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Unitary group approach to reduced density matrices

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A fully spin-adapted approach to many-electron density matrices is developed in the context of the unitary group approach to many-electron systems. An explicit expression for the single-electron spin-density operator, as a polynomial of degree two in the orbital $U(n)$ generators, is derived for the case of spin-independent systems. Extensions to spin-dependent systems are also considered, leading to the appearance of total-spin transition densities, whose general properties are investigated. A corresponding formalism for the two-electron density matrix, which is capable of further generalization, is also developed. The results of this paper, together with recent developments on the matrix elements of the $U(2n)$ generators in the electronic Gel'fand basis, afford a versatile method for the direct calculation of one- and two-body density matrices in the unitary group approach framework.

I. INTRODUCTION

Reduced density matrices and their application have a long history and were introduced, in the Hartree-Fock framework, by Dirac.¹ Subsequent work of Löwdin² and McWeeny^{3,4} demonstrated the wide power of such techniques, particularly for evaluating one- and two-electron expectation values and for the determination of effective spin Hamiltonians as required in ESR and NMR spectroscopy. Since then there have appeared many applications and extensions which are discussed in several books and review articles.⁴⁻⁷ We only mention here the numerous applications of density matrices to the definition of bond order matrices, various bond indices, and overlap populations,^{4,5,8-12} as well as their recent exploitation in theories of high- T_C superconductivity.¹³

It has been recognized for some time that molecular charge densities, in conjunction with x-ray-diffraction experiments, afford a powerful tool for the analysis of chemical bonding. Unfortunately, however, the valence electrons (in the bonding region) usually contribute only a small fraction to the overall charge density, so that it is first necessary to subtract out the dominant contribution from the core (leading to difference density maps). The latter is frequency modeled by spherically averaged atomic densities, although other possibilities, leading to different distributions, can occur, and hence great care needs to be exercised in their interpretation. An alternative approach, which enables one to experimentally observe the valence electrons directly, is afforded by polarized neutron-diffraction experiments, in which polarized neutrons are scattered by unpaired spins in a crystal-line lattice. These experiments yield magnetic structure factors which represent Fourier components of magnetization density, in complete analogy to Fourier components of the

electron density that are afforded by x-ray-diffraction structure factors. Assuming that in the ground state considered the orbital contribution to the magnetization is negligible, these magnetic structure factors provide a description of the spin density of the system. In this way valuable information on chemical bonding effect may be inferred, particularly for transition-metal compounds with unpaired d electrons. This technique has been developed and extensively exploited by Figgis and co-workers.¹⁴⁻¹⁶ The experiments and the interpretation of such neutron-diffraction data are, however, difficult and theoretical information on the distribution of unpaired spins, as afforded by the one- and two-electron spin densities, can be of crucial importance and help. We quote from the pioneering paper by Figgis, Reynolds, and Williams^{14(b)} in which spin density and bonding in the CoCl_4^{2-} ion were first explored: "the overlap spin-density component in the diffuse region is strongly correlated with possible spin-polarization effects, and within the accuracy of the experiment it is not possible to be clear about its origin without aid from theoretical chemistry."

Indeed, theoretical calculations have already proved a valuable adjunct for the interpretation of neutron-diffraction data¹⁷ but, to date, most calculations have been performed at the Hartree-Fock level. This leaves unexplained certain discrepancies with experiments, which are not removed when limited forms of *configuration-interaction* (CI) or multiconfiguration self-consistent-field (MCSCF) calculations are used.¹⁸ This is particularly the case for transition-metal compounds exhibiting a large degree of covalency.¹⁶ We note that although the CI methodology was employed to study the energetics, particularly in connection with optical spectra, in the transition-metal complexes, it was not employed in computation of charge or spin densities,¹⁸ which is rather demanding. The formalism developed in this paper can certainly facilitate such an undertaking.

In order to develop methods for efficiently obtaining

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molecular charge and spin densities in CI calculations, we investigate this problem within the framework of the unitary group approach (UGA), which currently affords a powerful and versatile method for large-scale CI calculations on molecules. The UGA, which arose from previous work of Moshinsky¹⁹ on the nuclear shell model, exploits the fact that the spin-independent (electronic) molecular Hamiltonian is expressible as a bilinear form in the orbital $U(n)$ generators. This enables the exploitation of $U(n)$ representation theory for the efficient spin adaptation and for calculation of Hamiltonian *matrix elements* (MEs) that are required in CI calculations. The initial development of UGA due to Paldus^{20,21} and Shavitt²² was followed by numerous important innovations and extensions, which are described in several review articles^{23–27} and books.^{28–30} The UGA formalism enabled numerous computational implementations, particularly in conjunction with direct CI,³¹ ranging from the integral-driven,^{32,33} loop-driven,³⁴ shape,³⁵ or internal interaction block-driven³⁶ to ME-driven³⁷ approaches based on harmonic level excitation diagrams.³⁸

Thus, as indicated above, the UGA affords a convenient method for the calculation of CI wave functions and hence provides an ideal framework in which to develop a spin- and charge-density matrix formalism. This is particularly the case since, as will be shortly seen, the general k -electron density matrix may be expressed naturally in terms of the $U(2n)$ generators. In the present and following papers we thus aim to develop a fully spin-adapted UGA to k -electron density matrices, with particular emphasis on the evaluation of one- and two-electron charge and spin densities.

In this paper we present a spin-adapted approach to one-electron density matrices. In particular, we show that, for spin-independent systems, the one-electron density matrix is determined completely by two density operators, namely the charge and (normalized) spin-density operators. We give an explicit expression for these operators in terms of the $U(n)$ matrix Δ of Ref. 39 (which is given by a polynomial of degree two in the orbital $U(n)$ matrix $E = [E_j^i]$). We then consider extensions to two-body density matrices which, for spin-independent systems, are shown to be completely determined by six density operators, which in turn are expressible in terms of the one-body charge and spin-density operators. The MEs of the entries Δ_j^i of the $U(n)$ matrix Δ in the electronic Gel'fand basis have been recently determined⁴⁰ and afford an efficient *direct* evaluation of one- and two-electron charge and spin densities in the UGA framework.

We also consider extensions to spin-dependent systems and demonstrate that the full one- and two-electron spin-density matrices are completely determined by certain total spin transition density operators, which are explicitly constructed in terms of the $U(2n)$ generators, together with the (scalar) densities discussed above. From the viewpoint of computer implementation, it is worth noting that the $U(2n)$ ME formalism developed in Refs. 39–41 affords a convenient method for the *direct* evaluation of these spin transition densities in the electronic spin-orbital basis.

The paper is set up as follows. We begin in Sec. II with the unitary group formulation of the one-electron density matrix. In Sec. III we investigate the reduction of this den-

sity matrix for spin-independent systems and obtain an explicit expression, in terms of the orbital $U(n)$ generators, for the normalized spin-density operator. In Secs. IV and V we consider extensions of the two-body density matrix and conclude with a brief discussion and suggestions for future research in Sec. VI. Throughout, repeated use is made of the characteristic identity methods of Green⁴² and Gould,^{43–45} which are shown to play a natural role in discussing density operators.

II. ONE-PARTICLE DENSITY MATRICES

We shall consider density matrices arising from wave functions constructed from $2n$ spin orbitals $\psi_{i\mu}(x)$, $1 \leq i \leq n$, $\mu = \pm 1/2$, where $x = (r, \xi)$ denotes the combined spatial and spin coordinates. We assume that the spin orbitals $\psi_{i\mu}(x)$ factor into the orbital and spin parts,

$$\psi_{i\mu}(x) = \phi_i(r)\chi_\mu(\xi),$$

where the molecular orbitals $\phi_i(r)$ are orthogonal and χ_μ denote the elementary spin column vectors

$$\chi_{1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi_{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

so that $\chi_\mu(\xi) = \delta_{\mu\xi}$. In the second quantized formulation, we introduce corresponding fermion creation and annihilation operators, $X_{i\mu}^\dagger$ and $X_{i\mu}$, respectively, satisfying the familiar anticommutation relations

$$\{X_{i\mu}^\dagger, X_{j\nu}\} = \delta_{ij}\delta_{\mu\nu}, \quad \{X_{i\mu}^\dagger, X_{j\nu}^\dagger\} = \{X_{i\mu}, X_{j\nu}\} = 0.$$

The space of N -particle states \mathcal{Y}_N , to which the N -electron wave functions belong, is then given by all N th-order products of fermion creation operators $X_{i\mu}^\dagger$ acting on the physical vacuum state $|0\rangle$.

Following the UGA,^{20–23} the particle number conserving operators

$$E_{j\nu}^{i\mu} = X_{i\mu}^\dagger X_{j\nu} \quad (1)$$

form the generators of the spin-orbital Lie group $U(2n)$. The space \mathcal{Y}_N of N -particle states then gives rise to an irreducible representation of $U(2n)$ with highest weight⁴⁴

$$(\dot{1}_N, \dot{0}) = (1, 1, \dots, 1, 0, \dots, 0),$$

with 1's in the first N positions, called the antisymmetric N th rank tensor representation. The spin-averaged operators

$$E_j^i = \sum_{\nu = -1/2}^{+1/2} E_{j\nu}^{i\nu} \quad (2)$$

form the generators of the orbital subgroup $U(n)$ of $U(2n)$, while the operators

$$E_\nu^\mu = \sum_{i=1}^n E_{i\nu}^{i\mu} \quad (3)$$

form the generators of the spin subgroup $U(2)$. The generators (2) and (3) collectively constitute the generators of the subgroup $U(n) \times U(2)$ (outer direct product) of $U(2n)$, referred to herein as the *spin-orbit* (SO) subgroup.

