

Direct Calculation of First- and Second-Order Density Matrices. The Higher RPA Method*

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We present a procedure for approximately determining the first- and second-order density matrices of pure-state N -fermion systems. A higher random-phase approximation is used to derive a method in which the resulting density matrices are approximated self-consistently in an iterative scheme. As test calculations, the method is applied to the ground states of the helium, lithium, and beryllium atoms. The possibility and importance of obtaining error bounds involving the density matrices are discussed.

I. INTRODUCTION

It is well known that the second-order reduced density matrix of the ground state is sufficient to determine all ground-state expectation values of one- and two-particle operators for systems composed of identical pairwise-interacting particles. In addition, the second-order density matrix is a function of only 12 continuous variables, whereas the system wavefunction depends on $3N$ continuous variables. These observations, together with the knowledge that accurate wavefunctions 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 *must* restrict the class of trial density matrices to those which can be expressed as

$$\Gamma(1, 2; 1', 2') = \binom{N}{2} \int \psi(1, 2, \dots, N) \times \psi^*(1', 2', \dots, N) d\tau_3 \dots d\tau_N, \quad (1.1)$$

where the normalized N -particle wavefunction $\psi(1, 2, \dots, N)$ is antisymmetric in all of the space spin variables represented by the integers $1, 2, \dots, N$. Such density matrices are said to be N representable.¹ The problem of determining necessary and sufficient conditions to guarantee that a proposed second-order density matrix Γ can be obtained from an antisymmetric wavefunction as in Eq. (1.1) is known as the pure state N -representability problem. The exact solution of this problem has not been found, but some progress has been made²⁻⁴ toward obtaining nearly N -representable density matrices which can be used in variational calculations. Very few numerical applications⁴ of these methods have been carried out.

Another more promising method which has been successfully applied to atomic^{5,6} and molecular⁷ 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 automatic computer, which is a distinct disadvantage of the method.

In this paper 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 wavefunction 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 higher random-phase approximation (HRPA) 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 HRPA is used to evaluate certain contributions to the second-order density matrix. Section 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. Section VII contains the results of applying the method to the helium, lithium, and beryllium atoms. We discuss possible error bounds involving the resultant density matrices in Sec. VIII. Section IX contains our concluding remarks.

II. THE HIGHER RANDOM-PHASE APPROXIMATION

The equations-of-motion method was originally developed by nuclear physicists⁸ as a technique for directly determining excitation energies and ground-state⁹ transition strengths for nuclei. It is expected that these relative quantities will not be as sensitive to correlations within the stationary-state wavefunctions 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 HRPAs occurs as a special case of the equations-of-motion method.

The equations-of-motion technique, which is discussed extensively by Rowe,¹⁰ is a method for approximating excitation operators which produce excited states of the system when operating on the *ground state* $|\phi\rangle$:

$$|k\rangle = O_k^+ |\phi\rangle, \quad (2.1)$$

where

$$H |\phi\rangle = E_g |\phi\rangle \quad (2.2)$$

and

$$H |k\rangle = E_k |k\rangle. \quad (2.3)$$

Starting with the fundamental equations defining excitation operators

$$[H, O_k^+] = \Delta E_k O_k^+, \quad (2.4)$$

$$[H, O_k] = -\Delta E_k O_k, \quad (2.5)$$

where

$$\Delta E_k = \omega_k \equiv E_k - E_g, \quad (2.6)$$

and the orthonormality statement for the states $|k\rangle$

$$\langle\phi| O_k O_l^+ |\phi\rangle = \delta_{kl}, \quad (2.7)$$

and the condition that O_k annihilate the ground state

$$O_k |\phi\rangle = 0, \quad (2.8)$$

$$\langle\phi| O_k^+ = 0, \quad (2.9)$$

Rowe obtains the following (exact) equations for O_k^+ :

$$\langle\phi| [R, [H, O_k^+]] |\phi\rangle = \Delta E_k \langle\phi| [R, O_k^+] |\phi\rangle, \quad (2.10)$$

$$\langle\phi| [R, [H, O_k]] |\phi\rangle = -\Delta E_k \langle\phi| [R, O_k] |\phi\rangle, \quad (2.11)$$

where R is an *arbitrary* operator. Equation (2.7) is also rewritten as

$$\langle\phi| [O_k, O_l^+] |\phi\rangle = \delta_{kl}. \quad (2.12)$$

To prepare for the possibility that $|\phi\rangle$ is not the exact ground-state wavefunction, but rather some approximate function, Rowe then combines Eqs. (2.10) and (2.11) into the single generalized equation

$$\langle\phi| [R, H, O_k^+] |\phi\rangle = \Delta E_k \langle\phi| [R, O_k^+] |\phi\rangle, \quad (2.13)$$

where the double commutator symbol is defined by

$$2[R, H, O_k^+] = [R, [H, O_k^+]] + [[R, H], O_k^+]. \quad (2.14)$$

The solutions O_k^+ of Eq. (2.13) are to be interpreted as excitation operators which generate excited state wavefunctions when operating on the ground state $|\phi\rangle$:

$$|k\rangle = O_k^+ |\phi\rangle. \quad (2.15)$$

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 higher random-phase

approximation we restrict the excitation operator to be of the following form:

$$O_k^+ = \sum_{m,\epsilon} [g_{m\epsilon}(k) C_m^+ C_\epsilon - h_{m\epsilon}(k) C_\epsilon^+ C_m], \quad (2.16)$$

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 Eq. (2.16) into Eq. (2.13) and using the fact that Eq. (2.13) must hold for any R within the space of operators spanned by $\{C_m^+ C_\epsilon, C_\epsilon^+ C_m\}$, 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:

$$\begin{pmatrix} A & B \\ -B^+ & -A^* \end{pmatrix} \begin{pmatrix} g \\ h \end{pmatrix} = \omega \begin{pmatrix} U & 0 \\ 0 & U^* \end{pmatrix} \begin{pmatrix} g \\ h \end{pmatrix} \quad (2.17)$$

with

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

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

$$U_{m\epsilon, n\theta} = \langle\phi| [C_\epsilon^+ C_m, C_n^+ C_\theta] |\phi\rangle. \quad (2.18)$$

