

the reasonableness of the two magnetic relaxation mechanisms discussed. It is especially important to examine the plausibility of important scalar contributions because of the implications of this mechanism for the use of NMR line broadening to elucidate the nature of both outer-sphere metal-solvent and metal-ion interactions. Two factors that make the scalar mechanism more competitive in  $^{17}\text{O}$  studies than it is in proton NMR are generally greater values of the scalar coupling constant,  $A$ , and the fact that  $\gamma$  is seven times greater for protons than for  $^{17}\text{O}$  nuclei. The disparity in

$\gamma$  values is quite significant, since the ratio of dipolar to scalar broadening goes as  $\gamma^2$ .

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## First- and Second-Order Density Matrices of Symmetry-Projected Single-Determinant Wavefunctions\*

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We derive the first- and second-order density matrices of symmetry-projected single-determinant wavefunctions, in the case of finite groups. We also give the first-order density matrices for functions projected in the axial-rotation group. A method is presented for extracting from a density matrix its totally symmetric component, and the eigenfunctions of this component are shown to be the same after projection as before.

### I. INTRODUCTION

It has been found that the effects of applying a spin projection operator to a determinantal wavefunction involving different orbitals for different spins can be conveniently summarized by considering the first- and second-order reduced density matrices.<sup>1,2</sup> In this paper we will be concerned with the density matrices of wavefunctions obtained by applying to a single-determinant projection operators of point groups or the axial-rotation group.

In Sec. 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 Sec. III. In Secs. 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 Sec. VI. In Sec. 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  $\Phi$  which we wish to adapt to the symmetry of a particular group:

$$\Phi(1 \cdots N) = \alpha \phi_1(1) \cdots \phi_N(N), \quad (1)$$

where  $\alpha$  is the  $N$ -particle antisymmetrizer,  $\phi_1 \cdots \phi_N$  are orthonormal spin-orbitals without any particular symmetry properties, and the arguments  $1 \cdots N$  refer to the space and spin coordinates of particles 1 through  $N$ , respectively. The normalized, symmetry-adapted wavefunction can be obtained by projection as

$$\Psi_\nu = \omega_\nu^{-1/2} \Theta_\nu \Phi, \quad (2)$$

where

$$\omega_\nu = \int (\Theta_\nu \Phi)^* (\Theta_\nu \Phi) d\tau. \quad (3)$$

The projection operator  $\Theta_\nu$  can be expressed as<sup>3</sup>

$$\Theta_\nu = \sum_R C_\nu(R) \mathbf{R}, \quad (4a)$$

where the sum is over all operations in the group. The

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<sup>1</sup> J. E. Harriman, *J. Chem. Phys.* **40**, 2827 (1964).

<sup>2</sup> A. Hardisson and J. E. Harriman, *J. Chem. Phys.* **46**, 3639 (1967).

<sup>3</sup> E. Wigner, *Group Theory and its Applications to the Quantum Mechanics of Atomic Spectra* (Academic Press Inc., New York, 1964).

index  $\nu$  refers to that irreducible representation which characterizes  $\Psi_\nu$ . The coefficients  $C_\nu(\mathbf{R})$  are defined in terms of the characters  $\chi_\nu(\mathbf{R})$ , the dimension  $n_\nu$  of irreducible representation  $\nu$ , and the order of the group  $g$ :

$$C_\nu(\mathbf{R}) = (n_\nu/g)\chi_\nu^*(\mathbf{R}). \quad (4b)$$

Since we are dealing with a many-particle system, the group operators  $\mathbf{R}$  will be of the form

$$\mathbf{R}(1 \dots N) = \mathbf{R}(1)\mathbf{R}(2) \dots \mathbf{R}(N), \quad (5)$$

where  $\mathbf{R}(k)$  operates only on the coordinates of the  $k$ th particle. For convenience, we adopt a special notation for the effect of a symmetry operation on a spin-orbital:

$$\mathbf{R}(k)\phi_i(k) = \phi_i^{\mathbf{R}}(k). \quad (6)$$

Then  $\Psi_\nu$  is seen to be

$$\Psi_\nu(1 \dots N) = \omega_\nu^{-1/2} \mathcal{G} \sum_{\mathbf{R}} C_\nu(\mathbf{R}) \phi_1^{\mathbf{R}}(1) \dots \phi_N^{\mathbf{R}}(N). \quad (7)$$