In terms of the $U(2)$ generators (3), the number operator \hat{N} and the total-spin vector operator \hat{S} may be expressed as²¹

$$\hat{S}_+ = E_{-1/2}^{1/2}, \quad \hat{S}_- = E_{1/2}^{-1/2}$$

$$\hat{S}_z = \frac{1}{2}(E_{1/2}^{1/2} - E_{-1/2}^{-1/2}), \quad \hat{N} = E_{1/2}^{1/2} + E_{-1/2}^{-1/2}, \quad (4)$$

where, as usual, $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$. We note that the operators \hat{S}_\pm, \hat{S}_z constitute the generators of the subgroup SU(2).

In this formulation of the many-electron problem, the general single-particle reduced density operator is given by⁴

$$\hat{\rho}_1(x; x') = \sum_{\mu, \nu = -1/2}^{1/2} \sum_{i, j = 1}^n \psi_{i\mu}^*(x) \psi_{j\nu}(x') E_{j\nu}^{\mu}, \quad (5)$$

which may be alternatively expressed as a 2×2 matrix with entries

$$\hat{\rho}_1(r; r')_{\nu}^{\mu} = \hat{\rho}_1((r, \mu); (r', \nu))$$

$$= \sum_{i, j = 1}^n \phi_i^*(r) \phi_j(r') E_{j\nu}^{\mu}. \quad (6)$$

Throughout we shall refer to the matrix (6) as the *single-electron density matrix*. We emphasize that in this approach the entries (6) of the density matrix are regarded as *operators*. The spin-density matrix $\rho_1(r)$ arising from a given molecular wave function Ψ is then given by the corresponding 2×2 matrix of expectation values

$$\rho_1(r)_{\nu}^{\mu} = \langle \Psi | \hat{\rho}_1(r; r)_{\nu}^{\mu} | \Psi \rangle. \quad (6')$$

It is of interest to investigate the behavior of the density operator (5) under convolution product. We have

$$\int \hat{\rho}_1(x; x') \hat{\rho}_1(x'; x'') dx'$$

$$= \sum_{i, j, k, l = 1}^n \sum_{\mu, \nu, \rho, \sigma = -1/2}^{+1/2} \psi_{i\mu}^*(x) \psi_{l\sigma}(x'')$$

$$\times \int \psi_{j\nu}(x') \psi_{k\rho}^*(x') dx' E_{j\nu}^{\mu} E_{l\sigma}^{k\rho}.$$

Using the orthonormality of spin orbitals

$$\int \psi_{j\nu}(x') \psi_{k\rho}^*(x') dx' = \delta_{jk} \delta_{\nu\rho},$$

we obtain

$$\int \hat{\rho}_1(x; x') \hat{\rho}_1(x'; x'') dx'$$

$$= \sum_{i, l = 1}^n \sum_{\mu, \sigma = -1/2}^{+1/2} \psi_{i\mu}^*(x) \psi_{l\sigma}(x'') (E^2)_{l\sigma}^{\mu}, \quad (7)$$

where E^2 is the $(2n) \times (2n)$ matrix with entries

$$(E^2)_{j\nu}^{\mu} = E_{k\sigma}^{\mu} E_{j\nu}^{k\sigma}$$

(summation over repeated indices is assumed). However, on the representation of U(2n) with highest weight $(\frac{1}{2}N, 0)$, which is pertinent to the N -electron problem, the U(2n) matrix $[E_{j\nu}^{\mu}]$ satisfies the quadratic identity⁴² (cf. the Appendix)

$$E(E - 2n - 1 + N) = 0, \quad (8)$$

so that

$$(E^2)_{j\nu}^{\mu} = (2n + 1 - N) E_{j\nu}^{\mu}. \quad (8')$$

Substituting into Eq. (7), we thus obtain

$$\int \hat{\rho}_1(x; x') \hat{\rho}_1(x'; x'') dx' = (2n + 1 - N) \hat{\rho}_1(x; x''),$$

which may be expressed in the matrix form

$$\sum_{\sigma = -1/2}^{+1/2} \int \hat{\rho}_1(r; r')_{\sigma}^{\mu} \hat{\rho}_1(r'; r'')_{\nu}^{\sigma} dr' = (2n + 1 - N) \hat{\rho}_1(r; r'')_{\nu}^{\mu}. \quad (9)$$

It follows, in particular, that the normalized density operator

$$\hat{\gamma}_1(x; x') \equiv (2n + 1 - N)^{-1} \hat{\rho}_1(x; x') \quad (10)$$

is idempotent, i.e.,

$$\int \hat{\gamma}_1(x; x') \hat{\gamma}_1(x'; x'') dx' = \hat{\gamma}_1(x; x'').$$

We emphasize that the idempotency of the density operator $\hat{\gamma}_1$, Eq. (10), should not be confused with the well-known^{2,3} idempotency of the molecular density matrix arising from a closed-shell Hartree-Fock wave function. Equation (9) is an *operator* equation and is a direct consequence of the reduced identities of Eq. (8). Such reduced identities, first encountered by Green⁴² (see also the Appendix), afford a natural tool for investigating density operators, as previously noted, and will be applied extensively throughout the paper.

Taking the trace of the density matrix (6) we obtain^{3,4} the familiar *charge-density operator*

$$\hat{\rho}_1^c(r; r') = \hat{\rho}_1(r; r')_{1/2}^{1/2} + \hat{\rho}_1(r; r')_{-1/2}^{-1/2}$$

$$= \sum_{i, j = 1}^n \phi_i^*(r) \phi_j(r') E_{j\nu}^{\mu}, \quad (11)$$

which is expressible solely in terms of the orbital U(n) generators $E_{j\nu}^{\mu}$, Eq. (2), and hence is obviously spin independent. In terms of the usual Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

the one-electron density matrix may be rewritten as

$$\hat{\rho}_1(r; r')_{\nu}^{\mu} = \frac{1}{2} \hat{\rho}_1^c(r; r') \delta_{\nu}^{\mu} + \mathbf{R} \cdot \boldsymbol{\sigma}_{\nu}^{\mu}, \quad (12)$$

where

$$\mathbf{R}(r; r') = \sum_{i, j = 1}^n \phi_i^*(r) \phi_j(r') \boldsymbol{\Gamma}_{ij}^i, \quad (13a)$$

and

$$(\boldsymbol{\Gamma}_x)_j^i = -\frac{1}{2}(E_{j, -1/2}^{i, 1/2} + E_{j, 1/2}^{i, -1/2}),$$

$$(\boldsymbol{\Gamma}_y)_j^i = -\frac{1}{2}i(E_{j, -1/2}^{i, 1/2} - E_{j, 1/2}^{i, -1/2}), \quad (13b)$$

$$(\boldsymbol{\Gamma}_z)_j^i = \frac{1}{2}(E_{j, 1/2}^{i, 1/2} - E_{j, -1/2}^{i, -1/2}).$$

Alternatively, we note that the one-body density matrix can be expressed in a convenient tensor form: This gives rise to a scalar density, which is given by the number density operator of Eq. (11), together with a vector density which, in terms of the SU(2) coupling coefficients, is defined by

$$\hat{\rho}_1(r; r')_{\alpha} = \hat{\rho}_1(r; r')_{\nu}^{\mu} \langle \frac{1}{2} \mu; \frac{1}{2} (-\nu) | 1\alpha \rangle (-1)^{1/2 + \nu}$$

$$(-1 \leq \alpha \leq 1). \quad (12')$$

where the summation over μ and ν is implied. Note that these components are explicitly given by

$$\begin{aligned}\hat{\rho}_1(r;r')_1 &= \hat{\rho}_1(r;r')_{-1/2}^{1/2}, \\ \hat{\rho}_1(r;r')_{-1} &= -\hat{\rho}_1(r;r')_{1/2}^{-1/2}, \\ \hat{\rho}_1(r;r')_0 &= -2^{1/2}R_z.\end{aligned}$$

We remark that this latter operator, defined by the z component of Eq. (13), determines the usual (single-electron) *spin density* of the molecule.^{3,4} This tensor form for reduced density matrices is useful, particularly for discussing two- and higher-electron density operators, which will be considered in Sec. IV and V. However, for one-body densities, it is just as convenient to work with the matrix formulation of Eq. (12), which we adopt throughout most of the paper.

It should be noted that the entries of the density matrix (6) are given in terms of the $U(2n)$ generators, Eq. (1), which do not conserve the total spin quantum number S . Consequently, in actual applications, we need a resolution of the density matrix into components which effect well-defined shifts on the total spin S . This is particularly the case when dealing with density matrices arising from wave functions with well-defined total spin (i.e., describing a spin-independent system). In the following section we present a solution to this problem using the spin-shift formalism of Refs. 44 and 45.

III. SPIN DENSITIES AND TOTAL-SPIN TRANSITION DENSITIES

In this section we consider the partitioning of the single-electron density matrix into components according to their shifts on the total-spin quantum number S . This leads to the appearance of total-spin *transition densities*, which increase or decrease the total-spin quantum number S , as well as a density-matrix component which commutes with the total spin S . Only this latter density matrix is required when dealing with wave functions possessing a well-defined total spin and is expected to yield the dominant contribution to the density matrix even for wave functions characterizing spin-dependent systems. In this latter case, however, the total-spin transition densities will contain useful information on transition probabilities between states with different total spins.