If we assume that the Hamiltonian can be written as

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

the expressions given in Eq. (2.18) can be evaluated exactly. Because the results are somewhat lengthy, we will not reproduce them here, but rather, we refer the interested readers to p. 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 to¹²

$$\begin{aligned} A_{m\epsilon, n\theta} &= \delta_{mn} \delta_{\epsilon\theta} (\bar{\epsilon}_m - \bar{\epsilon}_\theta) (\gamma_\theta - \gamma_m) \\ &\quad + \tilde{V}_{m\theta, \epsilon n} (\gamma_\epsilon + \gamma_\theta - \gamma_m - \gamma_n - 1), \\ B_{m\epsilon, n\theta} &= \tilde{V}_{mn, \epsilon\theta} (\gamma_\epsilon + \gamma_\theta - \gamma_m - \gamma_n - 1), \\ U_{m\epsilon, n\theta} &= \delta_{mn} \delta_{\epsilon\theta} (\gamma_\epsilon - \gamma_m), \end{aligned} \quad (2.19)$$

where all subscripts refer to the Hartree-Fock spin-orbitals. We have introduced the *exact* single-particle density

$$\begin{aligned} \gamma_m &= \langle\phi| C_m^+ C_m |\phi\rangle, \\ \gamma_\theta &= \langle\phi| C_\theta^+ C_\theta |\phi\rangle, \end{aligned} \quad (2.20)$$

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

$$\tilde{V}_{mn, \epsilon\theta} = V_{mn, \epsilon\theta} - V_{mn, \theta\epsilon}. \quad (2.21)$$

Equations (2.17) and (2.19) are referred to as the HRPAs 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 operators¹³

$$\begin{aligned} D_{m\epsilon}^{1+} &= (2)^{-1/2}(C_{m\alpha} + C_{\epsilon\alpha} + C_{m\beta} + C_{\epsilon\beta}), \\ D_{m\epsilon}^{3,0+} &= (2)^{-1/2}(C_{m\alpha} + C_{\epsilon\alpha} - C_{m\beta} - C_{\epsilon\beta}), \\ D_{m\epsilon}^{3,1+} &= C_{m\alpha} + C_{\epsilon\beta}, \\ D_{m\epsilon}^{3,-1+} &= C_{m\beta} + C_{\epsilon\alpha}, \end{aligned} \quad (2.22)$$

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

$$\begin{aligned} O_k^{1+} &= \sum_{m\epsilon} [g_{m\epsilon}^1(k) D_{m\epsilon}^{1+} - h_{m\epsilon}^1(k) D_{m\epsilon}^{1-}], \\ O_k^{3,M_S+} &= \sum_{m\epsilon} [g_{m\epsilon}^3(k) D_{m\epsilon}^{3,M_S+} - h_{m\epsilon}^3(k) D_{m\epsilon}^{3,M_S-}], \\ M_S &= 1, 0, -1. \end{aligned} \quad (2.23)$$

The HRPAs Eqs. (2.17) also separate into singlet and triplet equations, with the matrix elements being given by

$$\begin{aligned} A_{m\epsilon, n\theta}^{1(3)} &= (2)^{-1} [\delta_{mn} \delta_{\epsilon\theta} \\ &\quad \times (\bar{\epsilon}_m - \bar{\epsilon}_\theta) (\gamma_\theta^o - \gamma_m^o) + \tilde{V}_{m\theta, \epsilon n} \\ &\quad \times (\gamma_\epsilon^o + \gamma_\theta^o - \gamma_m^o - \gamma_n^o - 2) (\pm) V_{m\theta, \epsilon n} \\ &\quad \times (\gamma_\epsilon^o + \gamma_\theta^o - \gamma_m^o - \gamma_n^o - 2)], \\ B_{m\epsilon, n\theta}^{1(3)} &= (2)^{-1} [\tilde{V}_{mn, \epsilon\theta} \\ &\quad \times (\gamma_\epsilon^o + \gamma_\theta^o - \gamma_m^o - \gamma_n^o - 2) (\pm) V_{mn, \epsilon\theta} \\ &\quad \times (\gamma_\epsilon^o + \gamma_\theta^o - \gamma_m^o - \gamma_n^o - 2)], \\ U_{m\epsilon, n\theta}^{1(3)} &= (2)^{-1} \delta_{mn} \delta_{\epsilon\theta} (\gamma_\epsilon^o - \gamma_m^o). \end{aligned} \quad (2.24)$$

The diagonal elements of the charge density matrix are defined as

$$\begin{aligned} \gamma_\epsilon^o &= \langle \phi | C_{\epsilon\alpha} + C_{\epsilon\alpha} + C_{\epsilon\beta} + C_{\epsilon\beta} | \phi \rangle, \\ \gamma_m^o &= \langle \phi | C_{m\alpha} + C_{m\alpha} + C_{m\beta} + C_{m\beta} | \phi \rangle. \end{aligned} \quad (2.25)$$

To convert the HRPAs equations to their final form we premultiply Eq. (2.17) by the (diagonal) matrix

$$\begin{pmatrix} U^{-1/2} & 0 \\ 0 & U^{-1/2} \end{pmatrix}$$

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:

$$\begin{pmatrix} A & B \\ -B^+ & -A^* \end{pmatrix} \begin{pmatrix} \bar{g} \\ \bar{h} \end{pmatrix} = \omega \begin{pmatrix} \bar{g} \\ \bar{h} \end{pmatrix}, \quad (2.26)$$

with

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

and

$$\bar{h}_{m\epsilon}^{1(3)}(k) = (2)^{-1/2} (\gamma_\epsilon^o - \gamma_m^o)^{1/2} h_{m\epsilon}^{1(3)}(k). \quad (2.27)$$

The matrix elements appearing in Eq. (2.26) are given by¹⁵

$$\begin{aligned} A_{m\epsilon, n\theta}^{1(3)} &= \delta_{mn} \delta_{\epsilon\theta} (\bar{\epsilon}_m - \bar{\epsilon}_\theta) \\ &\quad + (2)^{-1} (\gamma_\epsilon^o - \gamma_m^o)^{1/2} (\gamma_\theta^o - \gamma_n^o)^{1/2} \\ &\quad \times (\tilde{V}_{m\theta, \epsilon n}(\pm) V_{m\theta, \epsilon n}) \end{aligned}$$

and

$$\begin{aligned} B_{m\epsilon, n\theta}^{1(3)} &= (2)^{-1} (\gamma_\epsilon^o - \gamma_m^o)^{1/2} (\gamma_\theta^o - \gamma_n^o)^{1/2} \\ &\quad \times (\tilde{V}_{mn, \epsilon\theta}(\pm) V_{mn, \epsilon\theta}). \end{aligned} \quad (2.28)$$

This is the working form of the HRPAs equations.¹⁶

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 *exact* charge density matrix, we could use Eq. (2.28) 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 HRPAs Eqs. (2.26) 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 (2.23) for O_k^+ are given by Eq. (2.27). The approximate "excited states" can then be written as follows:

$$\begin{aligned} |k, 0, 0\rangle &= O_k^{1+} | \phi \rangle, \\ |k, 1, M_S\rangle &= O_k^{3, M_S+} | \phi \rangle, \end{aligned} \quad (2.29)$$

with obvious notation.¹⁷

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.,

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

Using the fact that $| \phi \rangle$ is the ground state, we can write $O_k^{1+} | \phi \rangle = 0$ ¹⁸ to obtain the result

$$\langle \phi | Q | k, 0, 0 \rangle = \langle \phi | [Q, O_k^{1+}] | \phi \rangle. \quad (2.30)$$

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 HRPAs in Sec. IV.

