Unitary group approach to reduced density matrices

II. One-electron charge and spin density algebra

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Summary. The structure of the algebra generated by one-electron charge and spin density operators with an appropriately defined convolution product is investigated in the context of the unitary group approach (UGA) to the many-electron correlation problem. The new idempotent density operators, defined via the unitary group $U(n)$ projection operators, are introduced and employed to investigate the behavior of charge and spin density operators under the convolution product.

Key words: Reduced density matrices – Spin adaptation – Unitary group approach – Charge and spin density operator algebra

1. Introduction

It is certainly most fitting and appropriate to dedicate this paper to Professor Per-Olov Löwdin at the occasion of the forthcoming anniversary of his famous 1955 Physical Review Papers on Quantum Theory of Many-Particle systems [1]. His development and lucid pedagogical exposition of the density matrix formalism, originating from the pioneering work of Dirac [2] who introduced this concept in the framework of the Hartree–Fock approximation, and particularly the introduction of various new concepts, such as natural orbitals, correlation effects or the projection operator technique, had a far reaching influence on generations of quantum chemists to this very day.

Although the original hopes [3] to eliminate wave functions from quantum mechanics and replace them with reduced density matrices did not materialize, since the N-representability problem and the conditions it imposes on the second order density matrices of N-fermion systems proved to be too formidable to be – at least so far – of practical utility in computing molecular electronic structure properties [4], the conceptual and interpretative significance of the density matrix formalism as developed by Löwdin [1] and McWeeny [5–7]

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remains as important as ever, not to mention its utility in interpreting various experimental results as several books and review articles testify [4, 8–10] (see also a brief outline in our preceding communication [11]).

For this very reason we have addressed [11] the problem of efficient computation of molecular charge and spin density matrices using the configuration interaction (CI)-type wave function as determined by the unitary group approach (UGA) [12, 13]. We recall that UGA originated from Moshinsky's work [14] on the nuclear shell model and enabled an efficient spin-adaptation and CI matrix element evaluation [15, 16] for spin-independent molecular electronic Hamiltonians (for recent reviews see [17–19]). This versatile formalism afforded numerous computational implementations, particularly in connection with direct CI [20] (see [17–19] for references). We have thus developed [11] a spin-adapted approach to reduced density matrices based on the UGA formalism with particular emphasis on one- and two-electron charge and spin densities. We wish to mention here that the desirability of obtaining spin- and symmetry-adapted reduced density matrices, and corresponding natural orbitals and geminals, was recognized and addressed soon after the above mentioned seminal papers by Löwdin and McWeeny appeared. The initial work by Kutzelnigg [21] was soon followed by an exhaustive treatment by McWeeny and Kutzelnigg [22] within the standard wave function formalism. Approximately a decade later this problem was addressed by Harriman [23] in his series of papers on the geometry of density matrices [24]. Although this work again employs a standard first quantization formalism in constructing spin-tensorial components of one- and two-electron density matrices, it may be regarded as a "precursor" of the unitary group based formulation even though no representation theory or even Lie algebraic formulation was employed (cf., however, the Hermitian basis of Eq. (11) of [24a] with the corresponding skew-Hermitian basis, Eq. (2.25) of [25]).

The UGA based formalism for reduced density matrices [11] represents, therefore, not only a necessary framework for actual computation of one- and two-electron density matrices or their various reduced components when UGA CI methodology is exploited, but also a very concise and elegant framework for spin-adaptation of density matrices in general. In fact this approach naturally leads to an interesting charge and spin density algebra when an appropriate convolution product is introduced. In this paper we explore the structure of this algebra for the one-electron charge and spin density operators and derive basic relationships and sum rules. First, however, we shall briefly introduce necessary notation and recall basic results obtained in [11].

2. One- and two-body density matrices in the unitary group approach formalism

We consider the UGA formalism based on a set of $2n$ orthonormal spin-orbitals $\psi_{i\mu}(x)$, $1 \leqslant i \leqslant n$, $\mu = \pm \frac{1}{2}$, where $x = (r, \xi)$ designates the combined spatial (r) and spin (ξ) coordinates, and assume their factorization into molecular orbital $\phi_i(r)$ and spin function $\chi_\mu(\xi) = \delta_{\mu\xi}$ parts:

$$\psi_{i\mu}(x) = \phi_i(r)\chi_\mu(\xi). \tag{1}$$

Introducing the corresponding second quantization operators $X_{i\mu}^\dagger$ and $X_{i\mu}$ that satisfy the well-known anticommutation relations, we can represent the spin-orbital Lie group $U(2n)$ generators $E_{j\nu}^{i\mu}$ as:

$$E_{j\nu}^{i\mu} = X_{i\mu}^\dagger X_{j\nu}. \tag{2}$$

Taking the partial traces over the spin and orbital subspaces, we obtain the spin-averaged operators:

$$E_j^i = \sum_{\mu=-\frac{1}{2}}^{\frac{1}{2}} E_{j\mu}^{i\mu}, \tag{3}$$

constituting the generators of the orbital subgroup $U(n)$ of $U(2n)$, and the spin-group $U(2)$ generators:

$$E_\nu^\mu = \sum_{i=1}^{n} E_{i\nu}^{i\mu}. \tag{4}$$

Both sets of orbital and spin generators then constitute the generators of the spin-orbit subgroup $U(n) \times U(2)$ (outer direct product) of $U(2n)$. Thus, the spin generators are labeled by the lower case Greek indices while the Latin indices imply the orbital group generators. Similarly, the orbital indices are integral while the spin labels take on half-integral values $\pm\frac{1}{2}$. To simplify our notation we shall indicate the spin labels by the corresponding signs only, so that for example we set:

$$E_{j,-\frac{1}{2}}^{i,\frac{1}{2}} \equiv E_{j-}^{i+}, \qquad E_{\frac{1}{2}}^{\frac{1}{2}} \equiv E_+^+, \qquad \text{etc.} \tag{5}$$