We first evaluate the normalization constant  $\omega_\nu$ , making use of the facts that  $\mathcal{O}_\nu$  is self-adjoint and idempotent,<sup>4</sup> and that  $\mathcal{G}$  is self-adjoint and has

$$\mathcal{G}^2 = \sum_{\mathbf{P}} (-1)^{\mathbf{P}} \mathbf{P}, \quad (8)$$

the sum of all  $N!$  signed permutations of  $N$  particles. Then

$$\begin{aligned} \omega_\nu &= \sum_{\mathbf{R}} C_\nu(\mathbf{R}) \sum_{\mathbf{P}} (-1)^{\mathbf{P}} \\ &\times \int \phi_1^*(1) \dots \phi_N^*(N) \phi_{\mathbf{P}1}^{\mathbf{R}}(1) \dots \phi_{\mathbf{P}N}^{\mathbf{R}}(N) d\tau, \quad (9) \end{aligned}$$

where  $\mathbf{P}i$  is the index produced from  $i$  by  $\mathbf{P}^{-1}$ . The integral in (9) is a product of one-electron integrals of the form

$$\int \phi_i^*(i) \phi_{\mathbf{P}i}^{\mathbf{R}}(i) d\tau_i = \int \phi_i^*(i) \mathbf{R}(i) \phi_{\mathbf{P}i}(i) d\tau_i. \quad (10)$$

The expression for  $\omega_\nu$  therefore takes the form

$$\begin{aligned} \omega_\nu &= \sum_{\mathbf{R}} C_\nu(\mathbf{R}) \sum_{\mathbf{P}} (-1)^{\mathbf{P}} R_{1,\mathbf{P}1} \dots R_{N,\mathbf{P}N} \\ &= \sum_{\mathbf{R}} C_\nu(\mathbf{R}) \det \mathbf{R}. \quad (11) \end{aligned}$$

Notice that the determinants,  $\det \mathbf{R}$ , are to involve only the spin-orbitals appearing in  $\Phi$ . They are determinants of  $N \times N$  matrices. Thus if we know the matrix elements of the group operations in the spin-orbital basis, we can calculate  $\omega_\nu$ . 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  $\Omega$ , we can write its expectation value  $\langle \Omega \rangle_\nu$ ,

with respect to  $\Psi_\nu$  in two ways:

$$\langle \Omega \rangle_\nu = \int \Psi_\nu^* \Omega \Psi_\nu d\tau = \int' \Omega(1) \gamma_\nu(1 | 1') d\tau_1. \quad (12)$$

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  $\langle \Omega \rangle_\nu$  using the first expression, and then to identify  $\gamma_\nu$  as that which will correctly reproduce the second expression.

Therefore, we must calculate

$$\langle \Omega \rangle_\nu = \omega_\nu^{-1} \int \Phi^* \mathcal{O}_\nu \Omega \mathcal{O}_\nu \Phi d\tau. \quad (13)$$

First we examine the operator  $\mathcal{O}_\nu \Omega \mathcal{O}_\nu$ :

$$\begin{aligned} \mathcal{O}_\nu \Omega \mathcal{O}_\nu &= \sum_{\mathbf{R}} C_\nu(\mathbf{R}) \mathbf{R} \sum_{i=1}^N \Omega(i) \mathcal{O}_\nu \\ &= \sum_{\mathbf{R}} C_\nu(\mathbf{R}) \sum_{i=1}^N \mathbf{R}(i) \Omega(i) \mathbf{R}^{-1}(i) \mathcal{O}_\nu. \quad (14) \end{aligned}$$