III. DENSITY MATRICES IN THE OCCUPATION NUMBER REPRESENTATION

The first- and second-order density matrices correspond to the wavefunction $|\phi\rangle$ can be written as follows¹⁹:

$$\gamma(1; 1') = \langle \phi | \psi^+(1')\psi(1) | \phi \rangle$$

and

$$2\Gamma(1, 2; 1', 2') = \langle \phi | \psi^+(1')\psi^+(2')\psi(2)\psi(1) | \phi \rangle, \quad (3.1)$$

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 $\{\phi_i(r)\alpha, \beta\}$, we can decompose the above expressions for γ and Γ into spin components, e.g.,

$$\begin{aligned} \gamma(1; 1') &= \sum_{i,j} [\phi_i^*(r_1')\phi_j(r_1)\alpha^*\alpha\langle \phi | C_{i\alpha}^+C_{j\alpha} | \phi \rangle \\ &+ \phi_i^*(r_1')\phi_j(r_1)\beta^*\beta\langle \phi | C_{i\beta}^+C_{j\beta} | \phi \rangle]. \quad (3.2) \end{aligned}$$

There is an analogous expression for Γ involving six terms.²⁰ In writing Eq. (3.2) we have assumed that the state $|\phi\rangle$ is an eigenstate of the operator S_z . This allows us to write

$$\langle \phi | C_{i\sigma}^+C_{j\sigma'} | \phi \rangle = \delta_{\sigma\sigma'}\langle \phi | C_{i\sigma}^+C_{j\sigma} | \phi \rangle, \quad (3.3)$$

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,

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

$$\gamma_{ji}^0 = \langle \phi | C_{i\sigma}^+C_{j\alpha} + C_{i\beta}^+C_{j\beta} | \phi \rangle,^{21}$$

and

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

$$\gamma_{ji}^z = \langle \phi | C_{i\alpha}^+C_{j\alpha} - C_{i\beta}^+C_{j\beta} | \phi \rangle. \quad (3.4)$$

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

$$\begin{aligned} 2\Gamma_{kl,ij}^0 &= \langle \phi | C_{i\alpha}^+C_{j\alpha} + C_{l\alpha}C_{k\alpha} \\ &+ C_{i\beta}^+C_{j\beta} + C_{l\beta}C_{k\beta} + C_{i\alpha}^+C_{j\beta} + C_{l\beta}C_{k\alpha} \\ &+ C_{i\beta}^+C_{j\alpha} + C_{l\alpha}C_{k\beta} | \phi \rangle \end{aligned}$$

and

$$\begin{aligned} 2\Gamma_{kl,ij}^z &= \langle \phi | C_{i\alpha}^+C_{j\alpha} + C_{l\alpha}C_{k\alpha} \\ &- C_{i\beta}^+C_{j\beta} + C_{l\beta}C_{k\beta} + C_{i\alpha}^+C_{j\beta} + C_{l\beta}C_{k\alpha} \\ &- C_{i\beta}^+C_{j\alpha} + C_{l\alpha}C_{k\beta} | \phi \rangle. \quad (3.5) \end{aligned}$$

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^0 and Γ^z which will allow us to make use of the HRP, we use anticommutation relations to re-express the terms appearing in Eq. (3.5), e.g.,

$$\begin{aligned} \langle \phi | C_{i\alpha}^+C_{j\beta} + C_{l\beta}C_{k\alpha} | \phi \rangle \\ = (2)^{-1}(\langle \phi | C_{i\alpha}^+C_{k\alpha}C_{j\beta} + C_{l\beta} | \phi \rangle \\ - \langle \phi | C_{i\alpha}^+C_{l\beta}C_{j\beta} + C_{k\alpha} | \phi \rangle \\ + \delta_{jl}\langle \phi | C_{i\alpha}^+C_{k\alpha} | \phi \rangle), \quad (3.6) \end{aligned}$$

and so forth. In addition, we insert a complete orthonormal set of N -particle functions between the pairs of creation and annihilation operators in Eq. (3.6). For example,

$$\begin{aligned} \langle \phi | C_{i\alpha}^+C_{k\alpha}C_{j\beta} + C_{l\beta} | \phi \rangle \\ = \langle \phi | C_{i\alpha}^+C_{k\alpha} | \phi \rangle \langle \phi | C_{j\beta} + C_{l\beta} | \phi \rangle \\ + \sum_t \langle \phi | C_{i\alpha}^+C_{k\alpha} | t \rangle \langle t | C_{j\beta} + C_{l\beta} | \phi \rangle, \quad (3.7) \end{aligned}$$

where the sum is over a complete orthonormal set of functions which are orthogonal to $|\phi\rangle$. Eventually we will identify these functions²² with the approximate excited states of the HRP theory, and we will use Eq. (2.30) to evaluate the quantities $\langle \phi | C_{i\sigma}^+C_{j\sigma'} | t \rangle$. By using relationships such as Eqs. (3.6) and (3.7), we can write the previous expressions for Γ^0 and Γ^z as follows:

$$\begin{aligned} \Gamma_{kl,ij}^0 &= 4^{-1}[\gamma_{kj}^0(2\delta_{lj} + \gamma_{li}^0) - \delta_{kj}\gamma_{li}^0 \\ &- \frac{1}{2}(\gamma_{li}^0\gamma_{kj}^0 + \gamma_{li}^z\gamma_{kj}^z)] + \Delta_{kl,ij}^0 \end{aligned}$$

and

$$\begin{aligned} \Gamma_{kl,ij}^z &= 4^{-1}[\gamma_{ki}^z(2\delta_{lj} + \gamma_{li}^0) - \delta_{kj}\gamma_{li}^z \\ &- \frac{1}{2}(\gamma_{li}^0\gamma_{kj}^z + \gamma_{li}^z\gamma_{kj}^0)] + \Delta_{kl,ij}^z. \quad (3.8) \end{aligned}$$

Here Δ^0 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 HRP to evaluate Δ^0 and Δ^z . Because the above expressions for Γ^0 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 HRP