Recalling thus that the number operator $\hat{N}$ and the components of the total-spin operator $\hat{S}$ may be expressed in terms of $U(2)$ generators, we can write:

$$\hat{N} = \sum_\mu E_\mu^\mu = E_+^+ + E_-^-,$$
$$\hat{S}_z = \tfrac{1}{2}(E_+^+ - E_-^-), \tag{6}$$
$$\hat{S}_+ = E_-^+ \quad \text{and} \quad \hat{S}_- = \hat{S}_+^\dagger = E_+^-,$$

where $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$. The spin operators $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$ or $\hat{S}_+$, $\hat{S}_-$, $\hat{S}_z$ constitute the generators of the subgroup $SU(2)$.

Using this notation we can express the general one-body reduced density operator as:

$$\hat{\varrho}_1(x, x') = \sum_{\mu,\nu=-\frac{1}{2}}^{\frac{1}{2}} \sum_{i,j=1}^{n} \psi_{i\mu}^*(x)\psi_{j\nu}(x')E_{j\nu}^{i\mu} \tag{7}$$

or, alternatively, as a 2×2 matrix with entries:

$$\hat{\varrho}_1(r; r')_\nu^\mu = \hat{\varrho}_1((r, \mu); (r', \nu)) = \sum_{i,j=1}^{n} \phi_i^*(r)\phi_j(r')E_{j\nu}^{i\mu}, \tag{8}$$

which we refer to as the *one-electron density matrix*. We emphaize, however, that the entries of this density matrix, Eq. (8), are operators. Thus, the standard density matrix $\varrho_1(r)$ associated with a given wave function Ψ is given by the corresponding 2×2 matrix of expectation values:

$$\varrho_1(r)_\nu^\mu = \langle \Psi | \hat{\varrho}_1(r; r)_\nu^\mu | \Psi \rangle. \tag{8'}$$

Taking the trace of the density matrix of Eq. (8) over the spin space, we obtain the familiar [8, 9] *charge-density operator*:

$$\hat{\varrho}_1^c(r; r') = \hat{\varrho}_1(r; r')_+^+ + \hat{\varrho}_1(r; r')_-^- = \sum_{i,j=1}^{n} \phi_i^*(r)\phi_j(r')E_j^i, \tag{9}$$

that is obviously spin-independent. The one-electron density matrix of Eq. (8) may then be rewritten as:

$$\hat{\varrho}_1(r;r')^\mu_\nu = \tfrac{1}{2}\hat{\varrho}^c_1(r;r')\delta^\mu_\nu + \boldsymbol{R} \cdot \boldsymbol{\sigma}^\nu_\mu, \tag{10}$$

where $\boldsymbol{\sigma} \equiv (\sigma_x, \sigma_y, \sigma_z)$ are the usual Pauli spin matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{11}$$

and

$$\boldsymbol{R}(r;r') = \sum_{j,k=1}^n \phi^*_j(r)\phi_k(r')\boldsymbol{\Gamma}^j_k, \tag{12}$$

with $\boldsymbol{\Gamma} \equiv (\Gamma_x, \Gamma_y, \Gamma_z)$ defined by:

$$\begin{aligned}
(\Gamma_x)^j_k &= \tfrac{1}{2}(E^{j+}_{k-} + E^{j-}_{k+}), \\
(\Gamma_y)^j_k &= -\tfrac{1}{2}i(E^{j+}_{k-} - E^{j-}_{k+}), \\
(\Gamma_z)^j_k &= \tfrac{1}{2}(E^{j+}_{k+} - E^{j-}_{k-}).
\end{aligned} \tag{13}$$

Equivalently, we can write the one-body density matrix of Eq. (8) in a convenient tensor form: transforming with appropriate $SU(2)$ coupling (or Clebsch–Gordan) coefficients, we obtain a scalar component:

$$\hat{\varrho}_1(r;r')^{(0)}_0 = \hat{\varrho}_1(r;r')^\mu_\nu \langle\tfrac{1}{2}\mu\tfrac{1}{2}(-\nu)|00\rangle(-1)^{\frac{1}{2}+\nu}$$

$$= \sqrt{2}\hat{\varrho}^c_1(r;r'), \tag{14a}$$

given by the charge density operator, and a vector density with components:

$$\hat{\varrho}_1(r;r')^{(1)}_\alpha \equiv \hat{\varrho}_1(r;r')_\alpha = \hat{\varrho}_1(r;r')^\mu_\nu \langle\tfrac{1}{2}\mu\tfrac{1}{2}(-\nu)|1\alpha\rangle(-1)^{\frac{1}{2}+\nu},$$

$$(-1 < \alpha \leqslant 1), \quad (14b)$$

where in each case the summation over μ and ν is implied. Explicitly we easily find that

$$\begin{aligned}
\hat{\varrho}_1(r;r')_1 &= \hat{\varrho}_1(r;r')^+_-, \\
\hat{\varrho}_1(r;r')_0 &= -\sqrt{2}R_z(r;r'), \\
\hat{\varrho}_1(r;r')_{-1} &= -\hat{\varrho}_1(r;r')^-_+.
\end{aligned} \tag{14b'}$$

For the case of spin-dependent Hamiltonians, such as those arising when considering spin-orbit coupling or general relativistic effects, the spin-orbital $U(n) \times U(2)$ basis still represents a useful starting basis set as long as the spin-dependent interaction terms are relatively small. We must then represent the relevant operators in terms of $U(2n)$ generators $E^{i\mu}_{j\nu}$ and consider their matrix elements in the $U(n) \times U(2)$ basis [26]. Clearly, $U(2n)$ generators will mix different $U(n)$ irreps. It may be shown [26] that the $U(2n)$ generators $E^{i\mu}_{j\nu}$ may be resolved into spin-shift components:

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

where $E(+)$ $[E(-)]$ increases [decreases] the total spin of the spin-orbital states by one unit, while $E(0)$ leaves total spin unchanged, so that in fact:

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

while

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

This resolution of $U(2n)$ generators leads naturally to the corresponding partitioning of the density matrix of Eq. (8), namely:

$$\hat{\varrho}_1(r; r')_v^\mu = \hat{\varrho}_1^{(-)}(r; r')_v^\mu + \hat{\varrho}_1^{(0)}(r; r')_v^\mu + \hat{\varrho}_1^{(+)}(r; r')_v^\mu, \tag{17}$$

where

$$\hat{\varrho}_1^{(\varepsilon)}(r; r')_v^\mu = \sum_{i,j=1}^n \phi_i^*(r)\phi_j(r')E(\varepsilon)_{jv}^{i\mu}, \qquad \varepsilon = 0, \pm. \tag{17'}$$

In view of Eqs. (15) and (16) we have that:

$$\text{tr}[\hat{\varrho}_1^{(0)}(r; r')] = \text{tr}[\hat{\varrho}_1(r; r')] = \hat{\varrho}_1^c(r; r'), \tag{18a}$$

and

$$\text{tr}[\hat{\varrho}_1^{(\pm)}(r; r')] = 0. \tag{18b}$$

Relying on the decomposition (10) we can thus write:

$$\hat{\varrho}_1^{(0)}(r; r')_v^\mu = \tfrac{1}{2}\varrho_1^c(r; r')\delta_v^\mu + R^{(0)} \cdot \sigma_\mu^v, \tag{19a}$$

$$\hat{\varrho}_1^{(\pm)}(r; r')_v^\mu = R^{(\pm)} \cdot \sigma_\mu^v, \tag{19b}$$

where $R^{(\varepsilon)}$ is given by Eq. (13) with $E_{jv}^{i\mu}$ replaced by $E(\varepsilon)_{jv}^{i\mu}$.

The zero-shift component, Eq. (19a), is of a particular significance since it determines the full density matrix for wave functions with well-defined total spin S. It was shown [26] that the zero-shift components $E(0)_{jv}^{i\mu}$ of the $U(2n)$ generators $E_{jv}^{i\mu}$ may be expressed in terms of $U(n)$ and $U(2)$ generators and of a special second degree polynomial Δ in terms of $U(n)$ generators defined as follows:

$$\Delta = E(E + \tfrac{1}{2}\hat{N} - n - 2), \tag{20}$$

where $E = [E_j^i]$ designates the $n \times n$ matrix whose entries are $U(n)$ generators E_j^i. The powers of E are defined in the usual fashion [27, 28]:

$$(E^{m+1})_j^i = E_k^i(E^m)_j^k = (E^m)_k^i E_j^k; \qquad (E^0)_j^i = \delta_j^i, \tag{21}$$

where again summation over repeated indices is implied. With the help of this second degree polynomial, Eq. (20), we can thus express the zero-shift component $E(0)_{jv}^{i\mu}$ as follows:

$$E(0)_{jv}^{i\mu} = \tfrac{1}{2}E_j^i\delta_v^\mu - [2S(S + 1)]^{-1}\Delta_j^i\tilde{E}_v^\mu, \qquad (S \neq 0) \tag{22}$$

where $\tilde{E}_v^\mu$ designates the $SU(2)$ generator:

$$\tilde{E}_v^\mu = E_v^\mu - \tfrac{1}{2}\hat{N}\delta_v^\mu. \tag{23}$$

When $S = 0$, the second term on the right hand side of (22) does not contribute in agreement with the fact that $\Delta_j^i = 0$ $(1 \leqslant i, j \leqslant n)$ when $S = 0$ (see, for example, the Appendix of Ref. 26). Using this result for $E(0)_{jv}^{i\mu}$ we easily find the

zero-shift component of the vector R, Eq. (12), and thus we can express the zero-shift component, Eq. (19a), of the density matrix of Eq. (8) as follows:

$$\hat{\varrho}_1^{(0)}(r;r')_\nu^\mu = \tfrac{1}{2}\hat{\varrho}_1^c(r;r')\delta_\nu^\mu + \hat{\varrho}_1^s(r;r')S \cdot \sigma_\mu^\nu$$

$$= \tfrac{1}{2}\hat{\varrho}_1^c(r;r')\delta_\nu^\mu + \varrho_1^s(r;r')\tilde{E}_\nu^\mu, \tag{24}$$

since

$$S \cdot \sigma_\mu^\nu = \tilde{E}_\nu^\mu = E_\nu^\mu - \tfrac{1}{2}\hat{N}\delta_\nu^\mu. \tag{25}$$

Here $\hat{\varrho}_1^c$ designates the charge density operator of Eq. (9), while $\hat{\varrho}_1^s$ represents the normalized spin-density operator:

$$\hat{\varrho}_1^s(r;r') = -[2S(S+1)]^{-1}\sum_{i,j=1}^n \phi_i^*(r)\phi_j(r')\Delta_j^i; \qquad (S \neq 0). \tag{26}$$

Again, this operator vanishes when $S = 0$.