Substituting (14) into (13) and noting that  $\mathbf{R}$  and  $\mathcal{O}_\nu$  commute with  $\mathcal{G}$ , we obtain

$$\begin{aligned} \langle \Omega \rangle_\nu &= \omega_\nu^{-1} \sum_{\mathbf{R}} C_\nu(\mathbf{R}) \int \mathcal{G} \phi_1^*(1) \dots \phi_N^*(N) \\ &\times \sum_{i=1}^N \mathbf{R}(i) \Omega(i) \mathbf{R}^{-1}(i) \mathcal{G} \mathbf{R} \mathcal{O}_\nu \phi_1(1) \dots \phi_N(N) d\tau \\ &= \omega_\nu^{-1} \sum_{\mathbf{R}, \mathbf{S}} C_\nu(\mathbf{R}) C_\nu(\mathbf{S}) \sum_{i=1}^N \sum_{\mathbf{P}} (-1)^{\mathbf{P}} \\ &\times \int \phi_1^*(1) \dots \phi_N^*(N) \mathbf{R}(i) \Omega(i) \mathbf{R}^{-1}(i) \phi_{\mathbf{P}i}^{\mathbf{R}\mathbf{S}} \\ &\times (1) \dots \phi_{\mathbf{P}N}^{\mathbf{R}\mathbf{S}}(N) d\tau. \quad (15) \end{aligned}$$

Since the symmetry operators are unitary,

$$\begin{aligned} &\int \phi_i^*(i) \mathbf{R}(i) \Omega(i) \mathbf{R}^{-1}(i) \phi_{\mathbf{P}i}^{\mathbf{R}\mathbf{S}} d\tau_i \\ &= \int \phi_i^{\mathbf{R}^{-1}*}(i) \Omega(i) \phi_{\mathbf{P}i}^{\mathbf{S}}(i) d\tau_i. \quad (16) \end{aligned}$$

If we now let  $\mathbf{T} = \mathbf{R}\mathbf{S}$ , so that  $\mathbf{R} = \mathbf{T}\mathbf{S}^{-1}$ , we have

$$\begin{aligned} \langle \Omega \rangle_\nu &= \omega_\nu^{-1} \sum_{\mathbf{S}, \mathbf{T}} C_\nu(\mathbf{T}\mathbf{S}^{-1}) C_\nu(\mathbf{S}) \sum_{i,j=1}^N T(i | j) \\ &\times \int \phi_i^{\mathbf{S}\mathbf{T}^{-1}*}(1) \Omega(1) \phi_j^{\mathbf{S}}(1) d\tau_1, \quad (17) \end{aligned}$$

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  $\Phi$  and that for any  $R$  in the group,  $R\phi_i$  can be expressed as

$$R\phi_i = \sum_{k=1}^M R_{ki} \phi_k, \quad i=1, 2, \dots, M. \quad (18)$$

We can then write

$$\begin{aligned} & \int \phi_i^{ST^{-1}*}(1) \Omega(1) \phi_j^S(1) d\tau_1 \\ &= \sum_{k,l=1}^M (ST^{-1})_{ki} S_{lj} \int \phi_k^*(1) \Omega(1) \phi_l(1) d\tau_1 \\ &= \sum_{k,l=1}^M (TS^{-1})_{ik} S_{lj} \Omega_{kl}; \end{aligned} \quad (19)$$

and thus

$$\begin{aligned} \langle \Omega \rangle_\nu &= \omega_\nu^{-1} \sum_{S,T} C_\nu(TS^{-1}) C_\nu(S) \sum_{i,j=1}^N T(i|j) \\ & \quad \times \sum_{k,l=1}^M (TS^{-1})_{ik} S_{lj} \Omega_{kl} \\ &= \sum_{k,l=1}^M [\omega_\nu^{-1} \sum_{S,T} C_\nu(TS^{-1}) C_\nu(S) \\ & \quad \times \sum_{i,j=1}^N T(i|j) (TS^{-1})_{ik} S_{lj}] \Omega_{kl}. \end{aligned} \quad (20)$$

