell\beta} = \sum_{i,j=1}^{M} d^{1/2}_{ki} \, \hat{T}_{i\alpha,j\beta} \, d^{1/2}_{j\ell} \quad .$$

If we now vary the $\{V_{i\alpha}\}$ to make $\mu[\Psi]$ stationary, subject to the constraints

$$\sum_{\alpha=1}^{\binom{R}{N-2}} V_{i\alpha} V_{j\alpha}^{*} = d_{ij} \qquad i,j = 1,\ldots M \tag{33}$$

we obtain the set of equations

$$\sum_{\ell=1}^{M} \sum_{\beta=1}^{\binom{R}{N-2}} (\underset{\sim}{d}^{1/2} \, \hat{\underset{\sim}{T}} \, \underset{\sim}{d}^{1/2})_{k\alpha,\ell\beta} \, V_{\ell\beta} = \sum_{\ell=1}^{M} \varepsilon_{k\ell} \, V_{\ell\alpha} \quad . \tag{34}$$

The $\varepsilon_{k\ell}$ are Lagrange multipliers associated with the constraints of Eqn. (33). Since we initially know neither the elements of the optimum $\underset{\sim}{V}$ nor the Lagrange multipliers $\underset{\sim}{\varepsilon}$, Eqn. (34) would have to be solved iteratively, if at all. If this can be done, we obtain

$$\mu \left[\Psi\right] = \sum_{k,\ell=1}^{M} \sum_{\alpha=1}^{\binom{R}{N-2}} \varepsilon_{k\ell} \; V_{\ell\alpha} \; V_{k\alpha}^{*}$$

$$= \sum_{k,\ell=1}^{M} \varepsilon_{k\ell} \; \delta_{k\ell} = \sum_{k=1}^{M} \varepsilon_{kk} = \text{trace } \underset{\sim}{\varepsilon} \tag{35}$$

We conclude that if the trace of the Lagrange multiplier matrix $\underset{\sim}{\varepsilon}$ is 1, then the given density matrix is exactly N-representable. When trace $\underset{\sim}{\varepsilon} < 1$, we interpret its value as a measure of how nearly N-representable the density matrix is. Because of the large dimension of $\underset{\sim}{d}^{1/2} \underset{\sim}{T} \underset{\sim}{d}^{1/2}$, and because we do not know that Eqn. (34) can in fact be solved, there is little hope that this method will be computationally useful. This discussion has been presented only to establish the connection between our approach and the exact N-representability problem for a given density matrix.

There is another formulation of the exact N-representability problem for a given density matrix which avoids the difficulties associated with Eqn. (34), although again the solution provided is one in principle rather than one of practical utility. Given a hermitian, non-negative matrix $\underset{\sim}{d}$ of unit trace and a set of orthonormal, antisymmetric spin geminals $\{\phi_i\}$, we first construct the matrix $\underset{\sim}{\hat{T}}$ and find the δ different eigenvectors associated with the largest eigenvalue λ_o. If λ_o is not unity, the density matrix cannot be

N-representable, so the question is answered. If λ_o is equal to 1, we must determine whether the parameters $\{Y_a\}$ of Eqn. (22) can be chosen so the Eqn. (24) yields the <u>given</u> values of the d_{ij}. The density matrix will be N-representable if and only if such coefficients can be found. If we define

$$P_{ij,ab} = \sum_{\alpha=1}^{\binom{R}{N-2}} c_{i\alpha}^{(a)} \, c_{j\alpha}^{(b)*} \tag{36}$$

and

$$Z_{ab} = Y_a Y_b^* \ . \tag{37}$$

Eqn. (24) can be rewritten as

$$\sum_{a,b=1}^{\delta} P_{ij,ab} Z_{ab} = d_{ij} \qquad i,j = 1...M \tag{38}$$

This can be thought of as M^2 linear equations in the δ^2 unknowns Z_{ab}, of which only δ are independent. That is, if we know $Y_1 Y_1^*, Y_1 Y_2^*, ... Y_1 Y_\delta^*$ we can determine all of the coefficients to within a single arbitrary phase factor. As in all systems of linear equations, the existence of solutions is governed by the rank of the matrix P and the rank of the augmented matrix which is formed by adjoining the "column vector" $\underset{\sim}{d}$ to $\underset{\sim}{P}$,

$$\underset{\sim}{P}^a = \begin{pmatrix} d_{11} & P_{11,11} & \cdots & P_{11,\delta\delta} \\ d_{12} & P_{12,11} & & P_{12,\delta\delta} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ d_{MM} & P_{MM,11} & & P_{MM,\delta\delta} \end{pmatrix} \ . \tag{39}$$

From the ranks of $\underset{\sim}{P}$ and $\underset{\sim}{P}^d$ we can in principle learn how many, if any, of the unknowns Z_{ab} are determined and how many are arbitrary. If the density matrix is to be N-representable there must be a non-trivial solution to Eqn. (38) having the further property that

$$Z_{ab} = Z_{ba}^{\;*} \tag{40}$$

Methods, and even computational procedures, exist by which Eqn. (38) can be solved and the solutions tested to see if the necessary conditions are satisfied. We are thus able in principle to test the N-representability of a given density matrix. Because of the large dimensions of $\overset{\wedge}{\underset{\sim}{T}}$ and $\underset{\sim}{P}$, however, this approach is not useful, and is perhaps better characterized as a restatement rather than a solution of the N-representability problem.

Let us review what we have found in this section. To construct optimally N-representable 2-matrices from a given set of orthonormal, antisymmetric spin geminals, we must find the eigenvectors associated with the largest eigenvalue λ_0 of the $M\begin{pmatrix} R \\ N-2 \end{pmatrix}$ dimensional matrix $\overset{\wedge}{\underset{\sim}{T}}$. The required coefficient matrix is then given by Eqn. (24), and λ_0 is a measure of how N-representable the resultant density matrix is, with the value 1 corresponding to exact N-representability. Additional eigenvectors of $\overset{\wedge}{\underset{\sim}{T}}$ associated with eigenvalues nearly as large as λ_0 may also be included to increase the variational freedom, with some loss of N-representability. This approach can also be related to the exact N-representability problem for a given density matrix, but the resultant equations are not practical to work with.

III. CONSEQUENCES OF APPROXIMATE N-REPRESENTABILITY

As we remarked earlier, one reason for interest in the N-representability problem is the desire to do variational calculations directly with the reduced density matrix, which is a potentially simpler thing than the wave function. If the Hamiltonian for the system is of the form

$$\mathcal{H} = \sum_{i=1}^{N} f(i) + \sum_{\substack{i>j \\ =1}}^{N} g(ij) \tag{41}$$

Then a <u>reduced</u> Hamiltonian may be defined as[32]

$$\mathcal{K} = \frac{N}{2} [f(1) + f(2) + (N-1) g(1,2)] , \tag{42}$$

such that for an antisymmetric wave function Ψ

$$\tilde{E} \equiv \text{trace} (\underset{\sim}{K} \underset{\sim}{d}) = \int \Psi^* \mathcal{H} \Psi d\tau \tag{43}$$

where $\underset{\sim}{K}$ is the matrix of $\mathcal{K}$ in the $\{ \phi_i \}$ basis:

$$K_{ij} = \int \phi_i^*(1,2) \mathcal{K} \phi_j(1,2) d\tau_1 d\tau_2 . \tag{44}$$

If Ψ is not antisymmetric the two expressions for $\tilde{E}$ are not equivalent, and $\tilde{E}$ calculated from $\underset{\sim}{d}$ is not an upper bound to E_o, the ground state energy of a fermion system defined by $\mathcal{H}$.[33] Since $\underset{\sim}{d}$ is in any case so defined as to be a non-negative, hermitian matrix,

it will be true that

$$\tilde{E} \geq \epsilon_o \qquad (45)$$

where ϵ_o is the lowest eigenvalue of $\mathcal{K}$. However, ϵ_o is a
lower bound to the ground state energy of the N electron system.
In this section we will consider the errors which can arise from the
use of a density matrix that is only approximately N-representable.
We will show that the extent to which $\tilde{E}$ can fall below the ground
state energy is related to μ, the measure of N-representability
introduced in the previous section, and approaches zero as μ approaches 1.

We begin by introducing a remainder function $\Omega(1,2,\ldots N)$ defined
for any Ψ of the type in Eqn. (3) by

$$\Omega(1,\ldots N) = [\mathcal{O}_{1\ldots N} - \mu]\Psi \qquad (46)$$

With μ determined from Ψ by Eqn. (5). This function is antisymmetric
in the first two particles, and if only antisymmetric χ's are con-
sidered, it is also antisymmetric in the last N-2 particles:

$$\mathcal{O}_{1,2}\Omega = \mathcal{O}_{3\ldots N}\Omega = \Omega \quad . \qquad (47)$$

If the optimum χ's are used, corresponding to $\mu = \lambda_o$, then it also
follows from Eqn. (12) that Ω is orthogonal to all of the ϕ_i

$$\int \phi_i^*(1,2)\Omega(1,2,3\ldots N)d\tau_1 d\tau_2 = 0 \quad . \qquad (48)$$

The square of the norm of Ω is

$$\|\Omega\|^2 = \int |\Omega|^2 d\tau = \int [(\textcircled{0}_{1\ldots N} - \mu)\Psi]^* (\textcircled{0}_{1\ldots N} - \mu)\Psi d\tau$$

$$= \mu - 2\mu^2 + \mu^2 = \mu(1-\mu) . \tag{49}$$

For an antisymmetric function such as $\textcircled{0}\Psi$ it is readily shown by relabeling variables of integration that[34]

$$\hat{E} = \frac{\int (\textcircled{0}\Psi)^* \mathcal{H} \textcircled{0}\Psi d\tau}{\int |\textcircled{0}\Psi|^2 d\tau} = \frac{\int (\textcircled{0}\Psi)^* \mathcal{K} \textcircled{0}\Psi d\tau}{\int |\textcircled{0}\Psi|^2 d\tau} \tag{50}$$

It is clear also, by the variation principle, that $\hat{E} > E_o$. We will consider the possible difference between $\hat{E}$ and $\tilde{E}$ defined in terms of the density matrix. Of course any other symmetric one-or two-electron operator can be substituted for the Hamiltonian if an appropriate reduced operator is also defined, but the comparison with E_o has an analogy only for operators that are bounded below.

We look first at the expectation value of $\mathcal{K}$ with respect to Ω

$$\langle \Omega | \mathcal{K} | \Omega \rangle = \langle \textcircled{0}\Psi - \mu\Psi | \mathcal{K} | \textcircled{0}\Psi - \mu\Psi \rangle$$

$$= \langle \Psi | \textcircled{0}\mathcal{K}\textcircled{0} | \Psi \rangle - \mu[\langle \Psi | \mathcal{K} | \textcircled{0}\Psi \rangle + \langle \textcircled{0}\Psi | \mathcal{K} | \Psi \rangle] + \mu^2 \langle \Psi | \mathcal{K} | \Psi \rangle . \tag{51}$$

Making use of $\textcircled{0}\Psi = \Omega + \mu\Psi$ and the definitions of μ and Ω, we rewrite this as

$$\langle \Omega | \mathcal{K} | \Omega \rangle = \mu \frac{\langle \Psi | \textcircled{0}\mathcal{K}\textcircled{0} | \Psi \rangle}{\langle \Psi | \textcircled{0}\Psi \rangle} + \mu^2 \frac{\langle \Psi | \mathcal{K} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$- \mu [2\mu \frac{\langle \Psi | \mathcal{K} | \Psi \rangle}{\langle \Psi | \Psi \rangle} + \langle \Psi | \mathcal{K} | \Omega \rangle + \langle \Omega | \mathcal{K} | \Psi \rangle] \tag{52}$$

or

$$\langle\Omega|\hat{k}|\Omega\rangle + \mu[\langle\Psi|\hat{k}|\Omega\rangle + \langle\Omega|\hat{k}|\Psi\rangle] = \mu\hat{E} - \mu^2\tilde{E} , \qquad (53)$$

since

$$\langle\Psi|\hat{k}|\Psi\rangle/\langle\Psi|\Psi\rangle = \langle\Psi|\hat{k}|\Psi\rangle = \text{trace } (\underset{\sim}{d}\,\underset{\sim}{K}) = \tilde{E} . \qquad (54)$$

Then using the triangle inequality we find

$$|\mu\hat{E} - \mu^2\tilde{E}| \leq |\langle\Omega|\hat{k}|\Omega\rangle| + 2\mu|\langle\Omega|\hat{k}|\Psi\rangle|. \qquad (55)$$

A more useful relationship can be obtained by using bounds for the terms on the right hand side. By the Schwarz inequality

$$|\langle\Psi|\hat{k}|\Omega\rangle|^2 \leq \|\Omega\|^2 \|\hat{k}\Psi\|^2 = \mu(1-\mu) \langle\Psi|\hat{k}^2|\Psi\rangle \qquad (56)$$

It should be noted that $\hat{k}^2$, the square of a two-electron operator, is itself a two-electron operator. It follows that

$$\langle\Psi|\hat{k}^2|\Psi\rangle = \text{trace } (\underset{\sim}{K}^2\,\underset{\sim}{d}) . \qquad (57)$$

The remaining term can be bounded as

$$|\langle\Omega|\hat{k}|\Omega\rangle| \leq \langle\Omega|\Omega\rangle \cdot |e|_{max} = \mu(1-\mu)|e|_{max}, \qquad (58)$$

where $|e|_{max}$ is the eigenvalue of maximum absolute value associated with $\hat{k}$ in the space spanned by the Slater spin geminals $[\alpha_i\alpha_j]$. This follows from the expansion of Eqn. (15).

We have seen earlier that in the case of the optimum $\{\chi_i\}$ when $\mu = \lambda_o$, Ω is orthogonal to all the spin geminals ϕ_i. In this case it follows that

$$\left|<\Omega|\hat{k}|\Omega>\right| \leq \mu(1-\mu)\left|e'\right|_{max} \tag{59}$$

where $\left|e'\right|_{max}$ is the eigenvalue of maximum absolute value associated with $\hat{k}$ in the difference space between that spanned by all the Slater geminals and that spanned by the ϕ_i. The dimension of this difference space is $\binom{R}{2} - M$. Our bound on the energy difference is thus

$$\left|\hat{E} - \mu\tilde{E}\right| \leq (1-\mu)\left|e\right|_{max} + 2[\mu(1-\mu)]^{1/2}[\text{trace } (\underset{\sim}{K}^2 \underset{\sim}{d})]^{1/2} \tag{60}$$

and if the optimum χ_i are used, $\left|e\right|_{max}$ can be replaced by $\left|e'\right|_{max}$. The occurence of μ multiplying $\tilde{E}$ is somewhat unfortunate, but not really serious since presumably $\mu \sim 1$ in cases of interest.

Since both terms on the right hand side of Eqn. (60) contain $(1-\mu)$, the bound can be improved by modifying the spin geminal set to increase μ. In the limit when μ becomes equal to 1 the bound goes to zero and $\hat{E} = \tilde{E}$. For μ's somewhat less than 1, if the optimum χ_i have been used and the term involving $\left|e'\right|_{max}$ makes a significant contribution, the bound can be reduced by a particular augmentation of the spin geminal basis. We add to the set $\{\phi_i\}$ the eigenfunctions of $\hat{K}$, within the difference space, which are associated with large eigenvalues. Because the new difference space which remains does not contain these high energy functions, the effect of this

procedure will be to reduce $|e'|_{max}$ and thus to improve our bound. Such an augmentation will clearly not decrease the optimum value of μ.

Of course we could augment the spin geminal basis by adding <u>all</u> of the functions in the difference space. We would then have to deal with a set of $\binom{R}{2}$ functions equivalent to the full set of Slater geminals $[\alpha_i \alpha_j]$, and would again be in effect doing a complete CI calculation.

IV. METHODS OF CALCULATION AND EFFECTS OF TRUNCATION

Clearly the possible practical utility of the method described above for the construction of optimally N-representable density matrices is dependent on our ability to construct the $M\binom{R}{N-2}$ - dimensional matrix $\hat{\underset{\sim}{T}}$ and to find the eigenvectors $\{C_{i\alpha}^{(a)}\}$ associated with the largest eigenvalue λ_o. Let us first turn our attention to the evaluation of the elements of $\hat{\underset{\sim}{T}}$. The operator $\hat{T}$ is defined in Eqn. (18) and the matrix elements of interest are those of Eqn. (17). Using the well known rules for evaluating matrix elements of one- and two-particle operators between Slater determinants, we obtain the following expressions for contributions to $\hat{T}_{i\alpha,j\beta}$:

$$\int \phi_i^*[\alpha]^* \phi_j[\beta] d\tau = \delta_{ij} \delta_{\alpha\beta} \tag{61}$$

$$\int \phi_i^*[\alpha]^* P_{13} \phi_j[\beta] d\tau = \begin{cases} (N-2)^{-1} \sum_{k=3}^{N} \int \phi_i^*(1,2)\alpha_k^*(3)\phi_j(3,2)\alpha_k(1) \ d\tau & \text{if } \alpha=\beta \\[2ex] (N-2)^{-1} (-1)^{k+m} \int \phi_i^*(1,2)\alpha_k^*(3)\phi_j(3,2)\beta_m(1) \ d\tau \\ \qquad\qquad \text{if } \alpha-\alpha_k=\beta-\beta_m \\[2ex] 0 \qquad\qquad\qquad\qquad \text{otherwise} \end{cases} \tag{62}$$

$$\int \phi_i^*[\alpha]^* P_{13} P_{24} \phi_j[\beta] d\tau =$$

$$\begin{cases} \binom{N-2}{2}^{-1} \sum_{\substack{k<\ell \\ =3}}^{N} \int \phi_i^*(1,2)[\alpha_k \alpha_\ell](1,2) d\tau \int [\alpha_k \alpha_\ell]^*(3,4)\phi_j(3,4)d\tau & \text{if } \alpha = \beta \ . \\ \\ (-1)^{k+m} \binom{N-2}{2}^{-1} \sum_{\ell=3}^{N} \int \phi_i^*(1,2)[\beta_m \alpha_\ell](1,2)d\tau \int [\alpha_k \alpha_\ell]^*(3,4)\phi_j(3,4)d\tau \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{if } \alpha - \alpha_k = \beta - \beta_m \\ \\ (-1)^{k+\ell+m+n} \binom{N-2}{2}^{-1} \int \phi_i^*(1,2)[\beta_m \beta_n](1,2)d\tau \int [\alpha_k \alpha_\ell]^*(3,4)\phi_j(3,4)d\tau \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{if } \alpha - \alpha_k - \alpha_\ell = \beta - \beta_m - \beta_n \\ \\ \qquad\qquad 0 \qquad\qquad\qquad\qquad\qquad \text{otherwise} \end{cases}$$

$$(63)$$

The notation $\alpha = \beta$ means that the two sets $\{\alpha_3 \ldots \alpha_N\}$ and $\{\beta_3 \ldots \beta_N\}$ are identical; $\alpha - \alpha_k = \beta - \beta_m$ means that the two sets differ only in the unequal indices α_k and β_m, the other indices in the α set being the same as the other indices in the β set; and $\alpha - \alpha_k - \alpha_\ell = \beta - \beta_m - \beta_n$ means that the two sets differ in the two indices α_k, α_ℓ and β_m, β_n only. If strongly orthogonal geminals[35] are used, all the integrals are zero except in Eqn. (61) and the third case in Eqn. (63). Since the spin geminals $\{\phi_i\}$ can also be expanded in terms of the spin orbital set $\{\alpha\}$, these results can be expressed entirely in terms of the expansion coefficients of Eqn. (13), which are determined by

$$(i|\alpha_1 \alpha_2) = \int [\alpha_1 \alpha_2]^* \phi_i \, d\tau \qquad\qquad (64)$$

It should be noted that only the coefficients with $\alpha_1 < \alpha_2$ are required in Eqn. (13). It is convenient for the expressions we now want, and consistent with Eqns. (13) and (64), to allow either order with $(i|\alpha_2\alpha_1) = -(i|\alpha_1\alpha_2)$. The expressions for the integrals can then be written

$$\int \phi_i^*[\alpha]^* \phi_j[\beta] d\tau = \delta_{ij}\, \delta_{\alpha\beta} \tag{65}$$

$$\int \phi_i^*[\alpha]^* P_{13}\phi_j[\beta]d\tau = \begin{cases} \frac{1}{2}(N-2)^{-1} \sum\limits_{k=3}^{N} \sum\limits_{\alpha_1=1}^{R} (i|\alpha_k\alpha_1)^*(j|\alpha_k\alpha_1) & \text{if } \alpha=\beta \\[2ex] \frac{(-1)^{k+m}}{2}(N-2)^{-1} \sum\limits_{\alpha_1=1}^{R} (i|\beta_m\alpha_1)^*(j|\alpha_k\alpha_1) \\[2ex] \qquad\qquad\qquad\qquad \text{if } \alpha-\alpha_k=\beta-\beta_m \\[2ex] 0 \qquad\qquad \text{otherwise} \end{cases} \tag{66}$$

$$\int \phi_i^*[\alpha]^* P_{13}P_{24}\phi_j[\beta]d\tau = \begin{cases} \binom{N-2}{2}^{-1} \sum\limits_{\substack{k<\ell \\ =3}}^{N} (i|\alpha_k\alpha_\ell)^*(j|\alpha_k\alpha_\ell) & \text{if } \alpha=\beta \\[2ex] (-1)^{k+m}\binom{N-2}{2}^{-1} \sum\limits_{\ell=3}^{N} (i|\beta_m\alpha_\ell)^*(j|\alpha_k\alpha_\ell) \\[2ex] \qquad\qquad\qquad\qquad \text{if } \alpha-\alpha_k=\beta-\beta_m \\[2ex] (-1)^{k+\ell+m+n}\binom{N-2}{2}^{-1} (i|\beta_m\beta_n)^*(j|\alpha_k\alpha_\ell) \\[2ex] \qquad\qquad\qquad \text{if } \alpha-\alpha_k-\alpha_\ell = \beta-\beta_m-\beta_n \\[2ex] 0 \qquad\qquad \text{otherwise} \end{cases} \tag{67}$$

These integrals provide all the information we need to evaluate the elements of $\hat{\underset{\sim}{T}}$. Because of the large dimension of $\hat{\underset{\sim}{T}}$ it will be difficult, or at least time consuming, to find the largest eigenvalue and the eigenvectors associated with it. Many of the matrix elements are zero, but even though the matrix is quite sparse it does not appear to have any block structure which might aid in the diagonalization.

The trace of $\hat{\underset{\sim}{T}}$ is of some interest. Since the positive quantity $\mu[\Psi]$ is expressed in Eqn. (19) as a potentially arbitrary weighted average of the eigenvalues of $\hat{\underset{\sim}{T}}$, all the eigenvalues must be non-negative, and $\lambda_0 \delta$ thus cannot exceed the trace of $\hat{\underset{\sim}{T}}$. This quantity can be evaluated from the diagonal matrix element expressions included above. It is found that the expansion coefficients occur only in sums that can be put in the form $\sum\limits_{\substack{\alpha_1 < \alpha_2 \\ =1}}^{R} |(i|\alpha_1\alpha_2)|^2$, which is 1 if ϕ_i is normalized. The trace is thus independent of the expansion coefficients. It is

$$\text{trace } \hat{\underset{\sim}{T}} = 2M \frac{(R-2)!}{N!(R-N)!} \tag{68}$$

We note that it is simply proportional to M, the number of spin geminals in the set. If $M = \binom{R}{2}$, then the trace is $\binom{R}{N}$. We expect that in this case the eigenvalue 1 will occur with degeneracy $\binom{R}{N}$. If $M < \binom{R}{2}$ then trace $\hat{\underset{\sim}{T}} < \binom{R}{N}$.

We have noted previously that the number R of spin orbitals $\{\alpha_i\}$ may be very large or even, if correlated geminals are used, infinite. It may thus be necessary to truncate the set, using only some smaller number R'. In addition we may find it a practical necessity to use only $S < \binom{R'}{N-2}$ of the possible N-2 particle determinants made up from these

spin orbitals. Either of these truncations will affect our estimation

of μ and also the elements d_{ij} which we ascribe to the optimally

N-representable density matrix.

As an initial step in the estimation of the consequences of such

truncations, we note that much of what we have done above is in fact valid

for any choice of basis set. The particular choice $\{\alpha_i, i=1...R\}$ is

merely one which is convenient and is capable of leading to optimum results.

Eqn. (7) defines $\mu[\Psi]$ for any $\{\chi_i\}$, and so long as these functions are

antisymmetric, the expression of Eqn. (10) follows. If the χ_i are ex-

panded in terms of some set of Slater determinants built up from orthonormal

spin orbitals, we can arrive at Eqn. (19) and the optimum expansion co-

efficients are obtained from Eqn. (20). The optimum density matrix has $\underset{\sim}{d}$

given by Eqn. (24). None of this requires that the set of spin orbitals

be complete for the expansion of the spin geminals ϕ_i or that the sum

over the N-2 particle determinants include all possible choices. If

these conditions are not met, we will not be able in general to attain

the truly optimum μ or find the truly best $\underset{\sim}{d}$ possible for the given

set $\{\phi_i\}$. This loss of complete optimization may be offset by gains

in convenience, however. We will still be able to estimate the conse-

quences of only approximate N-representability and thus to decide in a

given case if the results are good enough.