We first discuss the problem of constructing states with well-defined total spin S , which has been extensively studied in the past (cf., e.g., Refs. 46–49). In the UGA this problem is automatically taken into account by considering a basis for the space \mathcal{Y}_N of N electron states which is symmetry adapted to the SO subgroup $U(n) \times U(2)$. The resulting SO basis states may be written as

$$|[P]\rangle_{M_S} \equiv |[P]\rangle \otimes |SM_S\rangle, \quad (14)$$

where $[P]$ designates an ABC (Refs. 20 and 21) or Gel'fand–Paldus^{22–30,41,44,45} (GP) tableau, labeling the orbital part of the state, and M_S is the azimuthal spin quantum number. The states $|SM_S\rangle$ constitute the usual basis for the *irreducible representations* (irreps) of $SU(2)$ and are also eigenstates of the number operator \hat{N} with eigenvalue N [and hence are also $U(2)$ states]. The total spin of the states (14) is given by $S = b/2$, where

$$p = [abc], \quad N = 2a + b, \quad a + b + c = n,$$

are the Paldus labels of the orbital group $U(n)$ (corresponding to the top row of the pattern $[P]$) that determine the irrep of $U(n)$ concerned.^{20,21,44}

The UGA was originally designed^{20,21} for spin-independent problems, in which case the electronic Hamiltonian is expressible solely in terms of the orbital $U(n)$ generators. For such problems it suffices to obtain the MEs of the $U(n)$ generators [Eq. (2)] (and of their products) in the orbital part of the SO basis, Eq. (14), with a fixed value of S and M_S . However, even when dealing with spin-dependent Hamiltonians, the SO basis, Eq. (14), represents an excellent starting point, since spin-dependent effects are usually small compared to the spin-independent Coulomb interactions. Consequently, in such a case, the MEs of the $U(2n)$ generators are required in the SO basis, Eq. (14). This latter problem, which has been addressed by Gould and Chandler^{41,45} and more recently by Gould and Paldus,³⁹ is also essential for the evaluation of the single-electron density matrix, Eq. (6'), in the SO basis, Eq. (14), to which we now turn.

Following Gould and Chandler^{41,45} (see also Ref. 39), we note that the $U(2n)$ generators transform, under commutation with the $U(n) \times U(2)$ generators, Eqs. (2) and (3), as the representation $Ad_{U(n)} \otimes Ad_{U(2)}$, where $Ad_{U(k)}$ denotes the adjoint representation of $U(k)$.^{45,50} It follows that the $U(2n)$ generators, Eq. (1), may be resolved into spin-shift components^{41,45}

$$E_{j\nu}^{\mu} = E(-)_{j\nu}^{\mu} + E(0)_{j\nu}^{\mu} + E(+)_{j\nu}^{\mu}, \quad (15)$$

where $E(\pm)$ increases (respectively decreases) the total spin S of the SO states, Eq. (14), by one unit, while $E(0)$ leaves S unchanged. Taking the $U(2)$ trace of Eq. (15) and equating spin-shift components, we immediately obtain that

$$E_j^i = \sum_{\mu} E_{j\mu}^{\mu} = \sum_{\mu} E(0)_{j\mu}^{\mu}, \quad (16a)$$

$$\sum_{\mu} E(+)_{j\mu}^{\mu} = \sum_{\mu} E(-)_{j\mu}^{\mu} = 0. \quad (16b)$$

This shift component resolution of Eq. (15) induces the following partitioning of the single-electron density matrix, Eq. (6):

$$\hat{\rho}_1(r;r')_{\nu}^{\mu} = \hat{\rho}_1^{(-)}(r;r')_{\nu}^{\mu} + \hat{\rho}_1^{(0)}(r;r')_{\nu}^{\mu} + \hat{\rho}_1^{(+)}(r;r')_{\nu}^{\mu}, \quad (17)$$

where

$$\hat{\rho}_1^{(\epsilon)}(r;r')_{\nu}^{\mu} = \sum_{i,j=1}^n \phi_i^*(r)\phi_j(r')E(\epsilon)_{j\nu}^{\mu}, \quad \epsilon = 0, \pm. \quad (18)$$

In view of Eq. (16) we obtain

$$\begin{aligned}\text{tr}[\hat{\rho}_1^{(0)}(r;r')] &= \text{tr}[\hat{\rho}_1(r;r')] = \hat{\rho}_1^c(r;r'), \\ \text{tr}[\hat{\rho}_1^{(\pm)}(r;r')] &= 0,\end{aligned} \quad (19)$$

where $\hat{\rho}_1^c(r;r')$ is the charge-density operator, Eq. (11). We may thus write, in view of Eq. (12),

$$\hat{\rho}_1^{(0)}(r;r')_{\nu}^{\mu} = \frac{1}{2} \delta_{\nu}^{\mu} \hat{\rho}_1^c(r;r') + \mathbf{R}^{(0)} \cdot \boldsymbol{\sigma}_{\nu}^{\mu}, \quad (20a)$$

$$\hat{\rho}_1^{(\pm)}(r;r')_{\nu}^{\mu} = \mathbf{R}^{(\pm)} \cdot \boldsymbol{\sigma}_{\nu}^{\mu}, \quad (20b)$$

where $\mathbf{R}^{(\epsilon)}$ is given by Eq. (13) with $E_{j\nu}^{\mu}$ replaced by the corresponding shift component $E(\epsilon)_{j\nu}^{\mu}$ ($\epsilon = 0, \pm$). A corresponding spin-shift resolution of the vector density of Eq. (12') also applies.

Of particular interest is the zero-shift component, Eq. (20a), which determines the full density matrix for wave functions with well-defined total spin S . Following Ref. 39, the zero-shift components of the $U(2n)$ generators are given by [Eq. (22) of Ref. 39]

$$E(0)_{j\nu}^{\mu} = \frac{1}{2} \delta_{\nu}^{\mu} E_j^{\nu} - [2S(S+1)]^{-1} \Delta_j^i \tilde{E}_{\nu}^{\mu} \quad (S \neq 0), \quad (21)$$

where \tilde{E}_{ν}^{μ} denote the $SU(2)$ generators [Eq. (20a) of Ref. 39]

$$\tilde{E}_{\nu}^{\mu} = E_{\nu}^{\mu} - \frac{\hat{N}}{2} \delta_{\nu}^{\mu}, \quad (21')$$

and Δ is the polynomial of degree 2 in the $U(n)$ matrix E given by [Eq. (18) of Ref. 39]

$$\Delta = E(E + \hat{N}/2 - n - 2), \quad (22)$$

where polynomials in the $U(n)$ matrix $E = [E_j^i]$ are defined recursively in the usual fashion^{42,44}

$$(E^{m+1})_j^i = E_k^i (E^m)_j^k, \quad (E^0)_j^i = \delta_j^i$$

(assuming summation over repeated indices). It is important to note that in the case $S=0$, the second term on the right-hand side of Eq. (21) does not contribute, which is consistent with the easily established result (see the Appendix)

$$\Delta_j^i = 0 \quad 1 \leq i, j \leq n \quad \text{for } S=0. \quad (23)$$

We thus obtain for the zero-shift component of the vector \mathbf{R} , Eq. (13), in view of Eq. (21), that

$$\mathbf{R}^{(0)}(r; r') = \hat{\rho}_1^s(r; r') \mathbf{S},$$

where \mathbf{S} is the total molecular spin vector and

$$\hat{\rho}_1^s(r; r') = -\frac{1}{2S(S+1)} \sum_{i,j=1}^n \phi_i^*(r) \phi_j(r') \Delta_j^i \quad (S \neq 0). \quad (24)$$

Here, again, the operator (24) vanishes when $S=0$. Substituting into Eq. (20a), we thus get for the zero-shift component of the density matrix, Eq. (6), the expression

$$\hat{\rho}_1^{(0)}(r; r')_{\nu}^{\mu} = \frac{1}{2} \delta_{\nu}^{\mu} \hat{\rho}_1^s(r; r') + \hat{\rho}_1^s(r; r') \mathbf{S} \cdot \boldsymbol{\sigma}_{\nu}^{\mu}. \quad (25a)$$

Alternatively, in terms of the $SU(2)$ generators \tilde{E}_{ν}^{μ} , we may write

$$\hat{\rho}_1^{(0)}(r; r')_{\nu}^{\mu} = \frac{1}{2} \hat{\rho}_1^s(r; r') \delta_{\nu}^{\mu} + \hat{\rho}_1^s(r; r') \tilde{E}_{\nu}^{\mu}, \quad (25b)$$

where we have used the easily established result

$$\mathbf{S} \cdot \boldsymbol{\sigma}_{\nu}^{\mu} = \tilde{E}_{\nu}^{\mu} = E_{\nu}^{\mu} - \frac{\hat{N}}{2} \delta_{\nu}^{\mu}.$$

The density operator (24) has a natural interpretation in terms of molecular spin densities. The spin-density operator is well known to be given by^{3,4}

$$R_z(r; r') = \frac{1}{2} [\hat{\rho}_1(r; r')^{1/2} - \hat{\rho}_1(r; r')^{-1/2}],$$

which, in the case of spin-independent CI, reduces to the corresponding zero-shift component

$$R_z^{(0)}(r; r') = \hat{\rho}_1^s(r; r') S_z.$$

Therefore, the density operator $\hat{\rho}_1^s(r; r')$, Eq. (24), determines the normalized spin density of the molecule and is referred to henceforth as the *normalized spin-density operator*. It is worth noting that, in tensor form, the zero-shift

component of the vector density operator (12') is given by

$$\hat{\rho}_1^{(0)}(r; r')_{\alpha} = \hat{\rho}_1^s(r; r') v_{\alpha}, \quad -1 \leq \alpha \leq 1 \quad (25')$$

where v_{α} denotes the rank-one $SU(2)$ tensor operator given by

$$v_1 = S_+, \quad v_0 = -\sqrt{2} S_z, \quad v_{-1} = -S_-. \quad (4')$$

Thus, for wave functions with well-defined total spin S , the single-electron density matrix reduces to the zero-shift component, Eq. (25), which is determined solely by two density operators, namely the charge-density operator, Eq. (11), and the normalized spin-density operator, Eq. (24). The former determines the distribution of electronic charge in the molecule and the latter the distribution of unpaired spins.⁴ For a wave function Ψ , with well-defined total spin S and azimuthal spin M_S , the spin M_S is regarded as smeared over the molecule with a distribution determined by⁴

$$\rho_1^s(r) = \langle \Psi | \hat{\rho}_1^s(r; r) | \Psi \rangle.$$

In the case of spin-dependent problems we also need to consider the nonzero-shift components

$$\hat{\rho}_1^{(\pm)}(r; r')_{\nu}^{\mu} = \mathbf{R}^{(\pm)} \cdot \boldsymbol{\sigma}_{\nu}^{\mu} = \sum_{i,j=1}^n \phi_i^*(r) \phi_j(r') E(\pm)_{j\nu}^{\mu i},$$

which we refer to herein as *total-spin transition density matrices*. These spin-shift components may be explicitly constructed with the help of the following polynomial identity, satisfied by the $U(n)$ matrix $E = [E_j^i]$ (see the Appendix and Green⁴²):

$$\prod_{i=1}^3 (E - \epsilon_i) = 0, \quad (26)$$

where, on an irrep of $U(n)$ with Paldus labels $[abc]$, the ϵ_i take constant values given by

$$\epsilon_1 = 1 + c, \quad \epsilon_2 = n + 2 - a, \quad \epsilon_3 = 0. \quad (26')$$