Therefore, we may identify  $\gamma_\nu$  as

$$\gamma_\nu(1|1') = \sum_{k,l=1}^M \gamma_{kl}^{(\nu)} \phi_l(1) \phi_k^*(1'), \quad (21)$$

where

$$\begin{aligned} \gamma_{kl}^{(\nu)} &= \omega_\nu^{-1} \sum_{S,T} C_\nu(TS^{-1}) C_\nu(S) \\ & \quad \times \sum_{i,j=1}^N T(i|j) (TS^{-1})_{ik} S_{lj}. \end{aligned} \quad (22)$$

In a similar fashion, we find the second-order density matrix to be given as

$$\begin{aligned} \Gamma_\nu(12|1'2') &= \sum_{p,q,r,t=1}^M \Gamma_\nu^{(pqr)} \phi_p(1) \phi_q(2) \phi_r^*(1') \phi_t^*(2') \end{aligned} \quad (23)$$

with

$$\begin{aligned} \Gamma_\nu^{(pqr)} &= \omega_\nu^{-1} \sum_{T,S} C_\nu(TS^{-1}) C_\nu(S) \sum_{i<j=1}^N \sum_{k<l=1}^N T(ij|kl) \\ & \quad \times S_{pk} S_{ql} (TS^{-1})_{ir} (TS^{-1})_{jt}, \end{aligned} \quad (24)$$

where  $T(ij|kl)$  is the  $ij|kl$  cofactor of  $T$ .<sup>4</sup>

<sup>4</sup> P.-O. Löwdin, Rev. Mod. Phys. 39, 259 (1967).

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  $\gamma_\nu$  and  $\Gamma_\nu$  is straightforward.

### III. EXAMPLE FOR FINITE POINT GROUPS

As an example we consider a wavefunction for the water molecule

$$\Phi = \mathcal{Q}[\phi_1^\alpha(1) \phi_1^\beta(2) \cdots \phi_4^\alpha(7) \phi_4^\beta(8) \phi_5^\alpha(9) \phi_5^\beta(10)],$$

where the orbitals are

$$\begin{aligned} \phi_1 &= (2+2\Delta)^{-1/2} (1S_A + 1S_B), & \Delta &= \int 1S_A 1S_B d\tau, \\ \phi_2 &= 1S_O, & \phi_3 &= 2S_O, & \phi_4 &= 2p_{z,O}, \\ \phi_5 &= 2^{-1/2} (2p_{x,O} + 2p_{y,O}), \\ \phi_6 &= 2^{-1/2} (2p_{x,O} - 2p_{y,O}). \end{aligned}$$

In what follows we will neglect the overlap between  $\phi_1, \phi_2$  and  $\phi_3$ , in order to preserve the simplicity of the example. 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  $\phi_1$  through  $\phi_4$  are thus symmetry adapted, but  $\phi_5$  and  $\phi_6$  are not. The last orbital is added to give a complete set in the sense of Eq. (18).

In this basis, the matrices of the symmetry operators decompose into pairs of  $6 \times 6$  matrices, a set of matrices involving  $\alpha$  spin, and an identical set involving  $\beta$  spin. These matrices are as follows:  $E$  is the  $6 \times 6$  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  $\Phi$ . Using Eq. (11), we find that

$$\begin{aligned} \omega_{A_2} &= \frac{1}{4} [\det \mathbf{E} + \det \mathbf{C}_2 - \det \sigma_v - \det \sigma_v'] \\ &= \frac{1}{4} [1 + 1 + 0 + 0] = \frac{1}{2}. \end{aligned}$$

Remember that in Eq. (11) the determinants are over the spin-orbitals appearing in  $\Phi$ ; so only the pairs of  $5 \times 5$  submatrices of our operator matrices are to be used to calculate  $\omega_{A_2}$ . We also find it helpful to construct a table of the various terms appearing in the expressions for  $\gamma_\nu$  and  $\Gamma_\nu$  (Table I).