In deciding which spin orbitals and which determinants to include

in the truncated sets we must be guided by the following considerations:

we want the largest eigenvalue of $\underset{\sim}{\hat{T}}$, λ_o, to be close to unity and its

degeneracy (or the number of other eigenvalues nearly degenerate with it)

to be sufficiently large to give good variational freedom, but not so large as to return us effectively to the CI problem. It is difficult to formulate specific criteria in the general case. The fact that we are trying to make Ψ as nearly antisymmetric as possible, together with the effect that various functions have in attaining this goal as indicated by the results above, suggests certain features of the criteria, however. Those spin orbitals which figure significantly in the $\{\phi_i\}$ must be included. For a general set of spin orbitals $\{\alpha'_i\}$, we can say that α'_i and α'_j must be included in any truncated set if $\int [\alpha'_i \alpha'_j]^* \phi_k d\tau$ is large for any k. Similarly, the determinants which are most important to include are those containing the greatest numbers of the most important spin orbitals.

Let us consider finally the problem of using the density matrices resulting from the above procedures to calculate properties of our system. We suppose that we have chosen not only the set of spin geminals $\{\phi_i\}$, but also a set of spin orbitals $\{\alpha'_i, i=1 \ldots R'\}$ and selected some S of the $N-2$ particle determinants made up from them. We suppose that $\hat{T}$ has been formed and the $q+1$ largest eigenvalues, $\lambda_0, \ldots \lambda_q$, together with their associated eigenvectors $\{c_{i\alpha}^{(t,a)}, t=0, \ldots q, a=1 \ldots \delta_t\}$ have been found. The 2-matrix is then given by Eqn. (2) with

$$d_{ij} = \sum_{\substack{\alpha'=1 \\ t,u \\ =0}}^{\delta} \sum_{t,u}^{q} \sum_{a=1}^{\delta_t} \sum_{b=1}^{\delta_u} Y_{at} Y_{bu}^* c_{i\alpha'}^{(t,a)} c_{j\alpha'}^{(u,b)*} . \tag{69}$$

The expectation value of a two particle operator G can be written as

$$\langle G \rangle = \binom{N}{2} \sum_{i,j=1}^{M} d_{ij} \, G_{ji} = \sum_{\substack{t,u \\ =o}}^{q} \sum_{a=1}^{\delta^t} \sum_{b=1}^{\delta^u} Y_{bu}^{*} \, \overline{G}_{bu,at} \, Y_{at} \tag{70}$$

with

$$G_{ji} = \int \phi_j^{*}(1,2) \, g_{12} \, \phi_i(1,2) \, d\tau_1 d\tau_2 \tag{71}$$

or

$$\overline{G}_{bu,at} = \binom{N}{2} \sum_{i,j=1}^{M} \sum_{\alpha'=1}^{S} c_{j\alpha}^{(u,b)*} \, G_{ji} \, c_{i\alpha'}^{(t,a)} \tag{72}$$

When our interest is in the energy of the system we introduce the reduced hamiltonian $\mathcal{K}$, as in Section III. We seek to make the value of $\tilde{E}$ stationary, subject to the normalization constraint of Eqn. (26). We obtain in the usual way an eigenvalue equation

$$\sum_{t=o}^{q} \sum_{a=1}^{\delta_t} K_{bu,at} \, Y_{at} = E Y_{bu} \tag{73}$$

The dimension of the matrix $\underset{\sim}{K}$ which must be considered is the sum of the degeneracies of the eigenvalues which have been included

$$\text{dimension } (\underset{\sim}{K}) = \sum_{t=o}^{q} \delta_t \quad . \tag{74}$$

The lowest eigenvalue in Eqn. (73) is our approximation to the ground
state energy of the system. Its associated, normalized eigenvector can
be substituted into Eqn. (69) to determine an approximation to the
2-matrix for the system in its ground state, and from this, other properties
can be determined. In the same way, higher eigenvalues and their associated
eigenvectors can be used to approximate properties of excited states of
the system. We would expect the approximation to get progressively worse
as we go higher, and it is obvious that to obtain a full description we
would have to work with a matrix of infinite dimension.

For the ground state, where our approximation should be the best,
we can calculate μ from Eqn. (27) and bound $\left| \hat{E} - \mu \tilde{E} \right|$ by using Eqn. (60).
Since $\hat{E}$ is an upper bound to the true ground state energy, this establishes
a maximum on the extent to which our estimate may fall below the true
value. Of course if the $\{\phi_i\}$ are poorly chosen or we have too few
linear variational parameters our value may be far above the true value.
This is common to all variational calculations, however.

V. DISCUSSION OF RESULTS

We have proposed here a method whereby, given some set of spin
geminals, we can find the 2-matrices expressible in terms of them which
are as nearly N-representable as possible. We introduce a family of
wave functions, not necessarily antisymmetric, which lead to 2-matrices
involving only the given set of spin geminals. The norm of the antisymmetric
component of such a normalized wave function is taken as a measure of the
N-representability of the corresponding density matrix. The wave functions

are then varied to maximize this quantity, and thus to obtain the most
nearly N-representable density matrix. The wave function itself need
not appear explicitly at any stage, however. The measure of N-repre-
sentability and the density matrix are determined from the eigenvalues
and eigenvectors of a matrix $\hat{T}$. We have given explicit expressions
for the elements of this matrix.

If the largest eigenvalue of $\hat{T}$ is degenerate, then variational
parameters occur in the density matrix. If there is no degeneracy, or
if more parameters are desired, other large eigenvalues of $\hat{T}$ may be
included. Variational freedom is then gained at the expense of N-repre-
sentability. Of course the spin geminals themselves can be varied, but
each change in the spin geminals requires a re-evaluation of N-represent-
ability. We have also investigated the N-representability of a density
matrix for which both spin geminals and expansion coefficients are given.
The problem here is more difficult and although a new restatement of the
exact N-representability problem results, it is doubtful that practical
utility will be found in this case. The treatment for a given density
matrix is thus of interest primarily in relating the present treatment
to other attacks on the N-representability problem. This is not a severe
limitation, however, since we are less interested in testing a _given_
density matrix than in obtaining density matrices with embedded variational
parameters, such that exact or approximate N-representability is main-
tained as the parameters are adjusted to minimize the energy of the system.

Because the energy calculated from a non-N-representable density
matrix is not an upper bound to the true ground state energy of the system,

it is necessary to estimate the consequences for such a calculation of having only approximate N-representability. We have obtained a bound on the difference between $\tilde{E}$, an energy determined from the density matrix, and $\hat{E}$, determined from an antisymmetric wave function. Since $\hat{E}$ is an upper bound to the true energy, this establishes a limit on how far $\tilde{E}$ could possibly be below the true energy. The difference between these two energies can be reduced in a systematic way by expanding the basis set, and becomes zero as exact N-representability is approached.

The principal difficulty with our approach lies in the large size of the matrix $\hat{T}$. It can be comparable in size to the full CI matrix for the problem of interest, for a basis set of a given size. We have thus considered the possibility of truncating the set of spin orbitals and the set of N-2 particle determinants which are used in estimating N-representability and in determining the optimum density matrix. Such truncations are possible and the calculation can be carried through, although the optimum results potentially available for the given spin geminal set will then not be obtained.

We have neglected the consequences of symmetry, other than permutational, in the density matrix or in the wave function. It is well known that symmetry restrictions on the wave function lead to certain limitations on N-representable density matrices.[2,36-45] These restrictions should probably be imposed if we want satisfactory descriptions of the physical system of interest. We have not included them in the present discussion because of the additional complications they would add to an already difficult problem. The consequences of symmetry should be further investigated.

It is clear that the method proposed here cannot be properly evaluated until an attempt has been made to actually apply it to a calculation. We have considered some model problems in an attempt to investigate and illustrate the features of the method, but we find that if the model is simple enough to be easily treated it does not fully reproduce the interesting parts of the problem. We are continuing to investigate more extensive models, and hope also to apply the method to an actual problem, probably the lithium atom. When this has been done we will be better able to assess the practical utility of the method. Even if it should prove to be comparable in difficulty to a conventional CI calculation, however, we feel that the concept of approximate N-representability is a useful one, and that this investigation has increased our understanding of the properties of reduced density matrices.

ACKNOWLEDGMENT

APPENDIX 1. Spin orbital expansion of the spin geminals.

The spin geminals with which we work are orthonormal and antisymmetric. Each such two particle function can be expanded in terms of an orthonormal set of spin orbitals as

$$\phi_i(1,2) = \sum_{\substack{k<\ell \\ =1}}^{r_i} F_{k\ell}^i \frac{1}{\sqrt{2}} [\xi_k^i(1)\xi_\ell^i(2) - \xi_\ell^i(1)\xi_k^i(2)] \ .$$

There are well known advantages to taking the ξ_k^i to be eigenfunctions of the 1-matrix associated with ϕ_i. They are the natural spin orbitals of ϕ_i and the pseudo natural spin orbitals of the full problem. The number of spin orbitals required, r_i, is the 1-rank of ϕ_i and may be infinite.

To choose a spin orbital basis for the whole problem we first form the space which is the union of the spaces spanned by the spin orbitals associated with the various spin geminals. We then find some orthonormal basis for this space. It might be convenient to start with the $\{\xi_k^1\}$ associated with ϕ_1, which we take to be the spin geminal we expect to be most important in the final density matrix. Any of the $\{\xi_\ell^2\}$ associated with the next spin geminal which cannot be expanded in terms of the $\{\xi_k^1\}$ are then orthogonalized to all the $\{\xi_k^1\}$ and added to the set. Any independent $\{\xi_j^3\}$ are then orthogonalized and added to the set, and this process continued until the set is sufficient to expand all the $\{\xi_k^i\}$. This final set will be labeled by $\{\alpha_i, i = 1...R\}$. Clearly

$$R \leq \sum_{i=1}^M r_i$$

and we expect that R will be much less than the sum unless strongly orthogonal spin geminals are used, in which case the equality holds. The expansion of Eqn. (13) is clearly possible because of the way in which the $\{\alpha_i\}$ have been chosen.

APPENDIX 2. The relationship between $\mathcal{J}$ and $\hat{T}$.

We want to show that the operators $\binom{N}{2}^{-1}\mathcal{J}$ and $\hat{T}$, defined by Eqns. (9) and (18), respectively, have the same matrix elements in the $\{\phi_i \chi_i\}$ basis. The common constant factor $\binom{N}{2}^{-1}$ and the initial term, 1, are clearly the same for both operators. The second terms in $\mathcal{J}$ are of the form $P_{1j} + P_{2j}$ and have matrix elements

$$\int \phi_k^*(1,2)\chi_k^*(3\ldots j\ldots N)[P_{1j}+P_{2j}]\phi_i(1,2)\chi_i(3\ldots j\ldots N)d\tau_1\ldots d\tau_N$$

$$= \int \phi_k^*(1,2)\chi_k^*(j\ldots 3\ldots N)P_{13}\phi_i(1,2)\chi_i(j\ldots 3\ldots N)d\tau_1\ldots d\tau_N$$

$$+ \int \phi_k(2,1)\chi_k^*(j\ldots 3\ldots N)P_{13}\phi_i(2,1)\chi_i(j\ldots 3\ldots N)d\tau_1\ldots d\tau_N$$

$$= 2\int \phi_k^*(1,2)\chi_k^*(3\ldots j\ldots N)P_{13}\phi_i(1,2)\chi_i(3\ldots j\ldots N)d\tau_1\ldots d\tau_N \quad .$$

The first transformation is obtained by relabeling the dummy variables of integration, and the second follows from the antisymmetry of ϕ_k, ϕ_i, χ_k and χ_i. There are $N-2$ terms in the sum for $3 \leq j \leq N$, so the second terms of $\binom{N}{2}^{-1}\mathcal{J}$ and $\hat{T}$ are equivalent.

The third terms in $\mathcal{J}$ are of the form $P_{1j}P_{2k}$, $j < k$, and have matrix elements

$$\int \phi_\ell^*(1,2)\chi_\ell^*(3\ldots j,k\ldots N)P_{1j}P_{2k}\phi_i(1,2)\chi_i(3\ldots j,k\ldots N)d\tau_1\ldots d\tau_N$$

$$= \int \phi_\ell^*(1,2)\chi_\ell^*(j,k\ldots 3,4\ldots N)P_{13}P_{24}\phi_i(1,2)\chi_i(j,k\ldots 3,4\ldots N)d\tau_1\ldots d\tau_N$$

$$= \int \phi_\ell^*(1,2)\chi_\ell^*(3,4\ldots j,k\ldots N)P_{13}P_{24}\phi_i(1,2)\chi_i(3,4\ldots j,k\ldots N)d\tau_1\ldots d\tau_N \quad .$$

Use has again been made of relabeling and of the antisymmetry of χ_k and χ_ℓ. There are $\binom{N-2}{2}$ terms in this sum, corresponding to $j < k$ between 3 and N. The final terms in the two operators are thus also equivalent.

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CHAPTER TWO

DIRECT CALCULATION OF SECOND-ORDER

DENSITY MATRICES USING GREEN'S FUNCTIONS

I. Introduction

In this chapter we show how one can obtain directly the second-order density matrix for a system of pairwise interacting fermions. We employ the Green's function method, which has recently[1] been used to calculate the first-order density matrix of the helium atom. The important advantage of this technique is that it permits the direct calculation of reduced quantities; it does not require the calculation of the N-particle wave function.

In Sec. II we demonstrate the connection between the two-particle Green's function $\mathcal{G}$ and the second-order density matrix Γ. The usual time-dependent perturbation treatment of the wave function and an introduction to the use of diagrams is presented in Sec. III. In Sec. IV we use Green's function diagrams to derive an exact integral equation for $\mathcal{G}$. Approximations to the so-called irreducible vertex potential are also introduced. We obtain a matrix equation for the Green's function in Sec. V using a specific approximation to the irreducible vertex potential. The second-order density matrix is then obtained from $\mathcal{G}$ by performing a contour integration. One contribution to this integral is evaluated analytically, but there remains a contribution which must be done numerically. Finally we discuss the application of these methods to the ground state of the helium atom.

II. Second-Order Density Matrix and Two-Particle Green's Function

The two-particle propogator (Green's function) $\mathcal{G}$ corresponding to the state vector $|\Psi\rangle$ is written in the Heisenberg representation

as follows:

$$\mathscr{G}(1,2,3,4 / t-t') = i^{-2} \frac{\langle \Psi | T \psi_H(1,t) \psi_H(2,t) \psi_H^\dagger(3,t') \psi_H^\dagger(4,t') | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad \text{(II.1)}$$

where $\psi_H^\dagger$ and ψ_H are fermion[2] field creation and annihilation operators respectively, T is the Wick time ordering operator, and the integers 1, 2, 3, 4, refer to space-spin coordinates. That $\mathscr{G}$ depends only on the difference $t-t'$ can easily be seen by recalling that we are in the Heisenberg picture (thus the subscript H) and that the hamiltonian is independent of time. The denominator of Eq. (II.1) is included so that we can obtain a linked-diagram expansion for $\mathscr{G}$. This is discussed in Sec. IV. The one-particle Green's function in the Heisenberg representation is defined as follows

$$G(1,2, t-t') = i^{-1} \frac{\langle \Psi | T \psi_H(1,t) \psi_H^\dagger(2,t') | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad \text{(II.1a)}$$

One-and two-particle operators can be written in the second-quantization language as is shown below

$$F_{S.Q.} = \int \psi^\dagger(1) f_{op}(1) \psi(1) \, d1 \quad ,$$

and

$$J_{S.Q.} = \frac{1}{2} \int\!\!\int \psi^\dagger(1) \psi^\dagger(2) j_{op}(1,2) \psi(2) \psi(1) \, d1 \, d2 \quad \text{(II.2a)}$$

where f_{op} and j_{op} are the usual "first-quantized" one-and two-particle operators respectively. If the operators defined above are to be in a particular representation (Heisenberg, Schrödinger, interaction, etc.), then we must use field creation and annihilation operators which are

expressed in this representation.

The first-and second-order density matrices belonging to the state vector $|\Psi>$ can be defined by the following relations:

$$\langle\Psi|F|\Psi\rangle = \int \delta(1-1') f_{op}(1) \gamma(1,1') \, d1 \, d1' \, ,$$

and

$$\langle\Psi|J|\Psi\rangle = \int \delta(1-1')\delta(2-2') \overset{\circ}{j}_{op}(1,2) \Gamma'(1,2,1',2') d1d1'd2d2' \quad \text{(II.2b)}.$$

If we use the second-quantized expressions given in Eq. (II.2a) for the operators and the second-quantized state vector, the expectation values in Eq. (II.2b) can be written as

$$\langle\Psi|F|\Psi\rangle = \int \langle\Psi| \psi^{\dagger}(1) f_{op}(1) \psi(1)|\Psi\rangle \, d1$$

$$= \int \delta(1-1') f_{op}(1) \langle\Psi| \psi^{\dagger}(1') \psi(1)|\Psi\rangle \, d1 \, d1' \quad ,$$

and

$$\langle\Psi|J|\Psi\rangle = \tfrac{1}{2} \int \langle\Psi| \psi^{\dagger}(1) \psi^{\dagger}(2) \overset{\circ}{j}_{op}(1,2) \psi(2) \psi(1)|\Psi\rangle \, d1 \, d2$$

$$= \tfrac{1}{2} \int \delta(1-1')\delta(2-2') \overset{\circ}{j}_{op}(1,2) \langle\Psi| \psi^{\dagger}(1') \psi^{\dagger}(2') \psi(2) \psi(1)|\Psi\rangle d1d2d1'd2' \quad \text{(II.2c)}$$

Thus the first-and second-order density matrices in the second quantization language can be identified as

$$\gamma(1,1') = \langle\Psi| \psi^{\dagger}(1') \psi(1)|\Psi\rangle \, ,$$

and

$$\Gamma(1,2,1',2') = \frac{1}{2} \langle \Psi | \psi^{\dagger}_{(1')} \psi^{\dagger}_{(2')} \psi_{(2)} \psi_{(1)} | \Psi \rangle \tag{II.2d}$$

respectively. To include the possibility of wave functions which are not normalized to unity, and in preparation for the deviation of a linked-diagram expansion of the density matrices, we can generalize the expressions in Eq. (II.2d) by dividing the right hand sides by $\langle \Psi | \Psi \rangle$.

From the definitions of the one-and two-particle Green's functions given in Eqs. (II.1a) and (II.1) respectively, the following relationships between Green's functions and density matrices can easily be established

$$\gamma(1,1') = -i \lim_{t' \to t_+} G(1,1', t-t')$$

and

$$\Gamma(1,2,1',2') = -\lim_{t' \to t_+} \mathcal{G}(1,2,1',2' | t-t') \tag{II.3}$$

We have made use of the antisymmetry of Γ and $\mathcal{G}^3$, and we take the limit t' approaches t from above ($t'>t$).

In the following sections, we will obtain an expression not for $\mathcal{G}(t-t')$ but rather for its fourier transform $\mathcal{G}(E)$ defined by the following equation:
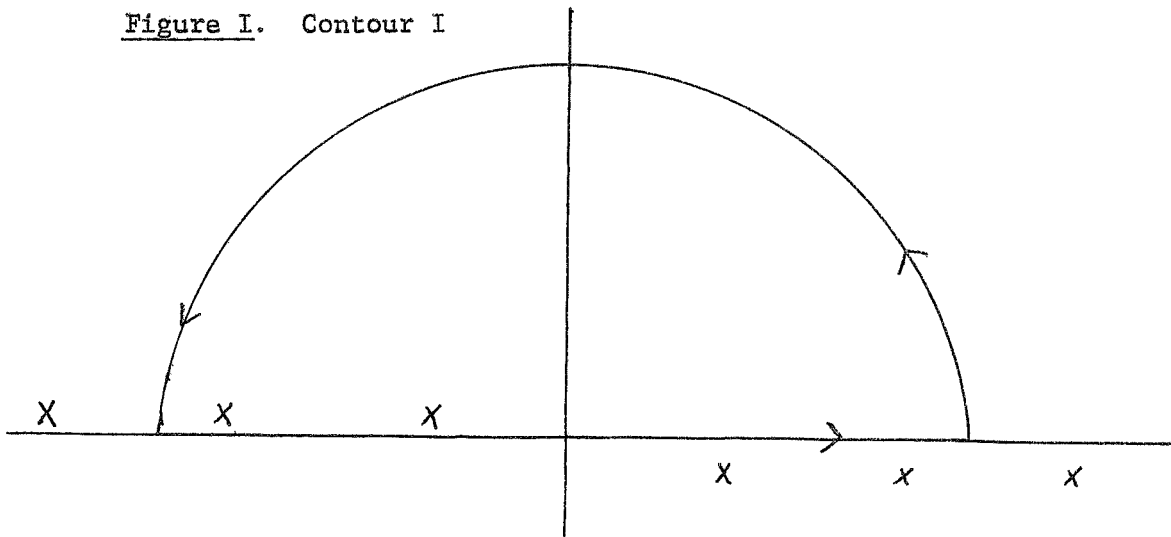
$$\mathcal{G}(1,2,3,4 | t-t') = (2\pi)^{-1} \int_{-\infty}^{\infty} \exp(-iE(t-t')) \mathcal{G}(1,2,3,4 | E) \, dE \tag{II.4}$$

With this, the expression for the second-order density matrix given in Eq. (II.3) becomes

$$\Gamma(1,2,1',2') = - (2\pi)^{-1} \lim_{\tau \to 0_+} \int_{-\infty}^{\infty} \exp(iE\tau) \mathcal{Y}(1,2,1',2' \mid E) \, dE \qquad (II.5)$$

This integral can be evaluated as a contour integral in the upper half complex E plane (Fig. (I)).

Figure I. Contour I

The upper half plane is chosen so that the integral over the arc vanishes due to the factor $e^{-\tau(\text{Im}E)}$. We will see later that $\mathcal{Y}$ (E) has poles both above the real axis to the left of the imaginary axis, and below the real axis to the right of the imaginary axis, as is shown in Fig. (I). Because the integral about contour I is difficult to carry out, we choose instead the contour shown in Fig. (II). Both contour I and contour II enclose the same poles of $\mathcal{Y}$ (E) and so they lead to the same result when substituted into Eq. (II.5). We choose the Coulson contour because the integral over the arc (E = Re$^{i\theta}$, $\frac{\pi}{2} \leq \theta \leq \frac{3\pi}{2}$) can be done analytically and the integral

Figure II. Coulson Contour[7] (Contour II)
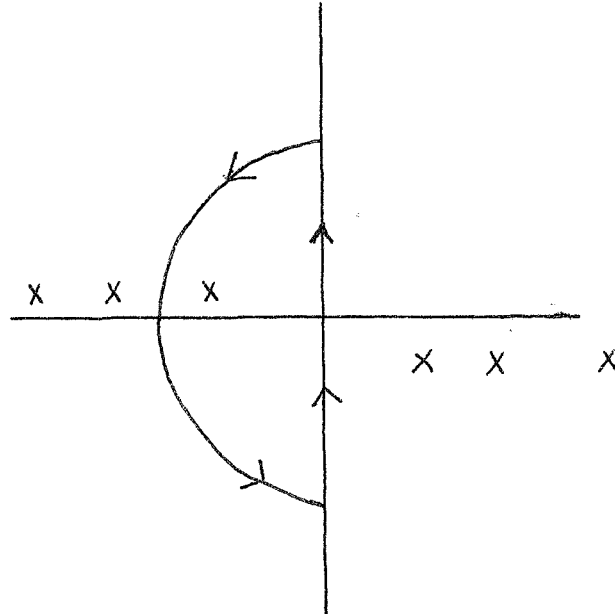
along the imaginary axis can be handled conveniently by standard

numerical techniques.

Hence we have reduced the problem of calculating the second-order

density matrix Γ to that of finding an expression for $\mathscr{G}$ (E) and

then evaluating the contour integral:

$$\Gamma(1,2,1',2') = - (2\pi)^{-1} \lim_{R \to \infty} \left\{ \int_{\pi/2}^{3\pi/2} \mathscr{G}(1,2,1',2' \mid R\,e^{i\theta})\, R\,e^{i\theta}\, i\,d\theta \right.$$

$$\left. + \int_{-R}^{R} \mathscr{G}(1,2,1',2' \mid i\,y)\, i\,d y \right\}$$

(II.6)

The evaluation of these two integrals is treated in Sec. V.

III. Time-dependent Perturbation Expansion of $|\Psi>$ and Diagrams

We assume that the hamiltonian of our system can be written as

$$H(t) = H^o + e^{-\alpha|t|} V \tag{III.1a}$$

where H^o is a sum of one-particle hamiltonians (perhaps Hartree-Fock or hydrogenic), and V is a two-particle time-independent perturbation:

$$H^o = \sum_{i=1}^{N} h(i) \quad ,$$

$$V = \sum_{\substack{i<j \\ =1}}^{N} V(i,j) \tag{III.1b}$$

We also assume that we know the eigenfunctions of h, and thus of H^o. In Eq. (III.1a) α is a positive real constant which we will eventually allow to approach zero.

The time-dependent Schrödinger equation is written as follows:

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = H(t) |\Psi\rangle \tag{III.2}$$

However, the problem is not yet completely specified. We must also stipulate the state vector $|\Psi>$ at some particular time. Therefore we decide that at $t = -\infty$, $|\Psi>$ is given by some eigenfunction of H^o,

$$|\Psi(t \to -\infty)\rangle = |\Phi\rangle \tag{III.3}$$

where

$$H^o \, |\Phi\rangle = E^o \, |\Phi\rangle \tag{III.4}$$

The function $|\Phi\rangle$ will usually be some Slater determinant composed of spin-orbitals which are eigenfunctions of h.