The explicit form of $\Delta_{kl,ij}^0$ can be determined from Eqs. (3.5)–(3.7). It is given by

$$\begin{aligned} \Delta_{kl,ij}^0 &= 4^{-1} \sum_t (\langle \phi | C_{i\alpha}^+C_{k\alpha} \\ &+ C_{i\beta}^+C_{k\beta} | t \rangle \langle t | C_{j\alpha} + C_{l\alpha} + C_{j\beta} + C_{l\beta} | \phi \rangle \\ &- \langle \phi | C_{i\alpha}^+C_{l\alpha} | t \rangle \langle t | C_{j\alpha} + C_{k\alpha} | \phi \rangle \\ &- \langle \phi | C_{i\beta}^+C_{l\beta} | t \rangle \langle t | C_{j\beta} + C_{k\beta} | \phi \rangle \\ &- \langle \phi | C_{i\alpha}^+C_{l\beta} | t \rangle \langle t | C_{j\beta} + C_{k\alpha} | \phi \rangle \\ &- \langle \phi | C_{i\beta}^+C_{l\alpha} | t \rangle \langle t | C_{j\alpha} + C_{k\beta} | \phi \rangle). \quad (4.1) \end{aligned}$$

There is a similar expression for $\Delta_{kl,ij}^z$ 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 $\Delta_{kl,ij}^o$ we will identify the functions $|t\rangle$ in Eq. (4.1) with the excited states of the HRP 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 HRP method provides a technique for determining the approximate excited states without requiring knowledge of $|\phi\rangle$. Because the HRP procedure was designed to accurately predict transition properties, it should provide reasonable approximations to the quantities $\langle\phi|C_{i\sigma}+C_{j\sigma'}|t\rangle$ which occur in the expression for Δ^o . Note that the functions $C_{j\sigma'}+C_{i\sigma}|\phi\rangle$ are single excitations from $|\phi\rangle$. Therefore, we need only consider excited states $|t\rangle$ which are single excitations of $|\phi\rangle$; the contributions from double and higher excitations vanishes. Thus the form of the excitation operator given in Eq. (2.16) is sufficient to exhaust the sum over certain excited states.²³ Also it is shown in Rowe's article that certain sum rules are satisfied exactly by the HRP excited states, even when a truncated set of orbitals is used. This supports our conviction that the HRP 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_k^+ are of either singlet or triplet character. Thus, the sum over excited states in Eq. (4.1) 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:

$$\begin{aligned} S_{ki}^o(s) &= \langle\phi|C_{i\alpha}+C_{k\alpha}+C_{i\beta}+C_{k\beta}|s, 0, 0\rangle, \\ S_{ki}^z(s) &= \langle\phi|C_{i\alpha}+C_{k\alpha}-C_{i\beta}-C_{k\beta}|s, 0, 0\rangle, \\ T_{ki}^o(t) &= \langle\phi|C_{i\alpha}+C_{k\alpha}+C_{i\beta}+C_{k\beta}|t, 1, 0\rangle, \\ T_{ki}^z(t) &= \langle\phi|C_{i\alpha}+C_{k\alpha}-C_{i\beta}-C_{k\beta}|t, 1, 0\rangle, \\ T_{ki}^{(+)}(t) &= \langle\phi|C_{i\alpha}+C_{k\beta}|t, 1, -1\rangle, \end{aligned}$$

and

$$T_{ki}^{(-)}(t) = \langle\phi|C_{i\beta}+C_{k\alpha}|t, 1, 1\rangle. \quad (4.2)$$

We have used the notation of Eq. (2.29) for the excited state wavefunctions. With these definitions Eq. (4.1) can be written in the following form:

$$\begin{aligned} \Delta_{kl,ij}^o &= 4^{-1} \sum_s [S_{ki}^o S_{jl}^{o*} - \frac{1}{2} (S_{li}^o S_{jk}^{o*} + S_{li}^z S_{jk}^{z*})] \\ &+ 4^{-1} \sum_t [T_{ki}^o T_{jl}^{o*} - \frac{1}{2} (T_{li}^o T_{jk}^{o*} + T_{li}^z T_{jk}^{z*})] \\ &- 4^{-1} \sum_t (T_{li}^{(+)} T_{jk}^{(+)*} + T_{li}^{(-)} T_{jk}^{(-)*}). \quad (4.3) \end{aligned}$$

The corresponding result for Δ^z is given by

$$\begin{aligned} \Delta_{kl,ij}^z &= 4^{-1} \sum_s [S_{ki}^z S_{jl}^{o*} - \frac{1}{2} (S_{li}^o S_{jk}^{z*} + S_{li}^z S_{jk}^{o*})] \\ &+ 4^{-1} \sum_t [T_{ki}^z T_{jl}^{o*} - \frac{1}{2} (T_{li}^o T_{jk}^{z*} + T_{li}^z T_{jk}^{o*})] \\ &- 4^{-1} \sum_t (T_{li}^{(+)} T_{jk}^{(+)*} - T_{li}^{(-)} T_{jk}^{(-)*}). \quad (4.4) \end{aligned}$$

In these equations the summation indices (s and t) have been eliminated for notational convenience. Equations (4.3) and (4.4) are the final expressions for Δ^o and Δ^z .

Let us now turn our attention to the evaluation of the six quantities defined in Eq. (4.2). This can be carried out in a relatively straightforward fashion by using (2.30), identifying Q with $C_{i\sigma}+C_{j\sigma'}$. Knowing the form of the excitation operator from Eq. (2.23), the commutator $[C_{i\sigma}+C_{j\sigma'}, O_k^+]$ 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:

$$\begin{aligned} S_{ji}^o(s) &= 2^{-1/2} \{ \sum_{\epsilon} [g_{j\epsilon}^1(s) \gamma_{\epsilon i}^o + h_{i\epsilon}^1(s) \gamma_{j\epsilon}^o] \\ &- \sum_m [g_{mi}^1(s) \gamma_{jm}^o + h_{mj}^1(s) \gamma_{mi}^o] \}, \\ S_{ji}^z(s) &= 2^{-1/2} \{ \sum_{\epsilon} [g_{j\epsilon}^1(s) \gamma_{\epsilon i}^z + h_{i\epsilon}^1(s) \gamma_{j\epsilon}^z] \\ &- \sum_m [g_{mi}^1(s) \gamma_{jm}^z + h_{mj}^1(s) \gamma_{mi}^z] \}, \\ T_{ji}^o(t) &= 2^{-1/2} \{ \sum_{\epsilon} [g_{j\epsilon}^3(t) \gamma_{\epsilon i}^z + h_{i\epsilon}^3(t) \gamma_{j\epsilon}^z] \\ &- \sum_m [g_{mi}^3(t) \gamma_{jm}^z + h_{mj}^3(t) \gamma_{mi}^z] \}, \\ T_{ji}^z(t) &= 2^{-1/2} \{ \sum_{\epsilon} [g_{j\epsilon}^3(t) \gamma_{\epsilon i}^o + h_{i\epsilon}^3(t) \gamma_{j\epsilon}^o] \\ &- \sum_m [g_{mi}^3(t) \gamma_{jm}^o + h_{mj}^3(t) \gamma_{mi}^o] \}, \\ T_{ji}^{(+)}(t) &= 2^{-1} \\ &\times \{ \sum_{\epsilon} [g_{j\epsilon}^3(t) (\gamma_{\epsilon i}^o + \gamma_{\epsilon i}^z) + h_{i\epsilon}^3(t) (\gamma_{j\epsilon}^o - \gamma_{j\epsilon}^z)] \\ &- \sum_m [g_{mi}^3(t) (\gamma_{jm}^o - \gamma_{jm}^z) + h_{mj}^3(t) (\gamma_{mi}^o + \gamma_{mi}^z)] \}, \\ T_{ji}^{(-)}(t) &= 2^{-1} \\ &\times \{ \sum_{\epsilon} [g_{j\epsilon}^3(t) (\gamma_{\epsilon i}^o - \gamma_{\epsilon i}^z) + h_{i\epsilon}^3(t) (\gamma_{j\epsilon}^o + \gamma_{j\epsilon}^z)] \\ &- \sum_m [g_{mi}^3(t) (\gamma_{jm}^o + \gamma_{jm}^z) + h_{mj}^3(t) (\gamma_{mi}^o - \gamma_{mi}^z)] \}. \quad (4.5) \end{aligned}$$

In evaluating these quantities, one must remember that $g_{ij}^{1(3)}(k)$ and $h_{ij}^{1(3)}(k)$ are nonzero only if the orbital ϕ_i is unoccupied and the orbital ϕ_j is occupied in the single-determinant approximation to $|\phi\rangle$. Notice that if the HRP calculation has been carried out and if the exact charge- and spin-density matrices are known, Δ^o and Δ^z can be determined from Eqs. (4.3)–

(4.5). We have thus succeeded in approximately evaluating Δ^o and Δ^z by using the HRP 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:

$$\gamma_{ki}^o = 2(N-1)^{-1} \sum_l \Gamma_{kl,il}^o$$

and

$$\gamma_{ki}^z = 2(N-1)^{-1} \sum_l \Gamma_{kl,il}^z. \quad (5.1)$$

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 Eq. (3.8) into Eq. (5.1), we obtain, after some rearrangement, the following closed expressions for γ^o and γ^z :

$$\gamma_{ki}^o = 2^{-1}(2M+1-N)^{-1} \times \sum_{l=1}^M (\gamma_{kl}^o \gamma_{li}^o + \gamma_{kl}^z \gamma_{li}^z - 8\Delta_{kl,il}^o)$$

and

$$\gamma_{ki}^z = 2^{-1}(2M+1-N)^{-1} \times \sum_{l=1}^M (\gamma_{kl}^z \gamma_{li}^o + \gamma_{kl}^o \gamma_{li}^z - 8\Delta_{kl,il}^z), \quad k, i = 1, 2, \dots, M. \quad (5.2)$$

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 Eq. (5.2) are the approximate Δ^o and Δ^z which we obtain by doing a HRP calculation. In the next section we will describe an iterative procedure which can be used to solve Eq. (5.2).

VI. SELF-CONSISTENT DETERMINATION OF Γ^o , Γ^z , γ^o , AND γ^z

In the preceding sections we have shown how the HRP method can be used to evaluate various components of the first- and second-order density matrices. Equation (5.2) provides us with a means of directly determining γ^o and γ^z by using the HRP approximations to Δ^o and Δ^z . Equations (3.8) and (4.3)–(4.5) can be used to evaluate Γ^o and Γ^z , if γ^o and γ^z are known. In this section we propose an iterative, self-consistent procedure for determining γ^o , γ^z , Γ^o , and Γ^z . The procedure is as follows:

(1) Set γ^o and γ^z equal to their single-determinant approximations.

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

(3) In Eq. (4.5) use the current γ^o and γ^z to evaluate S_{ji}^o , etc.

TABLE I. Slater basis for helium.

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

(4) Form Δ^o and Δ^z by using Eqs. (4.3) and (4.4).

(5) Use the current γ^o and γ^z on the *right-hand* side of Eq. (5.2) to obtain *new* values for γ^o and γ^z .

(6) In Eq. (3.8), use the *new* γ^o and γ^z to evaluate Γ^o and Γ^z .

(7) Compare the new γ^o and γ^z to the γ^o and γ^z obtained by reducing Γ^o and Γ^z [Eq. (5.1)]. If the agreement is satisfactory and if the *old* γ^o and γ^z agree well with the *new* γ^o and γ^z , then the calculation is complete. Otherwise return to step (2), using the *new* 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 calculation 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 *consistent* with the second-order density matrix.

One disadvantage of the iterative method is that matrix elements γ_{em}^o connecting occupied and unoccupied orbitals are difficult to calculate. If one begins the iteration process with a charge density matrix having $\gamma_{em}^o = 0$, the procedure never produces any non-zero γ_{em}^o . 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 CI expansion of the wavefunction $|\phi\rangle$ contains no single excitations, then the lowest order nonzero contributions to $\langle\phi|C_{m\alpha}^+C_{e\alpha}+C_{m\beta}^+C_{e\beta}|\phi\rangle$ will come from matrix elements of double excitations with triple excitations. Because the CI expansion coefficients of triple excitations are usually quite small, the elements γ_{em}^o will, in general, also be very small. To obtain approximate values for γ_{em}^o , 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.

TABLE II. Expectation values for helium.

(1) This work ^a	$2\langle -\frac{1}{2}\nabla^2 - (2/r) \rangle = -3.8822$ a.u. $\langle 1/r_{12} \rangle = +0.98766$ a.u. $\langle H \rangle = -2.8945$ a.u.
(2) Hartree-Fock ^b	$\langle H \rangle = -2.8617$ a.u.
(3) CI ^c	$\langle H \rangle = -2.8790$ a.u.
(4) Green's function ^d	$\langle H \rangle = -2.8780$ a.u.
(5) Exact ^e	$\langle H \rangle = -2.9037$ a.u.

^a These expectation values were calculated using the second-order density matrix of Eq. (3.8) and the first-order density matrix of Eq. (5.2) (after convergence of the iterative procedure). Γ^0 and γ^0 were normalized to

$$\binom{N}{2} \text{ and } N,$$

respectively.

^b C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1962).