Using this information and Eq. (22) we obtain

$$\begin{aligned} \gamma_{A_2}(1 | 1') &= \sum_{i=1}^4 \phi_i(1) \phi_i^*(1') [\alpha\alpha^* + \beta\beta^*] \\ &\quad + \frac{1}{2} \phi_5(1) \phi_5^*(1') [\alpha\alpha^* + \beta\beta^*] \\ &\quad + \frac{1}{2} \phi_6(1) \phi_6^*(1') [\alpha\alpha^* + \beta\beta^*]. \end{aligned}$$

Similarly, by using Eq. (24), we find that

$$\begin{aligned} \Gamma_{A_2}(12 | 1'2') &= \frac{1}{2} \sum_{i,j=1}^4 \{ |i\alpha j\alpha|^2 + |i\alpha j\beta|^2 + |i\beta j\alpha|^2 + |i\beta j\beta|^2 \} \\ &\quad + \frac{1}{2} \sum_{i=1}^4 \{ |i\alpha 5\alpha|^2 + |i\alpha 5\beta|^2 + |i\beta 5\alpha|^2 + |i\beta 5\beta|^2 \} \\ &\quad + \frac{1}{2} \sum_{i=1}^4 \{ |i\alpha 6\alpha|^2 + |i\alpha 6\beta|^2 + |i\beta 6\alpha|^2 + |i\beta 6\beta|^2 \} \\ &\quad + \frac{1}{4} \{ |5\alpha 5\beta|^2 + |5\beta 5\alpha|^2 + |6\alpha 6\beta|^2 + |6\beta 6\alpha|^2 \} \\ &\quad - \frac{1}{2} [\mathfrak{B}\phi_5^\alpha(1)\phi_5^\beta(2)] [\mathfrak{B}'\phi_5^\alpha(1')\phi_5^\beta(2')]^* \\ &\quad - \frac{1}{2} [\mathfrak{B}\phi_6^\alpha(1)\phi_6^\beta(2)] [\mathfrak{B}'\phi_6^\alpha(1')\phi_6^\beta(2')]^*, \end{aligned}$$

where

$$\mathfrak{B} = 2^{-1/2}(1 - \mathbf{P}_{12}), \quad \mathfrak{B}' = 2^{-1/2}(1 - \mathbf{P}_{1'2'}),$$

and

$$|i\alpha j\beta|^2 = [\mathfrak{B}\phi_i^\alpha(1)\phi_j^\beta(2)] [\mathfrak{B}'\phi_i^\alpha(1')\phi_j^\beta(2')]^*.$$

Equivalent results are of course obtainable more directly. The advantage of the present method increases with the number of nonsymmetry-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<sup>6</sup>

$$\mathcal{O}_m = \frac{1}{2\pi} \int_0^{2\pi} d\alpha \exp(-i\alpha m) \mathbf{R}_\alpha. \quad (25)$$

In this expression  $\mathbf{R}_\alpha$  is an operator which rotates through angle  $\alpha$ . If we define

$$\begin{aligned} Q_m(iklj | \alpha) &= (2\pi)^{-2} \exp(-i\alpha m) \int_0^{2\pi} d\phi (R_\phi)_{ik} (R_{\alpha-\phi})_{lj}, \quad (26) \end{aligned}$$

then we obtain for the coefficients

$$\gamma^{(m)}_{ik} = \omega_m^{-1} \int_0^{2\pi} d\alpha \sum_{i,j=1}^N R_\alpha(i | j) Q_m(iklj | \alpha), \quad (27)$$

where  $R_\alpha(i | j)$  is the  $i, j$  cofactor of  $R_\alpha$ . The normaliza-

<sup>6</sup> M. Hamermesh, *Group Theory and its Applications to Physical Problems* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1964).