To write the Schrödinger equation in a more useful form, we transform to the interaction representation. This is done by defining new state vectors and operators as follows:

$$|\Psi\rangle_I = \exp\left(\frac{i H^o t}{\hbar}\right) |\Psi\rangle \quad , \tag{III.5a}$$

$$V_I(t) = e^{-\alpha|t|} \exp\left(\frac{i H^o t}{\hbar}\right) V \exp\left(\frac{-i H^o t}{\hbar}\right) \quad , \tag{III.5b}$$

$$H_I^o(t) = \exp\left(\frac{i H^o t}{\hbar}\right) H^o \exp\left(\frac{-i H^o t}{\hbar}\right) = H^o \tag{III.5c}$$

The Schrödinger equation and its boundary condition in this representation become:

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle_I = V_I(t) |\Psi\rangle_I \quad , \tag{III.6}$$

$$|\Psi(t \to -\infty)\rangle_I = |\Phi\rangle \quad .$$

This differential equation and boundary condition are equivalent

to the following integral equation

$$|\Psi(t)\rangle_I = |\Phi\rangle - \frac{i}{\hbar}\int_{-\infty}^{t} dt_1\, V_I(t_1)\,|\Psi(t_1)\rangle_I \quad , \quad \text{(III.7)}$$

which can be iterated to yield the usual perturbation expression for

$|\Psi(t)\rangle_I$

$$|\Psi(t)\rangle_I = |\Phi\rangle - \frac{i}{\hbar}\int_{-\infty}^{t} dt_1\, V_I(t_1)\,|\Phi\rangle + \cdots$$

$$+ \left(\frac{-i}{\hbar}\right)^n (n!)^{-1}\int_{-\infty}^{t} dt_1 \cdots \int_{-\infty}^{t} dt_n\, T\, V_I(t_1)\cdots V_I(t_n)\,|\Phi\rangle$$

$$+ \cdots \quad\quad\quad\quad \text{(III.8)}$$

The Wick time ordering operator T arises by recognizing the identity

$$\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \cdots \int_{-\infty}^{t_{n-1}} dt_n\, V_I(t_1)\cdots V_I(t_n) =$$

$$(n!)^{-1}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 \cdots \int_{-\infty}^{t} dt_n\, T\, V_I(t_1)\cdots V_I(t_n) \quad\quad \text{(III.9)}$$

For convenience we write Eq. (III.8) in the form

$$|\Psi(t)\rangle_I = U_I(t,-\infty)|\Phi\rangle$$

$$= \left(1 + U_I^{(1)}(t,-\infty) + \cdots + U_I^{(n)}(t,-\infty) + \cdots\right)|\Phi\rangle , \quad \text{(III.10)}$$

where we have made the identification of terms in Eq. (III.8) involving $m-V_I$'s with $U_I^{(m)}$. Because we are interested in obtaining an eigenfunction of $H^o + V$, we integrate from $-\infty$ to 0 (at $t = 0$, $H = H^o + V$) and take the adiabatic limit ($\alpha \to 0$) of the terms in Eq. (III.8).

It may seem that the introduction of the time ordering operator T accomplished nothing, but as can be seen by reading any book on many-body theory, its presence is essential to the use of Wick's theorem and the techniques of Feynman diagrams.[4,5]

To illustrate the use of diagrams in expressing the terms given in Eq. (III.8) we consider the first order contribution $U_I^{(1)}(0,-\infty)|\Phi>$. This can be written in second-quantization notation as

$$-\frac{i}{\hbar} \frac{1}{2} \int_{-\infty}^{o} dt_1 \int\int d_1 \, d_2 \; T \, e^{-\alpha|t_1|} \, V(1,2)$$

$$\psi_I^\dagger(1,t_1) \, \psi_I^\dagger(2,t_1) \, \psi_I(2,t_1) \, \psi_I(1,t_1)|\Phi\rangle \qquad \text{(III.11)}$$

Each field operator is written in the particle-hole picture[8] as

$$\psi^\dagger(x,t) = \psi_+^\dagger(x,t) + \psi_-^\dagger(x,t) \, ,$$

$$\psi(x,t) = \psi_+(x,t) + \psi_-(x,t) \, ,$$

and each of these particle-hole operators is represented by a directed line segment as in Fig. (III).

Figure III   Particle and Hole Diagrams

$\psi_+^+(xt)$ xt   particle creation

$\psi^+(xt)$ xt   hole annihilation

$\psi_+(xt)$ xt   hole creation

$\psi_-(xt)$ xt   particle annihilation
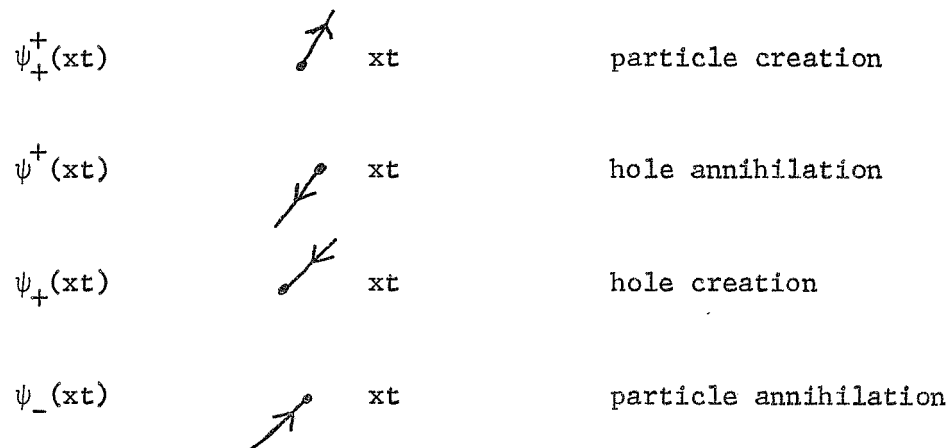
In these diagrams, time increases in the positive vertical direction, and a dot represents a space-spin-time point x,t. Recalling that in the particle-hole picture the unperturbed vector $|\Phi>$ becomes the vacuum state represented by $|0>$, we find by using Wick's theorem that the contributions to Eq. (III.11) can be written diagramatically as in Fig. (IV).

Figure IV   Contributions to $U_I^{(1)}(o,-\infty)\,|\Phi>$
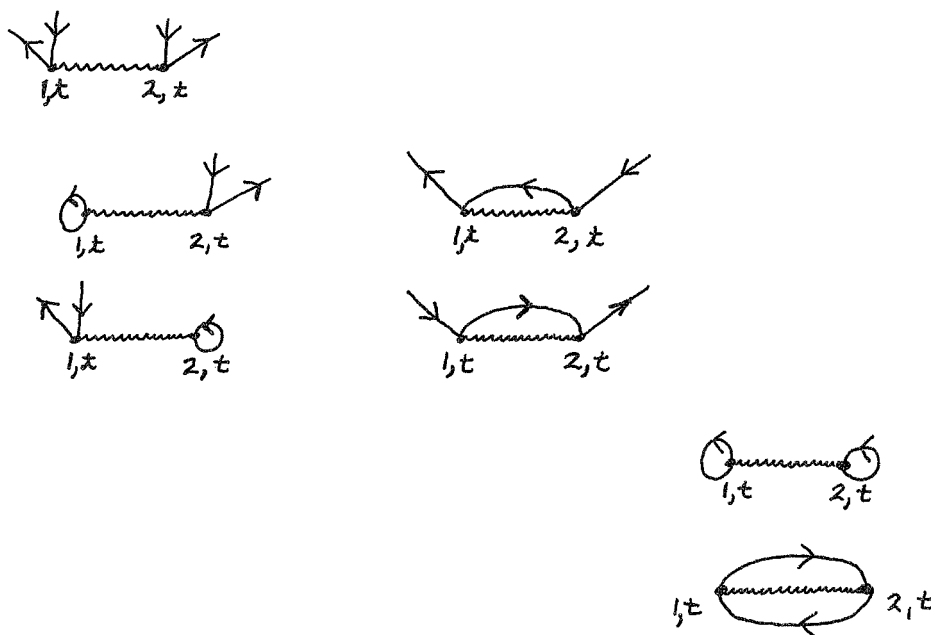
The wavy line represents $V(1,2)$, and integration over the space-spin-time variables is implied. The construction and use of such diagrams is discussed in a number of texts,[4] and so we will not pursue it further here. In the next section we use somewhat different diagrams (Green's function diagrams)[4] to derive an integral equation for the exact two-particle Green's function.

IV. Evaluation of Two-Particle Green's Function

The expression given in Eq. (II.1) for the exact two-particle Green's function $\mathcal{G}$ can be rewritten in a form more amenable to calculation by using the following relations between the Heisenberg and interaction pictures:

$$|\Psi\rangle_H = |\Psi(t=0)\rangle_I = U_I(0,-\infty)|\Phi\rangle \, , \tag{IV.1a}$$

and

$$\psi_H(1,t) = U_I(0,t)\,\psi_I(1,t)\,U_I(t,0) \, , \tag{IV.1b}$$

$$\psi_H^\dagger(1,t) = U_I(0,t)\,\psi_I^\dagger(1,t)\,U_I(t,0) \, . \tag{IV.1c}$$

These relations lead to the following expression for $\mathcal{G}$:

$$\mathcal{G}(1,2,3,4|t-t') = i^{-2}\langle\Phi|T\,U(\infty,t)\,\psi(1,t)\,\psi(2,t)\,U(t,t')$$

$$\psi^\dagger(3,t')\,\psi^\dagger(4,t')\,U(t',-\infty)|\Phi\rangle\left[\langle\Phi|U(\infty,-\infty)|\Phi\rangle\right]^{-1} \, , \tag{IV.2}$$

where the subscript (I) has been dropped for convenience.

The denominator in Eq. (IV.2) can be expressed as the sum of all time-integrated vacuum diagrams,[9] some of which are shown in Fig. (V).

Figure V   Vacuum Diagrams
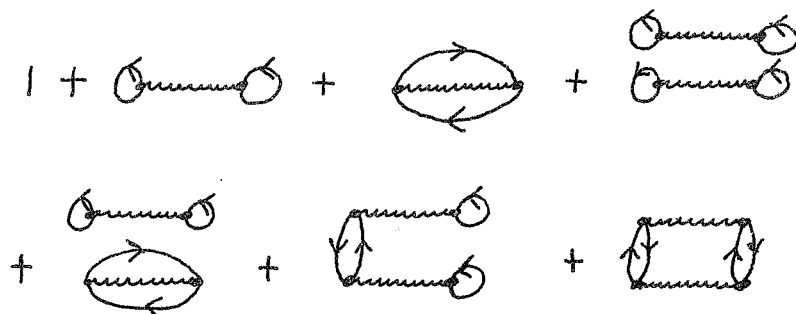
The numerator must be expressed in terms of the so called Green's function diagrams. These diagrams are obtained by expanding as in Eq. (III.10) each of the three U's appearing in the numerator and then using techniques similar to those used in writing the diagrams in Fig. (IV). Some of the Green's function diagrams are shown in Fig. (VI).

Figure VI   Green's Function Diagrams
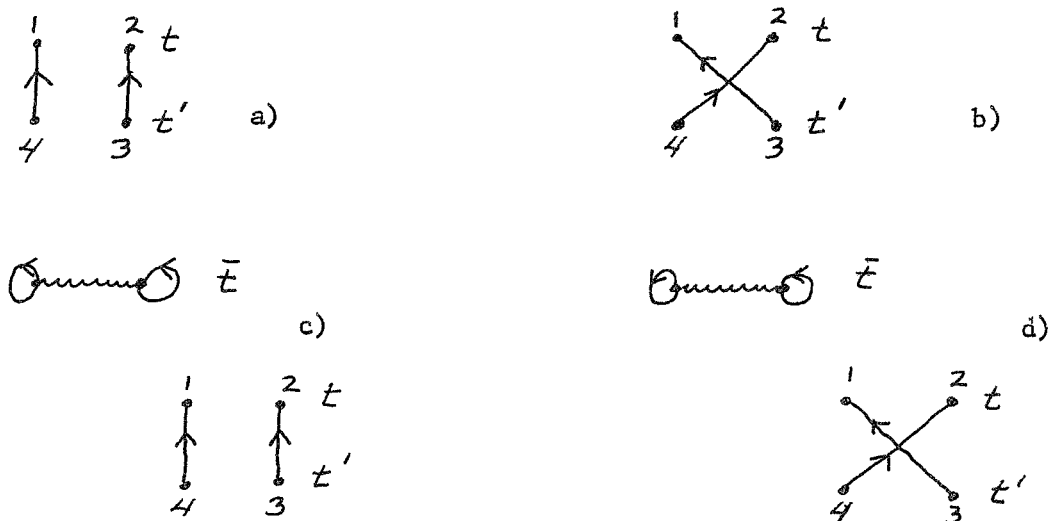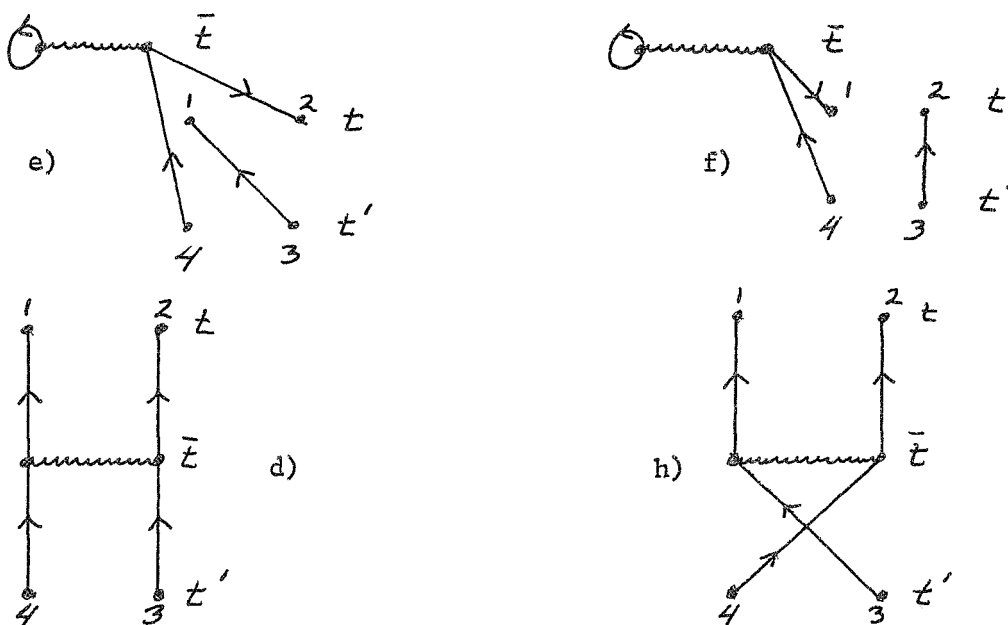
A directed line segment leading from x,t to x',t' represents the unperturbed one-particle Green's function $G^0(x',x,t'-t)$. In these diagrams all time orderings of $\bar{t}$ with respect to t and t' are implied. Then disconnected diagrams such as in c) and d) can be factored into their constituent parts, and, for example, diagrams a) and c) can be combined to give

If higher order diagrams were included in Fig. (VI), we would find that much more factorization of diagrams would occur and that the above

result would generalize to

$$\left(1 + \text{⟨}\cdots\text{⟩} + \text{⟨}\cdots\text{⟩} + \text{⟨}\cdots\text{⟩} + \text{⟨}\cdots\text{⟩} + \cdots \right) \left(\begin{array}{cc} \overset{1}{\uparrow} & \overset{2}{\uparrow} \\ _4 & _3 \end{array} \right)^t_{t'}$$

Notice that the first factor is exactly what we wrote in Fig. (V) for the denominator. This type of factorization occurs for all disconnected diagrams, and thus we can omit such diagrams from the list of Green's function diagrams since they only serve to cancel the denominator. This is the linked-cluster result for Green's functions.

Diagrams a) and b) represent contributions to the unperturbed two-particle Green's function $\mathcal{Y}^0$. Each directed line segment represents an unperturbed one-particle Green's function G^0

$$\uparrow \begin{array}{l} 1, t \\ 4, t' \end{array} = G^0 (1, 4, t - t') ,$$

and so diagrams a) and b) yield

$$\mathcal{Y}^0 (1, 2, 3, 4 | t - t') = G^0 (1, 4, t - t') \, G^0 (2, 3, t - t')$$

$$- G^0 (1, 3, t - t') \, G^0 (2, 4, t - t') .$$

(IV.3)

Diagrams such as e) and f) only serve to convert the unperturbed one-particle Green's function G^0 into the exact one-particle Green's function G. Therefore we can omit diagrams in which the

section containing the wavy line(s) is connected to only one of the directed line segments if we now interpret directed line segments to represent not G^{o} but the exact G .

With these considerations we can write the essential diagrams which contribute to $\mathcal{Y}$. Some of these are given in Fig. (VII).

Figure VII   Essential Contributions to $\mathcal{Y}$
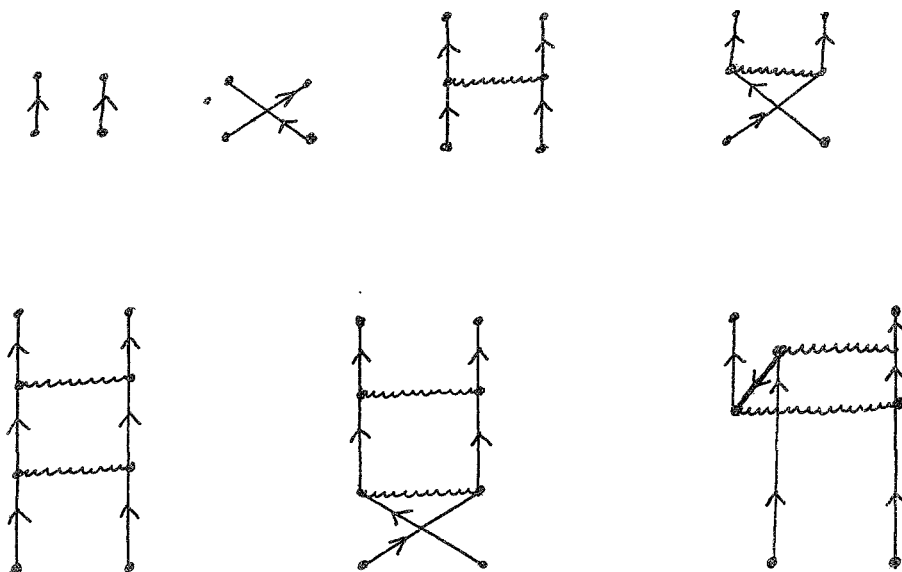
To understand how these diagrams lead to an integral equation for $\mathcal{Y}$ we have written their sum in a slightly different form in Fig. (VIII).

Figure VIII
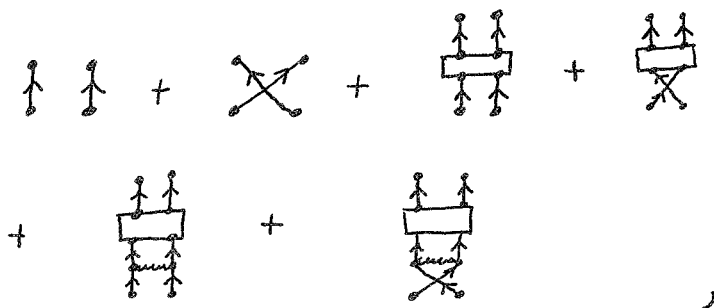
where

The box represents a generalized potential which is non-local in space and time. We recognize that the sum of the diagrams which are attached to the bottom of the box is identical to the sum of the Green's function diagrams given in Fig. (VII). Therefore we can immediately write an equation which $\mathcal{Y}$ must satisfy. From Fig. (VIII) we see that $\mathcal{Y}$ must be a solution of the following integral equation:

$$\mathcal{Y}(1,2,3,4\,|\,t-t') = G(1,4,t-t')\,G(2,3,t-t')$$

$$- G(1,3,t-t')\,G(2,4,t-t') + \int G(1,6,t-\bar{t})\,G(2,5,t-\bar{t})$$

$$\bar{V}(5,6,7,8,\bar{t}-\bar{t}')\,\mathcal{Y}(7,8,3,4\,|\,\bar{t}'-t)\,d5\,d6\,d7\,d8\,d\bar{t}\,d\bar{t}' , \quad \text{(IV.4)}$$

where $\bar{V}$, which is represented by the box in Fig. (VIII), is commonly referred to as the irreducible vertex potential. We can think of $\bar{V}$ as a non-local potential describing the interaction between two particles moving in the "sea" of the remaining particles.

The irreducible vertex potential can be evaluated to any desired order by simply writing all essential Green's function diagrams of that

order and then identifying the contributions to $\bar{V}$ as that which

multiples the factor

$$G(1,6,t-\bar{t})\; G(2,5,t-\bar{t})\; \Big[\; G(7,4,\bar{t}-t')\; G(8,3,\bar{t}-t')$$

$$-\; G(7,3,\bar{t}-t')\; G(8,4,\bar{t}-t')\Big]\;.$$

To prove this statement we expand $\mathcal{Y}$ and $\bar{V}$ in perturbation series

and then write the various orders of Eq. (IV.4) in symbolic notation:

$$\mathcal{Y} = \mathcal{Y}^{\,0} + \mathcal{Y}^{(1)} + \mathcal{Y}^{(2)} + \cdots \tag{IV.5a}$$

$$\bar{V} = \bar{V}^{(1)} + \bar{V}^{(2)} + \cdots \tag{IV.5b}$$

$$\mathcal{Y}^{\,0} = \Big[\, GG - GG \,\Big] \tag{IV.5c}$$

$$\mathcal{Y}^{(1)} = \int GG\; \bar{V}^{(1)} \Big[\, GG - GG \,\Big] \tag{IV.5d}$$

$$\mathcal{Y}^{(2)} = \int GG\; \bar{V}^{(1)} \mathcal{Y}^{(1)} + \int GG\; \bar{V}^{(2)} \Big[\, GG - GG \,\Big] \tag{IV.5e}$$

with

$$\int G G \, \overline{V}^{(1)} \, \underline{\mathcal{Y}}^{(1)} = \int G G \, \overline{V}^{(1)} \int G G \, \overline{V}^{(1)} [G G - G G] , \qquad \text{(IV.5f)}$$

etc.

Thus we see that we can identify $\overline{V}^{(1)}$ as that factor which multiplies GG[GG–GG] in the first-order diagrams; likewise $\overline{V}^{(2)}$ is the factor multiplying GG[GG–GG] in the second-order diagrams. This result can obviously be generalized to higher orders. As an example, let us consider the first-order contribution to $\overline{V}$:

$$\underline{\mathcal{Y}}^{(1)}(1,2,3,4/t-t') = \int G(1,6,t-\bar{t}) \, G(2,5,t-\bar{t})$$

$$\overline{V}^{(1)}(5,6,7,8,\bar{t}-\bar{t}') \, [G(7,4,\bar{t}'-t') \, G(8,3,\bar{t}'-t')$$

$$- G(7,3,\bar{t}'-t') \, G(8,4,\bar{t}'-t')] \, d5\,d6\,d7\,d8\,d\bar{t}\,d\bar{t}' \qquad \text{(IV.6)}$$

The first-order diagrams which contribute can be written as follows:
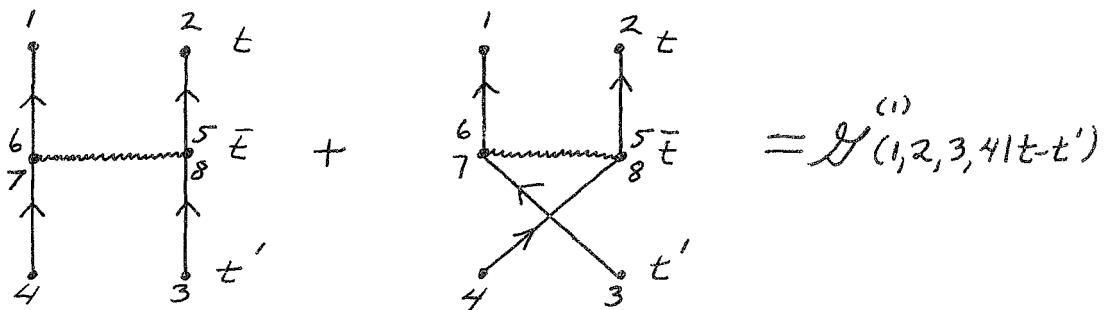
The sum of these two diagrams is equal to

$$
i \int G(1,6,t-\bar{t}) \, G(2,5,t-\bar{t}) \, V(5,6) \Big[G(6,4,\bar{t}-t')
$$

$$
G(5,3,\bar{t}-t') - G(6,3,\bar{t}-t') \, G(5,4,\bar{t}-t') \Big] \, d5 \, d6 \, d\bar{t}
$$

Therefore, we can identify $\bar{V}^{(1)}$ as

$$
\bar{V}^{(1)}(5,6,7,8,\bar{t}-\bar{t}') = i \, \delta(\bar{t}-\bar{t}') \delta(5-8) \delta(6-7) \, V(5,6) \qquad \text{(IV.7)}
$$

Higher order terms can be calculated in a similar fashion.

In the next section we will develop Eq. (IV.4) in more detail, using only the first-order irreducible vertex potential given by Eq. (IV.7). This approximation will be referred to as the extended random-phase approximation (ERPA).

V. ERPA in a Basis

Substituting the first-order approximation for the irreducible vertex potential into the exact Eq. (IV.4), we arrive at the following approximate equation

$$
\mathcal{Y}(1,2,3,4/t-t') = G(1,4,t-t') \, G(2,3,t-t') - G(1,3,t-t')
$$

$$
G(2,4,t-t') + i \int G(1,6,t-\bar{t}) \, G(2,5,t-\bar{t}) \, V(5,6)
$$

$$
\mathcal{Y}(6,5,3,4/\bar{t}-t') \, d5 \, d6 \, d\bar{t} . \qquad \text{(V.1)}
$$

We now assume that the fourier transform of the exact one-particle Green's function is known and is given in the form:[6]

$$G(1,4,E) = \sum_{\alpha=1}^{P_1} g_\alpha \left(E - E_\alpha^+\right)^{-1} \phi_\alpha(1) \, \phi_\alpha^*(4)$$

$$+ \sum_{s=P_1+1}^{P} g_s \left(E - E_s^-\right)^{-1} \phi_s(1) \, \phi_s^*(4) \quad , \tag{V.2}$$

where the E_α^+, and E_s^- are complex numbers with

$$E_\alpha^+ = E_\alpha + i \in \quad , \tag{V.3a}$$

$$E_s^- = E_s - i \in \quad , \tag{V.3b}$$

and the g_i are positive real constants. The number P_1 and the Greek and Roman subscripts are used in the summations to distinguish between those poles which lie above the real axis (E_α^+) and those which lie below (E_s^-). The (not necessarily linearly independent) functions ϕ_i are assumed to be expanded in some chosen basis set of spin-orbitals $\{ \chi_a \}$ as

$$\phi_i(1) = \sum_{a=1}^{M} C_{ia} \chi_a(1) \quad , \tag{V.4}$$

and the C_{ia} are assumed to be known.