^c A complete configuration interaction calculation within the basis of the same five Hartree-Fock functions which we used. This calculation was carried out by us.

^d J. Simons (unpublished results).

^e C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

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,²⁴ each of which is given as a linear combination of the five Slater orbitals (normalized) described in Table I. The convergence criterion used was that

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

Convergence was realized after two iterations, the complete calculation taking 30 sec on a Univac 1108 computer. Calculation of the necessary one- and two-

TABLE IV. Diagonal overlaps.

i	$(R-D_i S_i)$
1	1.00000
2	0.99817
3	0.99719
4	0.99901
5	0.99997

electron integrals required 20 sec, so the HRP calculation only required 10 sec. This is to be compared to our Green's function calculation²⁵ in which 4 min 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. The fact that our energy is below the energy of the complete CI 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. Expansion coefficients refer to the Hartree-Fock orbitals. In carrying out this calculation we first approximate the charge density matrix elements γ_{em}^0 (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 (S_i) and those of Reinhardt and Doll²⁶ ($R-D_i$) are given in Table IV. The two sets are in fairly good agreement. Although our natural orbitals seem to be reasonably accurate, the expectation value of the one-electron operators given in Table II is too low.²⁷ 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 nonnegative, 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

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^{-6}	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

occupation numbers are altered considerably. The new occupation numbers are given in Table V. With this γ^0 the predicted expectation value of the one-electron operators agrees very well with the correct result.²⁶ The fact that the total energy is not very good when compared to the CI 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 HRP 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 HRP calculation are compared to the CI results for singlet states in Table VI.

For the calculations on the ground states of lithium and beryllium, we used bases of six *s*-type Hartree-Fock orbitals²⁸ (restricted HF) which are expressed in terms of the (normalized) Slater orbitals described in Table VII. Convergence was realized in each case after four iterations. Both computations took 90 sec—

TABLE V. Occupation numbers with constraint.

1.9854
1.2441×10^{-2}
2.1319×10^{-3}
6.7217×10^{-5}
2.5378×10^{-7}

60 sec for integral evaluation and 30 sec for the HRP iterations. Again the convergence was not found to be sensitive to the initial choice of γ^0 , 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^0 be nonnegative was imposed. These natural orbitals and occupation numbers are similar to those obtained by other workers²⁹⁻³¹ using somewhat different basis functions. Notice that the block structure of the natural orbital expansion coefficients implies that the γ_{em}^0 , 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).³² 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^0 obtained by our method can be inaccurate, whereas the resultant γ^0 is usually rather good. This is not surprising because

TABLE VI. Singlet excitation spectrum for helium.

HRPA	CI
1.4243 a.u.	1.4068 a.u.
5.3068	5.3208
19.522	19.451
118.50	118.34

the detailed effects of particle correlation which enter into Γ^0 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 charge 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 constitute 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 CI 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 HRP method, the Green's function method, and other

TABLE VII. Slater bases for lithium and beryllium.

Lithium		Beryllium	
<i>n</i>	Exponent	<i>n</i>	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

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

“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 wavefunction $|\phi\rangle$ 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:

$$\mu = \int |\gamma(1; 1') - \gamma_T(1; 1')|^2 d\tau_1 d\tau_{1'}, \quad (8.1)$$

where γ is our approximation to the true γ_T

$$\gamma_T = N \int \phi(1, 2, \dots, N) \phi^*(1', 2, \dots, N) d\tau_2 \dots d\tau_N. \quad (8.2)$$

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 is 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

$$E(1; 1') = \gamma(1; 1') - \gamma_T(1; 1'), \quad (8.3)$$

then

$$\begin{aligned} \Delta F &\equiv \text{Tr}\{fE\} \\ &= \text{Tr}\{f\gamma\} - \text{Tr}\{f\gamma_T\} \end{aligned} \quad (8.4)$$

is the deviation of the calculated expectation value of F from its value for the wavefunction $|\phi\rangle$. Notice that $\text{Tr}\{f\gamma_T\}$ is not necessarily the expectation value of F for an *exact* wavefunction. If γ and γ_T are expanded in some orthonormal (probably finite) basis, then the quantity $|\Delta F|$ can be bounded as follows:

$$|\Delta F|^2 \leq \sum_{i,j=1}^M |f_{ij}|^2 \sum_{i,j=1}^M |E_{ij}|^2, \quad (8.5)$$

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 Eq. (8.1) that the second term in Eq. (8.5) is identical to what we have defined as μ :

$$\sum_{i,j=1}^M |E_{ij}|^2 = \mu. \quad (8.6)$$

The bound on $|\Delta F|$ can then be written in either of the following forms,

$$|\Delta F|^2 \leq \mu \sum_{i,j=1}^M |f_{ij}|^2 \leq \mu \sum_{i=1}^M (f^2)_{ii}, \quad (8.7)$$

where $(f^2)_{ii}$ is a matrix element of the operator f^2 which is still a one-particle operator. The second in-

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

equality in Eq. (8.7) 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 Eq. (8.7) 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^+ :

$$O_k |\phi\rangle = 0, \quad (8.8)$$

for all excited states $|k\rangle$. Equation (8.8) is a consequence of the fact that $|\phi\rangle$ is the HRP A ground state wavefunction 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 HRP A 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 $|0\rangle$ by the unitary operator given below:

$$|\phi\rangle = \exp(-S) |0\rangle, \quad (8.9)$$

where S is an antihermitian operator which is to be determined by using Eq. (8.8). The expression for an element of the second-order density matrix,

$$\Gamma_{kl,ij} = \frac{1}{2} \langle \phi | C_i^+ C_j^+ C_l C_k | \phi \rangle,$$

can be rearranged to give

$$\Gamma_{kl,ij} = \frac{1}{2} \delta_{jl} \langle \phi | C_i^+ C_k | \phi \rangle - \frac{1}{2} \langle \phi | C_i^+ C_l C_j^+ C_k | \phi \rangle. \quad (8.10)$$

By using the definition of the first-order density matrix and Eqs. (5.1) and (8.10), 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

$$(M+1-N) \gamma_{ki} = \sum_{j=1}^M \langle \phi | C_j^+ C_j C_j^+ C_k | \phi \rangle. \quad (8.11)$$