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
	$\sigma_v$	$\sigma_v$	-1	-1
	$\sigma_{v'}$	$\sigma_{v'}$	-1	-1
$C_2$	$E$	$C_2$	1	1
	$C_2$	$E$	1	1
	$\sigma_v$	$\sigma_{v'}$	-1	-1
	$\sigma_{v'}$	$\sigma_v$	-1	-1
$\sigma_v$	$E$	$\sigma_v$	1	-1
	$C_2$	$\sigma_{v'}$	1	-1
	$\sigma_v$	$E$	-1	1
	$\sigma_{v'}$	$C_2$	-1	1
$\sigma_{v'}$	$E$	$\sigma_{v'}$	1	-1
	$C_2$	$\sigma_v$	1	-1
	$\sigma_v$	$C_2$	-1	1
	$\sigma_{v'}$	$E$	-1	1

tion integral is given by

$$\omega_m = \frac{1}{2\pi} \int_0^{2\pi} d\alpha \exp(-i\alpha m) \det \mathbf{R}_\alpha. \quad (27a)$$

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

$$\Phi = \mathcal{Q} [1s^\alpha(1) 1s^\beta(2) 2s^\alpha(3) 2s^\beta(4) 2p_x^\alpha(5)].$$

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  $\xi$  can be written as

$$\begin{aligned} \mathbf{R}_\xi \Phi &= \mathcal{Q} [1s^\alpha(1) 1s^\beta(2) 2s^\alpha(3) 2s^\beta(4) \\ &\quad \times \{ 2^{-1/2}(e^{i\xi} 2p_{+1} + e^{-i\xi} 2p_{-1}) \}^\alpha(5)]. \end{aligned}$$

From this and Eq. (27),

$$\begin{aligned} \gamma_1(1 | 1') &= [1s(1) 1s^*(1') + 2s(1) 2s^*(1')] (\alpha\alpha^* + \beta\beta^*) \\ &\quad + \frac{1}{2} [\phi_3(1) \phi_3^*(1') + \phi_4(1) \phi_4^*(1') \\ &\quad + \phi_3(1) \phi_4^*(1') + \phi_4(1) \phi_3^*(1')] \alpha\alpha^*, \end{aligned}$$

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  $\Phi$  is given by

$$\Psi_1 = \mathcal{G}[1s^\alpha(1)1s^\beta(2)2s^\alpha(3)2s^\beta(4)2p_{+1}^\alpha(5)],$$

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 $\gamma_\nu$ AND $\Gamma_\nu$ <sup>6</sup>

The totally symmetric component  $\Gamma_\nu^0$  of  $\Gamma_\nu$  can be obtained as

$$\Gamma_\nu^0 = g^{-1} \sum_R \mathbf{R} \Gamma_\nu \mathbf{R}^{-1} \\ = g^{-1} \sum_R \mathbf{R}(12)\mathbf{R}(1'2')\Gamma_\nu(12 | 1'2') \quad (28)$$

and

$$\gamma_\nu^0 = g^{-1} \sum_R \mathbf{R}(1)\mathbf{R}(1')\gamma_\nu(1 | 1'). \quad (29)$$

We will consider  $\gamma_\nu^0$  first:

$$\gamma_\nu^0(1 | 1') \\ = g^{-1} \sum_Q \sum_{k,l=1}^M \gamma^{(\nu)}_{kl} Q(1)\phi_k(1)Q(1')\phi_l^*(1') \\ = \sum_{i,j=1}^M [g^{-1} \sum_Q \sum_{k,l=1}^M \gamma^{(\nu)}_{kl} Q_{ik} Q_{lj}^{-1}] \phi_i(1)\phi_j^*(1') \\ = \sum_{i,j=1}^M (\gamma_\nu^0)_{ij} \phi_i(1)\phi_j^*(1'), \quad (30)$$

where

$$(\gamma_\nu^0)_{ij} = g^{-1} \sum_Q \sum_{k,l=1}^M \gamma^{(\nu)}_{kl} Q_{ik} Q_{lj}^{-1}, \quad (31)$$

but

$$\sum_{k,l=1}^M Q_{ik} \gamma^{(\nu)}_{kl} Q_{lj}^{-1} \\ = \sum_{k,l=1}^M \omega_\nu^{-1} \sum_{S,T} C_\nu(TS^{-1})C_\nu(S) \sum_{p,q=1}^N T(p|q)(TS^{-1})_{pl} \\ \times S_{kq} Q^{-1}_{lj} Q_{ik} \\ = \omega_\nu^{-1} \sum_{S,T} C_\nu(TS^{-1})C_\nu(S) \sum_{p,q=1}^N T(p|q) \\ \times (TS^{-1}Q^{-1})_{pj}(QS)_{iq}. \quad (32)$$