Using the above identities, we may construct projection operators⁴⁴

$$P[r] = \prod_{k \neq r} \left(\frac{E - \epsilon_k}{\epsilon_r - \epsilon_k} \right), \quad (27a)$$

satisfying (assuming summation over repeated indices)

$$\sum_{r=1}^3 P[r]_j^i = \delta_j^i, \quad P[r]_k^i P[l]_j^k = \delta_{rl} P[l]_j^i. \quad (27b)$$

We then obtain, in view of Refs. 44 and 45, the following expressions for the spin-shift components of the $U(2n)$ generators:

$$\begin{aligned} E(+)_j^{\mu\nu} &= P[1]_k^i E_{j\nu}^{k\mu} P[2]_j^i, \\ E(-)_j^{\mu\nu} &= P[2]_k^i E_{j\nu}^{k\mu} P[1]_j^i, \end{aligned} \quad (28)$$

which follow from Eq. (27b) together with the easily established result (cf. Ref. 44)

$$P[3]_k^i E_{j\nu}^{k\mu} = E_{k\nu}^{\mu} P[3]_j^k = 0. \quad (29)$$

An alternative construction for the above shift components, using the characteristic identity of the spin group $U(2)$, was given in Ref. 39 [cf. Eqs. (8) and (9) of Ref. 39].

The MEs of the operators Δ_j^i and of the nonzero shift components $E(\pm)_{j\nu}^{\mu}$, in the SO basis, Eq. (14), have been determined in Ref. 40, which affords a convenient method

for the calculation of charge and spin densities in the UGA framework: In fact, this reference provides explicit expressions for the spin density associated with an arbitrary SO state, Eq. (14).

IV. TWO-BODY DENSITY OPERATORS

In this section we consider extensions of our previous results to two-body density matrices. Following Paldus and Jezierski,⁵¹ we introduce recursively defined symmetrized combinations of $U(2n)$ generators as follows:

$$E_{(j_1\nu_1)\dots(j_k\nu_k)(j\nu)}^{(i_1\mu_1)\dots(i_k\mu_k)(i\nu)} = E_{(j_1\nu_1)\dots(j_k\nu_k)}^{i_1\mu_1} E_{j\nu}^{i\nu} - \delta_{j_1}^i \delta_{\nu_1}^\nu E_{(j_1\nu_1)\dots(j_k\nu_k)}^{(i_1\mu_1)\dots(i_k\mu_k)} - \delta_{j_2}^i \delta_{\nu_2}^\nu E_{(j_1\nu_1)(j_2\nu_2)\dots(j_k\nu_k)}^{(i_1\mu_1)(i_2\mu_2)\dots(i_k\mu_k)} - \dots - \delta_{j_k}^i \delta_{\nu_k}^\nu E_{(j_1\nu_1)\dots(i_{k-1}\mu_{k-1})(j_k\nu_k)}^{(i_1\mu_1)\dots(i_{k-1}\mu_{k-1})(i_k\mu_k)} \quad (30)$$

so that, for example,

$$E_{(j\nu)(l\rho)}^{(i\mu)(k\sigma)} = E_{j\nu}^{i\mu} E_{l\rho}^{k\sigma} - \delta_j^k \delta_\nu^\rho E_{l\rho}^{i\mu}.$$

The operators (30) constitute a convenient basis for the universal enveloping algebra of $U(2n)$ which, as shall be discussed in Sec. V, is useful for investigating polynomial identities satisfied by the group generators. Our interest in the operators (30) stems from the fact that they determine the general k -electron density matrix in accordance with

$$\hat{\rho}_k(r_1, \dots, r_k; r'_1, \dots, r'_k)_{\nu_1 \dots \nu_k}^{\mu_1 \dots \mu_k} = \sum_{i_r, j_r=1}^n \phi_{i_1}^*(r_1) \dots \phi_{i_k}^*(r_k) \phi_{j_1}(r'_1) \dots \phi_{j_k}(r'_k) \times E_{(j_1\nu_1)\dots(j_k\nu_k)}^{(i_1\mu_1)\dots(i_k\mu_k)} \quad (31)$$

Taking the total trace of this tensor matrix, we obtain the k -electron charge-density operator

$$\hat{\rho}_k^c(r_1, \dots, r_k; r'_1, \dots, r'_k) = \sum_{i_r, j_r=1}^n \phi_{i_1}^*(r_1) \dots \phi_{i_k}^*(r_k) \phi_{j_1}(r'_1) \dots \phi_{j_k}(r'_k) E_{j_1 \dots j_k}^{i_1 \dots i_k} \quad (32)$$

where

$$E_{j_1 \dots j_k}^{i_1 \dots i_k} = E_{j_1 \dots j_k}^i E_j^{i_1 \dots i_k} - \delta_{j_1}^{i_1} E_{j_2 \dots j_k}^{i_2 \dots i_k} - \dots - \delta_{j_k}^{i_k} E_{j_1 \dots j_{k-1}}^{i_1 \dots i_{k-1}} \quad (33)$$

are the orbital $U(n)$ analogues of the $U(2n)$ operators, Eq. (30) (cf. Ref. 51).

In view of Eqs. (30) and (33), we have the following relation between k -electron density tensors and charge-density operators:

$$\hat{\rho}_{k+1}(r_1, \dots, r_k, r; r'_1, \dots, r'_k, r')_{\nu_1 \dots \nu_{k+1}}^{\mu_1 \dots \mu_{k+1}} = \hat{\rho}_k(r_1, \dots, r_k; r'_1, \dots, r'_k)_{\nu_1 \dots \nu_k}^{\mu_1 \dots \mu_k} \hat{\rho}_1(r; r')_{\nu}^{\mu} - \delta_{\nu_1}^{\mu_1} \hat{\rho}_k(r_1, \dots, r_k; r'_1, r'_2, \dots, r'_k)_{\nu_2 \dots \nu_k}^{\mu_2 \dots \mu_k} \delta(r; r'_1) - \dots - \delta_{\nu_k}^{\mu_k} \hat{\rho}_k(r_1, \dots, r_k; r'_1, \dots, r'_{k-1}, r')_{\nu_1 \dots \nu_{k-1} \nu}^{\mu_1 \dots \mu_{k-1} \mu_k} \delta(r; r'_k), \quad (34)$$

$$\hat{\rho}_{k+1}^c(r_1, \dots, r_k, r; r'_1, \dots, r'_k, r') = \hat{\rho}_k^c(r_1, \dots, r_k; r'_1, \dots, r'_k) \hat{\rho}_1^c(r; r') - \hat{\rho}_k^c(r_1, \dots, r_k; r'_1, r'_2, \dots, r'_k) \delta(r; r'_1) - \dots - \hat{\rho}_k^c(r_1, \dots, r_k; r'_1, \dots, r'_{k-1}, r') \delta(r; r'_k), \quad (35)$$

where

$$\delta(r; r') = \sum_{i=1}^n \phi_i^*(r) \phi_i(r'). \quad (36)$$

Also by setting $r = r'$ above and integrating, we obtain the additional relations (assuming again summation over repeated indices)

$$\int \hat{\rho}_{k+1}(r_1, \dots, r_k, r; r'_1, \dots, r'_k, r)_{\nu_1 \dots \nu_{k+1}}^{\mu_1 \dots \mu_{k+1}} dr = (N - k) \hat{\rho}_k(r_1, \dots, r_k; r'_1, \dots, r'_k)_{\nu_1 \dots \nu_k}^{\mu_1 \dots \mu_k} \int \hat{\rho}_{k+1}^c(r_1, \dots, r_k, r; r'_1, \dots, r'_k, r) dr = (N - k) \hat{\rho}_k^c(r_1, \dots, r_k; r'_1, \dots, r'_k).$$

In particular, for the two-electron density matrix, which is our main concern here, Eqs. (31) and (34) simplify to

$$\hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\nu\rho}^{\mu\sigma} = \sum_{i,j,k,l=1}^n \phi_i^*(r_1) \phi_k^*(r_2) \phi_j(r'_1) \phi_l(r'_2) \times (E_{j\nu}^{i\mu} E_{l\rho}^{k\sigma} - \delta_j^k \delta_\nu^\rho E_{l\rho}^{i\mu}) = \hat{\rho}_1(r_1; r'_1)_{\nu}^{\mu} \hat{\rho}_1(r_2; r'_2)_{\rho}^{\sigma} - \delta_\nu^\rho \hat{\rho}_1(r_1; r'_1)_{\rho}^{\mu} \delta(r_2; r'_2). \quad (37)$$