The time-dependent one-particle Green's function can be obtained by fourier transform from Eq. (V.2). This gives the following result:

$$G(1,4,t-t') = \Theta(t-t') \, G_+ (1,4,t-t') + \Theta(t'-t) \, G_- (1,4,t-t') \, , \qquad (V.5)$$

where we have defined

$$G_- (1,4,t-t') = -i^{-1} \sum_{\alpha=1}^{P_1} g_\alpha \, exp\left(-i E_\alpha^+ (t-t')\right) \phi_\alpha (1) \, \phi_\alpha^* (4) \qquad (V.6a)$$

$$G_+ (1,4,t-t') = i^{-1} \sum_{s=P_1+1}^{P} g_s \, exp\left(-i E_s^- (t-t')\right) \phi_s (1) \phi_s^* (4) \, , \qquad (V.6b)$$

and $\Theta(t)$ is the unit step function.

With this, we can rewrite Eq. (V.1) as follows:

$$\mathcal{H}(1,2,3,4/t-t') = \Theta(t-t') \Big[G_+ (1,4,t-t') \, G_+ (2,3, t-t') -$$

$$G_+ (1,3,t-t') \, G_+ (2,4,t-t') \Big] + \Theta(t'-t) \Big[G_- (1,4, t-t') G_- (2,3,t-t') -$$

$$G_- (1,3,t-t') \, G_- (2,4,t-t') \Big] + i \int \Big\{ \Theta(t-\bar{t}) \, G_+ (1,6,t-\bar{t})$$

$$G_+ (2,5,t-\bar{t}) + \Theta(t'-t) \, G_- (1,6,t-\bar{t}) \, G_- (2,5, t-\bar{t}) \Big\}$$

$$V(5,6) \, \mathcal{H}(6,5,3,4/\bar{t}-t') \, d\bar{t} \, d5 \, d6. \qquad (V.7)$$

We can then fourier transform this equation to yield the more useful result given below:

$$\mathcal{G}(1,2,3,4|E) = (1 - P_{34})\, G(1,2,3,4|E) + i \int G(1,2,5,6|E)$$

$$V(5,6)\, \mathcal{G}(6,5,3,4|E)\, d5\, d6 , \tag{V.8}$$

where we have defined $G(1,2,3,4|E)$ as the fourier transform of $G(1,4,t-t')\, G(2,3,t-t')$. The operator P_{34} permutes the space-spin variables 3 and 4. Let us now examine the permutation symmetry of factors in Eq. (V.8), remembering that $\mathcal{G}(1,2,3,4|E)$ is anti-symmetric in variables $(1,2)$ and $(3,4)$.

First we consider the integral term:

$$P_{12} \int G(1,2,5,6|E)\, i\, V(5,6)\, \mathcal{G}(6,5,3,4|E)\, d5\, d6 =$$

$$\int G(2,1,5,6|E)\, i\, V(5,6)\, \mathcal{G}(6,5,3,4|E)\, d5\, d6 =$$

$$\int G(1,2,6,5|E)\, i\, V(5,6)\, \mathcal{G}(6,5,3,4|E)\, d5\, d6 =$$

$$\int G(1,2,5,6|E)\, i\, V(6,5)\, \mathcal{G}(5,6,3,4|E)\, d5\, d6 =$$

$$- \int G(1,2,5,6|E)\, i\, V(5,6)\, \mathcal{G}(6,5,3,4|E)\, d5\, d6 \tag{V.9}$$

We have used the fact that $G(1,2,3,4|E)$ is the fourier transform of the product $G(1,4,t)\, G(2,3,t)$, and we recognized that the variables $(5,6)$ are dummy. Hence the integral term is antisymmetric in variables $(1,2)$ and $(3,4)$. Therefore the first term in Eq. (V.8) must also be antisymmetric in $(1,2)$ and $(3,4)$.

Thus we can expand Eq. (V.8) in the following basis of antisymmetric functions:

$$[ab](1,2) = 2^{-1/2}\left(\chi_a(1)\chi_b(2) - \chi_a(2)\chi_b(1) \right) \qquad \text{(V.10)}$$

This results in the matrix equation given below:

$$\mathcal{H}_{ab,cd}(E) = G_{ab,cd}(E) - \sum_{\substack{e<f \\ g<h \\ =1}}^{M} G_{ab,ef}(E)\, V_{ef,gh}\, \mathcal{H}_{gh,cd}(E) \qquad \text{(V.11)}$$

We have made the following identifications:

$$\mathcal{H}(1,2,3,4|E) = \sum_{\substack{a<b \\ c<d \\ =1}}^{M} i^{-1} \mathcal{H}_{ab,cd}(E)\, [ab](1,2)\, [cd]^{*}(3,4) \qquad \text{(V.12a)}$$

$$G_{ab,cd}(E) = \sum_{s,t=P_1+1}^{P} g_s\, g_t\, (E - E_s - E_t)^{-1}\, C_{sa}\, C_{tb}\, C_{tc}^{*}\, C_{sd}^{*}$$

$$- \sum_{\alpha,\beta=1}^{P_1} g_\alpha\, g_\beta\, (E - E_\alpha - E_\beta)^{-1}\, C_{\alpha a}\, C_{\beta b}\, C_{\beta c}^{*}\, C_{\alpha d}^{*} \qquad \text{(V.12b)}$$

and

$$V_{ef,gh} = \int \chi_e(1) \chi_f(2) V(1,2) \left[\chi_g(1) \chi_h(2) - \chi_g(2) \chi_h(1) \right]^* d_1 \, d_2 \quad \text{(V.12c)}$$

Thus given any basis $\left\{ \chi_a, \ a = 1\ldots M \right\}$ and the exact one-particle Green's function as in Eq. (V.2), we can calculate the matrix elements $G_{ab,cd}(E)$ (for any E) and $V_{er,gh}$. Eq. (V.11) is then a simple matrix equation which determines $\mathcal{Y}_{ab,cd}(E)$. We write this equation in matrix form as

$$\mathcal{Y}(E) = G(E) - G(E) \, V \, \mathcal{Y}(E) \quad \text{(V.13)}$$

from which it follows that

$$\mathcal{Y}(E) = \left[G^{-1}(E) + V \right]^{-1} \quad \text{(V.14)}$$

This is the final expression for $\mathcal{Y}(E)$.

Let us now return to the problem of evaluating the second-order density matrix as discussed in Sec. II. Being careful to notice the $1/i$ in Eq. (V.12a), we write the previous expression (Eq. (II.6))

for Γ in matrix notation as follows:

$$\underline{\Gamma} = -(2\pi i)^{-1} \lim_{R \to \infty} \left\{ \int_{\pi/2}^{3\pi/2} \underline{G}(Re^{i\theta}) \, Re^{i\theta} \, i \, d\theta \right.$$

$$\left. + \int_{-R}^{R} \underline{G}(iy) \, i \, dy \right\}, \tag{V.15}$$

with the matrix $\underline{\Gamma}$ defined by

$$\Gamma(1,2,1',2') = \sum_{\substack{a<b \\ c<d \\ =1}}^{M} \underline{\Gamma}_{ab,cd} \; [ab](1,2) \; [cd]^*(1',2') \tag{V.16}$$

The evaluation of the arc integral can be done analytically by noticing (see Eq. (V.12b)) that for large R

$$G_{ab,cd}(Re^{i\theta}) = (Re^{i\theta})^{-1} \left\{ \sum_{s,t=P_1+1}^{P} g_s g_t \, C_{sa} C_{tb} C_{tc}^* C_{sd}^* \right.$$

$$\left. - \sum_{\alpha,\beta=1}^{P_1} g_\alpha g_\beta \, C_{\alpha a} C_{\beta b} C_{\beta c}^* C_{\alpha d}^* \right\}$$

$$= (Re^{i\theta})^{-1} \; B_{ab,cd} \tag{V.17}$$

This defines the matrix $\underset{\sim}{B}$. Therefore the arc integral reduces to

$$\underset{\sim}{\Gamma}_{arc} = -(2\pi i)^{-1} \lim_{R \to \infty} \int_{\pi/2}^{3\pi/2} \left[R e^{i\theta} \underset{\sim}{B}^{-1} + \underset{\sim}{V} \right]^{-1} R e^{i\theta} i \, d\theta$$

$$= -(2\pi)^{-1} \int_{\pi/2}^{3\pi/2} \underset{\sim}{B} \, d\theta$$

$$= -\frac{1}{2} \underset{\sim}{B} \tag{V.18}$$

This result is exact, and is easily evaluated if the exact one-particle Green's function is known.

To calculate the integral along the imaginary axis we resort to the use of numerical integration techniques. However we first write the integral in a form which is most amenable to computer treatment. We notice that each term in $G_{ab,cd}(iy)$ contains factors of the form

$$(iy - E_s - E_t)^{-1} = -\left(y^2 + (E_s + E_t)^2 \right)^{-1} (E_s + E_t + iy) \tag{V.19}$$

Therefore we can write $\underset{\sim}{G}(iy)$ as

$$\underset{\sim}{G}(iy) = \underset{\sim}{G}^{(1)}(y) + i \underset{\sim}{G}^{(2)}(y)$$

where

$$G_{ab,cd}^{(1)}(y) = -\sum_{s,t=P_1+1}^{P} g_s g_t (E_s + E_t)(y^2 + (E_s + E_t)^2)^{-1} C_{sa} C_{tb} C_{tc}^* C_{sd}^*$$

$$+ \sum_{\alpha,\beta=1}^{P_1} {}' g_\alpha g_\beta (E_\alpha + E_\beta)(y^2 + (E_\alpha + E_\beta)^2)^{-1} C_{\alpha a} C_{\beta b} C_{\beta c}^* C_{\alpha d}^* ,$$

(V.20a)

and

$$G_{ab,cd}^{(2)}(y) = -\sum_{s,t=P_1+1}^{P} g_s g_t y (y^2 + (E_s + E_t)^2)^{-1} C_{sa} C_{tb} C_{tc}^* C_{sd}^*$$

$$+ \sum_{\alpha,\beta=1}^{P_1} {}' g_\alpha g_\beta y (y^2 + (E_\alpha + E_\beta)^2)^{-1} C_{\alpha a} C_{\beta b} C_{\beta c}^* C_{\alpha d}^*$$

(V.20b)

We also decompose $\underset{\sim}{G}^{-1}(iy)$ and $\underset{\sim}{\mathscr{G}}(iy)$ into real and imaginary components as

$$\underset{\sim}{G}^{-1}(iy) = \underset{\sim}{T}(y) + i \underset{\sim}{U}(y) ,$$

(V.21a)

and

$$\underset{\sim}{\mathscr{G}}(iy) = \underset{\sim}{\mathscr{G}}^{(1)}(y) + i \underset{\sim}{\mathscr{G}}^{(2)}(y) .$$

(V.21b)

To determine $\underset{\sim}{T}(y)$ and $\underset{\sim}{U}(y)$ we write the real and imaginary parts of the identity

$$\left(\underset{\sim}{G}^{(1)}(y) + i \underset{\sim}{G}^{(2)}(y) \right)\left(\underset{\sim}{T}(y) + i \underset{\sim}{U}(y) \right) = \underset{\sim}{1} \qquad (V.22)$$

This results in the following matrix equations:

$$\underset{\sim}{T}(y) = \left[\underset{\sim}{G}^{(1)}(y) + \underset{\sim}{G}^{(2)}(y) \underset{\sim}{G}^{(1)}(y)^{-1} \underset{\sim}{G}^{(2)}(y) \right]^{-1} \qquad (V.23a)$$

and

$$\underset{\sim}{U}(y) = - \underset{\sim}{G}^{(1)}(y)^{-1} \underset{\sim}{G}^{(2)}(y) \underset{\sim}{T}(y) \qquad (V.23b)$$

Then knowing $\underset{\sim}{T}(y)$, $\underset{\sim}{U}(y)$, and $\underset{\sim}{V}$ we can write Eq. (V.14) as

$$\left[\underset{\sim}{T}(y) + \underset{\sim}{V} + i \underset{\sim}{U}(y) \right]\left[\underset{\sim}{\mathcal{Y}}^{(1)}(y) + i \underset{\sim}{\mathcal{Y}}^{(2)}(y) \right] = \underset{\sim}{1}$$

which yields the following equations for $\underset{\sim}{\mathcal{Y}}^{(1)}(y)$ and $\underset{\sim}{\mathcal{Y}}^{(2)}(y)$:

$$\underset{\sim}{\mathcal{Y}}^{(1)}(y) = \left[\underset{\sim}{T}(y) + \underset{\sim}{V} + \underset{\sim}{U}(y) \left(\underset{\sim}{T}(y) + \underset{\sim}{V} \right)^{-1} \underset{\sim}{U}(y) \right]^{-1} \qquad (V.24a)$$

$$\underset{\sim}{\mathcal{Y}}^{(2)}(y) = - \left(\underset{\sim}{T}(y) + \underset{\sim}{V} \right)^{-1} \underset{\sim}{U}(y) \underset{\sim}{\mathcal{Y}}^{(1)}(y) \ . \qquad (V.24b)$$

Because $G^{(1)}(y)$ is an even function of y (see Eq. (V.20a))
and $G^{(2)}(y)$ is an odd function of y, it can easily be seen that
$\mathscr{Y}^{(1)}(y)$ is even in y and $\mathscr{Y}^{(2)}(y)$ is odd in y. Therefore
$\mathscr{Y}^{(2)}(y)$ will not contribute to the integral along the imaginary
axis because we integrate from -R to R. As a result of the above
analysis we can now write the imaginary axis integral as follows:

$$\Gamma_{axis} = -\pi^{-1} \lim_{R \to \infty} \int_{0}^{R} \left[T(y) + V + U(y)\left(T(y) + V\right)^{-1} U(y) \right]^{-1} dy \qquad (V.25)$$

where we have used the fact that $\mathscr{Y}^{(1)}(y)$ is an even function of y.
This integral is evaluated numerically.

To review our formal discussion of the calculation of density
matrices using Green's function techniques, we now outline the method
for determining the second-order density matrix Γ.

We assume that we are given the one-particle Green's
function as in Eq. (V.2) as well as a set of basis
functions $\left\{ \chi_a, a=1,2,\ldots M \right\}$. The procedure then is
as follows:

1) Form the matrix B defined in Eq. (V.17). The contribution
to Γ from the arc integral is immediately written as:

$$\Gamma_{arc} = -\frac{1}{2} B .$$

2) Calculate the matrix V defined in Eq. (V.12c).

3) Set y equal to zero.

4) Use Eq. (V.20a) and Eq. (V.20b) to evaluate $G^{(1)}(y)$ and

$\underline{G}^{(2)}(y)$ for the current value of y.

5)   Use Eqs. (V.23) and (V.24) to obtain $\underline{\mathscr{Y}}^{(1)}(y)$.

6)   Increase y by some small increment, and return to step 4) after adding the contribution to $\underline{\Gamma}$ from this iteration.

The results of such a calculation are presented in the next section.   Hopefully this method will prove to be very useful for calculating second-order density matrices of reasonable accuracy for atomic systems.   Certainly it represents a new and interesting method which should be investigated a great deal more in the future.

VI   Results and Discussion

We have applied the Green's function method described above to the ground state ('S) of the helium atom.   The basis[10] of five S-type Slater orbitals (normalized) which were used in the present calculation are described in Table I.

Table I.   Slater Basis

n	exponent
1	1.4191
1	2.5722
2	4.2625
3	3.9979
3	5.4863

It was found to be sufficient to take the upper limit (Rmax.) of the numerical integration equal to 1000 atomic units. The total calculation took five minutes on a Univac 1108 computer.

Because helium is a two-electron system we can extract the wave function from our calculation of the second-order density matrix. The radial part of the singlet wave function can be expanded in the following set of symmetrized functions:

$$\Phi_{ii} = \eta_i (1) \, \eta_i (2)$$

$$\Phi_{ij} = (2)^{-1/2} \left[\eta_i (1) \eta_j (2) + \eta_j (1) \eta_i (2) \right], \quad i < j$$

where the η_i are the five Hartree-Fock orbitals constructed from the above Slater orbitals. In Table II the expansion coefficients for the wave function obtained from the Green's function technique are compared to those for a complete C.I. wave function within the same basis.

Table II.   Expansion Coefficients for the Wave Function

i	j	C.I.	Green's Function
1	1	.99969	.99968
1	2	-.02327	-.02330
1	3	.00697	.00699
1	4	-.00318	-.00323
1	5	.00245	.00250
2	2	.00303	.00313
2	3	-.00151	-.00155
2	4	.00078	.00084
2	5	.00066	.00071
3	3	.00050	.00060
3	4	-.00039	-.00042
3	5	-.00040	-.00044
4	4	-.00009	-.00014
4	5	.00024	.00026
5	5	-.00020	-.00028

The wave function obtained from the Green's function calculation seems to be in excellent agreement with the C.I. wave function.   It is not surprising then that the energies reported in Table III are in such close agreement for the two calculations.

Table III. Predicted Energy

Method	Energy
Hartree-Fock	-2.8617 a.u.
C.I.	-2.8790 a.u.
Green's Function	-2.8780 a.u.

It is important to note that we must compare our results to the
complete C.I. calculation within the original basis rather than to
the results of more extensive computations.

Although the results of this calculation are encouraging they do
not constitute a proof that the Green's function method will be a
useful tool for larger systems. In order to intelligently evaluate
the method, we must have numerical results from many more computations.
Hopefully these calculations will be performed in the near future.

In review then we see that in this chapter we have described
in considerable detail the application of Green's function techniques
to the calculation of the second-order density matrix for an interacting
N-fermion system. We derived an integral equation for the two-particle
Green's function $\mathcal{H}$ which was reduced, after making the extended
random-phase approximation, to a matrix equation. We then obtained
an expression for the density matrix Γ involving a contour integral
of $\mathcal{H}$. The evaluation of this integral was discussed.

We have also presented the results of applying this method to the
ground state of the helium atom. Although such calculations have never
before been carried out, we believe that these techniques will prove
to be very useful in atomic and molecular problems. The most appealing

aspect of Green's functions is that they provide a means of directly calculating reduced quantities without ever having to obtain an N-particle wave function. Certainly this reason alone is sufficient to justify further research.

References

1. W. P. Reinhardt and J. D. Doll, J. Chem. Phys. $\underline{50}$, 2767 (1969).

2. Because of the fermi statistics, we have the following equal time commutation relations: $[\psi^+(x,t), \psi(y,t)]_+ = \delta(x-y)$ $[\psi^+(x,t), \psi^+(y,t)]_+ = 0 = [\psi(x,t), \psi(y,t)]_+$, where the symbol $[,]_+$ means anticommutator.

3. $\Gamma(1,2,1',2') = - \Gamma(2,1,1',2') = - \Gamma(1,2,2',1')$. Similarly for $\mathscr{Y}$.

4. March, Young, and Sampanthar, _The Many-Body Problem in Quantum Mechanics_, Cambridge Univ. Press, 1967.

5. Thouless, _The Quantum Mechanics of Many-Body Systems_, Academic Press (1961).

6. See for example: A. J. Layzer, Phys. Rev. $\underline{129}$, 897 (1963).

7. C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) $\underline{A191}$, 39 (1947).

8. Holes are vacancies in the one-particle functions that are occupied in $|\bar{\Phi}>$; particles are one-particle functions which are unoccupied in $|\bar{\Phi}>$.

9. Vacuum diagrams are those with no free creation or annihilation lines.

10. We are grateful to Prof. W. P. Reinhardt for providing us with his one-particle Green's function results.

CHAPTER THREE

CONSTRUCTION OF APPROXIMATELY

N-REPRESENTABLE DENSITY MATRICES

I. Introduction

It is well-known that the second-order reduced density matrix is sufficient to determine all observable properties for systems composed of pairwise interacting particles. In addition the second-order density matrix is a function of only twelve continuous variables, whereas the system wave function[1] depends on 3N continuous variables. These observations, together with the knowledge that accurate wave functions become much more difficult to obtain as the number of particles increases, lead us to investigate possible methods for directly determining reduced density matrices.

One cannot merely use trial second-order density matrices in a variational calculation of the energy; there is no variational principle for arbitrary density matrices. One $\underline{\text{must}}$ restrict the class of trial density matrices to those which can be expressed as

$$\Gamma(1,2;1',2') = \binom{N}{2} \int \psi(1,2,\cdots N) \, \psi^{*}(1',2',\cdots N) \, d\tau_3 \cdots d\tau_N, \quad \text{(I.1)}$$

where the normalized N-particle wave function ψ (1,2,..N) is anti-symmetric in all of the space-spin variables represented by the integers 1,2,..N. Such density matrices are said to be N-representable. The problem of determining necessary and sufficient conditions to guarantee that a proposed second-order density matrix Γ can be obtained from an antisymmetric wave function as in Eqn. (I.1) is known as the pure state N-representability problem. The exact solution of this problem has not been found, but some progress has been made[2,3,4] toward obtaining nearly N-representable density matrices which can be used in variational

calculations. Very few numerical applications[4] of these methods have

been carried out.

Another more promising method which has been successfully applied

to atomic[5,6] and molecular[7] problems is the Green's function technique.

This is a potentially exact scheme in which the first-order (second-

order) density matrix is obtained as a contour integral involving the

Fourier transform of the one-particle (two-particle) Green's function.

The evaluation of the contour integral is done numerically on an auto-

matic computer, which is a distinct disadvantage of the method.

In this chapter we present a new method for approximating, in a self-

consistent fashion, the first- and second-order reduced density matrices

for systems of N pairwise-interacting fermions. Unlike the Green's

function technique, this method requires no time-consuming numerical

integration.

Within this scheme, one can bound the errors in expectation values obtained

by using the resultant density matrices which might not be N-representable.

This test involves formally generating a special wave function whose

reduced density matrices are then compared to the density matrices

obtained using the proposed procedure.

Before developing the formalism of our method, we briefly review in

Sec. II the generalized random-phase approximation (GRPA) as presented

by Rowe[8]. In Sec. III we discuss the occupation number representation

of density matrices and their spin components. In Sec. IV the GRPA

is used to evaluate certain contributions to the second-order density

matrix. Sec. V contains closed expressions for the spin components

of the first-order density matrix. In Sec. VI we discuss a scheme which

allows the self-consistent determination of the first- and second-order

density matrices. Sec. VII contains the results of applying the method to the helim, lithium, and beryllium atoms. We discuss possible error bounds involving the resultant density matrices in Sec. VIII. Sec. IX contains our concluding remarks.

II. The Generalized Random-Phase Approximation

The equations-of-motion method was originally developed by nuclear physicists[8] as a technique for directly determining excitation energies and ground state[9] transition strengths for nuclei. It is expected that these relative quantities will not be as sensitive to correlations within the stationary-state wave functions as, for example, the energies of the individual states. Thus the results of such calculations often imply a higher order of ground-state correlation than would be expected by considering the approximations made within the method. The GRPA occurs as a special case of the equations-of-motion method.

As an approach[10] to the equations-of-motion technique, let us recall the operator equations for a harmonic oscillator of frequency ω, and Hamiltonian H :

$$[H, \mathcal{O}^{\dagger}] = \omega \mathcal{O}^{\dagger}, \quad [H, \mathcal{O}] = -\omega \mathcal{O}, \qquad \text{(II.1)}$$

$$[\mathcal{O}, \mathcal{O}^{\dagger}] = 1, \qquad \text{(II.2)}$$

where we have chosen to use units in which $\hbar = 1$. In attempting to approximately solve Eqns. (II.1) and (II.2) we will expand the unknown operators ($\mathcal{O}$ and $\mathcal{O}^{\dagger}$) and the Hamiltonian in a basis of known operators. These equations will then allow us to determine the expansion coefficients and the excitation energies . Before doing this we transform Egns. (II.1) and (II.2) into forms which will be more easily used.

If we define the usual set of eigenfunctions and eigenvalues by

$$\Theta |o\rangle = 0, \qquad \Theta^\dagger |o\rangle = |1\rangle,$$

$$\Theta^\dagger |n\rangle = (n+1)^{1/2} |n+1\rangle,$$

$$E_n = (n + 1/2) \omega, \tag{II.3}$$

the solution to Eqns. (II.1) and (II.2) is given as follows:

$$\Theta^\dagger = \sum_{n=0}^{\infty} (n+1)^{1/2} |n+1\rangle\langle n|,$$

and therefore

$$\Theta = \sum_{n=0}^{\infty} (n+1)^{1/2} |n\rangle\langle n+1| \tag{II.4}$$

It is easily seen that these operators are raising and lowering operators respectively with respect to the Hamiltonian (energy).

To extend this type of treatment to more general Hamiltonians, we assume that the spectrum of our Hamiltonian is harmonic up to the mth ·level, i.e.

$$E_{n+1} - E_n = \omega, \qquad n \le m, \tag{II.5}$$

where ω is a constant. The space spanned by the (m+1) lowest eigenfunctions of H is referred to as the harmonic region of Hilbert space. If the spectrum of H is not at all harmonic, then m=o and the harmonic region is the one-dimensional space spanned by the ground state. In any case Eqn. (II.5) serves to define ω.