Letting  $\mathbf{R} = \mathbf{Q}\mathbf{S}$ , and using the orthogonality properties

of the  $C_\nu(R)$ , we obtain

$$(\gamma_\nu^0)_{ij} = g^{-1} \omega_\nu^{-1} \sum_{R,S,T} C_\nu(TS^{-1})C_\nu(S) \\ \times \sum_{k,l=1}^N T(k|l)R_{il}(TR^{-1})_{kj} \\ = g^{-1} \omega_\nu^{-1} \sum_{R,T} C_\nu(T) \sum_{k,l=1}^N T(k|l)R_{il}(TR^{-1})_{kj}. \quad (33)$$

In a similar way we obtain the matrix elements of the symmetric component of the second-order density matrix

$$(\Gamma_\nu^0)_{rsnq} = g^{-1} \omega_\nu^{-1} \sum_{R,T} C_\nu(T) \\ \times \sum_{i < j=1, k < l=1}^N T(ij|kl)R_{ri}R_{sj}(TR^{-1})_{kp}(TR^{-1})_{lq}. \quad (34)$$

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 Eqs. (33) and (34) are slightly simpler than Eqs. (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 projection.<sup>1</sup> 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  $\rho^0$ . With  $\gamma_\nu^0$  from Eq. (33), we have for an element of the commutator of  $\rho^0$  and  $\gamma_\nu^0$

$$[\gamma_\nu^0, \rho^0]_{ij} = \sum_{k=1}^M \{ (\gamma_\nu^0)_{ik}(\rho^0)_{kj} - (\rho^0)_{ik}(\gamma_\nu^0)_{kj} \} \\ = g^{-1} \omega_\nu^{-1} \sum_{R,T} C_\nu(T) \sum_{m,n=1}^N T(m|n) \\ \times \{ R_{in}(TR^{-1}\rho^0)_{mj} - (\rho^0 R)_{in}(TR^{-1})_{mj} \}. \quad (35)$$

Because both  $\rho^0$  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  $\{\eta^{\alpha a_i}\}$  related to the original spin-orbital basis  $\{\phi_i\}$  by a unitary transformation

$$\phi_j = \sum_{\alpha} \sum_{a=1}^{J_{\alpha}} \sum_{i=1}^{n_{\alpha}} U^{-1}(\alpha a i)_{,j} \eta^{\alpha a_i}. \quad (36)$$

<sup>6</sup> R. McWeeny and W. Kutzelnigg, Intern. J. Quantum Chem. 2, 186 (1968).

The set  $\alpha ai$  can be thought of as constituting a single index labeling  $\eta$  or as a set of indicies. The irreducible representation is identified by  $\alpha$  and further labeled by  $a$  if  $J_\alpha$ , the number of times the  $\alpha$ th 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 ( $\alpha$  and  $a$ ) must be a multiple of the  $n_\alpha \times n_\alpha$  unit matrix

$$\langle \eta^{\alpha ai} | \Omega^0 | \eta^{\alpha aj} \rangle = \delta_{ij} \xi(\alpha a), \quad (37)$$

where  $\Omega^0$  can be  $\rho^0$ ,  $\gamma_\nu^0$ , or their commutator and  $\xi(\alpha a)$  depends on the operator,  $a$  and  $\alpha$ , 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  $\alpha$  and  $a$ .