In the HRP A method we approximate the right-hand

side of Eq. (8.11) as follows:

$$\langle \phi | C_i^+ C_j C_j^+ C_k | \phi \rangle \rightarrow \langle \phi | C_i^+ C_j P C_j^+ C_k | \phi \rangle, \quad (8.12)$$

where the projection operator P is given by

$$P = |\phi\rangle \langle \phi| + \sum_{\lambda} O_{\lambda}^+ |\phi\rangle \langle \phi| O_{\lambda}, \quad (8.13)$$

and the O_{λ}^+ are the known HRP A excitation operators. Thus, the deviation of γ_{ki} (HRP A) from the true $(\gamma_T)_{ki}$ can be written formally as

$$\begin{aligned} (M+1-N) E_{ki} &= (M+1-N) (\gamma_T - \gamma)_{ki} \\ &= \sum_{j=1}^M \langle \phi | C_i^+ C_j Q C_j^+ C_k | \phi \rangle, \end{aligned} \quad (8.14)$$

with

$$Q = 1 - P. \quad (8.15)$$

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 operator³³ of the form $C_i^+ C_j$ can be expanded as follows:

$$C_i^+ C_j = W_{ij}'' + \sum_{\lambda} [W_{ij}(\lambda) O_{\lambda}^+ + W_{ij}'(\lambda) O_{\lambda}]. \quad (8.16)$$

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 Eq. (8.16), it is easily shown that each element E_{ki} vanishes. Therefore, as the spin-orbital 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 Eq. (8.9) in evaluating the parameter μ , we recall the following identity for exponential operators³⁴:

$$\begin{aligned} B \exp(-A) &= \exp(-A) \\ &\times \{B + [A, B] + (1/2)[A, [A, B]] + \dots\}. \end{aligned} \quad (8.17)$$

With Eq. (8.9) the expression for E_{ki} can be rewritten in the form:

$$\begin{aligned} (M+1-N) E_{ki} &= \sum_{j=1}^M \{ \langle 0 | \exp(S) C_i^+ C_j C_j^+ C_k \exp(-S) | 0 \rangle \\ &\quad - \langle 0 | \exp(S) C_i^+ C_j \exp(-S) | 0 \rangle \\ &\quad \times \langle 0 | \exp(S) C_j^+ C_k \exp(-S) | 0 \rangle \\ &\quad - \sum_{\lambda} \langle 0 | \exp(S) [C_i^+ C_j, O_{\lambda}^+] \exp(-S) | 0 \rangle \\ &\quad \times \langle 0 | \exp(S) [O_{\lambda}, C_j^+ C_k] \exp(-S) | 0 \rangle \}. \end{aligned} \quad (8.18)$$

Before this equation can be simplified by using Eq. (8.17), we must investigate in more detail the form of the operator S .

In the nuclear literature^{33,36} the wavefunction $|0\rangle$ is usually written as

$$|\phi\rangle = K \exp(-S) |0\rangle, \quad (8.19)$$

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 ^a a.u.	-14.592 ^b a.u.

^a A. Weiss, Phys. Rev. **122**, 1826 (1961). This might not be the exact radial limit.

^b C. F. Bunge, Phys. Rev. **168**, 92 (1968).

where K is a normalization constant and

$$S = \sum_{m,n,\alpha,\beta} S_{m\alpha,n\beta} C_m^\dagger C_\alpha C_n^\dagger C_\beta. \quad (8.20)$$

We are using the subscript convention of Sec. II.

This form of the wavefunction is not especially useful because the operator S is not anti-Hermitian. This means that Eq. (8.18) can not be used to evaluate E_{ki} if we insist on using the above wavefunction. To avoid this problem we can express $|\phi\rangle$ as in Eq. (8.9) with the anti-Hermitian operator S given by

$$S = \sum_{m,n,\alpha,\beta} (S_{m\alpha,n\beta} C_m^\dagger C_\alpha C_n^\dagger C_\beta - S_{m\alpha,n\beta}^* C_\beta^\dagger C_n C_\alpha^\dagger C_m). \quad (8.21)$$

Once the coefficients $S_{m\alpha,n\beta}$ have been determined, Eqs. (8.17) and (8.18) can be used to calculate E_{ki} . We will return to this calculation shortly.

To obtain an equation for the coefficients $S_{m\alpha,n\beta}$ we make use of Eqs. (8.9) and (8.17) to write Eq. (8.8) in the form

$$O_\lambda |\phi\rangle = \exp(-S) \{O_\lambda + [S, O_\lambda] + (1/2!)[S, [S, O_\lambda]] + \dots\} |0\rangle = 0. \quad (8.22)$$

By substituting the explicit expressions for O_λ and S given in Eqs. (2.6) and (8.21), respectively, and carry-out the commutations indicated above, we can equate to zero the coefficients of the various independent functions $|0\rangle$, $C_i^\dagger C_j |0\rangle$, $C_i^\dagger C_j^\dagger C_k C_l |0\rangle$, etc. This leads to the following equation involving $S_{m\alpha,n\beta}$:

$$\begin{aligned} 4 \sum_{n\beta} S_{m\alpha,n\beta} g_{n\beta}^*(\lambda) &= -h_{m\alpha}^*(\lambda), \\ \alpha &= 1, 2, \dots, N; \quad m = N+1, \dots, M; \\ \lambda &= 1, 2, \dots, N(M-N). \end{aligned} \quad (8.23)$$

In our HRP 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 Eq. (8.23) 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 HRP coefficients $g_{n\beta}(\lambda)$ and $h_{m\alpha}(\lambda)$ can be thought of as forming square $N(M-N)$ dimensional matrices, and so Eq. (7.23) is a simple matrix equation which can be solved by standard matrix inversion techniques to yield the coefficients $S_{m\alpha,n\beta}$,

$$4S_{\mu\lambda} = - \sum_{\kappa=1}^{N(M-N)} h_{\mu\kappa}^* g_{\kappa\lambda}^{-1}. \quad (8.24)$$

It should be pointed out that Eq. (8.23) is identical to the equation which would result if the wavefunction given in Eq. (8.19) had been used. In other words, no additional complications arise when we introduce the antihermitian form for S given in Eq. (8.21).

With the coefficients $S_{m\alpha,n\beta}$ given by Eq. (8.24), we now return to the evaluation of the E_{ki} . By using the identity given in Eq. (8.17) and carrying out the indicated commutations, the right-hand side of Eq. (8.18) 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

$$\begin{aligned} (M+1-N)E_{ki}^{(0)} &= - \sum_{\lambda} \sum_{\alpha} h_{i\alpha}(\lambda) h_{k\alpha}^*(\lambda), \quad \text{if } i, k > N \\ &= - \sum_{\lambda} \sum_{m} h_{mi}(\lambda) h_{mk}^*(\lambda), \quad \text{if } i, k \leq N \\ &= 0, \quad \text{otherwise.} \end{aligned} \quad (8.25)$$

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 $E_{ki}^{(0)}$ given in Eq. (8.25) 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 Eq. (8.6) with Eq. (8.25) is of the order of 10^{-12} . Therefore, unless the quantity

$$\sum_{i,j=1}^M |f_{ij}|^2$$

which enters into Eq. (8.7) 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 HRP 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 CI 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^2 . 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^0 be nonnegative, the calculated natural orbitals were essentially unaltered but the occupation numbers were significantly changed.³⁷ 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^0 . 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 CI calculation. Let us recall that the HRP A technique was developed to predict properties which do not depend strongly on the complex correlations within wavefunctions. Therefore, in our use of the HRP A 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 HRP A 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.