Based on the above discussion, we choose to consider the following

proposed form for the excitation operator:

$$O^\dagger = \sum_{n=0}^{m} (n+1)^{1/2} |n+1\rangle\langle n| + \sum_{p,q > m} C_{pq} |p\rangle\langle q|, \tag{II.6}$$

with arbitrary C_{pq}. For this operator we can write equations which resemble Eqns. (II.1) and (II.2):

$$[H, O^\dagger] = \omega O^\dagger + P,$$
$$[H, O] = -\omega O - P^\dagger, \tag{II.7}$$
$$[O, O^\dagger] = 1 + Q, \tag{II.8}$$

where

$$P|n\rangle = P^\dagger|n\rangle = Q|n\rangle = Q^\dagger|n\rangle = 0, \quad n \leq m. \tag{II.9}$$

It is clear from the above results that Eqns. (II.7) and (II.8) are identical with Eqns. (II.1) and (II.2), provided that we restrict the operators to the harmonic region of Hilbert space. This is important because we are eventually going to take expectation values of all equations with respect to functions belonging to the harmonic region. Although the excitation operator given by Eqn. (II.6) does not exactly obey Eqn. (II.1), it does satisfy Eqn. (II.1) within the harmonic space.

To obtain more useful equations we premultiply the first equation of (II.7) by an _arbitrary_ operator R and the second by $R^\dagger$. Then take the expectation value of the first plus the adjoint of the second with respect to a wave function $|\phi\rangle$ lying within the harmonic space. This gives the following result:

$$\langle\phi| [R, [H, O^\dagger]] |\phi\rangle = \omega \langle\phi| [R, O^\dagger] |\phi\rangle, \tag{II.10}$$

for arbitrary R . In a similar fashion we obtain an analogous

equation involving Θ:

$$\langle \phi | [R, [H, \Theta]] | \phi \rangle = -\omega \langle \phi | [R, \Theta] | \phi \rangle, \qquad \text{(II.11)}$$

for arbitrary R. Also it follows directly from Eqns. (II.8) and

(II.9) that

$$\langle \phi | [\Theta, \Theta^\dagger] | \phi \rangle = 1 . \qquad \text{(II.12)}$$

If the harmonic region is one-dimensional, $|\phi\rangle$ must be the <u>exact</u>

<u>ground state of the system</u>. In this case Eqn. (II.11) is the Hermitian

conjugate of Eqn. (II.10), so we need only consider one of them. If

$|\phi\rangle$ is only an approximation to the ground state wave function, Eqns.

(II.10) and (II.11) are not simply Hermitian conjugates of one another.

To regain this Hermitian relationship, we generalize Eqn. (II.10) in

the following way:

$$\langle \phi | [R, H, \Theta^\dagger] | \phi \rangle = \omega \langle \phi | [R, \Theta^\dagger] | \phi \rangle \qquad \text{(II.13)}$$

for arbitrary R. The double commutator symbol $[R, H, \Theta^\dagger]$ is defined

by

$$2[R, H, \Theta^\dagger] = [R, [H, \Theta^\dagger]] + [[R, H], \Theta^\dagger]. \qquad \text{(II.14)}$$

If $|\phi\rangle$ is the exact ground state, Eqn. (II.13) is identical to

Eqn. (II.10).

The solutions $\Theta_k^\dagger$ of Eqn. (II.13) are to be interpreted as

excitation operators which generate excited state wave functions when

operating on the ground state $|\phi\rangle$:

$$|k\rangle = O_k^+ \; |\phi\rangle \qquad (II.15)$$

The energy ω_k associated with O_k^+ then represents the excitation energy

from the ground state $|\phi\rangle$ to the excited state $|k\rangle$. To derive the

generalized random-phase approximation we restrict the excitation

operator to be of the following form:

$$O_k^+ = \sum_{m,\epsilon} \left(g_{m\epsilon}(k) C_m^+ C_\epsilon - h_{m\epsilon}(k) C_\epsilon^+ C_m \right), \qquad (II.16)$$

where the C_i^+ and C_i are fermion creation and annihilation operators

respectively and the $g_{m\epsilon}(k)$, $h_{m\epsilon}(k)$ are coefficients. The index m

is summed over all single-particle functions (spin orbitals) which

are unoccupied in the single-determinant approximation to the exact

ground state function[11]. Similarly ϵ is summed over all occupied spin-

orbitals. Inserting Eqn. (II.16) into Eqn. (II.13) and using the fact

that Eqn. (II.13) must hold for any R within the space of operators

spanned by $\left\{ C_m^+ C_\epsilon, C_\epsilon^+ C_m \right\}$, we arrive at a set of equations for the

coefficients $g_{m\epsilon}(k)$, $h_{m\epsilon}(k)$, which can be written in matrix form:

$$\begin{pmatrix} A & B \\ -B^+ & -A^* \end{pmatrix} \begin{pmatrix} g \\ h \end{pmatrix} = \omega \begin{pmatrix} U & O \\ O & U^* \end{pmatrix} \begin{pmatrix} g \\ h \end{pmatrix} \qquad (II.17)$$

with

$$A_{m\epsilon, n\theta} = \langle \phi | [C_\epsilon^+ C_m, H, C_n^+ C_\theta] | \phi \rangle,$$

$$B_{m\epsilon, n\theta} = \langle \phi | [C_\epsilon^+ C_m, H, C_\theta^+ C_n] | \phi \rangle,$$

$$U_{m\epsilon, n\theta} = \langle \phi | [C_\epsilon^+ C_m, C_n^+ C_\theta] | \phi \rangle. \qquad (II.18)$$

If we assume that the Hamiltonian can be written as

$$H = \sum_{ij} f_{ij} \, C_i^\dagger C_j + 2^{-1} \sum_{ijkl} V_{ijkl} \, C_i^\dagger C_j^\dagger C_l C_k \, ,$$

the expressions given in Eqn. (II.18) can be evaluated exactly.
Because the results are somewhat lengthy we will not reproduce them
here, but rather we refer the interested readers to page 161 of Rowe's
article.

If we now assume that the Hartree-Fock single-particle density is
reasonably close to the true single-particle density, the expressions
given by Rowe reduce to[37]

$$A_{m\epsilon, n\theta} = \delta_{mn} \delta_{\epsilon\theta} (\bar{\epsilon}_m - \bar{\epsilon}_\theta)(\gamma_\theta - \gamma_m) + \tilde{V}_{m\theta, \epsilon n}$$

$$\cdot (\gamma_\epsilon + \gamma_\theta - \gamma_m - \gamma_m - 1) \, ,$$

$$B_{m\epsilon, n\theta} = \tilde{V}_{mn \, \epsilon\theta} (\gamma_\epsilon + \gamma_\theta - \gamma_m - \gamma_n - 1) \, ,$$

$$U_{m\epsilon, n\theta} = \delta_{mn} \delta_{\epsilon\theta} (\gamma_\epsilon - \gamma_m) \, , \tag{II.19}$$

where all subscripts refer to the Hartree-Fock spin orbitals. We
have introduced the <u>exact</u> single-particle density

$$\gamma_m = \langle \phi | C_m^\dagger C_m | \phi \rangle \, ,$$

$$\gamma_\theta = \langle \phi | C_\theta^\dagger C_\theta | \phi \rangle \, , \tag{II.20}$$

the Hartree-Fock eigenvalues $\bar{\epsilon}_i$, and the two-particle interaction
including exchange

$$\tilde{V}_{mn, \epsilon\theta} = V_{mn, \epsilon\theta} - V_{mn, \theta\epsilon} \, . \tag{II.21}$$

Equations (II.17) and (II.19) are referred to as the GRPA equations.

When the spin of the particles (assumed to be spin 1/2) is taken into consideration, the set of excitation operators $\{ O_k^+ \}$ can be separated into singlets and triplets. By defining a basis of singlet and triplet operators[12]

$$D_{m\epsilon}^{1\,\dagger} = (2)^{-1/2} \left(C_{m\alpha}^{\dagger} C_{\epsilon\alpha} + C_{m\beta}^{\dagger} C_{\epsilon\beta} \right),$$

$$D_{m\epsilon}^{3,0\,\dagger} = (2)^{-1/2} \left(C_{m\alpha}^{\dagger} C_{\epsilon\alpha} - C_{m\beta}^{\dagger} C_{\epsilon\beta} \right),$$

$$D_{m\epsilon}^{3,1\,\dagger} = C_{m\alpha}^{\dagger} C_{\epsilon\beta},$$

$$D_{m\epsilon}^{3,-1\,\dagger} = C_{m\beta}^{\dagger} C_{\epsilon\alpha}, \tag{II.22}$$

we can write the singlet and triplet excitation operators as follows:

$$O_k^{1\,\dagger} = \sum_{m\epsilon} \left(g_{m\epsilon}^1(k) D_{m\epsilon}^{1\,\dagger} - h_{m\epsilon}^1(k) D_{m\epsilon}^1 \right),$$

$$O_k^{3,M_s\,\dagger} = \sum_{m\epsilon} \left(g_{m\epsilon}^3(k) D_{m\epsilon}^{3,M_s\,\dagger} - h_{m\epsilon}^3(k) D_{m\epsilon}^{3,M_s} \right) \quad M_s = 1,0,-1.[13] \tag{II.23}$$

The GRPA equations (II.17) also separate into singlet and triplet equations, with the matrix elements being given by

$$A_{m\epsilon,n\theta}^{1(3)} = (2)^{-1} \left(\delta_{mn} \delta_{\epsilon\theta} \left(\bar{\epsilon}_m - \bar{\epsilon}_\theta \right) \left(\gamma_\theta^0 - \gamma_m^0 \right) + \tilde{V}_{m\theta,\epsilon n} \left(\gamma_\epsilon^0 + \gamma_\theta^0 - \gamma_m^0 - \gamma_n^0 - 2 \right) \overset{+}{(-)} V_{m\theta,\epsilon n} \left(\gamma_\epsilon^0 + \gamma_\theta^0 - \gamma_m^0 - \gamma_n^0 - 2 \right) \right),$$

$$B_{m\epsilon,n\theta}^{1(3)} = (2)^{-1} \left(\tilde{V}_{mn,\epsilon\theta} \left(\gamma_\epsilon^0 + \gamma_\theta^0 - \gamma_m^0 - \gamma_n^0 - 2 \right) \overset{+}{(-)} V_{mn,\epsilon\theta} \left(\gamma_\epsilon^0 + \gamma_\epsilon^0 - \gamma_m^0 - \gamma_n^0 - 2 \right) \right),$$

$$U_{m\epsilon,n\theta}^{1(3)} = (2)^{-1} \delta_{mn} \delta_{\epsilon\theta} \left(\gamma_\epsilon^0 - \gamma_m^0 \right). \tag{II.24}$$

The diagonal elements of the charge density matrix are defined as

$$\gamma_\epsilon^0 = \langle \phi | C_{\epsilon\alpha}^\dagger C_{\epsilon\alpha} + C_{\epsilon\beta}^\dagger C_{\alpha\beta} | \phi \rangle ,$$

$$\gamma_m^0 = \langle \phi | C_{m\alpha}^\dagger C_{m\alpha} + C_{m\beta}^\dagger C_{m\beta} | \phi \rangle . \tag{II.25}$$

To convert the GRPA equations to their final form we premultiply

Eqn. (II.17) by the (diagonal) matrix

$$\begin{pmatrix} U^{-1/2} & O \\ O & U^{-1/2} \end{pmatrix}$$

which is well-defined because the elements of the (diagonal) matrix U

are positive. This leads to a set of equations which can be written

in matrix form as follows:

$$\begin{pmatrix} A & B \\ -B^\dagger & -A^* \end{pmatrix} \begin{pmatrix} \bar{g} \\ \bar{h} \end{pmatrix} = \omega \begin{pmatrix} \bar{g} \\ \bar{h} \end{pmatrix} , \tag{II.26}$$

with

$$\bar{g}_{m\epsilon}^{1(3)}(k) = (2)^{-1/2} \left(\gamma_\epsilon^0 - \gamma_m^0 \right)^{1/2} g_{m\epsilon}^{1(3)}(k) ,$$

and

$$\bar{h}_{m\epsilon}^{1(3)}(k) = (2)^{-1/2} \left(\gamma_\epsilon^0 - \gamma_m^0 \right)^{1/2} h_{m\epsilon}^{1(3)}(k) . \tag{II.27}$$

The matrix elements appearing in Eqn. (II.26) are given by

$$A_{m\epsilon,n\theta}^{1(3)} = \delta_{mn} \delta_{\epsilon\theta} \left(\bar{\epsilon}_m - \bar{\epsilon}_\theta \right) + (2)^{-1} \left(\gamma_\epsilon^0 - \gamma_m^0 \right)^{1/2}$$

$$\left(\gamma_\theta^0 - \gamma_n^0 \right)^{1/2} \left(\tilde{V}_{m\theta,\epsilon n} \overset{+}{(-)} V_{m\theta,\epsilon n} \right) ,$$

and

$$B_{m\epsilon,n\theta}^{1(3)} = (2)^{-1}(\gamma_\epsilon^0 - \gamma_m^0)^{1/2}(\gamma_\theta^0 - \gamma_n^0)^{1/2}(\tilde{V}_{mn,\epsilon\theta} \overset{+}{\underset{\omega}{}} V_{mn,\epsilon\theta}). \qquad (II.28)$$

This is the working form of the GRPA equations[14].

We have thus reduced the problem of finding the approximate excitation operators O_k^+ and their associated energies ω_k to a fairly simple matrix eigenvalue equation. Given the Hartree-Fock orbitals and eigenvalues and the <u>exact</u> charge density matrix, we could use Eqn. (II.28) to form the A and B matrices. Standard numerical techniques would then yield the eigenvalues and eigenvectors of the (unsymmetric) matrix

$$\begin{pmatrix} A & B \\ -B^+ & -A^* \end{pmatrix}.$$

We defer until Sec. VI the problem of obtaining the exact charge density matrix. Orthogonality and normalization of the eigenvectors of matrices such as the above are discussed clearly in Rowe's article, as are the conditions which guarantee that the eigenvalues ω_k will be real. We will not go into these details here.

Let us assume that the GRPA equations (II.26) have been solved and that the exact charge density matrix is known. The coefficients $g_{m\epsilon}^{1(3)}(k)$, $h_{m\epsilon}^{1(3)}(k)$ which appear in the expression (II.23) for O_k^+ are given by Eqn. (II.27). The approximate "excited states" can then be written as follows:

$$|k,0,0\rangle = O_k^{1\,+}|\phi\rangle$$
$$|k,1,M_s\rangle = O_k^{3,M_s\,+}|\phi\rangle, \qquad (II.29)$$

with obvious notation[15]

Suppose now that we wish to evaluate the transition value of some operator Q between the ground state $|\phi\rangle$ and one of these approximate excited states, e.g.

$$\langle\phi|Q|k,0,0\rangle = \langle\phi|Q\,O_k^{1\dagger}|\phi\rangle .$$

Using the fact that $|\phi\rangle$ is the ground state, we can write

$$O_k^{1}|\phi\rangle = 0 \qquad \text{to obtain the result}$$

$$\langle\phi|Q|k,0,0\rangle = \langle\phi|[Q,O_k^{1\dagger}]|\phi\rangle . \tag{II.30}$$

Thus to calculate transition values of Q we need only know the ground state expectation value of the commutator of Q with the appropriate excitation operator. This is the use which will be made of the GRPA in Sec. IV.

III. Density Matrices in the Occupation Number Representation

The first-and second-order density matrices corresponding to the wave function $|\phi\rangle$ can be written as follows[16]:

$$\gamma(1;1') = \langle\phi|\psi^{\dagger}(1')\psi(1)|\phi\rangle ,$$

and

$$2\,\Gamma(1,2;1',2') = \langle\phi|\psi^{\dagger}(1')\psi^{\dagger}(2')\psi(2)\psi(1)|\phi\rangle , \tag{III.1}$$

where the arguments $1,2,1',2'$ refer to space-spin coordinates, and the expectation value is taken with respect to the occupation number

representative of $|\phi\rangle$. ψ^+ and ψ are fermion field creation and annihilation operators respectively. By expanding the field operators in a complete orthonormal set of spin orbitals $\{\phi_i(r) \frac{\alpha}{\beta}\}$ we can decompose the above expressions for γ and Γ into spin components, e.g.

$$\gamma(1; 1') = \sum_{ij} \{ \phi_i^*(r_1') \phi_j(r_1) \alpha^\dagger \alpha \langle \phi| C_{i\alpha}^\dagger C_{j\alpha} |\phi\rangle$$

$$+ \phi_i^*(r_1') \phi_j(r_1) \beta^* \beta \langle \phi| C_{i\beta}^\dagger C_{j\beta} |\phi\rangle \}. \qquad \text{(III.2)}$$

There is an analogous expression for Γ involving six terms[17]. In writing Eqn. (III.2) we have assumed that the state $|\phi\rangle$ is an eigenstate of the operator S_z . This allows us to write:

$$\langle\phi| C_{i\sigma}^\dagger C_{j\sigma'} |\phi\rangle = \delta_{\sigma\sigma'} \langle\phi| C_{i\sigma}^\dagger C_{j\sigma} |\phi\rangle , \qquad \text{(III.3)}$$

where σ and σ' represent either of the one-electron spin functions α, β .

As a matter of choice we will restrict the remainder of the development to the most frequently used spin components of Γ . This restriction is by no means necessary to the treatment; the method can be applied to any other spin components with minor modifications.

The one-electron charge-and spin-density matrices are respectively:

$$\gamma^0(1; 1') = \sum_{ij} \gamma_{ji}^0 \phi_i^*(r_1') \phi_j(r_1),$$

$$\gamma_{ji}^0 = \langle\phi| C_{i\alpha}^\dagger C_{j\alpha} + C_{i\beta}^\dagger C_{j\beta} |\phi\rangle,[18]$$

and

$$\gamma^{z}(1;1') = \sum_{ij} \gamma_{ji}^{z} \phi_i^*(r_1') \phi_j(r_1),$$

$$\gamma_{ji}^{z} = \langle \phi | C_{i\alpha}^{\dagger} C_{j\alpha} - C_{i\beta}^{\dagger} C_{j\beta} | \phi \rangle. \qquad (III.4)$$

The analogous components of the second-order density matrix are defined as follows:

$$2\Gamma_{k\ell,ij}^{o} = \langle \phi | C_{i\alpha}^{\dagger} C_{j\alpha}^{\dagger} C_{\ell\alpha} C_{k\alpha} + C_{i\beta}^{\dagger} C_{j\beta}^{\dagger} C_{\ell\beta} C_{k\beta}$$

$$+ C_{i\alpha}^{\dagger} C_{j\beta}^{\dagger} C_{\ell\beta} C_{k\alpha} + C_{i\beta}^{\dagger} C_{j\alpha}^{\dagger} C_{\ell\alpha} C_{k\beta} | \phi \rangle,$$

and

$$2\Gamma_{k\ell,ij}^{z} = \langle \phi | C_{i\alpha}^{\dagger} C_{j\alpha}^{\dagger} C_{\ell\alpha} C_{k\alpha} - C_{i\beta}^{\dagger} C_{j\beta}^{\dagger} C_{\ell\beta} C_{k\beta}$$

$$+ C_{i\alpha}^{\dagger} C_{j\beta}^{\dagger} C_{\ell\beta} C_{k\alpha} - C_{i\beta}^{\dagger} C_{j\alpha}^{\dagger} C_{\ell\alpha} C_{k\beta} | \phi \rangle. \qquad (III.5)$$

These are the four components of γ and Γ with which we will concern ourselves. They are chosen because they are sufficient to determine the expectation values of all spin-free operators and the spin density of the system.

To obtain forms for Γ^{o} and Γ^{z} which will allow us to make use of the GRPA, we use anticommutation relations to reexpress the terms appearing in Eqn. (III.5), e.g.

$$\langle \phi | C_{i\alpha}^{\dagger} C_{j\beta}^{\dagger} C_{\ell\beta} C_{k\alpha} | \phi \rangle = (2)^{-1} (\langle \phi | C_{i\alpha}^{\dagger} C_{k\alpha} C_{j\beta}^{\dagger} C_{\ell\beta} | \phi \rangle$$

$$- \langle \phi | C_{i\alpha}^{\dagger} C_{\ell\beta} C_{j\beta}^{\dagger} C_{k\alpha} | \phi \rangle + \delta_{j\ell} \langle \phi | C_{i\alpha}^{\dagger} C_{k\alpha} | \phi \rangle), \qquad (III.6)$$

and so forth. In addition we insert a complete orthonormal set of
N-particle functions between the pairs of creation and annihilation
operators in Eqn. (III.6). For example,

$$\langle\phi|C^{\dagger}_{i\alpha}C_{k\alpha}C^{\dagger}_{j\beta}C_{\ell\beta}|\phi\rangle = \langle\phi|C^{\dagger}_{i\alpha}C_{k\alpha}|\phi\rangle\langle\phi|C^{\dagger}_{j\beta}C_{\ell\beta}|\phi\rangle$$

$$+ \sum_{t} \langle\phi|C^{\dagger}_{i\alpha}C_{k\alpha}|t\rangle\langle t|C^{\dagger}_{j\beta}C_{\ell\beta}|\phi\rangle, \qquad (III.7)$$

where the sum is over a complete orthonormal set of functions which
are orthogonal to $|\phi\rangle$. Eventually we will identify these functions
with the approximate excited states of the GRPA theory, and we will
use Eqn. (II.30) to evaluate the quantities $\langle\phi|C^{\dagger}_{i\sigma}C_{j\sigma'}|t\rangle$.
By using relationships such as Eqns. (III.6) and (III.7), we can write
the previous expressions for Γ^{o} and Γ^{z} as follows:

$$\Gamma^{o}_{k\ell,ij} = 4^{-1}\left(\gamma^{o}_{ki}\left(2\delta_{\ell j} + \gamma^{o}_{\ell j}\right) - \delta_{kj}\gamma^{o}_{\ell i} - \frac{1}{2}\left(\gamma^{o}_{\ell i}\gamma^{o}_{kj}\right.\right.$$

$$\left.\left.+ \gamma^{z}_{\ell i}\gamma^{z}_{kj}\right)\right) + \Delta^{o}_{k\ell,ij},$$

and

$$\Gamma^{z}_{k\ell,ij} = 4^{-1}\left(\gamma^{z}_{ki}\left(2\delta_{\ell j} + \gamma^{o}_{\ell j}\right) - \delta_{kj}\gamma^{z}_{\ell i} - \frac{1}{2}\left(\gamma^{o}_{\ell i}\gamma^{z}_{kj}\right.\right.$$

$$\left.\left.+ \gamma^{z}_{\ell i}\gamma^{o}_{kj}\right)\right) + \Delta^{z}_{k\ell,ij}. \qquad (III.8)$$

Here Δ^{o} and Δ^{z} contain the contributions from the sum over all
states orthogonal to $|\phi\rangle$. In the next section we will make use of
the GRPA to evaluate Δ^{o} and Δ^{z} . Because the above expressions
for Γ^{o} and Γ^{z} contain the exact charge-and spin-density matrices,

we must find an independent method to determine these quantities. This will be discussed in Sec. V.

IV. Use of the GRPA

The explicit form of $\Delta^o_{kl,ij}$ can be determined from Eqns. (III.5), (III.6) and (III.7). It is given by:

$$\Delta^o_{kl,ij} = 4^{-1} \sum_\lambda \left(\langle\phi| C^\dagger_{i\alpha} C_{k\alpha} + C^\dagger_{i\beta} C_{k\beta} |\lambda\rangle\langle\lambda| C^\dagger_{j\alpha} C_{l\alpha} \right.$$

$$+ C^\dagger_{j\beta} C_{l\beta} |\phi\rangle - \langle\phi| C^\dagger_{i\alpha} C_{l\alpha} |\lambda\rangle\langle\lambda| C^\dagger_{j\alpha} C_{k\alpha} |\phi\rangle$$

$$- \langle\phi| C^\dagger_{i\beta} C_{l\beta} |\lambda\rangle\langle\lambda| C^\dagger_{j\beta} C_{k\beta} |\phi\rangle - \langle\phi| C^\dagger_{i\alpha} C_{l\beta} |\lambda\rangle$$

$$\langle\lambda| C^\dagger_{j\beta} C_{k\alpha} |\phi\rangle - \langle\phi| C^\dagger_{i\beta} C_{l\alpha} |\lambda\rangle\langle\lambda| C^\dagger_{j\alpha} C_{k\beta} |\phi\rangle \right). \quad (IV.1)$$

There is a similar expression for $\Delta^z_{kl,ij}$ which we will not present here. Rather we will carry through the evaluation of Δ^o and just quote the result for Δ^z. The techniques employed to obtain Δ^z are identical to those described below, so the interested reader can verify our result.

To approximate $\Delta^o_{kl,ij}$ we will identify the functions $|\lambda\rangle$ in Eqn. (IV.1) with the excited states of the GRPA theory. This identification is not unique; any orthonormal set of states orthogonal to $|\phi\rangle$ is equally acceptable. The difficulty in finding such states is contained in the restriction that they be orthogonal to the unknown $|\phi\rangle$. The GRPA method provides a technique for determining the

approximate excited states without requiring knowledge of $|\phi\rangle$.

Because the GRPA procedure was designed to accurately predict transition properties, it should provide reasonable approximations to the quantities $\langle\phi|C^{\dagger}_{i\sigma}C_{j'\sigma'}|\mathcal{X}\rangle$ which occur in the expression for Δ^{o}. Note that the functions $C^{\dagger}_{j\sigma'}C_{i\sigma}|\phi\rangle$ are single excitations from $|\phi\rangle$. Therefore we need only consider excited states $|\mathcal{X}\rangle$ which are single excitations of $|\phi\rangle$; the contributions from double and higher excitations vanishes. Thus the form of the excitation operator given in Eqn. (II.6) is sufficient to exhaust the sum over excited states. Also it is shown in Rowe's article that certain sum rules are satisfied exactly by the GRPA excited states, even when a truncated set of orbitals is used. This supports our conviction that the GRPA method, carried out in a finite basis, can yield reasonable approximations to Δ^{o} and Δ^{z}.