The corresponding charge-density operator is then given by the total trace of Eq. (37), namely

$$\hat{\rho}_2^c(r_1, r_2; r'_1, r'_2) = \sum_{i,j,k,l=1}^n \phi_i^*(r_1) \phi_k^*(r_2) \phi_j(r'_1) \phi_l(r'_2) (E_j^i E_l^k - \delta_j^k E_l^i) = \hat{\rho}_1^c(r_1; r'_1) \hat{\rho}_1^c(r_2; r'_2) - \hat{\rho}_1^c(r_1; r'_2) \delta(r_2; r'_1). \quad (38)$$

Following McWeeny and Mizuno,³ it is appropriate in this case to express the two-body density matrix $\hat{\rho}_2$, Eq. (37), in the convenient $SU(2)$ tensor form. This leads to the number density operator $\hat{\rho}_2^c$, Eq. (38), which is an $SU(2)$ scalar, together with the two vector densities [cf. Eq. (12')]

$$\hat{V}_1(r_1, r_2; r'_1, r'_2)_{\alpha} = \hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\nu\sigma}^{\mu\alpha} \langle \frac{1}{2} \mu; \frac{1}{2}(-\nu) | 1\alpha \rangle (-1)^{1/2+\nu}, \quad (39a)$$

$$\hat{V}_2(r_1, r_2; r'_1, r'_2)_{\alpha} = \hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\nu\sigma}^{\alpha\mu} \langle \frac{1}{2} \mu; \frac{1}{2}(-\nu) | 1\alpha \rangle (-1)^{1/2+\nu} \quad (-1 \leq \alpha \leq 1) \quad (39b)$$

(summation over repeated indices is assumed here and below), as well as the three-tensor densities

$$\hat{Q}(r_1, r_2; r'_1, r'_2)_{\alpha\beta}^{(l)} = \hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\alpha\beta} \langle 1\alpha; 1\beta | lm \rangle \quad (l = 0, 1, 2; -l \leq m \leq l) \quad (40)$$

where

$$\hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\alpha\beta} = \hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\nu\sigma}^{\mu\alpha} \langle \frac{1}{2} \mu; \frac{1}{2}(-\nu) | 1\alpha \rangle \times \langle \frac{1}{2} \sigma; \frac{1}{2}(-\tau) | 1\beta \rangle (-1)^{1+\nu+\tau} \quad (-1 \leq \alpha, \beta \leq 1).$$

This gives rise, in all, to two scalar densities $\hat{\rho}_1^c, \hat{Q}_0^{(0)}$, three vector densities $\hat{V}_1, \hat{V}_2, \hat{Q}^{(1)}$, as well as a rank-two tensor density $\hat{Q}^{(2)}$: The total number of spin components is easily seen to be 16, in agreement with the number of entries of the density matrix $\hat{\rho}_2$, Eq. (37).

Following the one-electron case, our aim is to determine the zero spin-shift component of the above tensor densities, which determine the full density matrix for spin-independent systems. In particular, for the scalar density $\hat{Q}_0^{(0)}$, we obtain, using SU(2) coupling coefficients,⁵² the result

$$\hat{Q}(r_1, r_2; r'_1, r'_2)_0^{(0)} = 3^{-1/2} [\hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\nu\mu}^{\mu\nu} - \frac{1}{2} \hat{\rho}_2^c(r_1, r_2; r'_1, r'_2)]. \quad (42)$$

To determine the zero-shift components of the vector densities \hat{V}_i , Eqs. (39), we follow Steven's method of operator equivalents,⁵³ according to which we may write, for the zero-shift components,

$$\hat{V}_i^{(0)}(r_1, r_2; r'_1, r'_2)_\alpha = \hat{v}_i(r_1, r_2; r'_1, r'_2) v_\alpha, \quad i = 1, 2 \quad (43)$$

where v_α denotes the SU(2) vector with components [cf. Eq. (4')]]

$$v_1 = S_+, \quad v_0 = -\sqrt{2}S_z, \quad v_{-1} = -S_-. \quad (44)$$

To determine the scalar density operators \hat{v}_i ($i = 1, 2$) on the right-hand side of Eq. (43) we multiply both sides by v_α^\dagger and sum on α to obtain

$$\hat{v}_i(r_1, r_2; r'_1, r'_2) = [2(S+1)S]^{-1} \times v_\alpha^\dagger \hat{V}_i^{(0)}(r_1, r_2; r'_1, r'_2)_\alpha, \quad (45)$$

where we have used the result

$$v_\alpha^\dagger v_\alpha = S_- S_+ + S_+ S_- + 2S_z^2 = 2S(S+1).$$

Similarly, to obtain the zero-shift components of the tensor densities (40), we employ the method of operator equivalents⁵³ and construct the zero-shift tensors

$$T_m^{(l)} = v_\alpha v_\beta \langle 1\alpha; 1\beta | lm \rangle, \quad l = 0, 1, 2; \quad -l \leq m \leq l \quad (46)$$

with v_α as in Eq. (44). The above tensors are given explicitly by

$$T_0^{(0)} = -2 \cdot 3^{-1/2} S(S+1), \quad (47a)$$

$$T_m^{(1)} = v_m, \quad -1 \leq m \leq 1, \quad (47b)$$

together with

$$T_2^{(2)} = (T_{-2}^{(2)})^\dagger = (v_1)^2, \quad (47c)$$

$$T_1^{(2)} = -(T_{-1}^{(2)})^\dagger = 2^{-1/2}(v_0 v_1 + v_1 v_0),$$

$$T_0^{(2)} = 6^{-1/2}(v_{-1} v_1 + v_1 v_{-1} + 2v_0^2).$$

We may therefore write, for the zero-shift components of the tensor densities (40), for the case $l = 1, 2$,

$$\hat{Q}^{(l)}(r_1, r_2; r'_1, r'_2)_m^{(l)} = \hat{q}^{(l)}(r_1, r_2; r'_1, r'_2) T_m^{(l)}, \quad (48)$$

where the scalar densities $\hat{q}^{(l)}$ are given by

$$\hat{q}^{(l)}(r_1, r_2; r'_1, r'_2) = \alpha_l^{-1} T_m^{\dagger(l)} \hat{Q}(r_1, r_2; r'_1, r'_2)_m^{(l)}, \quad l = 1, 2 \quad (49)$$

and the constants α_l are given by

$$\alpha_1 = v_\alpha^\dagger v_\alpha = 2S(S+1), \quad (50a)$$

$$\alpha_2 = T_m^{\dagger(2)} T_m^{(2)} = \frac{3}{2} S(S+1)(2S-1)(2S+3). \quad (50b)$$

It follows that the zero-shift component of the two-body density matrix is determined solely by six density operators, namely the charge-density operator $\hat{\rho}_2^c$, Eq. (38), the scalar density $\hat{Q}_0^{(0)}$, Eq. (42), and the density operators \hat{v}_i and $\hat{q}^{(l)}$ of Eqs. (45) and (49), respectively. These six density operators, thus, determine the full density matrix for wave functions with well-defined total spin S (corresponding to a given spin-independent system), and will be explicitly determined in terms of the one-body charge- and spin-density operators in the following section.

From the viewpoint of spin-dependent extensions, it is also necessary to construct the appropriate spin-transition densities: We note that such transition densities can only occur for the vector densities \hat{V}_1, \hat{V}_2 and the tensor densities $\hat{Q}^{(1)}, \hat{Q}^{(2)}$. As in the one-electron case, we find it convenient to employ the projection operators constructed on the basis of characteristic identities:⁴² In the present case we consider the SU(2) tensor identities, which have been previously discussed in Ref. 54 (where generalizations to arbitrary semi-simple Lie algebras were obtained).

Following Ref. 54, corresponding to each non-negative integer or half-integer l we consider the matrix

$$a_l = \frac{1}{2} [\pi_l(S_-) \otimes S_+ + \pi_l(S_+) \otimes S_- + 2\pi_l(S_z) \otimes S_z],$$

where π_l denotes the $(2l+1)$ -dimensional irrep of SU(2). The matrix a_l may thus be regarded as a $(2l+1) \times (2l+1)$ matrix with entries

$$[a_l]_{ij} = \frac{1}{2} \delta_{ij-1} \sqrt{(l+j)(l-j+1)} S_+ + \frac{1}{2} \delta_{ij+1} \sqrt{(l-j)(l+j+1)} S_- + j \delta_{ij} S_z, \\ -l \leq i, j \leq l.$$

Thus, for example, for $l = 1$ we obtain the 3×3 matrix

$$a_1 = 2^{-1/2} \begin{pmatrix} 2^{1/2} S_z & S_- & 0 \\ S_+ & 0 & S_- \\ 0 & S_+ & -2^{1/2} S_z \end{pmatrix}.$$

Polynomials in the matrix a_l may then be defined recursively according to (assuming summation over repeated indices)

$$(a_l^m)^+_{ij} = (a_l)_{ik} (a_l^m)_{kj}.$$

Acting on the irrep π_s of SU(2), the matrix a_l may be expressed in the invariant form⁴³

$$a_l = \frac{1}{2} [\pi_l \otimes \pi_s(S^2) - \pi_l(S^2) \otimes 1 - 1 \otimes \pi_s(S^2)],$$

from which it follows that a_l has eigenvalues

$$\alpha_{l,m} = \frac{1}{2} [(m+s)(m+s+1) - s(s+1) - l(l+1)] \\ = \frac{1}{2} [2ms - (l-m)(l+m+1)]. \quad (51)$$

Thus, acting on the irrep π_s , the matrix a_l satisfies the polynomial identity

$$\prod_{m=-l}^l (a_l - \alpha_{l,m}) = 0.$$

The projection operators

$$P[l, m] = \prod_{k \neq m} \left(\frac{a_l - \alpha_{l,k}}{\alpha_{l,m} - \alpha_{l,k}} \right) \quad (52)$$

then project onto the $[2(s+m)+1]$ -dimensional irreducible

ble SU(2) submodules of the corresponding tensor product space.