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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 From this point on the unknown wavefunction $|\phi\rangle$ will probably not be exact. However, we will often refer to $|\phi\rangle$ as the exact function in the sense that $O_k|\phi\rangle=0$ (see Eq. (8.8)).

¹³ The notation "singlet and triplet operators" is based upon the fact that $D_{m,1^+}$ operating on a singlet yields a singlet and $D_{m,3^+}$ operating on a singlet yields a triplet.

¹⁴ We assume that there are no effects which split the degeneracy of the triplet level.

¹⁵ We use the same notation (A and B) here as in Eq. (2.24) even though the elements of the A and B matrices are different. This is done for notational ease.

¹⁶ Notice that the dimension of the matrix to be diagonalized is given by $2N_0(M-N_0)$, where N_0 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 CI matrix. This is an important computational advantage of the method.

¹⁷ The function $|k, S, M_s\rangle$ is not necessarily an eigenfunction of S^2 . The notation only implies that $|k_1, S, M_s\rangle$ is obtained by $O_k S, M_s^+$ 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 $|\phi\rangle$.

¹⁸ One can use this equation and Eqs. (2.26)-(2.28) to iteratively calculate $|\phi\rangle$ and the O_k^+ . That is, one guesses a starting $|\phi\rangle$ whose charge density γ^0 allows the formation of the A and B matrices of Eq. (2.28). The solution of Eq. (2.26) then gives the excitation energies and the O_k^+ (of the first iteration). $O_k|\phi\rangle=0$ can then be solved for a new $|\phi\rangle$ giving a new charge density γ^0 for use in the next iteration. Because we are trying to make progress without ever calculating $|\phi\rangle$, we adopt the following different iterative procedure. We guess a starting charge density γ^0 which allows us to obtain the O_k^+ from Eqs. (2.26)-(2.28). Knowing the O_k^+ , Eq. (5.2) gives us a new charge density which is used in the next iteration to form the A and B matrices of Eq. (2.28). We have made the assumption that the charge density calculated by Eq. (5.2) is a reasonable approximation to the correct charge density of $|\phi\rangle$ (which can be calculated by solving $O_k|\phi\rangle=0$), at each stage of the iteration. Thus, we bypass the problem of solving $O_k|\phi\rangle=0$ by using Eq. (5.2) to calculate new charge densities in the iterative procedure. The consequences of this approximation should be investigated further by comparing the charge densities calculated from the solution of $O_k|\phi\rangle=0$ with those given by Eq. (5.2).

¹⁹ We use the following normalization:

$$\text{Tr}\gamma = N, \quad \text{Tr}\Gamma = \binom{N}{2}.$$

²⁰ See, for example, R. McWeeny, *Rev. Mod. Phys.* **32**, 335 (1960).

²¹ We sometimes use γ_i^0 to represent a diagonal element of the charge density matrix: $\gamma_i^0 = \gamma_{ii}^0$. This is done for notational convenience.

²² The reader should be cautioned that these approximate excited states are not generally going to form a complete set. This is an approximation.

²³ Because the form of O_k^+ given in Eq. (2.16) does not contain $C_m^+C_n$ or $C_i^+C_\theta$ excitations, this statement is not strictly true. However, if the ground state $|\phi\rangle$ is well approximated by a single Slater determinant, contributions from these terms will be small.

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Dynamics of Protons in Hydrogen-Bonded Systems: Propynoic and Acrylic Acid Dimers

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This paper is part of a study of the origin of the abnormal infrared spectra of the stretching vibrations of protons in H-bonded species. An experimental ir study of the $2000\text{--}3000\text{ cm}^{-1}$ region of propynoic and acrylic acid dimers and of their deuterated analogs is presented. These ir spectra have been recorded with high resolution and intensity in order to be compared with a theoretical model which predicts positions and intensities of the lines. This model is briefly recalled, and the fit between theory and experiment is discussed. It is suggested that the theoretical model considered here, although in its first stage of development, represents the basic features of the mechanism of oscillation of protons in weak and moderate H bonds.

I. INTRODUCTION

The elucidation of the mechanism of vibration of the proton in a H bond $\text{X-H}\cdots\text{Y}$ is one of the intriguing problems set up by the existence of the hydrogen bond. Most of the vibrations of nuclei in an ordinary molecule may be considered as harmonic and thus correspond to a simple narrow line in the infrared spectra of the molecule. By contrast, the stretching vibration of the proton in the H bond $\text{X-H}\cdots\text{Y}$ is strongly anharmonic,¹ and its corresponding infrared spectrum is broad, with a well defined structure; and when a D atom is substituted for the H atom, a strong isotope effect appears.²

A qualitative explanation of these abnormal features in the infrared spectrum has been previously proposed.¹ Recently, a more quantitative model of the dynamics of the proton in the H bond $\text{X-H}\cdots\text{Y}$ has been used with apparent success³⁻⁵ to simulate the infrared spectrum of the stretching vibrations of the protons in acetic acid dimers in the gas phase. The carboxylic acids, which form hydrogen-bonded cyclic dimers in the gas phase, are ideal species for testing these theoretical models.

Except for the spectrum of acetic acid,⁶ the infrared spectra of the stretching vibration of the H-bonded proton in carboxylic acids which exist in the literature are not precise enough (with regard to the intensities of their lines) to be transformed to the optical absorption $\log(I_0/I)$. Consequently, they can hardly be compared with a theoretical model which predicts positions and intensities of the lines. We have thus been led to record precise spectra of different carboxylic acids in the gas phase, and the object of this paper is to report an experimental study of the ir spectra of the proton stretching vibrations in propynoic and acrylic acids, together with a theoretical interpretation of these spectra. This work is a part of a more general study of the dynamics of protons in H bonds⁷ with a view to testing the validity of the previously cited model,³⁻⁵ where it was assumed that the originality of the motions of the proton in a H bond $\text{X-H}\cdots\text{Y}$ is due to the coupling of this latter motion with the "hydrogen-bond vibration" $\text{X}\cdots\text{H}\cdots\text{Y}^{\leftarrow}$. This model might furthermore give an idea of the effect of π electrons on the hydrogen bond, which might be related later with an electronic study of the H bond.