We recall from Sec. II that the excitation operators $O^{\dagger}_{k}$ are of either singlet or triplet character. Thus the sum over excited states in Eqn. (IV.1) reduces to a sum over singlet excitations and three sums over the triplet excitations. It is therefore convenient to define six new quantities in terms of which Δ^{o} and Δ^{z} are easily expressed:

$$S^{o}_{ki}(a) = \langle\phi|C^{\dagger}_{i\alpha}C_{k\alpha} + C^{\dagger}_{i\beta}C_{k\beta}|a,0,0\rangle,$$

$$S^{z}_{ki}(a) = \langle\phi|C^{\dagger}_{i\alpha}C_{k\alpha} - C^{\dagger}_{i\beta}C_{k\beta}|a,0,0\rangle,$$

$$T^{o}_{ki}(x) = \langle\phi|C^{\dagger}_{i\alpha}C_{k\alpha} + C^{\dagger}_{i\beta}C_{k\beta}|x,1,0\rangle,$$

$$T^{\bar{z}}_{ki}(\vec{\mathcal{H}}) = \langle \phi | C^{\dagger}_{i\alpha} C_{k\alpha} - C^{\dagger}_{i\beta} C_{k\beta} | \vec{\mathcal{H}}, 1, 0 \rangle,$$

$$T^{(+)}_{ki}(\vec{\mathcal{H}}) = \langle \phi | C^{\dagger}_{i\alpha} C_{k\beta} | \vec{\mathcal{H}}, 1, -1 \rangle,$$

and

$$T^{(-)}_{ki}(\vec{\mathcal{H}}) = \langle \phi | C^{\dagger}_{i\beta} C_{k\alpha} | \vec{\mathcal{H}}, 1, 1 \rangle. \tag{IV.2}$$

We have used the notation of Eqn. (II.29) for the excited state wave functions. With these definitions Eqn. (IV.1) can be written in the following form:

$$\Delta^{o}_{kl,ij} = 4^{-1} \sum_{a} \left(S^{o}_{ki} S^{o*}_{jl} - \tfrac{1}{2} \left(S^{o}_{li} S^{o*}_{jk} + S^{\bar{z}}_{li} S^{\bar{z}*}_{jk} \right) \right)$$

$$+ 4^{-1} \sum_{\mathcal{H}} \left(T^{o}_{ki} T^{o*}_{jl} - \tfrac{1}{2} \left(T^{o}_{li} T^{o*}_{jk} + T^{\bar{z}}_{li} T^{\bar{z}*}_{jk} \right) \right)$$

$$- 4^{-1} \sum_{\mathcal{H}} \left(T^{(+)}_{li} T^{(+)*}_{jk} + T^{(-)}_{li} T^{(-)*}_{jk} \right). \tag{IV.3}$$

The corresponding result for $\Delta^{\bar{z}}$ is given by:

$$\Delta^{\bar{z}}_{kl,ij} = 4^{-1} \sum_{a} \left(S^{\bar{z}}_{ki} S^{o*}_{jl} - \tfrac{1}{2} \left(S^{o}_{li} S^{\bar{z}*}_{jk} + S^{\bar{z}}_{li} S^{o*}_{jk} \right) \right)$$

$$+ 4^{-1} \sum_{\mathcal{H}} \left(T^{\bar{z}}_{ki} T^{o*}_{jl} - \tfrac{1}{2} \left(T^{o}_{li} T^{\bar{z}*}_{jk} + T^{\bar{z}}_{li} T^{o*}_{jk} \right) \right)$$

$$- 4^{-1} \sum_{\mathcal{H}} \left(T^{(+)}_{li} T^{(+)*}_{jk} - T^{(-)}_{li} T^{(-)*}_{jk} \right). \tag{IV.4}$$

In these equations the summation indices (s and t) have been eliminated for notational convenience. Eqns. (IV.3) and (IV.4) are the final expressions for $\triangle^0$ and $\triangle^{\bar{z}}$.

Let us now turn our attention to the evaluation of the six quantities defined in Eqn. (IV.2). This can be carried out in a relatively straightforward fashion by using Eqn. (II.30), identifying Q with $C_{i\sigma}^{\dagger} C_{j\sigma'}$. Knowing the form of the excitation operator from Eqn. (II.23), the commutator $[C_{i\sigma}^{\dagger} C_{j\sigma'}, O_k^{\dagger}]$ can easily be evaluated by using anticommutation relations. All that remains then is to take the expectation value of the commutator with respect to the exact ground state $/\phi\rangle$. The results of performing these steps are given below:

$$S_{ji}^0(a) = 2^{-1/2}\left(\sum_{\epsilon} \left(g_{j\epsilon}^1(a) \gamma_{\epsilon i}^0 + h_{i\epsilon}^1(a) \gamma_{j\epsilon}^0 \right) \right.$$

$$\left. - \sum_m \left(g_{mi}^1(a) \gamma_{jm}^0 + h_{mj}^1(a) \gamma_{mi}^0 \right)\right),$$

$$S_{ji}^{\bar{z}}(a) = 2^{-1/2}\left(\sum_{\epsilon} \left(g_{j\epsilon}^1(a) \gamma_{\epsilon i}^{\bar{z}} + h_{i\epsilon}^1(a) \gamma_{j\epsilon}^{\bar{z}} \right) \right.$$

$$\left. - \sum_m \left(g_{mi}^1(a) \gamma_{jm}^{\bar{z}} + h_{mj}^1(a) \gamma_{mi}^{\bar{z}} \right)\right),$$

$$T_{ji}^0(t) = 2^{-1/2}\left(\sum_{\epsilon} \left(g_{j\epsilon}^3(t) \gamma_{\epsilon i}^{\bar{z}} + h_{i\epsilon}^3(t) \gamma_{j\epsilon}^{\bar{z}} \right) \right.$$

$$\left. - \sum_m \left(g_{mi}^3(t) \gamma_{jm}^{\bar{z}} + h_{mj}^3(t) \gamma_{mi}^{\bar{z}} \right)\right),$$

$$T_{j'i}^{\bar{z}}(\lambda) = 2^{-1/2} \left(\sum_{\epsilon} \left(g_{j'\epsilon}^{3}(\lambda) \gamma_{\epsilon i}^{0} + h_{i\epsilon}^{3}(\lambda) \gamma_{j\epsilon}^{0} \right) \right.$$

$$\left. - \sum_{m} \left(g_{mi}^{3}(\lambda) \gamma_{jm}^{0} + h_{mj}^{3}(\lambda) \gamma_{mi}^{0} \right) \right),$$

$$T_{j'i}^{(+)}(\lambda) = 2^{-1} \left(\sum_{\epsilon} \left(g_{j'\epsilon}^{3}(\lambda) (\gamma_{\epsilon i}^{0} + \gamma_{\epsilon i}^{\bar{z}}) + h_{i\epsilon}^{3}(\lambda) (\gamma_{j\epsilon}^{0} - \gamma_{j\epsilon}^{\bar{z}}) \right) \right.$$

$$\left. - \sum_{m} \left(g_{mi}^{3}(\lambda) (\gamma_{jm}^{0} - \gamma_{jm}^{\bar{z}}) + h_{mj}^{3}(\lambda) (\gamma_{mi}^{0} + \gamma_{mi}^{\bar{z}}) \right) \right),$$

$$T_{j'i}^{(-)}(\lambda) = 2^{-1} \left(\sum_{\epsilon} \left(g_{j'\epsilon}^{3}(\lambda) (\gamma_{\epsilon i}^{0} - \gamma_{\epsilon i}^{\bar{z}}) + h_{i\epsilon}^{3}(\lambda) (\gamma_{j\epsilon}^{0} + \gamma_{j\epsilon}^{\bar{z}}) \right) \right.$$

$$\left. - \sum_{m} \left(g_{mi}^{3}(\lambda) (\gamma_{jm}^{0} + \gamma_{jm}^{\bar{z}}) + h_{mj}^{3}(\lambda) (\gamma_{mi}^{0} - \gamma_{mi}^{\bar{z}}) \right) \right). \quad \text{(IV.5)}$$

In evaluating these quantities one must remember that $g_{i'j'}^{1(3)}(k)$ and $h_{ij}^{1(3)}(k)$ are nonzero only if the orbital $\phi_{i'}$ is unoccupied and the orbital $\phi_{j'}$ is occupied in the single-determinant approximation to $|\phi\rangle$. Notice that if the GRPA calculation has been carried out and if the exact charge-and spin-density matrices are known, Δ^{0} and $\Delta^{\bar{z}}$ can be determined from Eqns. (IV.3), (IV.4), and (IV.5). We have thus succeeded in approximately evaluating Δ^{0} and $\Delta^{\bar{z}}$ by using the GRPA method.

V. First-Order Density Matrix

The components of the first-order density matrix are related to those of the second-order density matrix through the following identities:

$$\gamma^{o}_{ki} = 2(N-1)^{-1} \sum_{\ell} \Gamma^{o}_{k\ell,i\ell} \quad ,$$

and

$$\gamma^{z}_{ki} = 2(N-1)^{-1} \sum_{\ell} \Gamma^{z}_{k\ell,i\ell} \quad . \tag{V.1}$$

Let us assume that a truncated basis of M orbitals has been chosen, and that we wish to evaluate the first-and second-order density matrices within this basis. If we substitute the expressions for Γ^{o} and Γ^{z} given in Eqn. (III.8) into Eqn. (V.1), we obtain, after some rearrangement, the following closed expressions for γ^{o} and γ^{z} :

$$\gamma^{o}_{ki} = 2^{-1}(2M+1-N)^{-1} \sum_{\ell=1}^{M} \left(\gamma^{o}_{k\ell}\gamma^{o}_{\ell i} + \gamma^{z}_{k\ell}\gamma^{z}_{\ell i} - 8\Delta^{o}_{k\ell,i\ell} \right),$$

and

$$\gamma^{z}_{ki} = 2^{-1}(2M+1-N)^{-1} \sum_{\ell=1}^{M} \left(\gamma^{z}_{k\ell}\gamma^{o}_{\ell i} + \gamma^{o}_{k\ell}\gamma^{z}_{\ell i} - 8\Delta^{z}_{k\ell,i\ell} \right),$$

$$k,i = 1,2,\cdots M. \tag{V.2}$$

Because Δ^{o} and Δ^{z} are completely determined by γ^{o} and γ^{z} the above equations are closed, and they can be used to evaluate γ^{o} and γ^{z} . The only approximations in Eqn. (V.2) are the approximate Δ^{o} and Δ^{z} which we obtain by doing a GRPA calculation. In

the next section we will describe an iterative procedure which can be used to solve Eqn. (V.2).

VI. Self-Consistent Determination of Γ^{o}, $\Gamma^{\bar{z}}$, γ^{o}, and $\gamma^{\bar{z}}$

In the preceding sections we have shown how the GRPA method can be used to evaluate various components of the first-and second-order density matrices. Eqn. (V.2) provides us with a means of directly determining γ^{o} and $\gamma^{\bar{z}}$ by using the GRPA approximations to Δ^{o} and $\Delta^{\bar{z}}$. Eqns. (III.8), (IV.3), (IV.4), and (IV.5) can be used to evaluate Γ^{o} and $\Gamma^{\bar{z}}$, if γ^{o} and $\gamma^{\bar{z}}$ are known. In this section we propose an iterative, self-consistent procedure for determining γ^{o}, $\gamma^{\bar{z}}$, Γ^{o}, and $\Gamma^{\bar{z}}$. The procedure is as follows:

(1) Set γ^{o} and $\gamma^{\bar{z}}$ equal to their single-determinant approximations.

(2) Carry out the singlet and triplet GRPA calculations, using the present value of γ^{o}.

(3) In Eqn. (IV.5) use the current γ^{o} and $\gamma^{\bar{z}}$ to evaluate $S_{j\lambda}^{o}$, etc.

(4) Form Δ^{o} and $\Delta^{\bar{z}}$ by using Eqns. (IV.3) and (IV.4)

(5) Use the current γ^{o} and $\gamma^{\bar{z}}$ on the <u>right</u> <u>hand</u> side of Eqn. (V.2) to obtain <u>new</u> values for γ^{o} and $\gamma^{\bar{z}}$.

(6) In Eqn. (III.8), use the <u>new</u> γ^{o} and $\gamma^{\bar{z}}$ to evaluate Γ^{o} and $\Gamma^{\bar{z}}$.

(7) Compare the new γ^{o} and $\gamma^{\bar{z}}$ to the γ^{o} and $\gamma^{\bar{z}}$ obtained by reducing Γ^{o} and $\Gamma^{\bar{z}}$ (Eqn. (V.1)). If

the agreement is satisfactory and if the <u>old</u> γ^o

and γ^z agree well with the <u>new</u> γ^o and γ^z then

the calculation is complete. Otherwise return to step

(2), using the <u>new</u> γ^o and γ^z.

That this procedure is an iterative method is clear from the above

description. It is also called self-consistent because half of the

convergence criterion is that the first-order density matrix calculated

in step (5) must agree with the first-order density matrix obtained by

reducing Γ (step (7)). That is, the first-order density matrix must

be <u>consistent</u> with the second-order density matrix.

One disadvantage of the iterative method is that matrix elements

$\gamma^o_{\epsilon m}$ connecting occupied and unoccupied orbitals are difficult to

calculate. If one begins the iteration process with a charge density

matrix having $\gamma^o_{\epsilon m} = 0$, the procedure never produces any nonzero

$\gamma^o_{\epsilon m}$. However if exact Hartree-Fock orbitals are being used, such

matrix elements should be quite small due to Brillouin's theorem. That

is, if the C. I. expansion of the wave function $/\phi\rangle$ contains no single

excitations, then the lowest order nonzero contributions to

$$\langle \phi | C^\dagger_{m\alpha} C_{\epsilon\alpha} + C^\dagger_{m\beta} C_{\epsilon\beta} | \phi \rangle$$
will come from matrix elements

of double excitations with triple excitations. Because the C. I. expansion

coefficients of triple excitations are usually quite small, the elements

$\gamma^o_{\epsilon m}$ will, in general, also be very small. To obtain approximate

values for $\gamma^o_{\epsilon m}$, which could then be used in the first step of the

iterative procedure, one can use first-order perturbation theory. This

only requires a knowledge of the Hartree-Fock orbitals and energies.

There is no formal proof that an iterative procedure such as we have

proposed will converge to any meaningful result. Therefore we must test

the convergence by using the method to carry out numerical calculations on systems of interest. In the next section we report the results of such calculations on the helium, lithium and beryllium atoms.

VII. Application to Helium, Lithium, and Beryllium

There are a number of reasons behind our decision to choose the ground state of the helium atom as our first test case. In the first place, helium is the simplest atomic system to which our method is applicable. In addition the second-order density matrix which we obtain can easily be tested for N-representability, because necessary and sufficient conditions are known for the two-electron case. Finally, we want to compare the results of the present method to results which we have previously obtained for helium using Green's function techniques.

We have chosen as a basis five s-type Hartree-Fock orbitals[19], each of which is given as a linear combination of the five Slater orbitals (normalized) described in Table I.

Table I. Slater Basis for Helium

n	exponent
1	1.4191
1	2.5722
2	4.2625
3	3.9979
3	5.4863

The convergence criterion used was that

$$\sum_{i,j=1}^{M} |\gamma_{ij}^{o}(new) - \gamma_{ij}^{o}(old)|^2 < 10^{-6}.$$

Convergence was realized after two iterations; the complete calculation

taking thirty seconds on a Univac 1108 computer. Calculation of the necessary one- and two-electron integrals required twenty seconds, so the GRPA calculation only required ten seconds. This is to be compared to our Green's function calculation[20] in which four minutes were used in the numerical integration step. The convergence was not found to be very sensitive to the initial choice of γ^0. The expectation values of the one- and two-electron operators which occur in the Hamiltonian, along with the results of other work, are given in Table II.

<u>Table II. Expectation Values for Helium</u>

1)	This work:	$2\left\langle -\frac{1}{2}\nabla^2 - \frac{2}{r}\right\rangle$	$=-3.8822$ a.u.
		$\left\langle \frac{1}{r_{12}}\right\rangle$	$=+0.98766$ a.u.
		$\langle H\rangle$	$=-2.8945$ a.u
2)	Hartree-Fock[20]	$\langle H\rangle$	$=-2.8617$ a.u.
3)	C. I. [21]	$\langle H\rangle$	$=-2.8790$ a.u.
4)	Green's function[22]	$\langle H\rangle$	$=-2.8780$ a.u.
5)	Exact[23]	$\langle H\rangle$	$=-2.9037$ a.u.

The fact that our energy is below the energy of the complete C. I. immediately tells us that the second-order density matrix which we have calculated is not N-representable. We will defer further comments concerning this problem until the next section.

The eigenvectors (natural orbitals) and eigenvalues (occupation numbers) of the charge density matrix γ^0 are given in Table III. Of course, the spin density matrix is identically zero.

Table III. Natural Orbitals and Occupation Numbers for Helium

Occupation Numbers

1.9974	1.0000	-0.0004	0.0001	0.0000	0.0000
2.5025×10^{-3}	0.0004	0.9286	-0.3688	-0.0419	-0.0007
4.9696×10^{-5}	0.0001	0.3612	0.8717	0.3311	0.0053
2.1833×10^{-6}	0.0000	-0.0853	-0.3216	0.9386	0.0914
2.2919×10^{-8}	0.0000	0.0066	0.0246	-0.0880	0.9958

Expansion coefficients refer to the Hartree-Fock orbitals. In carrying out this calculation we first approximate the charge density matrix elements $\gamma_{\epsilon m}^{o}$ (see the end of Sec. VI) by using first-order perturbation theory. These approximate values were then used to begin the iterative procedure. This was found to have negligible effect on our results. The diagonal overlaps between our natural orbitals (Si) and those of Reinhardt and Doll[24] (R-Di) are given in Table IV. The two sets are in fairly good agreement.

Table IV. Diagonal Overlaps

i	$(R\text{-}D_i | S_i)$
1	1.00000
2	0.99817
3	0.99719
4	0.99901
5	0.99997

Although our natural orbitals seem to be reasonably accurate, the

expectation value of the one-electron operators given in Table II is too low.[25] This is evidence that the occupation numbers of the second through fifth natural orbitals are not large enough.

By imposing the additional constraint (necessary for N-representability) that the diagonal elements of Γ^0 be non-negative, we obtain an energy of $-3.8496 + 0.9877 = -2.8619$ a. u. for helium. In this case the natural orbitals are essentially unchanged, but the occupation numbers are altered considerably. The new occupation numbers are given in Table V.

Table V. Occupation Numbers with Constraint

$$1.9854$$
$$1.2441 \times 10^{-2}$$
$$2.1319 \times 10^{-3}$$
$$6.7217 \times 10^{-5}$$
$$2.5378 \times 10^{-7}$$

With this γ^0 the predicted expectation value of the one-electron operators agrees very well with the correct result.[25] The fact that the total energy is not very good when compared to the C. I. result indicates that the second-order density matrix Γ^0 which our method yields is probably not very accurate in this case.

In addition to the first- and second-order density matrices of the ground state, the GRPA calculation yields an approximate electronic excitation spectrum of the system. The energy differences

between the ground state and excited states which are obtained by doing the GRPA calculation are compared to the C. I. results for singlet states in Table VI.

Table VI. Singlet Excitation Spectrum for Helium

GRPA	C. I.
1.4243 a.u.	1.4068 a.u.
5.3068	5.3208
19.522	19.451
118.50	118.34

For the calculations on the ground states of lithium and beryllium we used bases of six s-type Hartree Fock orbitals[26] (restricted H.F.) which are expressed in terms of the (normalized) Slater orbitals described in Table VII.

Table VII. Slater Bases for Lithium and Beryllium

Lithium		Beryllium	
n	exponent	n	exponent
1	2.4803	1	3.4703
1	4.7071	1	6.3681
2	0.3500	2	0.7516
2	0.6600	2	0.9084
2	1.0000	2	1.4236
2	1.7350	2	2.7616

Convergence was realized in each case after four iterations. Both computations took ninty seconds; sixty seconds for integral evaluation and thirty seconds for the GRPA iterations. Again the convergence was not found to be sensitive to the initial choice of γ^o , and for lithium the calculation was quite insensitive to the initial spin-density matrix γ^{z} . The natural orbitals and occupation numbers for lithium and beryllium which are obtained by our method are given in Tables VIII and IX respectively. In both cases the constraint that the diagonal elements of Γ^o be non-negative was imposed.

Table VIII. Natural Orbitals and Occupation Numbers for Lithium

Occupation Numbers	Expansion Coefficients (rows)					
1.9979	1.0000	−0.0002	0.0001	−0.0002	0.0003	−0.0001
0.9976	0.0002	0.9994	0.0282	−0.0186	0.0003	0.0000
2.9614×10^{-3}	−0.0001	−0.0088	0.6743	0.5608	0.3341	−0.3451
1.1524×10^{-3}	0.0002	0.0319	−0.6121	0.7862	−0.0784	0.0047
3.0561×10^{-4}	−0.0003	0.0067	−0.3946	−0.2232	0.8264	−0.3338
8.5726×10^{-5}	−0.0001	−0.0010	0.1184	0.1315	0.4463	0.8772

Table IX. Natural Orbitals and Occupation Numbers for Beryllium

Occupation Numbers	Expansion Coefficients (rows)					
1.9998	0.9339	0.3575	0.0000	0.0000	0.0000	0.0000
1.9968	−0.3575	0.9339	0.0000	0.0000	0.0000	0.0000
2.4175×10^{-3}	0.0000	0.0000	0.7697	−0.6304	0.0986	−0.0205
2.7226×10^{-4}	0.0000	0.0000	0.5626	0.7327	0.2285	−0.3072
4.2424×10^{-5}	0.0000	0.0000	−0.2849	−0.2006	0.8675	−0.3551
7.8827×10^{-6}	0.0000	0.0000	0.0991	0.1596	0.4308	0.8827

These natural orbitals and occupation numbers are similar to those obtained by other workers[27,28,29] using somewhat different basis functions. Notice that the block structure of the natural orbital expansion coefficients implies that the $\gamma_{\epsilon m}^{o}$, which are more difficult to obtain by our iterative scheme, are, as we anticipated, quite small in the three cases considered here. The ground state energies for lithium and beryllium calculated by using our density matrices are presented in Table X. For lithium our spin density at the nucleus (2.8006) agrees fairly well with the correct value (2.9096).[30]

Table X. Ground State Energy of Lithium and Beryllium

Method	Lithium	Beryllium
This work	-7.4419 a.u.	-14.579 a.u.
Hartree Fock	-7.4327 a.u.	-14.572 a.u.
Radial Limit	-7.4420[32] a.u.	-14.592[31] a.u.

In both calculations the expectation values of the one-electron operators agree very well with the exact results. Almost all of the error in the calculated energy is due to error in the two-electron energy. This supports our earlier proposal that the Γ^{o} obtained by our method can be inaccurate, whereas the resultant γ^{o} is usually rather good. This is not surprising because the detailed effects of particle correlation which enter into Γ^{o} can not be adequately described by the limited basis sets which we have chosen. On the other hand it is well known that correlation does not appreciably alter the change density, and so the limited bases should not prohibit us from obtaining accurate first-order density matrices.

We have also studied the behavior of the resulting density matrices for helium as the basis set is expanded. It was observed that the natural orbitals and occupation numbers converged smoothly to the radial limit results reported in Table III. Such calculations were carried out with two, three, four, and five s-type basis functions.

Although the results of these examples do not consititute a proof that the proposed iteration scheme will always converge, they do indicate that the method can be a useful tool for determining first- and second-order density matrices of atomic and molecular systems. Even though the energy which our method predicts is not accurate, the resulting natural orbitals can be used in C. I. calculations to obtain better expectation values of two-electron operators.

VIII. Error Bounds

We have seen from the results of the helium calculation that our method does not necessarily yield density matrices which are exactly N-representable. However this does not mean that these density matrices can not be used for predicting the properties of atomic and molecular systems. We learned from the calculations reported that our method can yield first-order density matrices which are reasonably accurate. However density matrices which are obtained by the GRPA method, the Green's function method, and other "direct calculation" techniques might not be N-representable, therefore it is important to examine the consequences of possible approximate N-representability. In a recent paper[2] we have shown that the errors introduced in calculating expectation values with non-N-representable density matrices can be

bounded, and that these errors decrease to zero as the density matrices
become more nearly N-representable.