Using Eqs. (35) and (36), and the fact that  $\rho^0$  commutes with all symmetry operations, we obtain

$$\begin{aligned} [\gamma_\nu^0, \rho^0]_{ij} &= g^{-1} \omega_\nu^{-1} \sum_{R,T} C_\nu(T) \sum_{m,n=1}^N T(m|n) \\ &\times \sum_{\alpha,a,g,r} \sum_{\beta,b,t,s} \{ U_{i,(aaq)} \langle \eta^{\alpha aq} | R | \eta^{\alpha ar} \rangle \\ &\times U^{-1}(\alpha ar, n) U_{m,(\beta bs)} \langle \eta^{\beta bs} | \rho^0 T R^{-1} | \eta^{\beta bt} \rangle \\ &\times U^{-1}(\beta bt, j) - U_{i,(\alpha aq)} \langle \eta^{\alpha aq} | R \rho^0 | \eta^{\alpha ar} \rangle U^{-1}(\alpha ar, n) U_{m,(\beta bs)} \\ &\times \langle \eta^{\beta bs} | T R^{-1} | \eta^{\beta bt} \rangle U^{-1}(\beta bt, j) \}. \quad (38) \end{aligned}$$

Therefore, we may identify the matrix element in the symmetry-adapted basis as

$$\begin{aligned} \langle \eta^{\alpha aq} | [\gamma_\nu^0, \rho^0] | \eta^{\beta bt} \rangle &= g^{-1} \omega_\nu^{-1} \sum_{R,T} C_\nu(T) \sum_{m,n=1}^N T(m|n) \\ &\times \sum_{r,s} \{ \langle \eta^{\alpha aq} | R | \eta^{\alpha ar} \rangle \langle \eta^{\beta bs} | \rho^0 T R^{-1} | \eta^{\beta bt} \rangle \\ &- \langle \eta^{\alpha aq} | R \rho^0 | \eta^{\alpha ar} \rangle \langle \eta^{\beta bs} | T R^{-1} | \eta^{\beta bt} \rangle \} U^{-1}(\alpha ar, n) U_{m,(\beta bs)}. \quad (39) \end{aligned}$$

From Eq. (37) we have

$$\begin{aligned} \langle \eta^{\alpha aq} | R \rho^0 | \eta^{\alpha ar} \rangle &= \sum_{\epsilon, \epsilon, u} \langle \eta^{\alpha aq} | R | \eta^{\epsilon eu} \rangle \langle \eta^{\epsilon eu} | \rho^0 | \eta^{\alpha ar} \rangle \\ &= \langle \eta^{\alpha aq} | R | \eta^{\alpha ar} \rangle \langle \eta^{\alpha ar} | \rho^0 | \eta^{\alpha ar} \rangle, \quad (40) \end{aligned}$$

where  $\langle \eta^{\alpha ar} | \rho^0 | \eta^{\alpha ar} \rangle$  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

$$\begin{aligned} \langle \eta^{\alpha aq} | [\gamma_\nu^0, \rho^0] | \eta^{\beta bt} \rangle &= \delta_{\alpha\beta} \delta_{at} \delta_{qt} g^{-1} \omega_\nu^{-1} \sum_{R,T} C_\nu(T) \\ &\times \sum_{m,n=1}^N T(m|n) \sum_{r,s} \langle \eta^{\alpha aq} | R | \eta^{\alpha ar} \rangle \langle \eta^{\alpha as} | T R^{-1} | \eta^{\alpha aq} \rangle \\ &\times \{ \langle \eta^{\alpha as} | \rho^0 | \eta^{\alpha as} \rangle - \langle \eta^{\alpha ar} | \rho^0 | \eta^{\alpha ar} \rangle \} U^{-1}(\alpha ar, n) U_{m,(\alpha as)}. \quad (41) \end{aligned}$$

Because  $\langle \eta^{\alpha ar} | \rho^0 | \eta^{\alpha ar} \rangle$  does not depend on  $r$ ,

$$\langle \eta^{\alpha aq} | [\gamma_\nu^0, \rho^0] | \eta^{\beta bt} \rangle = 0 \quad (42)$$

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 paper we have shown how to calculate the first- and second-order density matrices of symmetry-projected wavefunctions. Our technique does not require the explicit calculation of the projected wavefunction. The method should prove very useful when applied to point-group projection in polyatomic molecules and  $L_z$  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 nonsymmetry-adapted single-determinant wavefunction.

(2) As the first step in obtaining a variationally useful energy expression for an extended Hartree-Fock calculation in which nonsymmetry-adapted orbitals are used to obtain a lower energy without sacrificing the symmetry properties of the total wavefunction.