In the case of spin-dependent problems we also need non-zero components $\hat{\varrho}_1^{(\pm)}$, referred to as total spin transition density matrices [11]:

$$\hat{\varrho}_1^{(\pm)}(r;r')_\nu^\mu = R^{(\pm)} \cdot \sigma_\mu^\nu = \sum_{i,j=1}^n \phi_i^*(r)\phi_j(r')E(\pm)_{j\nu}^{i\mu}. \tag{27}$$

To construct these shift components we employed [11] Green's polynomial identity for $E = [E_{ij}]$ (see Appendix of Ref. [11] and Ref. [27]):

$$\prod_{i=1}^3 (E - \varepsilon_i) = 0, \tag{28}$$

where the roots ε_i on a $U(n)$ irreducible representation (irrep) with the highest weight $\langle 2^a 1^b 0^c \rangle \equiv [a\,b\,c]$, $a + b + c = n$ take the values:

$$\varepsilon_1 = 1 + c, \qquad \varepsilon_2 = n + 2 - a, \qquad \varepsilon_3 = 0. \tag{29}$$

With the help of this identity we can construct orthogonal projection operators [28] (recall classical Lagrange interpolation polynomials):

$$P[r] = \prod_{k(\neq r)} \frac{E - \varepsilon_k}{\varepsilon_r - \varepsilon_k}, \tag{30}$$

$$P[r]_k^i P[l]_j^k = \delta_{rl}P[l]_j^i, \tag{31}$$

(the summation convention is implied) providing resolution of the identity:

$$\sum_{r=1}^3 P[r]_j^i = \delta_j^i. \tag{32}$$

It was shown in Refs. [28] and [29] that with the help of these projectors, the spin-shift components of $U(2n)$ generators are given by the following expressions:

$$E(+)_{j\nu}^{i\mu} = P[1]_k^i E_{l\nu}^{k\mu} P[2]_j^l, \tag{33a}$$

$$E(-)_{j\nu}^{i\mu} = P[2]_k^i E_{l\nu}^{k\mu} P[1]_j^l. \tag{33b}$$

Alternatively, we may also exploit the $U(2)$ Green's characteristic identity and obtain [26]:

$$E(+)_{j\nu}^{i\mu} = P[1]_\tau^\mu E_{j\sigma}^{i\tau} P[2]_\nu^\sigma, \tag{33'a}$$

$$E(-)_{j\nu}^{i\mu} = P[2]_\tau^\mu E_{j\sigma}^{i\tau} P[1]_\nu^\sigma, \tag{33'b}$$

where now:

$$P[r]^{\mu}_{\nu} = \frac{E^{\mu}_{\nu} - \alpha_{\bar{r}}\delta^{\mu}_{\nu}}{\alpha_r - \alpha_{\bar{r}}}, \qquad (1 \leqslant r \neq \bar{r} \leqslant 2) \qquad (30')$$

and

$$\alpha_1 = n + 1 - c = \tfrac{1}{2}N + S + 1, \qquad \alpha_2 = a = \tfrac{1}{2}N - S. \qquad (29')$$

Let us finally mention that we can handle two-electron density matrices in a completely analogous way [11], although it is very convenient in this case to exploit a special basis for the universal enveloping algebra of $U(2n)$ constituted by the so-called replacement operators [30]. Following McWeeny and Mizuno [6] we can then express the two-body density matrix $\hat{\varrho}_2$:

$$\hat{\varrho}_2(1, 2; 1', 2')^{\mu\sigma}_{\nu\varrho} = \sum_{i,j,k,l=1}^{n} \phi^{*}_{i}(1)\phi^{*}_{k}(2)\phi_{j}(1')\phi_{l}(2')[E^{i\mu}_{j\nu}E^{k\sigma}_{l\varrho} - \delta^{k}_{j}\delta^{\sigma}_{\nu}E^{i\mu}_{l\varrho}]$$

$$= \hat{\varrho}_1(1; 1')^{\mu}_{\nu}\hat{\varrho}_1(2; 2')^{\sigma}_{\varrho} - \delta^{\sigma}_{\nu}\hat{\varrho}_1(1; 2')\delta(2; 1'), \qquad (34)$$

where we now write $1, 2, 1', 2'$ for r_1, r_2, r'_1, r'_2, in convenient $SU(2)$ tensor form. This will consist of the number density:

$$\hat{\varrho}_2(1, 2; 1', 2') = \hat{\varrho}^{c}_1(1; 1')\hat{\varrho}^{c}_1(2; 2') - \hat{\varrho}^{c}_1(1; 2')\delta(2; 1'), \qquad (35)$$

two vector densities:

$$V_1(1; 2; 1', 2')_{\alpha} = \hat{\varrho}_2(1, 2; 1', 2')^{\mu\sigma}_{\nu\sigma}\langle\tfrac{1}{2}\mu\tfrac{1}{2}(-\nu)|1\alpha\rangle(-1)^{\frac{1}{2}+\nu}, \qquad (36a)$$

$$V_2(1, 2; 1', 2')_{\alpha} = \hat{\varrho}_2(1, 2; 1', 2')^{\sigma\mu}_{\sigma\nu}\langle\tfrac{1}{2}\mu\tfrac{1}{2}(-\nu)|1\alpha\rangle(-1)^{\frac{1}{2}+\nu},$$

$$(-1 \leqslant \alpha \leqslant 1), \quad (36b)$$

and three tensor densities:

$$\hat{Q}(1, 2; 1', 2')^{(l)}_{m} = \hat{\varrho}_2(1, 2; 1', 2')_{\alpha\beta}\langle1\alpha1\beta|lm\rangle, \qquad (l = 0, 1, 2; \; -l \leqslant m \leqslant l) \quad (37)$$

where:

$$\hat{\varrho}_2(1, 2; 1', 2')_{\alpha\beta} = \hat{\varrho}_2(1, 2; 1', 2')^{\mu\sigma}_{\nu\tau}\langle\tfrac{1}{2}\mu\tfrac{1}{2}(-\nu)|1\alpha\rangle\langle\tfrac{1}{2}\sigma\tfrac{1}{2}(-\tau)|1\beta\rangle(-1)^{1+\nu+\tau},$$

$$(-1 \leqslant \alpha, \beta \leqslant 1). \quad (38)$$

This gives rise to two scalar densities $\hat{\varrho}^{c}_1$ and $\hat{Q}^{(0)}_0$, three vector densities $\hat{V}_1, \hat{V}_2, \hat{Q}^{(1)}$ and one rank two tensor density $\hat{Q}^{(2)}$, altogether comprising 16 components. Clearly $16 = 2^4$ is the number of entries in the density matrix $\hat{\varrho}_2$, Eq. (34).