In the method which has been presented in this paper, approximations
to the first- and second-order density matrices belonging to the
unknown wave function $|\phi\rangle$ are obtained by an iterative procedure.
Hopefully these approximate density matrices are quite close to the
true (N-representable) density matrices of $|\phi\rangle$. Concentrating on the
first-order density matrix γ , we can define a measure of deviation
from the density matrix belonging to $|\phi\rangle$ as follows:

$$\mu = \int |\gamma(1;1') - \gamma_T(1;1')|^2 \, d\tau_1 \, d\tau_{1'}, \qquad \text{(VIII.1)}$$

where γ is our approximation to the true γ_T

$$\gamma_T = \int \phi(1,2,\cdots N) \phi^*(1',2,\cdots N) \, d\tau_2 \cdots d\tau_N \qquad \text{(VIII.2)}$$

It should be kept in mind that we are trying to bound the differences
in expectation values which are calculated using our γ and the γ_T
belonging to $|\phi\rangle$. Neither of these expectation values are necessarily
exact. Suppose now that we are interested in calculating the expectation
value of some one-particle operator $F = \sum_{i=1}^{N} f_i$. If we define the
difference function $E(1,1')$ by

$$E(1;1') = \gamma(1;1') - \gamma_T(1;1'), \qquad \text{(VIII.3)}$$

then

$$\Delta F \equiv \text{Trace} \{f E\}$$

$$= \text{Trace}\{f \gamma\} - \text{Trace}\{f \gamma_T\} \qquad \text{(VIII.4)}$$

is the deviation of the calculated expectation value of F from its value for the wave function $|\phi\rangle$. Notice that Trace $\{f\,\gamma_T\}$ is not necessarily the expectation value of F for an _exact_ wave function. If γ and γ_T are expanded in some orthonormal (probably finite) basis, then the quantity $|\Delta F|$ can be bounded as follows:

$$|\Delta F|^2 \le \sum_{i,j=1}^{M} |f_{ij}|^2 \sum_{i,j=1}^{M} |E_{ij}|^2 \,, \qquad\qquad (VIII.5)$$

where M is the dimension of the basis and f_{ij} and E_{ij} are the representatives of f and E within this basis. The bound on $|\Delta F|$ is thus written as a factor depending on the operator F times a factor which depends only on the difference function E. It is easy to see from Egn. (VIII.1) that the second term in Eqn. (VIII.5) is identical to what we have defined as μ :

$$\sum_{i,j=1}^{M} |E_{ij}|^2 = \mu \qquad\qquad (VIII.6)$$

The bound on $|\Delta F|$ can then be written in either of the following forms

$$|\Delta F|^2 \le \mu \sum_{i,j=1}^{M} |f_{ij}|^2 \le \mu \sum_{i=1}^{M} (f^2)_{ii} \,, \qquad\qquad (VIII.7)$$

where $(f^2)_{ii}$ is a matrix element of the operator f^2 which is still a one-particle operator. The second inequality in Eqn. (VIII.7) follows from the fact that the basis in which γ and γ_T are expanded is probably not complete. If we can find a means of evaluating the parameter μ , either form of Eqn. (VIII.7) will allow us to bound the quantity $|\Delta F|$. We do not mean to imply that the bounds given above are in any sense good bounds; we only wish to show that knowledge of μ can lead to error bounds for expectation values.

In order to calculate the value of μ corresponding to a given γ, we must somehow obtain γ_T, at least formally. This can be done by using the following property of the known excitation operators O_k^+:

$$O_k \, |\phi\rangle = 0 \, , \qquad\qquad (VIII.8)$$

for all excited states $|k\rangle$. Eqn. (VIII.8) is a consequence of the fact that $|\phi\rangle$ is the GRPA ground state wave function which must be orthogonal to all of the excited states $O_k^+ |\phi\rangle$. Because the O_k^+ and hence the O_k are known once the GRPA calculation has been performed, the above equation can be used to determine $|\phi\rangle$.

For what follows we find it convenient to relate $|\phi\rangle$ to its single determinant approximation $|o\rangle$ by the unitary operator given below:

$$|\phi\rangle = \exp\,(-S)\,|o\rangle , \qquad\qquad (VIII-9)$$

where S is an antihermitian operator which is to be determined by using Eqn. (VIII.8). The expression for an element of the second-order density matrix

$$\Gamma_{kl,ij} = \tfrac{1}{2} \langle\phi|\, c_i^+ c_j^+ \, c_l \, c_k \,|\phi\rangle ,$$

can be rearranged to give

$$\Gamma_{kl,ij} = \tfrac{1}{2}\, \delta_{jl} \langle\phi|\, c_i^+ \, c_k \,|\phi\rangle$$
$$- \tfrac{1}{2} \langle\phi|\, c_i^+ \, c_l \, c_j^+ \, c_k\,|\phi\rangle \, . \qquad\qquad (VIII.10)$$

By using the definition of the first-order density matrix and Eqns.

(V.1) and (VIII.10) we can write

$$\frac{1}{2}(N-1)\gamma_{ki} = \frac{1}{2}M\gamma_{ki} - \frac{1}{2}\sum_{j=1}^{M}\langle\phi|c_i^+ c_j c_j^+ c_k|\phi\rangle,$$

or $\quad (M+1-N)\gamma_{ki} = \sum_{j=1}^{M}\langle\phi|c_i^+ c_j c_j^+ c_k|\phi\rangle.$ \hfill (VIII.11)

In the GRPA method we approximate the right hand side of Eqn. (VIII.11) as follows:

$$\langle\phi|c_i^+ c_j c_j^+ c_k|\phi\rangle \rightarrow \langle\phi|c_i^+ c_j P c_j^+ c_k|\phi\rangle, \hfill (VIII.12)$$

where the projection operator P is given by

$$P = |\phi\rangle\langle\phi| + \sum_{\lambda} O_\lambda^+ |\phi\rangle\langle\phi| O_\lambda, \hfill (VIII.13)$$

and the O_λ^+ are the known GRPA excitation operators. Thus the deviation of γ_{ki} (GRPA) from the true $(\gamma_T)_{ki}$ can be written formally as

$$(M+1-N)E_{ki} = (M+1-N)(\gamma_T - \gamma)_{ki}$$

$$= \sum_{j=1}^{M}\langle\phi|c_i^+ c_j Q c_j^+ c_k|\phi\rangle, \hfill (VIII.14)$$

with

$$Q = 1 - P. \hfill (VIII.15)$$

If the spin-orbital basis used in constructing O_λ^+ is complete, the operators O_λ^+ and O_λ form a complete set in terms of which any operator of the form $c_i^+ c_j$ can be expanded as follows:

$$c_i^+ c_j = W_{ij}'' + \sum_{\lambda}\left(W_{ij}(\lambda) O_\lambda^+ + W_{ij}'(\lambda) O_\lambda\right). \hfill (VIII.16)$$

The $W_{ij}(\lambda)$, $W_{ij}'(\lambda)$, and W_{ij}'' are expansion coefficients. By using the orthogonality properties of the states $O_\lambda^+|\phi\rangle$ and the

expansion given in Eqn. (VIII.16), it is easily shown that each element E_{ki} vanishes. Therefore as the spin-oribtal basis approaches completeness, it is expected that the E_{ki} will approach zero and the approximate γ will approach the true γ_T.

To make use of Eqn. (VIII.9) in evaluating the parameter μ , we recall the following identity for exponential operators[33]:

$$B \exp(-A) = \exp(-A)\left\{ B + [A,B] + \frac{1}{2!}[A,[A,B]] + \cdots \right\}.$$ (VIII.17)

With Eqn. (VIII.9) the expression for E_{ki} can be rewritten in the form:

$$
(M+1-N)E_{ki} = \sum_{j=1}^{M} \left\{ \langle o | \exp(s) c_i^+ c_j \cdot c_j^+ c_k \exp(-s) | o \rangle \right.
$$
$$
- \langle o | \exp(s) c_i^+ c_j \exp(-s) | o \rangle \langle o | \exp(s) c_j^+ c_k \exp(-s) | o \rangle
$$
$$
- \sum_{\lambda} \langle o | \exp(s) [c_i^+ c_j, O_\lambda^+] \exp(-s) | o \rangle
$$
$$
\langle o | \exp(s) [O_\lambda, c_j^+ c_k] \exp(-s) | o \rangle \left. \right\}.
$$ (VIII.18)

Before this equation can be simplified by using Eqn. (VIII.17), we must investigate in more detail the form of the operator S.

In the nuclear literature[34,35] the wave function $|\phi\rangle$ is usually written as

$$|\phi\rangle = K \exp(-s) |o\rangle,$$ (VIII.19)

where K is a normalization constant and

$$S = \sum_{\substack{m,n \\ \alpha,\beta}} S_{m\alpha,n\beta} c_m^+ c_\alpha c_n^+ c_\beta.$$ (VIII.20)

We are using the subscript convetion of Sec. II.

This form of the wave function is not especially useful because the

operator S is not antihermitian. This means that Eqn. (VIII.18)

can not be used to evaluate $E_{\hbar i}$ if we insist on using the above

wave function. To avoid this problem we can express $/\phi\rangle$ as in Eqn.

(VIII.9) with the antihermitian operator S given by

$$S = \sum_{\substack{m,n \\ \alpha,\beta}} \left(S_{m\alpha,n\beta}\, C_m^\dagger\, C_\alpha\, C_n^\dagger\, C_\beta - S_{m\alpha,n\beta}^*\, C_\beta^\dagger\, C_n\, C_\alpha^\dagger\, C_m \right). \qquad \text{(VIII.21)}$$

Once the coefficients $S_{m\alpha,n\beta}$ have been determined, Eqns. (VIII.17)

and (VIII.18) can be used to calculate $E_{\hbar i}$. We will return to this

calculation shortly.

To obtain an equation for the coefficients $S_{m\alpha,n\beta}$ we make use

of Eqn. (VIII.9) and Eqn. (VIII.17) to write Eqn (VIII.8) in the form

$$O_\lambda\,|\phi\rangle = \exp(-s)\left\{ O_\lambda + [S, O_\lambda] + \tfrac{1}{2!}[S,[S,O_\lambda]] + \cdots \right\}|0\rangle = 0 \qquad \text{(VIII.22)}$$

By substituting the explicit expressions for O_λ and S given in Eqn. (II.6)

and Eqn. (VII.21) respectively, and carrying out the commutations

indicated above we can equate to zero the coefficients of the various

independent functions $|0\rangle$, $C_i^\dagger C_j|0\rangle$, $C_i^\dagger C_j^\dagger C_k C_\ell |0\rangle$, etc.

This leads to the following equation involving $S_{m\alpha,n\beta}$:

$$4 \sum_{n\beta} S_{m\alpha,n\beta}\, g_{n\beta}^*(\lambda) = - h_{m\alpha}^*(\lambda),$$

$$\alpha = 1,2,\cdots N \; ; \; m = N+1,\cdots M \; ; \; \lambda = 1,2,\cdots N(M-N). \qquad \text{(VIII.23)}$$

In our GRPA calculations all of the $h_{m\alpha}(\lambda)$ turned out to be quite

small $(\sim 10^{-3})$ as did most of the $g_{m\alpha}(\lambda)$. For each value of λ there

was one $g_{m\alpha}(\lambda)$ whose value was near unity. These results are typical

of RPA calculations on atomic systems. Based on these observations

Eqn. (VIII.23) implies that the magnitude of the $S_{m\alpha,n\beta}$ will generally be at least as small as the $h_{m\alpha}(\lambda)$.

If we represent each of the (M-N) N pairs $n\beta$ by a single Greek index μ , the set of GRPA coefficients $g_{n\beta}(\lambda)$ and $h_{m\alpha}(\lambda)$ can be thought of as forming square N(M-N) dimensional matrices, and so Eqn. (VII.23) is a simple matrix equation which can be solved by standard matrix inversion techniques to yield the coefficients $S_{m\alpha,n\beta}$:

$$4 S_{\mu\lambda} = - \sum_{\chi=1}^{N(M-N)} h_{\mu\chi}^{*} g_{\chi\lambda}^{*-1} .$$

(VIII.24)

It should be pointed out that Eqn. (VIII.23) is identical to the equation which would result if the wave function given in Eqn. (VIII.19) had been used. In other words no additional complications arise when we introduce the antihermitian form for S given in Eqn. (VIII.21).

With the coefficients $S_{m\alpha,n\beta}$ given by Eqn. (VII-24) we now return to the evaluation of the E_{ki}. By using the identity given in Eqn. (VIII.17) and carrying out the indicated commutations, the right hand side of Eqn. (VIII.18) can be written as a sum of terms involving various powers of the coefficients $S_{m\alpha,n\beta}$. Because the $S_{m\alpha,n\beta}$ are generally quite small the use of powers of $S_{m\alpha,n\beta}$ for ordering purposes is justified. The sum of all terms which do not contain any $S_{m\alpha,n\beta}$ is given by

$$(M+I-N) E_{ki}^{(0)} \begin{cases} -\sum_{\lambda}\sum_{\alpha} h_{i\alpha}(\lambda) h_{k\alpha}^{*}(\lambda), \text{ if } i,k > N \\ -\sum_{\lambda}\sum_{m} h_{mi}(\lambda) h_{mk}^{*}(\lambda), \text{ if } i,k \leq N \\ 0, \text{ otherwise} \end{cases}$$

(VIII.25)

Notice that there are no contributions in the zeroth order to $E_{m\alpha}$.
This supports our earlier claim that the quantities $\gamma_{m\alpha}$ should be
quite small in general. In addition all terms which are first order
in $S_{m\alpha, n\beta}$ are found to vanish identically. Thus the factors $S_{m\alpha, n\beta}$
contribute to E_{ki} only in the second and higher orders. Because
the $S_{m\alpha, n\beta}$ are generally smaller in magnitude than 10^{-3}, the second
order contributions to E_{ki} will be of the order of 10^{-6} or smaller.
This is a negligible contribution for our purposes, and so we need not
obtain explicit expressions for these second order terms.

Because the zeroth order contributions $E_{ki}^{(o)}$ given in Eqn.
(VIII.25) are also quite small, it is not surprising that the expectation
values of the one-electron operators which we have calculated are in
good agreement with the correct values. The fact that the magnitudes
of all the $h_{m\alpha}(\lambda)$ are 10^{-3} or less implies that the value of μ given
by Eqn. (VIII.6) with Eqn. (VIII.25) is of the order of 10^{-12}. Therefore
unless the quantity $\sum_{i,j=1}^{M} |f_{ij}|^2$ which enters into Eqn. (VIII.7) is
quite large, the deviation $|\Delta F|$ should be very small.

It is our opinion that error bounds such as have been discussed
in this section are necessary components of any complete and workable
method which attempts the direct calculation of reduced quantities.

IX. Conclusions

In this paper we have shown how the GRPA method can be used to
approximately determine the first- and second-order density matrices
of atomic and molecular systems. In our method there are no numerical

integrations and the size of the arrays to be diagonalized increases
much less rapidly with the number of particles than in the C. I.
technique. Besides these computational advantages there exists the
possibility of obtaining error bounds involving the resultant density
matrices. These bounds allow us to estimate the deviations in
calculated expectation values caused by using density matrices that
might not be exactly N-representable.

From the application of our method to the ground states of the
helium, lithium, and beryllium atoms, we learned that the iterative
procedure which we proposed can converge to a meaningful result. In
these cases convergence was realized after a few iterations. We
also found that the results of the method are not very sensitive to
the initial approximations for the charge density matrix. In the case
of lithium the results were also insensitive to the initial choice of
γ^z. This indicates that there are probably no inherent instabilities
in the iterative method.

We observed that by imposing the additional constraint that the
diagonal elements of Γ^o be non-negative, the calculated natural
orbitals were essentially unaltered but the occupation numbers were
significantly changed.[36] With this constraint the resulting charge
density matrices gave nearly exact results for the expectation values
of the one-electron operators occurring in the Hamiltonian. From
this observation we inferred that nearly all of the error in the
predicted energy is caused by error in Γ^o. These results also
indicate that the occupation numbers which we obtain are probably of

reasonable accuracy.

Although our method might not yield accurate second-order density matrices or ground state energies which are competitive with the best results, it does show promise as a method for obtaining first-order density matrices and natural orbitals which can then be used in a C. I. calculation. Let us recall that the GRPA technique was developed to predict properties which do not depend strongly on the complex correlations within wave functions. Therefore in our use of the GRPA for evaluating certain contributions to the first- and second-order density matrices, we should not expect to be able to accurately describe detailed particle correlation effects. Because such detailed effects contribute significantly to the second-order density matrix, it is not reasonable to think that our method can consistently yield reasonable second-order density matrices. On the other hand, it is well known that particle correlations have relatively little effect on the first-order density matrix. Thus it is not surprising to find that the GRPA method is capable of predicting the small corrections to the Hartree-Fock first-order density matrix.

In order to better assess the value of our method as a tool for calculating first- and second-order density matrices, many more numerical calculations are needed. Hopefully such results will become plentiful in the future.

Acknowledgments

Notes and References

1. We restrict the discussion to pure states of N fermions.

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9. The GRPA, as presented, is only applicable to the ground state. Therefore we restrict our treatment ot this case. One can generalize the GRPA method to apply to excited states, but we will not do so here.

10. Our treatment follows closely that of Rowe.

11. It is assumed that the ground state wave function can be approximately represented by a single Slater determinant. One can generalize the treatment to cover a combination of Slater determinants but the bookkeeping becomes very messy.

12. The notation "singlet and triplet-operators" is based upon the fact that $D_{m\epsilon}^{1\dagger}$ operating on a singlet yields a singlet and $D_{m\epsilon}^{3,M_s\dagger}$ operating on a singlet yields a triplet.

13. We assume that there are no effects which split the degeneracy of the triplet level.

14. Notice that the dimension of the matrix to be diagonalized is given by $2N_o(M-N_o)$, where N_o is the number of occupied orbitals and M is the number of basis functions which we use. The size of this matrix does not increase nearly as rapidly with the number of particles as, for example, the C. I. matrix. This is an important computational advantage of the method.

15. The function $|k,S,M_s\rangle$ is <u>not necessarily</u> an eigenfunction of S^2. The notation only implies that $|k,S,M_s\rangle$ is obtained by $O_k^{S,M_s\dagger}$ operating on the ground state $|\phi\rangle$. The S^2-dependence of $|k,S,M_s\rangle$ has no effect on our problem; we are just using the $\{|k,S,M_s\rangle\}$ as a set of orthonormal functions which are also orthogonal to $|\phi\rangle$.

16. We use the following normalization: $\text{Trace}\,\gamma = N,\ \text{Trace}\,\Gamma = \binom{N}{2}$

17. See, for example, R. McWeeny, Rev. Mod. Phys. <u>32</u>, 335 (1960).

18. We sometimes use γ_i^o to represent a diagonal element of the charge density matrix: $\gamma_i^o = \gamma_{ii}^o$. This is done for notational convenience.

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36. Reinhardt and Doll find that accurate occupation numbers are

difficult to obtain. Private communication.

37. From this point on the unknown wave function $|\phi\rangle$ will probably not be exact. However we will often refer to $|\phi\rangle$ as the exact function in the sense that $\mathcal{O}_{\hbar} |\phi\rangle = 0$ (see Eqn. (VIII.8)).

Chapter Four

First- and Second-Order Density Matrices

of Symmetry-Projected Single Determinants

I. Introduction

It has been found that the effects of applying a spin projection operator to a determinental wave function involving different orbitals for different spins can be conveniently summarized by considering the first and second order reduced density matrices.[1,2] In this chapter we will be concerned with the density matrices of wave functions obtained by applying to a single determinant projection operators of point-groups or the axial-rotation group.

In section II we consider the effects of point-group symmetry projection, and obtain expressions for the elements of the first and second order density matrices of the projected function. An example is considered in section III. In sections IV and V we treat the axial-rotation group and an example of this group.

It is also of interest to obtain the totally symmetric components of density matrices, since only these components contribute to the expectation values of symmetric operators. We consider this problem in section VI. In section VII, we consider the effect of projection on the eigenfunctions of the totally symmetric component of the first order density matrix. We find that these eigenfunctions can be taken to be the same after projection as before.

II. Derivation of the Density Matrices for Point-Group Projection

We start with a function Φ which we wish to adapt to the symmetry of a particular group:

$$\Phi(1\ldots N) = \mathcal{A}\,\phi_1(1)\ldots\phi_N(N), \tag{1}$$

where $\mathcal{A}$ is the N-particle antisymmetrizer, $\phi_1 \cdots \phi_N$ are orthonormal spin-orbitals without any particular symmetry properties, and the arguments 1 ... N refer to the space and spin coordinates of particles 1 through N, respectively. The normalized, symmetry-adapted wave function can be obtained by projection as

$$\Psi_\nu = \omega_\nu^{-1/2} \mathcal{O}_\nu \Phi \tag{2}$$

where

$$\omega_\nu = \int (\mathcal{O}_\nu \Phi)^* (\mathcal{O}_\nu \Phi) \, d\tau \, , \tag{3}$$

The projection operator $\mathcal{O}_\nu$ can be expressed as[3]

$$\mathcal{O}_\nu = \sum_R C_\nu(R) \, \underset{\sim}{R}, \tag{4a}$$

where the sum is over all operations in the group. The index ν refers to that irreducible representation which characterizes Ψ_ν. The coefficients $C_\nu(R)$ are defined in terms of the characters $\chi_\nu(R)$, the dimension n_ν of irreducible representation ν, and the order of the group, g.

$$C_\nu(R) = (n_\nu/g)\chi_\nu^*(R) \, . \tag{4b}$$

Since we are dealing with a many-particle system the group operators $\underset{\sim}{R}$ will be of the form

$$\underset{\sim}{R}(1\ldots N) = \underset{\sim}{R}(1)\underset{\sim}{R}(2)\ldots\underset{\sim}{R}(N), \tag{5}$$

where $\underset{\sim}{R}(k)$ operates only on the coordinates of the kth particle. For convenience, we adopt a special notation for the effect of a symmetry operation on a spin-orbital:

$$\underset{\sim}{R}(k)\phi_i(k) = \phi_i{}^R(k). \tag{6}$$

Then Ψ_ν is seen to be

$$\Psi_\nu(1\ldots N) = \omega_\nu{}^{-1/2}\sum_R C_\nu(R)\ \phi_1{}^R(1)\ldots\phi_N{}^R(N). \tag{7}$$

We first evaluate the normalization constant ω_ν, making use of the facts that $\mathcal{O}_\nu$ is self-adjoint and idempotent,[4] and that $\mathcal{A}$ is self-adjoint and has

$$\mathcal{A}^2 = \sum_P (-1)^P \underset{\sim}{P}, \tag{8}$$

the sum of all $N!$ signed permutations of N-particles. Then

$$\omega_\nu = \sum_R C_\nu(R)\sum_P(-1)^P \int\phi_1{}^*(1)\ldots\phi_N{}^*(N)\phi_{P1}{}^R(1)\ldots\phi_{PN}{}^R(N)d\tau \tag{9}$$

where P_i is the index produced from i by $\underset{\sim}{P}^{\pm 1}$. The integral in (9) is a product of one-electron integrals of the form

$$\int \phi_i^{*}(i)\phi_{Pi}^{R}(i)d\tau_i = \int \phi_i^{*}(i)R(i)\phi_{Pi}(i)d\tau_i \ , \tag{10}$$

The expression for ω_ν therefore takes the form

$$\begin{aligned}
\omega_\nu &= \sum_R C_\nu(R)\sum_P (-1)^P R_{1,P1}\cdots R_{N,PN} \\
&= \sum_R C_\nu(R) \ \det \underset{\sim}{R} \ , \tag{11}
\end{aligned}$$

Notice that the determinants, $\det \underset{\sim}{R}$, are to involve only the spin-orbitals appearing in Φ . They are determinants of N x N matrices. Thus if we know the matrix elements of the group operations in the spin-orbital basis, we can calculate ω_ν . We will assume that these matrix elements are known.

We now proceed to the calculation of the first order density matrix. Given a symmetric, one-particle operator Ω, we can write its expectation value $< \Omega >_\nu$, with respect to Ψ_ν in two ways:

$$<\Omega>_\nu = \int \Psi_\nu^{*}\Omega\Psi_\nu d\tau = \int' \Omega(1)\gamma_\nu(1|1')d\tau_1 . \tag{12}$$

The first expression is the usual definition of the expectation value, and the second is the density matrix equivalent. The prime on the integral means that $\Omega(1)$ first operates on the unprimed coordinates only, then the primed coordinates are set equal to the unprimed and integration is carried out. Our method will be to calculate $< \Omega >_\nu$ using the first expression, and then to identify $\underset{\sim}{\gamma}_\nu$ as that which will correctly reproduce the second expression.

Therefore, we must calculate

$$\langle \Omega \rangle_\nu = \omega_\nu^{-1} \int \phi^* \mathcal{O}_\nu \Omega \mathcal{O}_\nu \phi \, d\tau \tag{13}$$

First we examine the operator $\mathcal{O}_\nu \Omega \mathcal{O}_\nu$.

$$\mathcal{O}_\nu \Omega \mathcal{O}_\nu = \sum_R C_\nu(R) R \sum_{i=1}^N \Omega(i) \mathcal{O}_\nu$$

$$= \sum_R C_\nu(R) \sum_{i=1}^N R(i) \, \Omega(i) R^{-1}(i) R \mathcal{O}_\nu \tag{14}$$

Substituting (14) into (13) and noting that R and $\mathcal{O}_\nu$ commute with $\mathscr{A}$, we obtain

$$\langle \Omega \rangle_\nu = \omega_\nu^{-1} \sum_R C_\nu(R) \int \mathscr{A} \phi_1^*(1) \ldots \phi_N^*(N) \sum_{i=1}^N R(i) \, \Omega(i) R^{-1}(i)$$

$$\times \mathscr{A} R \mathcal{O}_\nu \phi_1(1) \ldots \phi_N(N) d\tau$$

$$= \omega_\nu^{-1} \sum_{R,S} C_\nu(R) C_\nu(S) \sum_{i=1}^N \sum_P (-1)^P \int \phi_1^*(1) \ldots \phi_N^*(N) \tag{15}$$

$$\times R(i) \Omega(i) R^{-1}(i) \phi_{P1}^{RS}(1) \ldots \phi_{PN}^{RS}(N) d\tau \; .$$

Since the symmetry operators are unitary,

$$\int \phi_i^*(i) R(i) \Omega(i) R^{-1}(i) \phi_{Pi}^{RS} d\tau_i = \int \phi_i^{R^{-1}*}(i) \Omega(i) \phi_{Pi}^S(i) d\tau_i \tag{16}$$

If we now let $T = RS$, so that $R = TS^{-1}$, we have

$$\langle\Omega\rangle_\nu = \omega_\nu^{-1} \sum_{S,T} C_\nu(TS^{-1}) C_\nu(S) \sum_{i,j=1}^{N} T(i|j) \int \phi_i^{ST^{-1}*}(1)\Omega(1)\phi_j^{S}(1)\tau_1 \tag{17}$$

where $T(i|j)$ is the i,j cofactor of T.