In the following, we find it convenient to regard the roots $\alpha_{l,m}$ in a representation-independent way as operators belonging to a quadratic extension of the universal enveloping algebra of SU(2), whose eigenvalues, on the $(2s+1)$ -dimensional irrep π_s , are given by Eq. (51). It follows, from the arguments given in Refs. 42, 43, and 54, that if $T^{(l)}$ ($-l \leq i \leq l$) is an SU(2) tensor operator of rank l , then $T^{(l)}$ may be resolved into shift components

$$T^{(l)}[m]_i = T_j^{(l)} P[l, m]_{ji},$$

which increase the total spin quantum number S by m units ($-l \leq m \leq l$).

Utilizing the tensor projectors $P[l, m]$, Eq. (52), we thus arrive at the following spin transition density matrices (notation as above):

$$\begin{aligned} \hat{V}_i^{(\pm)}(r_1, r_2; r'_1, r'_2)_\alpha &= \hat{V}_i(r_1, r_2; r'_1, r'_2)_\beta P[1, \pm 1]_{\beta\alpha}, \\ & i = 1, 2; \quad -1 \leq \alpha \leq 1 \\ \hat{Q}^{(\pm)}(r_1, r_2; r'_1, r'_2)_\alpha^{(1)} &= \hat{Q}(r_1, r_2; r'_1, r'_2)_\beta^{(1)} P[1, \pm 1]_{\beta\alpha}, \\ & -1 \leq \alpha \leq 1 \\ \hat{Q}^{(\epsilon)}(r_1, r_2; r'_1, r'_2)_m^{(2)} &= \hat{Q}(r_1, r_2; r'_1, r'_2)_m^{(2)} P[2, \epsilon]_{m'm}, \\ & -2 \leq m \leq 2 \end{aligned} \quad (53)$$

where $\epsilon = \pm 1, \pm 2$. We note that the vector densities can only increase or decrease the total spin S by one unit, while the rank-two tensor densities may also increase or decrease S by two units.

We have thus demonstrated that the full two-electron density matrix is completely determined by the six scalar densities, Eqs. (38), (42), (45), and (49), together with the ten spin transition density operators, Eq. (53). For wave functions with well-defined total spin S , these latter transition densities do not contribute and the density matrix is fully determined by the scalar densities, as noted earlier. Finally, it is clear that the spin transition density operators may be conveniently expressed using the off-diagonal operator equivalent method, which has been extensively investigated⁵⁵⁻⁵⁹ in the hyperbolic operator formalism of Schwinger⁶⁰

V. TWO-BODY DENSITY MATRIX: SPIN-INDEPENDENT CASE

Here we consider the explicit determination of the scalar density operators, Eqs. (38), (42), (45), and (49), which determine the full two-body density matrix for wave functions with well-defined total spin S . We start by expressing the SU(2) vector operator components v_α , Eq. (44), in terms of the U(2) generators E_ν^μ , Eq. (3), as follows:

$$v_\alpha = E_\nu^\mu \langle \frac{1}{2} \mu; \frac{1}{2} (-\nu) | 1\alpha \rangle (-1)^{1/2 + \nu},$$

which may be inverted to give

$$\tilde{E}_\nu^\mu = v_\alpha \langle 1\alpha | \frac{1}{2} \mu; \frac{1}{2} (-\nu) \rangle (-1)^{1/2 + \nu}, \quad (54)$$

where \tilde{E}_ν^μ denote the SU(2) generators, Eq. (21'),

$$\tilde{E}_\nu^\mu = E_\nu^\mu - \frac{\hat{N}}{2} \delta_\nu^\mu. \quad (55)$$

We next recall Eq. (25'), expressing the zero-shift com-

ponent of the one-body density vector $\hat{\rho}_1$, Eq. (12'), in terms of the spin-density operator $\hat{\rho}_1^s$, Eq. (24), namely

$$\hat{\rho}_1^{(0)}(r; r')_\alpha = \hat{\rho}_1^s(r; r') v_\alpha, \quad (56)$$

from which we obtain

$$\hat{\rho}_1^s(r; r') = [2S(S+1)]^{-1} v_\alpha^\dagger \hat{\rho}_1^{(0)}(r; r')_\alpha, \quad (57a)$$

or, equivalently

$$\hat{\rho}_1^s(r; r') = [2S(S+1)]^{-1} \tilde{E}_\nu^\mu \hat{\rho}_1^{(0)}(r; r')_\mu. \quad (57b)$$

Note that we can replace here $\hat{\rho}_1^{(0)}$ by $\hat{\rho}_1$ since from U(2) invariance we have that

$$\tilde{E}_\nu^\mu \hat{\rho}_1^{(\pm)}(r; r')_\mu = 0.$$

These equations enable us to immediately determine the scalar densities of Eq. (45). In view of Eqs. (37) and (12'), we may rewrite the vector density $\hat{V}_1(r_1, r_2; r'_1, r'_2)$, Eq. (39a), as

$$\begin{aligned} \hat{V}_1(r_1, r_2; r'_1, r'_2)_\alpha &= \hat{\rho}_1(r_1; r'_1)_\alpha \hat{\rho}_1^c(r_2; r'_2) \\ & - \delta(r_2; r'_1) \hat{\rho}_1(r_1; r'_2)_\alpha, \end{aligned}$$

whose zero-shift component, in view of Eq. (56), is given by

$$\begin{aligned} \hat{V}_1^{(0)}(r_1, r_2; r'_1, r'_2)_\alpha &= [\hat{\rho}_1^s(r_1; r'_1) \hat{\rho}_1^c(r_2; r'_2) \\ & - \delta(r_2; r'_1) \hat{\rho}_1^s(r_1; r'_2)] v_\alpha. \end{aligned}$$

By comparison with Eq. (43), we thus obtain for the scalar density \hat{v}_1 , Eq. (45), the expression

$$\begin{aligned} \hat{v}_1(r_1, r_2; r'_1, r'_2) &= \hat{\rho}_1^s(r_1; r'_1) \hat{\rho}_1^c(r_2; r'_2) - \delta(r_2; r'_1) \hat{\rho}_1^s(r_1; r'_2) \\ &= \frac{-1}{2S(S+1)} \sum_{i,j,k,l} \phi_i^*(r_1) \phi_k^*(r_2) \phi_j(r'_1) \phi_l(r'_2) \\ & \quad \times (\Delta_j^i E_l^k - \delta_j^k \Delta_l^i). \end{aligned} \quad (58a)$$

Similarly for the scalar density \hat{v}_2 , we have

$$\begin{aligned} \hat{v}_2(r_1, r_2; r'_1, r'_2) &= \hat{\rho}_1^c(r_1; r'_1) \hat{\rho}_1^s(r_2; r'_2) - \delta(r_2; r'_1) \hat{\rho}_1^s(r_1; r'_2) \\ &= \frac{-1}{2S(S+1)} \sum_{i,j,k,l} \phi_i^*(r_1) \phi_k^*(r_2) \phi_j(r'_1) \phi_l(r'_2) \\ & \quad \times (E_j^i \Delta_l^k - \delta_j^k \Delta_l^i). \end{aligned} \quad (58b)$$

As to remaining scalar densities of Eqs. (42) and (49) a bit more work is required. We first note that the U(2n) operators

$$E_{(j\nu)(l\tau)}^{(i\mu)(k\sigma)} = E_{j\nu}^{i\mu} E_{l\tau}^{k\sigma} - \delta_j^k \delta_\nu^\sigma E_{l\tau}^{i\mu}$$

of Eq. (30) are symmetric under interchange of the two columns of indices. It follows that on the antisymmetric tensor irrep of U(2n), pertinent to the many-electron problem, these operators must satisfy the relations⁵¹

$$E_{(j\nu)(l\tau)}^{(i\mu)(k\sigma)} + E_{(j\nu)(l\tau)}^{(k\sigma)(i\mu)} = 0. \quad (59)$$

For the orbital U(n) generators, such relations have been already discussed by Paldus and Jeziorski.⁵¹ In particular, setting $\sigma = \tau$ in Eq. (59) and summing, we obtain the following useful relations:

$$E_{(j\nu)(l\tau)}^{(k\tau)(i\mu)} = E_{(l\tau)(j\nu)}^{(i\mu)(k\tau)} = -E_{(j\nu)(l\tau)}^{(i\mu)(k\tau)} = \delta_j^k E_{l\tau}^{i\mu} - E_{j\nu}^{i\mu} E_l^k. \quad (60)$$

It is now interesting to note that if we set $k = l$ in the above Eq. (60) and sum, we obtain the result

$$E(E - 2n)_{\nu}^{\mu} = E_{(k\tau)(j\nu)}^{(i\mu)(k\tau)} = (1 - N)E_{\nu}^{\mu},$$

which may be rearranged to give

$$E(E - 2n - 1 + N) = 0,$$

which is just the $U(2n)$ reduced identity, Eq. (8). Thus, the relations of Eq. (59) imply the $U(2n)$ identities, Eq. (8), but also contain extra information which we utilize below. The reduced identities (cf. the Appendix) satisfied by the unitary group generators on a given k -column irrep may similarly be derived and will be investigated elsewhere.