For the spin-independent case, the explicit expressions for all these density operators were given in [11]. With the help of these expressions one can evaluate the actual density matrices once the wave function in UGA form has been determined.

We shall now turn our attention to an interesting algebraic structure of charge and spin density operators that arises when we introduce a convenient convolution product. We shall also show that the projection operators defined by Eq. (30) give rise to new idempotent density operators.

3. Single electron charge and spin density algebra

We have seen that, for spin-independent systems, the single electron density matrix is given by the zero shift component, Eq. (24), which is determined solely

by the charge density operator, Eq. (9), and the normalized spin density operator, Eq. (26). These operators in fact generate an algebra, which is closed under multiplication by scalars and addition, together with the *convolution product* "∗", defined by:

$$[\hat{\varrho} * \hat{\tau}](r; r') = \int \hat{\varrho}(r; r'')\hat{\tau}(r''; r') \, dr''. \tag{39}$$

Before investigating the general structure of this algebra, let us consider the behavior of the one-body density operator of Eq. (7) under the spin-orbital convolution product, that we designate by "$\bar{*}$", i.e.

$$
\begin{aligned}
[\hat{\varrho}_1 \bar{*} \hat{\varrho}_1](x; x') &= \int \hat{\varrho}_1(x; x'')\hat{\varrho}_1(x''; x') \, dx'' \\
&= \sum_{i,j,k,l=1}^{n} \sum_{\mu,\nu,\varrho,\sigma=-\frac{1}{2}}^{\frac{1}{2}} \psi_{i\mu}^*(x)\psi_{l\sigma}(x') \int \psi_{j\nu}(x'')\psi_{k\varrho}^*(x'') \, dx'' E_{j\nu}^{i\mu} E_{l\sigma}^{k\varrho} \\
&= \sum_{i,l=1}^{n} \sum_{\mu,\sigma=-\frac{1}{2}}^{\frac{1}{2}} \psi_{i\mu}^*(x)\psi_{l\sigma}(x')(E^2)_{l\sigma}^{i\mu}, \tag{40}
\end{aligned}
$$

where in the last step we used the orthonormality of spin orbitals $\psi_{i\mu}(x)$. However, on the totally antisymmetric irrep of $U(2n)$ with the highest weight $\langle 1^N \dot{0} \rangle \equiv \langle 1^N 0^{2n-N} \rangle$, which is pertinent to the N-electron problem, the $U(2n)$ matrix $E = [E_{j\nu}^{i\mu}]$ satisfies the quadratic identity[1] [11, 16, 27]:

$$E(E - 2n - 1 + N) = 0. \tag{41}$$

We can thus reduce the required entry of E^2 to that of E, namely:

$$(E^2)_{j\nu}^{i\mu} = (2n + 1 - N)E_{j\nu}^{i\mu}. \tag{42}$$

Using this identity in Eq. (40), we get that:

$$[\hat{\varrho}_1 \bar{*} \hat{\varrho}_1](x; x') = (2n + 1 - N)\hat{\varrho}_1(x; x'), \tag{43}$$

which we can also write in the following matrix form:

$$\sum_{\sigma=-\frac{1}{2}}^{\frac{1}{2}} \int \hat{\varrho}_1(r; r'')_{\sigma}^{\mu}\hat{\varrho}_1(r''; r')_{\nu}^{\sigma} \, dr'' = (2n + 1 - N)\hat{\varrho}_1(r; r')_{\nu}^{\mu}. \tag{43'}$$

This immediately implies that we can define the normalized density operator:

$$\hat{\gamma}_1(x; x') \equiv (2n + 1 - N)^{-1}\hat{\varrho}_1(x; x') \tag{44}$$

that is idempotent:

$$[\hat{\gamma}_1 \bar{*} \hat{\gamma}_1](x; x') = \int \hat{\gamma}_1(x; x'')\hat{\gamma}_1(x''; x') \, dx'' = \gamma_1(x; x'). \tag{45}$$

It must be emphasized (see also [11]) that the idempotency of the density operator $\hat{\gamma}_1$, Eq. (44), must not be confused with the well-known [1, 6] idempotency of the molecular density matrix associated with a closed-shell Hartree–Fock wave function. Indeed, Eq. (43) is an *operator equation* and is a direct consequence of Green's identity (41).

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[1] It may be shown [11] that this identity is a simple consequence of a trivial identity between replacement operators, namely $E_{(j\nu)(k\varrho)}^{(i\mu)(k\sigma)} + E_{(j\nu)(k\varrho)}^{(k\sigma)(i\mu)} = 0$

Let us now proceed with the investigation of the structure of the algebra of one-body density matrices that were introduced in the preceding section with the binary operation defined by the orbital convolution product of Eq. (39). We shall treat the cases $S = 0$ and $S \neq 0$ separately and begin with the case $S \neq 0$.