We now assume the existence of an orthonormal set of spin-orbitals $\phi_1 \cdots \phi_N, \phi_{N+1} \cdots \phi_M$, such that $\phi_1 \cdots \phi_N$ are the spin-orbitals occurring in Φ and that for any $\underset{\sim}{R}$ in the group, $\underset{\sim}{R}\phi_i$ can be expressed as

$$\underset{\sim}{R}\phi_i = \sum_{k=1}^{M} R_{ki}\phi_k , \qquad i = 1,2,\ldots M. \tag{18}$$

We can then write

$$\int \phi_i^{ST^{-1}*}(1)\Omega(1)\phi_j^{S}(1)d\tau_1$$

$$= \sum_{k,\ell=1}^{M} (ST^{-1})_{ki}^{*} S_{\ell j} \int \phi_k^{*}(1)\Omega(1)\phi_\ell(1)d\tau_1 \tag{19}$$

$$= \sum_{k,\ell=1}^{M} (TS^{-1})_{ik} S_{\ell j} \Omega_{k\ell};$$

and thus

$$\langle\Omega\rangle_\nu = \omega_\nu^{-1} \sum_{S,T} C_\nu(TS^{-1}) C_\nu(S) \sum_{i,j=1}^{N} T(i|j) \sum_{k,\ell=1}^{M} (TS^{-1})_{ik} S_{\ell j} \Omega_{k\ell}$$

$$\tag{20}$$

$$= \sum_{k,\ell=1}^{M} \left\{ \omega_\nu^{-1} \sum_{S,T} C_\nu(TS^{-1}) C_\nu(S) \sum_{i,j=1}^{N} T(i|j)(TS^{-1})_{ik} S_{\ell j} \right\} \Omega_{k\ell}.$$

Therefore, we may identify γ_ν as

$$\gamma_\nu(1|1') = \sum_{k,\ell=1}^{M} \gamma^{(\nu)}{}_{k\ell} \, \phi_\ell(1) \phi_k^*(1') \tag{21}$$

where

$$\gamma^{(\nu)}{}_{k\ell} = \omega_\nu^{-1} \sum_{S,T} C_\nu(TS^{-1}) C_\nu(S) \sum_{i,j=1}^{N} T(i|j)(TS^{-1})_{ik} S_{\ell j} \tag{22}$$

In a similar fashion, we find the second order density matrix to be given as

$$\Gamma_\nu(12|1'2') = \sum_{\substack{p,q,r,t \\ =1}}^{M} \Gamma^{(\nu)}{}_{pqrt} \phi_p(1)\phi_q(2)\phi_r^*(1')\phi_t^*(2') \tag{23}$$

with

$$\Gamma^{(\nu)}{}_{pqrt} = \omega_\nu^{-1} \sum_{T,S} C_\nu(TS^-) C_\nu(S) \sum_{i<j=1}^{N} \sum_{k<\ell=1}^{N} T(ij|k\ell)$$

$$\tag{24}$$

$$\times S_{pk} S_{q\ell} (TS^{-1})_{ir} (TS^{-1})_{jt},$$

where T(ij|kl) is the ij;kl cofactor of T^4.

Equations (21), (22), (23), and (24) are the final expressions for the desired first and second order density matrices in the case of finite groups. Notice that we only need know the matrices of the group operations in the spin-orbital basis, and the appropriate character table (the group multiplication table must also be known, but can be determined if necessary from the orbital-basis representation). Once

we have this information, calculation of $\underset{\sim}{\gamma}_\nu$ and $\underset{\sim}{\Gamma}_\nu$ is straight-forward.

III. Example for Finite Point Groups

As an example we consider a wave function for the water molecule

$$\Phi = \mathscr{A} [\phi_1{}^\alpha(1)\phi_1{}^\beta(2)\ldots\phi_4{}^\alpha(7)\phi_4{}^\beta(8)\phi_5{}^\alpha(9)\phi_5{}^\beta(10)]$$

where the orbitals are

$$\phi_1 = (2+2\Delta)^{-1/2}(1S_A + 1S_B), \qquad \Delta = \int 1S_A 1S_B d\tau$$

$$\phi_2 = 1S_O, \qquad \phi_3 = 2S_O, \qquad \phi_4 = 2p_{z,O}$$

$$\phi_5 = 2^{-1/2}(2p_{x,O} + 2p_{y,O})$$

$$\phi_6 = 2^{-1/2}(2p_{x,O} - 2p_{y,O})$$

The molecule is assumed to have C_{2v} symmetry and to lie in the yz plane. Subscripts A and B refer to the two hydrogen atoms and O to the oxygen atom. Orbitals ϕ_1 through ϕ_4 are thus symmetry adapted but ϕ_5 and ϕ_6 are not. The last orbital is added to give a complete set in the sense of equation (18).

In this basis, the matrices of the symmetry operators decompose into pairs of 6 x 6 matrices, a set of matrices involving α spin and an identical set involving β spin. These matrices are as follows:

E is the 6 x 6 unit matrix. Each of C_2, $\sigma_v = \sigma_{xz}$ and $\sigma_v' = \sigma_{yz}$ has diagonal elements 1,1 through 4,4 equal to 1. In addition, $(C_2)_{5,5} = (C_2)_{6,6} = -1$, $(\sigma_v)_{5,6} = (\sigma_v)_{6,5} = 1$, and $(\sigma_v')_{5,6} = (\sigma_v')_{6,5} = -1$. Other elements are zero.

We will illustrate the formulas developed in the previous section by obtaining the density matrices for the A_2 component of Φ. Using equation (11), we find that

$$\omega_{A_2} = \tfrac{1}{4}[\ \det E + \det C_2 - \det \sigma_v - \det \sigma_v'\ ]$$

$$= \tfrac{1}{4}[\ 1 + 1 + 0 + 0\ ] = \tfrac{1}{2}$$

Remember that in equation (11) the determinants are over only the spin-orbitals appearing in Φ; so only the pairs of 5 x 5 submatrices of our operator matrices are to be used to calculate ω_{A_2}. We also find it helpful to construct a table of the various terms appearing in the expressions for γ_v and Γ_v (Table I).

Using this information and equation (22) we obtain

$$\gamma_{A_2}(1|1') = \sum_{i=1}^{4} \phi_i(1)\phi_i^*(1')[\alpha\alpha^*+\beta\beta^*] + \tfrac{1}{2}\phi_5(1)\phi_5^*(1')[\alpha\alpha^*+\beta\beta^*]$$

$$+ \tfrac{1}{2}\phi_6(1)\phi_6^*(1')[\alpha\alpha^*+\beta\beta^*]\ .$$

Similarly, by using equation (24), we find that

Table I. Combinations of Group Operations

Used to Calculate Density Matrices

T	S^{-1}	TS^{-1}	$\chi_{A_2}(S)$	$\chi_{A_2}(TS^{-1})$
E	E	E	1	1
	C_2	C_2	1	1
	σ_v	σ_v	-1	-1
	$\sigma_{v'}$	$\sigma_{v'}$	-1	-1
C_2	E	C_2	1	1
	C_2	E	1	1
	σ_v	$\sigma_{v'}$	-1	-1
	$\sigma_{v'}$	σ_v	-1	-1
σ_v	E	σ_v	1	-1
	C_2	$\sigma_{v'}$	1	-1
	σ_v	E	-1	1
	$\sigma_{v'}$	C_2	-1	1
$\sigma_{v'}$	E	$\sigma_{v'}$	1	-1
	C_2	σ_v	1	-1
	σ_v	C_2	-1	1
	$\sigma_{v'}$	E	-1	1

$$\Gamma_{A_2}(12|1'2') = \frac{1}{2} \sum_{i,j=1}^{4} \{|i\alpha j\alpha|^2 + |i\alpha j\beta|^2 + |i\beta j\alpha|^2 + |i\beta j\beta|^2\}$$

$$+ \frac{1}{2} \sum_{i=1}^{4} \{|i\alpha 5\alpha|^2 + |i\alpha 5\beta|^2 + |i\beta 5\alpha|^2 + |i\beta 5\beta|^2\}$$

$$+ \frac{1}{2} \sum_{i=1}^{4} \{|i\alpha 6\alpha|^2 + |i\alpha 6\beta|^2 + |i\beta 6\alpha|^2 + |i\beta 6\beta|^2\}$$

$$+ \frac{1}{4} \{|5\alpha 5\beta|^2 + |5\beta 5\alpha|^2 + |6\alpha 6\beta|^2 + |6\beta 6\alpha|^2\}$$

$$- \frac{1}{2} [\mathcal{B}\phi_5{}^\alpha(1)\phi_5{}^\beta(2)][\mathcal{B}'\phi_6{}^\alpha(1')\phi_6{}^\beta(2')]^*$$

$$- \frac{1}{2} [\mathcal{B}\phi_6{}^\alpha(1)\phi_6{}^\beta(2)][\mathcal{B}'\phi_5{}^\alpha(1')\phi_5{}^\beta(2')]^*,$$

where

$$\mathcal{B} = 2^{-1/2}(1 - \underset{\sim}{P}_{12}), \qquad \mathcal{B}' = 2^{-1/2}(1 - \underset{\sim}{P}_{1'2'})$$

and

$$|i\alpha j\beta|^2 = [\mathcal{B}\phi_i{}^\alpha(1)\phi_j{}^\beta(2)][\mathcal{B}'\phi_i{}^\alpha(1')\phi_j{}^\beta(2')]^*.$$

Equivalent results are of course obtainable more directly. The advantage of the present method increases with the number of non-symmetry adapted orbitals, and is much more apparent for non-Abelian groups.

IV. The Axial-Rotation Group

To extend the above treatment for the first order density matrix to the axial-rotation group, we need only change the formula for the projection operator. The proper projection operator is[5]

$$\mathcal{O}_m = \frac{1}{2\pi} \int_0^{2\pi} d\alpha \; e^{-im\alpha} R_\alpha .$$ (25)

In this expression R_α is an operator which rotates through angle α. If we define

$$Q_m(ik\ell j|\alpha) = (2\pi)^{-2} e^{-im\alpha} \int_0^{2\pi} d\phi (R_\phi)_{ik} (R_{\alpha-\phi})_{\ell j} ,$$ (26)

then we obtain for the coefficients

$$\gamma^{(m)}_{\ell k} = \omega_m^{-1} \int_0^{2\pi} d\alpha \sum_{i,j=1}^{N} R_\alpha(i|j) Q_m(ik\ell j|\alpha)$$ (27)

where $R_\alpha(i|j)$ is the i,j cofactor of R_α. The normalization integral is given by

$$\omega_m = \frac{1}{2\pi} \int_0^{2\pi} d\alpha \; e^{-im\alpha} \det R_\alpha .$$ (27a)

The evaluation of the second order density matrix is somewhat more difficult and will not be presented here.

V. Example for Axial-Rotation Group

As an example in this case we will calculate the first order density matrix of the $L_z = 1$ component of an atomic function (we

will not consider the L^2 behavior). We take

$$\Phi = \mathcal{A}[1s^{\alpha}(1)1s^{\beta}(2)2s^{\alpha}(3)2s^{\beta}(4)2p_x^{\alpha}(5)]$$

Since $2P_x = 2^{-1/2}(2P_{+1} + 2P_{-1})$ and the S orbitals are symmetric, the effect of a rotation about the Z-axis by angle ξ can be written as

$$\underset{\sim}{R}_{\xi}\Phi = \mathcal{A}[1s^{\alpha}(1)1s^{\beta}(2)2s^{\alpha}(3)2s^{\beta}(4)\{2^{-1/2}(e^{i\xi}2p_{+1}+e^{-i\xi}2p_{-1})\}^{\alpha}(5)].$$

From this and equation (27),

$$\gamma_1(1|1') = [1s(1)1s^*(1')+2s(1)2s^*(1')](\alpha\alpha^*+\beta\beta^*)$$

$$+\frac{1}{2}[\phi_3(1)\phi_3^*(1')+\phi_4(1)\phi_4^*(1')$$
$$+\phi_3(1)\phi_4^*(1')+\phi_4(1)\phi_3^*(1')]\alpha\alpha^*$$

where

$$\phi_3 = 2^{-1/2}(2p_{+1}+2p_{-1}) = 2p_x$$

and

$$\phi_4 = 2^{-1/2}(2p_{+1}-2p_{-1}) = i2p_y$$

But this can be written as

$$\gamma_1(1|1') = [1s(1)1s^*(1')+2s(1)2s^*(1')](\alpha\alpha^*+\beta\beta^*)$$

$$+2p_{+1}(1)2p_{+1}^*(1')\alpha\alpha^*.$$

This result is of course expected because the $L_z = 1$ component of Φ is given by

$$\Psi_1 = \mathscr{A} [1s^\alpha(1)1s^\beta(2)2s^\alpha(3)2s^\beta(4)2p_{+1}{}^\alpha(5)],$$

and the first order density matrix above follows directly. For a more complicated function, however, the density matrix method can be simpler than the direct method.

VI. The Totally Symmetric Components of $\underset{\sim\sim}{\gamma}_\nu$ and $\underset{\sim\sim}{\Gamma}_\nu$.

The totally symmetric component $\underset{\sim\sim}{\Gamma}_\nu{}^0$ of $\underset{\sim\sim}{\Gamma}_\nu$ can be obtained as

$$\underset{\sim\sim}{\Gamma}_\nu{}^0 = g^{-1} \underset{R}{\Sigma} \underset{\sim\sim\sim}{R}\underset{\sim\sim}{\Gamma}_\nu \underset{\sim\sim}{R}{}^{-1}$$

$$= g^{-1} \underset{R}{\Sigma} \underset{\sim}{R}(12)\underset{\sim}{R}(1'2')\Gamma_\nu(12|1'2') \tag{28}$$

and

$$\underset{\sim\sim}{\gamma}_\nu{}^0 = g^{-1} \underset{R}{\Sigma} \underset{\sim}{R}(1)\underset{\sim}{R}(1')\gamma_\nu(1|1'). \tag{29}$$

We will consider $\underset{\sim\sim}{\gamma}_\nu{}^0$ first.

$$\gamma_\nu{}^0(1|1') = g^{-1}\underset{Q}{\Sigma} \underset{k,\ell=1}{\overset{M}{\Sigma}} \gamma^{(\nu)}{}_{k\ell}Q(1)\phi_k(1)Q(1')\phi_\ell{}^*(1')$$

$$= \underset{i,j=1}{\overset{M}{\Sigma}} [g^{-1}\underset{Q}{\Sigma} \underset{k,\ell=1}{\overset{M}{\Sigma}} \gamma^{(\nu)}{}_{k\ell}Q_{ik}Q^{-1}{}_{\ell j}]\phi_i(1)\phi_j{}^*(1')$$

$$= \underset{i,j=1}{\overset{M}{\Sigma}} (\gamma_\nu{}^0)_{ij}\phi_i(1)\phi_j{}^*(1') \tag{30}$$

Where

$$(\gamma_\nu{}^0)_{ij} = g^{-1} \sum_Q \sum_{k,\ell=1}^{M} \gamma^{(\nu)}{}_{k\ell} Q_{ik} Q^{-1}{}_{\ell j} \quad , \tag{31}$$

But

$$\sum_{k,\ell=1}^{M} Q_{ik} \gamma^{(\nu)}{}_{k\ell} Q^{-1}{}_{\ell j}$$

$$= \sum_{k,\ell=1}^{M} \omega_\nu{}^{-1} \sum_{S,T} C_\nu(TS^{-1}) C_\nu(S) \sum_{p,q=1}^{N} T(p|q)(TS^{-1})_{p\ell}$$

$$\times S_{kq} Q^{-1}{}_{\ell j} Q_{ik} \tag{32}$$

$$= \omega_\nu{}^{-1} \sum_{S,T} C_\nu(TS^{-1}) C_\nu(S) \sum_{p,q=1}^{N} T(p|q)(TS^{-1}Q^{-1})_{pj} (QS)_{iq} \quad .$$

Letting $R = QS$, and using the orthogonality properties of the $C_\nu(R)$, we obtain

$$(\gamma_\nu{}^0)_{ij} = g^{-1} \omega_\nu{}^{-1} \sum_{R,S,T} C_\nu(TS^{-1}) C_\nu(S) \sum_{k,\ell=1}^{N} T(k|\ell) R_{i\ell} (TR^{-1})_{kj}$$

$$\tag{33}$$

$$= g^{-1} \omega_\nu{}^{-1} \sum_{R,T} C_\nu(T) \sum_{k,\ell=1}^{N} T(k|\ell) R_{i\ell} (TR^{-1})_{kj} \quad ,$$

In a similar way we obtain the matrix elements of the symmetric component of the second order density matrix

$$(\Gamma_\nu{}^0)_{rspq} = g^{-1} \omega_\nu{}^{-1} \sum_{R,T} C_\nu(T) \sum_{\substack{i<j=1 \\ k<\ell=1}}^{N} T(ij|k\ell) R_{ri} R_{sj} (TR^{-1})_{kp} (TR^{-1})_{\ell q} \quad .$$

$$\tag{34}$$

Equations (33) and (34) are the final expressions for the coefficients

in the expansion of $\gamma_\nu{}^0$ and $\Gamma_\nu{}^0$, respectively. Again a knowledge

of the matrices of the group operations and the appropriate character

table is all that is needed to perform the calculations. Because

equations (33) and (34) are slightly simpler than equations (22) and

(24), the totally symmetric components should prove more convenient

for performing numerical calculations involving symmetric operators.

VII. Totally Symmetric Components of First Order Density Matrices

Before and After Projection

It has been noticed in spin-projection calculations that the

natural orbitals of the charge density matrix are not changed by pro-

jection.[1] In what follows, we will examine the corresponding problem

in the point-group case.

Let the totally symmetric component of the first order density

matrix before projection be denoted by ρ^0 . With $\gamma_\nu{}^0$ from

equation (33), we have for an element of the commutator of ρ^0 and $\gamma_\nu{}^0$

$$[\gamma_\nu{}^0, \rho^0]_{ij} = \sum_{k=1}^{M} \{ (\gamma_\nu{}^0)_{ik}(\rho^0)_{kj} - (\rho^0)_{ik}(\gamma_\nu{}^0)_{kj} \}$$

$$= g^{-1}\omega_\nu{}^{-1} \sum_{R,T} C_\nu(T) \sum_{m,n=1}^{N} T(m|n)$$

$$\times \{ R_{in}(TR^{-1}\rho^0)_{mj} - (\rho^0 R)_{in}(TR^{-1})_{mj} \} \quad . \tag{35}$$

Because both ρ^0 and $\gamma_\nu{}^0$ are by definition totally symmetric,

they will commute with all symmetry operations and so will their

commutator. We can transform to a symmetry adapted basis $\{\eta^{\alpha}_{ai}\}$ related to the original spin-orbital basis $\{\phi_i\}$ by a unitary transformation

$$\phi_j = \sum_{\alpha}\sum_{a=1}^{J_\alpha}\sum_{i=1}^{n_\alpha} U^{-1}{}_{(\alpha ai),j}\,\eta^{\alpha}_{ai} \,, \tag{36}$$

The set $\alpha a i$ can be thought of as constituting a single index labeling η or as a set of indicies. The irreducible representation is identified by α and further labeled by a if J_α, the number of times the αth irreducible representation occurs in the reduction of the $\{\phi_i\}$ representation, is greater than 1. The functions transforming among themselves within a given irreducible representation are indexed by i.

In this symmetry-adapted basis, symmetric operators will have zero matrix elements between functions belonging to different irreducible representations. Further, the block associated with a given irreducible representation (α and a) must be a multiple of the $n_\alpha \times n_\alpha$ unit matrix

$$<\eta^{\alpha}_{ai}|\Omega^0|\eta^{\alpha}_{aj}> = \delta_{ij}\xi(\alpha a) \tag{37}$$

where Ω^0 can be ρ^0, γ_ν^0, or their commutator and $\xi(\alpha a)$ depends on the operator, a and α, but not on i or j. The matrices of the symmetry operations themselves will be zero outside each $n_\alpha \times n_\alpha$ block labeled by α and a.

Using equations (35) and (36), and the fact that ρ^0 commutes with all symmetry operations, we obtain

$$[\gamma_\nu{}^0, \rho^0]_{ij} = g^{-1}\omega_\nu{}^{-1} \sum_{R,T} C_\nu(T) \sum_{m,n=1}^{N} T(m|n) \sum_{\substack{\alpha,a \\ q,r}} \sum_{\substack{\beta,b \\ t,s}} \{U_{i,(\alpha a q)}$$

$$\times \langle \eta^\alpha{}_{aq}|R|\eta^\alpha{}_{ar}\rangle U^{-1}{}_{(\alpha a r),n} U_{m,(\beta b s)} \quad (38)$$

$$\times \langle \eta^\beta{}_{bs}|\rho^0 T R^{-1}|\eta^\beta{}_{bt}\rangle U^{-1}{}_{(\beta b t),j} - U_{i,(\alpha a q)}\langle \eta^\alpha{}_{aq}|R\rho^0|\eta^\alpha{}_{ar}\rangle$$

$$\times U^{-1}{}_{(\alpha a r),n} U_{m,(\beta b s)}\langle \eta^\beta{}_{bs}|T R^{-1}|\eta^\beta{}_{bt}\rangle U^{-1}{}_{(\beta b t),j}\}.$$

Therefore, we may identify the matrix element in the symmetry-adapted basis as

$$\langle \eta^\alpha{}_{aq}|[\gamma_\nu{}^0, \rho^0]|\eta^\beta{}_{bt}\rangle = g^{-1}\omega_\nu{}^{-1} \sum_{R,T} C_\nu(T) \sum_{m,n=1}^{N} T(m|n)$$

$$\quad (39)$$

$$\times \sum_{r,s} \{\langle \eta^\alpha{}_{aq}|R|\eta^\alpha{}_{ar}\rangle\langle \eta^\beta{}_{bs}|\rho^0 T R^{-1}|\eta^\beta{}_{bt}\rangle$$

$$- \langle \eta^\alpha{}_{aq}|R\rho^0|\eta^\alpha{}_{ar}\rangle\langle \eta^\beta{}_{bs}|T R^{-1}|\eta^\beta{}_{bt}\rangle\} U^{-1}{}_{(\alpha a r),n} U_{m,(\beta b s)}.$$

From equation (37) we have

$$\langle \eta^\alpha{}_{aq}|R\rho^0|\eta^\alpha{}_{ar}\rangle = \sum_{\epsilon,e,u} \langle \eta^\alpha{}_{aq}|R|\eta^\epsilon{}_{eu}\rangle\langle \eta^\epsilon{}_{eu}|\rho^0|\eta^\alpha{}_{ar}\rangle \quad (40)$$

$$= \langle \eta^\alpha{}_{aq}|R|\eta^\alpha{}_{ar}\rangle\langle \eta^\alpha{}_{ar}|\rho^0|\eta^\alpha{}_{ar}\rangle ,$$

where $<\eta^{\alpha}_{ar}|\rho^0|\eta^{\alpha}_{ar}>$ is in fact independent of r.

Because $[\gamma_{\nu}{}^0, \rho^0]$ is anti-Hermitian, it can be diagonalized by a unitary transformation. The set $\{\eta^{\alpha}_{ai}\}$ has not yet been completely specified, so we now use our freedom to choose it so that $[\gamma_{\nu}{}^0, \rho^0]$ is diagonal. Equation (39) then becomes

$$<\eta^{\alpha}_{aq}|[\gamma_{\nu}{}^0, \rho^0]|\eta^{\beta}_{bt}> = \delta_{\alpha\beta}\delta_{ab}\delta_{qt} g^{-1}\omega_{\nu}{}^{-1} \sum_{R,T} C_{\nu}(T) \sum_{m,n=1}^{N} T(m|n)$$

$$\times \sum_{r,s} <\eta^{\alpha}_{aq}|R|\eta^{\alpha}_{ar}><\eta^{\alpha}_{as}|TR^{-1}|\eta^{\alpha}_{aq}> \qquad (41)$$

$$\times \{<\eta^{\alpha}_{as}|\rho^0|\eta^{\alpha}_{as}> - <\eta^{\alpha}_{ar}|\rho^0|\eta^{\alpha}_{ar}>\} U^{-1}{}_{(\alpha ar),n} U_{m,(\alpha as)}.$$

Because $<\eta^{\alpha}_{ar}|\rho^0|\eta^{\alpha}_{ar}>$ does not depend on r,

$$<\eta^{\alpha}_{aq}|[\gamma_{\nu}{}^0, \rho^0]|\eta^{\beta}_{bt}> = 0 \qquad (42)$$

and from this we deduce that the eigenfunctions of the totally symmetric component of the first order density matrix will not be changed by projection.

VIII. Discussion of Results

In this chapter we have shown how to calculate the first and second order density matrices of symmetry-projected wave functions. Our technique does not require the explicit calculation of the projected wave function. The method should prove very useful when applied to point-group projection in polyatomic molecules and L^2 projection in diatomics.

We have also shown how to project from a given density matrix the totally symmetric component. This component is all that is needed in the calculation of expectation values of symmetric operators. Finally, we have shown that the NSO's of the totally symmetric component of the first order density matrix are unchanged by projections.

These results are of potential use in two ways:

(1) As a practical method of obtaining expectation values of symmetric operators for the component of a particular symmetry, projected from a non-symmetry adapted single-determinant wave function.

(2) As the first step in obtaining a variationally-useful energy expression for an extended Hartree-Fock calculation in which non-symmetry adapted orbitals are used to obtain a lower energy without sacrificing the symmetry properties of the total wave function.

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