Our interest in the relation (60) stems from the fact that it implies the following result for the entries of the density matrix (37):

$$\begin{aligned} \hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\nu\tau}^{\mu} \\ = \sum_{i,j,k,l} \phi_i^*(r_1) \phi_k^*(r_2) \phi_j(r'_1) \phi_l(r'_2) E_{(j\nu)(l\tau)}^{(i\mu)(k\mu)} \\ = \delta(r_1; r'_1) \hat{\rho}_1(r_2; r'_2)_{\nu}^{\mu} - \hat{\rho}_1(r_2; r'_1)_{\nu}^{\mu} \hat{\rho}_1^c(r_1; r'_2), \end{aligned} \quad (61a)$$

$$\begin{aligned} \hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\nu\tau}^{\mu} \\ = \sum_{i,j,k,l} \phi_i^*(r_1) \phi_k^*(r_2) \phi_j(r'_1) \phi_l(r'_2) E_{(j\tau)(l\nu)}^{(i\mu)(k\tau)} \\ = \delta(r_2; r'_2) \hat{\rho}_1(r_1; r'_1)_{\nu}^{\mu} - \hat{\rho}_1(r_1; r'_2)_{\nu}^{\mu} \hat{\rho}_1^c(r_2; r'_1). \end{aligned} \quad (61b)$$

In particular, setting $\mu = \nu$ into the above and summing we obtain

$$\begin{aligned} \hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\nu\tau}^{\nu\tau} \\ = \delta(r_1; r'_1) \hat{\rho}_1^c(r_2; r'_2) - \hat{\rho}_1^c(r_2; r'_1) \hat{\rho}_1^c(r_1; r'_2) \\ = -\hat{\rho}_2^c(r_2, r_1; r'_1, r'_2) = -\hat{\rho}_2^c(r_1, r_2; r'_2, r'_1), \end{aligned}$$

from which we can immediately deduce for the scalar density of Eq. (42)

$$\begin{aligned} \hat{Q}(r_1, r_2; r'_1, r'_2)_0^{(0)} \\ = 3^{-1/2} [\hat{\rho}_2^c(r_2, r_1; r'_1, r'_2) + \frac{1}{2} \hat{\rho}_2^c(r_1, r_2; r'_1, r'_2)]. \end{aligned} \quad (62)$$

As to the tensor densities of Eq. (40), we note that the components of $\hat{Q}^{(1)}$ are easily seen to be given by

$$\begin{aligned} \hat{Q}(r_1, r_2; r'_1, r'_2)_{\alpha}^{(1)} \\ = \frac{1}{2} [\hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\nu\tau}^{\mu\tau} - \hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\nu\tau}^{\mu\tau}] \\ \times \langle \frac{1}{2} \mu; \frac{1}{2}(-\nu) | 1\alpha \rangle (-1)^{1/2+\nu}, \end{aligned}$$

which, in view of Eqs. (12') and (61), may be expressed as

$$\begin{aligned} \hat{Q}(r_1, r_2; r'_1, r'_2)_{\alpha}^{(1)} \\ = -\frac{1}{2} [\delta(r_1; r'_1) \hat{\rho}_1(r_2; r'_2)_{\alpha} - \delta(r_2; r'_2) \hat{\rho}_1(r_1; r'_1)_{\alpha} \\ + \hat{\rho}_1(r_1; r'_2)_{\alpha} \hat{\rho}_1^c(r_2; r'_1) - \hat{\rho}_1(r_2; r'_1)_{\alpha} \hat{\rho}_1^c(r_1; r'_2)]. \end{aligned}$$

It then follows from Eqs. (48) and (56) that the corresponding density operator $\hat{q}^{(1)}$, Eq. (49), is given by

$$\begin{aligned} \hat{q}^{(1)}(r_1, r_2; r'_1, r'_2) \\ = \frac{1}{2} [\delta(r_2; r'_2) \hat{\rho}_1^c(r_1; r'_1) - \delta(r_1; r'_1) \hat{\rho}_1^c(r_2; r'_2) \\ + \hat{\rho}_1^c(r_2; r'_1) \hat{\rho}_1^c(r_1; r'_2) - \hat{\rho}_1^c(r_1; r'_2) \hat{\rho}_1^c(r_2; r'_1)], \end{aligned} \quad (63)$$

where we have used Eq. (47b).

It finally remains to evaluate the scalar density $\hat{q}^{(2)}$, Eq. (49). We first note that in view of Eq. (37), the operators of Eq. (41) may be expressed as

$$\begin{aligned} \hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\alpha\beta} = \hat{\rho}_1(r_1; r'_1)_{\alpha} \hat{\rho}_1(r_2; r'_2)_{\beta} - T_{\alpha\beta} \\ (-1 \leq \alpha, \beta \leq 1), \end{aligned} \quad (64)$$

where

$$\begin{aligned} T_{\alpha\beta} = \delta_{\nu}^{\sigma} \hat{\rho}_1(r_1; r'_2)_{\tau}^{\mu} \delta(r_2; r'_1) \langle \frac{1}{2} \mu; \frac{1}{2}(-\nu) | 1\alpha \rangle (-1)^{1/2+\nu} \\ \times \langle \frac{1}{2} \sigma; \frac{1}{2}(-\tau) | 1\beta \rangle (-1)^{1/2+\tau}. \end{aligned}$$

We note the following property of this latter tensor (summation over repeated indices is assumed as usual):

$$\begin{aligned} T_{\alpha\beta} v_{\alpha}^{\dagger} v_{\beta}^{\dagger} \\ = \delta_{\nu}^{\sigma} \hat{\rho}_1(r_1; r'_2)_{\tau}^{\mu} \delta(r_2; r'_1) \langle \frac{1}{2} \mu; \frac{1}{2}(-\nu) | 1\alpha \rangle \\ \times (-1)^{1/2+\nu} v_{\alpha}^{\dagger} \langle \frac{1}{2} \sigma; \frac{1}{2}(-\tau) | 1\beta \rangle (-1)^{1/2+\tau} v_{\beta}^{\dagger} \\ = \delta_{\nu}^{\sigma} \hat{\rho}_1(r_1; r'_2)_{\tau}^{\mu} \tilde{E}_{\mu}^{\nu} \tilde{E}_{\sigma}^{\tau} \delta(r_2; r'_1), \end{aligned}$$

which may be rearranged to give

$$\begin{aligned} T_{\alpha\beta} v_{\alpha}^{\dagger} v_{\beta}^{\dagger} = \delta(r_2; r'_1) \hat{\rho}_1(r_1; r'_2)_{\tau}^{\mu} [S(S+1) + \tilde{E}]_{\mu}^{\tau} \\ = S(S+1) \delta(r_2; r'_1) [\hat{\rho}_1^c(r_1; r'_2) + 2\hat{\rho}_1^c(r_1; r'_2)], \end{aligned} \quad (65)$$

where we have employed the $SU(2)$ identity³⁹

$$(\tilde{E} + S)(\tilde{E} - S - 1) = 0,$$

together with Eq. (57b) and the Hermitian conjugate of Eq. (54).

We may therefore write (summation over m is assumed)

$$\begin{aligned} \sum_{l=0}^2 T_m^{\dagger(l)} \hat{Q}(r_1, r_2; r'_1, r'_2)_m^{(l)} \\ = \hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\alpha\beta} \sum_{l=0}^2 \langle 1\alpha; 1\beta | lm \rangle \\ \times \langle lm | 1\alpha'; 1\beta' \rangle v_{\alpha}^{\dagger} v_{\beta}^{\dagger} \\ = \hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{\alpha\beta} v_{\alpha}^{\dagger} v_{\beta}^{\dagger} \\ = \hat{\rho}_1(r_1; r'_1)_{\alpha} v_{\alpha}^{\dagger} \hat{\rho}_1(r_2; r'_2)_{\beta} v_{\beta}^{\dagger} - T_{\alpha\beta} v_{\alpha}^{\dagger} v_{\beta}^{\dagger}, \end{aligned}$$

where we have employed Eq. (40) together with Eq. (64). Application of Eqs. (57) and (65) then yields

$$\begin{aligned} \sum_{l=0}^2 T_m^{\dagger(l)} \hat{Q}(r_1, r_2; r'_1, r'_2)_m^{(l)} \\ = [2S(S+1)]^2 \hat{\rho}_1^c(r_1; r'_1) \hat{\rho}_1^c(r_2; r'_2) \\ - S(S+1) \delta(r_2; r'_1) [\hat{\rho}_1^c(r_1; r'_2) + 2\hat{\rho}_1^c(r_1; r'_2)]. \end{aligned} \quad (66)$$

On the other hand, for $l = 0$ we have from Eq. (47a) that

$$\begin{aligned} T_0^{\dagger(0)} \hat{Q}(r_1, r_2; r'_1, r'_2)_0^{(0)} \\ = -2 \cdot 3^{-1/2} S(S+1) \hat{Q}(r_1, r_2; r'_1, r'_2)_0^{(0)}, \end{aligned}$$

with $\hat{Q}_0^{(0)}$ as in Eq. (62), and for $l = 1$ we have from Eqs. (49) and (63)

$$T_m^{\dagger(1)} \hat{Q}(r_1, r_2; r'_1, r'_2)_m^{(1)} = 2S(S+1) \hat{q}^{(1)}(r_1, r_2; r'_1, r'_2).$$