We shall find it convenient to introduce new density operators:

$$\hat{e}_\alpha(r; r') = \sum_{i,j=1}^{n} \phi_i^*(r)\phi_j(r')P[\alpha]_j^i, \qquad (\alpha = 1, 2, 3) \tag{46}$$

where $P[\alpha]$ are the $U(n)$ projection operators, Eq. (30). The convolution product of these operators equals

$$[\hat{e}_\alpha * \hat{e}_\beta](r; r') = \int \hat{e}_\alpha(r; r'')\hat{e}_\beta(r''; r') \, dr''$$

$$= \sum_{i,j,k,l=1}^{n} \phi_i^*(r) \int \phi_j(r'')\phi_k^*(r'') \, dr'' \phi_l(r')P[\alpha]_j^i P[\beta]_l^k. \tag{47}$$

Using the orbital orthonormality:

$$\int \phi_j(r'')\phi_k^*(r'') \, dr'' = \delta_{jk}, \tag{48}$$

the right-hand side above reduces to:

$$\sum_{i,l=1}^{n} \phi_i^*(r)\phi_l(r')(P[\alpha]_k^i \,|\, P[\beta]_l^k) = \delta_{\alpha\beta} \sum_{i,l=1}^{n} \phi_i^*(r)\phi_l(r')P[\beta]_l^i, \tag{49}$$

where we have employed Eq. (31). We thus find:

$$[\hat{e}_\alpha * \hat{e}_\beta](r; r') = \delta_{\alpha\beta}\hat{e}_\beta(r; r'), \tag{50}$$

which shows that the density operators $\hat{e}_\alpha$, Eq. (46), form an orthogonal set of idempotent density operators. Moreover, in view of the identity resolution, Eq. (32), we have that:

$$\sum_{\alpha=1}^{3} \hat{e}_\alpha(r; r') = \hat{\delta}(r; r'), \tag{51}$$

where

$$\hat{\delta}(r; r') = \sum_{i=1}^{n} \phi_i^*(r)\phi_i(r') \tag{52}$$

determines the identity operator on the one electron Hilbert space. The above special properties of the idempotent density operators $\hat{e}_\alpha$, Eq. (46), make them particularly convenient to work with.

We may express the charge and normalized spin density operators, Eqs. (9) and (26):

$$\hat{\varrho}_1^c(r; r') = \sum_{i,j=1}^{n} \phi_i^*(r)\phi_j(r')E_j^i, \tag{9'}$$

and

$$\hat{\varrho}_1^s(r; r') = \frac{-1}{2S(S+1)} \sum_{i,j=1}^{n} \phi_i^*(r)\phi_j(r')\Delta_j^i, \qquad (S \neq 0) \tag{26}$$

respectively, in terms of the density operators $\hat{e}_\alpha$, Eq. (46), by noting that the $U(n)$ matrices E and Δ may be expanded as follows:

$$E = \varepsilon_1 P[1] + \varepsilon_2 P[2],$$

$$\Delta = \varepsilon_1 \left(\varepsilon_1 + \frac{N}{2} - n - 2 \right) P[1] + \varepsilon_2 \left(\varepsilon_2 + \frac{N}{2} - n - 2 \right) P[2],$$

where we used the Green's identity of Eq. (28) together with the identity resolution, Eq. (32), as well as the fact that $\varepsilon_3 = 0$. We thereby obtain that:

$$\hat{\varrho}_1^c(r; r') = \varepsilon_1 \hat{e}_1(r; r') + \varepsilon_2 \hat{e}_2(r; r'),$$

$$\hat{\varrho}_1^s(r; r') = \frac{\varepsilon_1}{2S} \hat{e}_1(r; r') - \frac{\varepsilon_2}{2(S+1)} \hat{e}_2(r; r'),$$

(53)

where we employed the relations:

$$\varepsilon_1 + \frac{N}{2} - n - 2 = -(S+1), \qquad \varepsilon_2 + \frac{N}{2} - n - 2 = S. \qquad (29')$$

Inverting Eqs. (53) we may also write:

$$\hat{e}_1(r; r') = \frac{S}{(2S+1)\varepsilon_1} [\hat{\varrho}_1^c(r; r') + 2(S+1)\hat{\varrho}_1^s(r; r')],$$

$$\hat{e}_2(r; r') = \frac{S+1}{(2S+1)\varepsilon_2} [\hat{\varrho}_1^c(r; r') - 2S\hat{\varrho}_1^s(r; r')].$$

(54)

Equations (53) and (54) enable us to move between the physically important operators $\hat{\varrho}_1^c$, $\hat{\varrho}_1^s$ and the mathematically more convenient operators $\hat{e}_\alpha$, Eq. (46).

In view of Eqs. (53) and (54) and the idempotency of the operators $\hat{e}_\alpha$, Eqs. (46) and (50), we deduce the following properties of the operators $\hat{\varrho}_1^c$ and $\hat{\varrho}_1^s$ under convolution, namely:

$$\hat{\varrho}_1^c * \hat{\varrho}_1^c = \left(n + 2 - \frac{N}{2} \right) \hat{\varrho}_1^c - 2S(S+1)\hat{\varrho}_1^s,$$

$$\hat{\varrho}_1^c * \hat{\varrho}_1^s = \hat{\varrho}_1^s * \hat{\varrho}_1^c = \left(n + 1 - \frac{N}{2} \right) \hat{\varrho}_1^s - \tfrac{1}{2}\hat{\varrho}_1^c,$$

$$\hat{\varrho}_1^s * \hat{\varrho}_1^s = \frac{(n+1-N/2)}{4S(S+1)} (\hat{\varrho}_1^c + 2\hat{\varrho}_1^s) - \tfrac{1}{2}\hat{\varrho}_1^s.$$

(55)

Thus, unlike the full (normalized) single electron density operator, Eq. (44), the charge and spin density operators are not generally idempotent, although they close to form a two dimensional algebra under convolution product. However, the density operators $\hat{e}_\alpha$, Eq. (46), are idempotent and orthogonal [and represent, moreover, the unique density operators of this type yielding the spectral decomposition, Eq. (51)] and, in this sense, afford natural spin-independent generalization of the full (normalized) density operator, Eq. (44). It would thus be worthwhile to investigate the possible physical significance of these operators, particularly for the idempotent density operator $\hat{e}_3(r; r')$, which is orthogonal to both the charge and spin density operators.