We thereby arrive at

$$T_m^{(2)} \hat{Q}(r_1, r_2; r'_1, r'_2)_m^{(2)} = [2S(S+1)]^2 \hat{\rho}_1^s(r_1; r'_1) \hat{\rho}_1^s(r_2; r'_2) - S(S+1) \delta(r_2; r'_1) [\hat{\rho}_1^s(r_1; r'_2) + 2\hat{\rho}_1^s(r_1; r'_2)] \\ + 2 \cdot 3^{-1/2} S(S+1) \hat{Q}(r_1, r_2; r'_1, r'_2)_0^{(0)} - 2S(S+1) \hat{q}^{(1)}(r_1, r_2; r'_1, r'_2),$$

from which we obtain, in view of Eqs. (49) and (50), the scalar density $\hat{q}^{(2)}$

$$(2S-1)(2S+3) \hat{q}^{(2)}(r_1, r_2; r'_1, r'_2) \\ = 6S(S+1) \hat{\rho}_1^s(r_1; r'_1) \hat{\rho}_1^s(r_2; r'_2) - \frac{3}{2} \delta(r_2; r'_1) [\hat{\rho}_1^c(r_1, r'_2) + 2\hat{\rho}_1^s(r_1; r'_2)] + \hat{\rho}_2^c(r_2, r_1; r'_1, r'_2) \\ + \frac{1}{2} \hat{\rho}_2^c(r_1, r_2; r'_1, r'_2) - \frac{3}{2} [\hat{\rho}_1^s(r_1; r'_1) \delta(r_2; r'_2) - \hat{\rho}_1^s(r_2; r'_2) \delta(r_1; r'_1) \\ + \hat{\rho}_1^s(r_2; r'_1) \hat{\rho}_1^s(r_1, r'_2) - \hat{\rho}_1^s(r_1; r'_2) \hat{\rho}_1^s(r_2; r'_1)]. \quad (67)$$

The six scalar densities, which completely determine the full two-body density matrix for spin-independent systems, are thus given explicitly by Eqs. (38), (58), (62), (63), and (67) in terms of the one-body charge- and spin-density operators. In particular, we note that these latter operators determine the full two-body density matrix, and in this sense we see that for spin-independent systems, the one-body density matrix determines also the two (and presumably higher) order density matrices. We draw particular attention to the density operator $\hat{Q}_0^{(2)}$, Eq. (40), whose zero-shift component, Eq. (48), may be written in the form

$$\hat{Q}_0^{(0)}(r_1, r_2; r'_1, r'_2)_0^{(2)} \\ = (\frac{3}{2})^{1/2} [3S_z^2 - S(S+1)] \hat{q}^{(2)}(r_1, r_2; r'_1, r'_2). \quad (68)$$

As noted previously by McWeeny,^{3,4} this density operator determines the anisotropy of the spin distribution and plays an important role⁴ in connection with spin-spin coupling in the ESR spectra of transition-metal ions. Another operator of interest is the two-electron spin-density operator

$$\hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{1/2, 1/2} - \hat{\rho}_2(r_1, r_2; r'_1, r'_2)_{-1/2, -1/2} \\ = -2^{-1/2} [\hat{V}_1(r_1, r_2; r'_1, r'_2)_0 + \hat{V}_2(r_1, r_2; r'_1, r'_2)_0], \quad (69)$$

whose zero-shift component is given by $S_z \hat{\rho}_2^s$, where $\hat{\rho}_2^s$ is the normalized two-electron spin density operator

$$\hat{\rho}_2^s(r_1, r_2; r'_1, r'_2) = \hat{v}_1(r_1, r_2; r'_1, r'_2) + \hat{v}_2(r_1, r_2; r'_1, r'_2) \\ = \frac{-1}{2S(S+1)} \sum_{i,j,k,l} \phi_i^*(r_1) \phi_k^*(r_2) \phi_j(r'_1) \\ \times \phi_l(r'_2) [\Delta_i^j E_l^k + E_j^i \Delta_l^k - 2\delta_j^k \Delta_l^i]. \quad (70)$$

Other two-electron operators of physical interest are discussed in Refs. 2-7.

VI. CONCLUSIONS

A fully spin-adapted approach to one- and two-electron density matrices has been presented in the framework of the UGA. In particular, the one-electron density matrix, arising from a wave function with well-defined total spin S , was shown to be completely determined by the charge and normalized spin-density operators for which we obtained an explicit expression in terms of the orbital $U(n)$ generators. We draw particular attention to Eq. (24), which determines the normalized molecular spin density in terms of the entries Δ_j^i of the $U(n)$ matrix Δ defined in Eq. (22).

Extensions to two-body density matrices were also ob-

tained, and it was shown that, in the case of spin-independent systems, the two-electron density matrix is completely determined by the six scalar densities of Eqs. (38), (58), (62), (63), and (67). These scalar densities were derived in terms of the one-electron charge- and spin-density operators, which in turn are expressible in terms of the orbital $U(n)$ generators in accordance with Eqs. (11) and (24). It follows that the $U(n)$ matrix Δ , Eq. (22), plays a fundamental role in the determination of the spin density of a molecule and hence also of two- (and higher-order) electron densities. The matrix elements of the operators Δ_j^i , in the SO basis (14), have been explicitly evaluated in Ref. 40 as a simple segment level product. This then provides a convenient method for the evaluation of one- and two-electron density operators in the UGA framework.

In the case of spin-dependent systems, it is also necessary to consider the one- and two-electron total-spin transition density operators. These transition density operators are given explicitly in terms of the $U(2n)$ generators by Eqs. (18) and (53). Since the MEs of the $U(2n)$ generators have been derived in Refs. 39-41, as a simple segment level product, this enables the complete determination of the one- and two-electron spin transition densities, as required for spin-dependent systems, within the UGA framework.

Let us finally mention that the above introduced charge-, spin-, and transition-density operators possess a great deal of additional interesting structural properties and form a spin-density algebra when the convolution product is introduced. Moreover, it can be shown that the projection operators, Eq. (27a), give rise to a new set of idempotent and orthogonal density operators, which provide a resolution of the identity and represent a particularly suitable basis for this algebra. We have investigated this algebra for one-electron density operators and will present these results elsewhere. We also intend to extend these investigations to two- (and higher) electron spin-density operators, in order to achieve a fully spin-adapted approach to a k -electron density matrix in the UGA framework. In this regard we note that the graphical methods of spin algebras⁶¹ may provide a convenient tool for treating this problem. In particular, it is of interest to determine the k -electron density matrix, for wave functions with well-defined total spin S , in terms of the one-body charge- and spin-density operators, as required when dealing with spin-independent systems. As noted earlier, this problem has already been solved for the one- and two-electron case in Secs. III and V. Finally, it would be also of interest to investigate the role of the off-diagonal operator

equivalent method⁵⁵⁻⁵⁸ for the determination of total spin transition densities.

APPENDIX: REDUCED IDENTITIES

We recall from Refs. 42 and 44, that acting on the irrep π_λ of $U(n)$ with highest weight

$$\lambda = (\lambda_1, \dots, \lambda_n),$$

the $U(n)$ matrix $E = [E_j^i]$ may be written in the invariant form

$$E = -\frac{1}{2}[\pi \otimes \pi_\lambda(I_2) - \pi(I_2) \otimes 1 - 1 \otimes \pi_\lambda(I_2)],$$

where π denotes the contragredient vector representation⁴⁴ of $U(n)$ [with highest weight $(0, \dots, -1)$] and I_2 denotes the second-order Casimir invariant

$$I_2 = E_j^i E_i^j,$$

whose eigenvalue on the irrep π_λ is given by^{42,44}

$$\langle I_2 \rangle_\lambda = \sum_{r=1}^n \lambda_r (\lambda_r + n + 1 - 2r). \quad (\text{A1})$$

We have the Clebsch–Gordan decomposition⁴⁴

$$\pi \otimes \pi_\lambda = \bigoplus_{r=1}^n \pi_{\lambda - \epsilon_r}, \quad (\text{A2})$$

where ϵ_r denotes the elementary weight

$$\epsilon_r = (0, \dots, 0, 1, 0, \dots, 0),$$

with 1 in the r th position, and the sum in Eq. (A2) is over all r such that $\lambda - \epsilon_r$ is *dominant*: We recall^{42,44} that a weight μ is called dominant if the components μ_i of μ satisfy

$$\mu_1 \geq \mu_2 \geq \dots \geq \mu_n, \quad \mu_i - \mu_j \in \mathbb{Z}. \quad (\text{A3})$$

It follows that on each irrep $\pi_{\lambda - \epsilon_r}$, occurring in the decomposition (A2), E takes the constant value

$$\lambda_r + n - r = -\frac{1}{2}[\langle I_2 \rangle_{\lambda - \epsilon_r} - \langle I_2 \rangle_\lambda - \langle I_2 \rangle],$$

with $\langle I_2 \rangle_\lambda$ as in Eq. (A1) and $\langle I_2 \rangle = \langle I_2 \rangle_{-\epsilon_n}$. Therefore, on the irrep π_λ , the $U(n)$ matrix E satisfies the minimum polynomial identity

$$\prod_{r=1}^n (E - \lambda_r - n + r) = 0,$$

where the product is over all r such that $\lambda - \epsilon_r$ is dominant, i.e., satisfies the conditions of Eq. (A3). These polynomial identities have been previously discussed in Refs. 27, 42, and 44.

The minimum polynomial identities, corresponding to some highest weights $\lambda = (\lambda_1, \dots, \lambda_n)$ of interest, are listed below (see also Ref. 42):

$$(\dot{1}_N, \dot{0}): E(E + N - n - 1) = 0,$$

$$(\dot{2}_a, \dot{0}): E(E - n - 2 + a) = 0,$$

$$(\dot{2}_a, \dot{1}_b, \dot{0}): E(E - n - 2 + a)(E - 1 - c) = 0,$$

$$c = n - a - b.$$

We remark that this latter identity corresponds to the characteristic identity of Eq. (26), while the first identity corresponds to the identity (8), satisfied by the $U(2n)$ matrix $E = [E_{\mu\nu}^{\mu\nu}]$ on the antisymmetric N th-rank tensor representation. Finally, the second identity given above corresponds

to the zero-spin case $S = 0$, and yields the identity of Eq. (23). It is particularly interesting, in this latter case, that the matrix Δ of Eq. (22), which determines the single-electron spin-density operator, is simply the left-hand side of the above reduced identity. This suggests generalizations of such density operators in the framework of reduced identities.

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