It remains to consider the $S = 0$ case, when (cf. Appendix of Ref. [11]):

$$\Delta = P[1] = 0, \qquad (S = 0)$$

and the remaining projection matrices reduce to:

$$P[2] = E/\varepsilon_2, \qquad P[3] = 1 - P[2], \qquad \varepsilon_2 = n + 2 - \frac{N}{2}, \qquad (S = 0).$$

Thus

$$\hat{\varrho}_1^s(r; r') = \hat{e}_1(r; r') = 0, \qquad (S = 0)$$

and the charge density reduces to:

$$\hat{\varrho}_1^c(r; r') = \left(n + 2 - \frac{N}{2} \right) \hat{e}_2(r; r'), \qquad (S = 0),$$

which is a scalar multiple of a projection density, $\hat{e}_2$. As in the case $S \neq 0$, the density operator $\hat{e}_3(r; r')$ is orthogonal to $\hat{\varrho}_1^c(r; r')$.

It is worth noting that in the special case when $N = 2S$ (i.e. when $a = 0$, $b = N$, corresponding to completely unpaired spins) the $U(n)$ matrix E satisfies the reduced identity (cf. Appendix of Ref. [11]):

$$P[2] = 0,$$

so that

$$\hat{e}_2(r; r') = 0.$$

In this case we have:

$$\hat{\varrho}_1^c(r; r') = N\hat{\varrho}_1^s(r; r') = (n + 1 - N)\hat{e}_1(r; r'),$$

where we have used, for the case at hand [cf. Eq. (53)], that $\varepsilon_1 = n + 1 - 2S = n + 1 - N$. Thus, for this particular case, both the spin and charge density operators are proportional to the same idempotent density $\hat{e}_1(r; r')$, as we would expect. For the general case, however, corresponding to $a \neq 0$, $b \neq 0$, both the charge and spin density operators are independent.

We are now in a position to consider the behavior, under the convolution product, of the spin-shift densities $\hat{\varrho}_1^{(\pm)}$, Eqs. (19b) and (27), which, unlike the charge and normalized spin densities discussed above, depend explicitly on the spin coordinates. For such density operators we defined the convolution product $\bar{*}$ as follows [cf., Eq. (40)]:

$$[\hat{\varrho} \,\bar{*}\, \hat{\tau}](x; x') = \int \hat{\varrho}(x; x'') \hat{\tau}(x''; x') \, dx'',$$

where x, as usual, denotes the combined spatial and spin coordinates.

By equating the spin-shift components of Eq. (43) we immediately obtain the equations:

$$\hat{\varrho}_1^{(+)} \,\bar{*}\, \hat{\varrho}_1^{(+)} = \hat{\varrho}_1^{(-)} \,\bar{*}\, \hat{\varrho}_1^{(-)} = 0,$$

$$\hat{\varrho}_1^{(0)} \,\bar{*}\, \hat{\varrho}_1^{(\pm)} + \hat{\varrho}_1^{(\pm)} \,\bar{*}\, \hat{\varrho}_1^{(0)} = (2n + 1 - N)\hat{\varrho}_1^{(\pm)}, \qquad (56)$$

$$\hat{\varrho}_1^{(+)} \,\bar{*}\, \hat{\varrho}_1^{(-)} + \hat{\varrho}_1^{(-)} \,\bar{*}\, \hat{\varrho}_1^{(+)} + \hat{\varrho}_1^{(0)} \,\bar{*}\, \hat{\varrho}_1^{(0)} = (2n + 1 - N)\hat{\varrho}_1^{(0)}.$$

This last equation is a direct consequence of Eq. (42), whose zero-shift component gives:

$$[E(+)E(-)]_{j\nu}^{i\mu} + [E(-)E(+)]_{j\nu}^{i\mu} + [E(0)^2]_{j\nu}^{i\mu} = (2n + 1 - N)E(0)_{j\nu}^{i\mu}, \qquad (57)$$

where (assuming summation over repeated indices):

$$[E(\varepsilon)E(\varepsilon')]_{jv}^{i\mu} = E(\varepsilon)_{k\sigma}^{i\mu}E(\varepsilon')_{jv}^{k\sigma}; \qquad \varepsilon, \varepsilon' = 0, \pm.$$

Now, from Eq. (24) we have (note that $S \equiv S \cdot \hat{1}$):

$$P[1]_k^i E(0)_{jv}^{k\mu} = E(0)_{kv}^{i\mu} P[1]_j^k = \frac{\varepsilon_1}{2S}(\tilde{E} + S)_v^\mu P[1]_j^i,$$

$$P[2]_k^i E(0)_{jv}^{k\mu} = E(0)_{kv}^{i\mu} P[2]_j^k = -\frac{\varepsilon_2}{2(S+1)}(\tilde{E} - S - 1)_v^\mu P[2]_j^i,$$
(58)

from which we immediately obtain, in view of Eq. (33):

$$[E(0)E(+)]_{jv}^{i\mu} = \frac{\varepsilon_1}{2S}(\tilde{E} + S)_\sigma^\mu E(+)_{jv}^{i\sigma}.$$

However, from the $SU(2)$ identity [26]:

$$(\tilde{E} + S)(\tilde{E} - S - 1) = 0,$$
(59)

and Ref. [26], we know that:

$$P[1]_\sigma^\mu = \frac{(\tilde{E} + S)_\sigma^\mu}{2S + 1},$$

so that

$$E(+)_{jv}^{i\mu} = P[1]_\sigma^\mu E(+)_{jv}^{i\sigma} = \frac{(\tilde{E} + S)_\sigma^\mu}{2S + 1} E(+)_{jv}^{i\sigma}.$$

Substituting into the above we arrive at:

$$[E(0)E(+)]_{jv}^{i\mu} = \frac{2S + 1}{2S} \varepsilon_1 E(+)_{jv}^{i\mu},$$

and, in a similar way, we obtain:

$$[E(0)E(-)]_{jv}^{i\mu} = \frac{2S + 1}{2S + 2} \varepsilon_2 E(-)_{jv}^{i\mu}.$$

We thus deduce the convolution laws:

$$\hat{\varrho}_1^{(0)} \bar{\ast} \hat{\varrho}_1^{(+)} = \frac{2S + 1}{2S} \varepsilon_1 \hat{\varrho}_1^{(+)},$$

$$\hat{\varrho}_1^{(0)} \bar{\ast} \hat{\varrho}_1^{(-)} = \frac{2S + 1}{2S + 2} \varepsilon_2 \hat{\varrho}_1^{(-)},$$
(60)

and similarly:

$$\hat{\varrho}_1^{(+)} \bar{\ast} \hat{\varrho}_1^{(0)} = \hat{\varrho}_1^{(+)} \varepsilon_2 \frac{2S + 1}{2S + 2},$$

$$\hat{\varrho}_1^{(-)} \bar{\ast} \hat{\varrho}_1^{(0)} = \hat{\varrho}_1^{(-)} \varepsilon_1 \frac{2S + 1}{2S}.$$
(61)

We note that $\hat{\varrho}^{(\pm)}$ do not commute with the total spin S so that the ordering on the right-hand side of Eqs. (60) and (61) is important. Recalling that $\hat{\varrho}^{(\pm)}$ shift

the total spin by one unit and employing the values of the roots ε_i, Eq. (29'), we can also write Eqs. (61) in the form:

$$\hat{\varrho}_1^{(+)} \mp \hat{\varrho}_1^{(0)} = \left(n + 1 - \frac{N}{2} + S\right)\frac{2S - 1}{2S}\,\hat{\varrho}_1^{(+)} = (\varepsilon_2 - 1)\frac{2S - 1}{2S}\,\hat{\varrho}_1^{(+)},$$

$$\hat{\varrho}_1^{(-)} \mp \hat{\varrho}_1^{(0)} = \left(n - \frac{N}{2} - S\right)\frac{2S + 3}{2S + 2}\,\hat{\varrho}_1^{(-)} = (\varepsilon_1 - 1)\frac{2S + 3}{2S + 2}\,\hat{\varrho}_1^{(-)},$$

$$(61')$$

and verify that these convolution laws, Eqs. (60) and (61), or (61'), satisfy the second Eq. (56).

If we next multiply Eq. (57) on the left by the $U(n)$ projector $P[1]$, we obtain, in view of Eqs. (58), (59), and (33), the result:

$$[E(+)E(-)]^{i\mu}_{j\nu} = P[1]^i_k[(2n + 1 - N)E(0) - E(0)^2]^{k\mu}_{j\nu}$$

$$= \alpha_+ P[1]^i_j(\tilde{E} + S)^\mu_\nu,$$

where

$$\alpha_+ = \frac{\varepsilon_1}{4S^2}[2S(2n + 1 - N) - \varepsilon_1(2S + 1)]. \tag{62}$$

In matrix notation, this yields the convolution law:

$$(\hat{\varrho}_1^{(+)} \mp \hat{\varrho}_1^{(-)})^\mu_\nu = \alpha_+ \hat{e}_1(\tilde{E} + S)^\mu_\nu, \tag{63a}$$

with α_+ as in Eq. (62) and $\hat{e}_1$ given by Eq. (46). We similarly deduce the convolution law:

$$(\hat{\varrho}_1^{(-)} \mp \hat{\varrho}_1^{(+)})^\mu_\nu = \alpha_- \hat{e}_2(\tilde{E} - S - 1)^\mu_\nu, \tag{63b}$$

where

$$\alpha_- = \frac{\varepsilon_2}{4(S + 1)^2}[(2S + 1)\varepsilon_2 - 2(S + 1)(2n + 1 - N)]. $$

Finally, for the zero shift components, we arrive at:

$$(\hat{\varrho}_1^{(0)} \mp \hat{\varrho}_1^{(0)})^\mu_\nu = \tfrac{1}{4}\delta^\mu_\nu\hat{\varrho}_1^c * \hat{\varrho}_1^c + \tilde{E}^\mu_\nu\hat{\varrho}_1^c * \hat{\varrho}_1^s + [\tilde{E} + S(S + 1)]^\mu_\nu\hat{\varrho}_1^s * \hat{\varrho}_1^s, \tag{64}$$

which may be evaluated with the help of Eqs. (55). Expressing the right-hand-side in terms of idempotent density operators $\hat{e}_\alpha$, Eq. (46), we get:

$$(\hat{\varrho}_1^{(0} \mp \hat{\varrho}_1^{(0)})^\mu_\nu = (2S + 1)\left[\left(\frac{\varepsilon_1}{2S}\right)^2(\tilde{E} + S)^\mu_\nu\hat{e}_1 - \left(\frac{\varepsilon_2}{2(S + 1)}\right)^2(\tilde{E} - S - 1)^\mu_\nu\hat{e}_2\right]. \tag{64'}$$

Again, we can easily verify that these convolution laws satisfy the sum rule given by the third Eq. (56).

The above results, particularly Eqs. (56) and (60)–(64), summarize the behavior of the spin-density matrices $\hat{\varrho}_1^{(e)}$, Eq. (19), under convolution product. As noted previously, we obtain an interesting algebra, in which the idempotent densities $\hat{e}_\alpha$, Eq. (46), play a central role. A further investigation of the properties of these operators, and particularly of their physical significance, would be highly desirable.

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