Magnitude and Significance of the Higher-Order Reduced Density Matrix Cumulants

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ABSTRACT: Using full configuration interaction wave functions for Be and LiH, in both minimal and extended basis sets, we examine the absolute magnitude and energetic significance of various contributions to the three-electron reduced density matrix (3-RDM) and its connected (size-consistent) component, the 3-RDM cumulant (3-RDMC). Minimal basis sets are shown to suppress the magnitude of the 3-RDMC in an artificial manner, whereas in extended basis sets, 3-RDMC matrix elements are often comparable in magnitude to the corresponding 3-RDM elements, even in cases where this result is not required by spin angular momentum coupling. Formal considerations suggest that these observations should generalize to higher-order p-RDMs and p-RDMCs ($p > 3$). This result is discussed within the context of electronic structure methods based on the contracted Schrödinger equation (CSE), as solution of the CSE relies on 3- and 4-RDM "reconstruction functionals" that neglect the 3-RDMC, the 4-RDMC, or both. Although the 3-RDMC is responsible for at most 0.2% of the total electronic energy in Be and LiH, it accounts for up to 70% of the correlation energy, raising questions regarding whether (and how) the CSE can offer a useful computational methodology. © 2006 Wiley Periodicals, Inc. Int J Quantum Chem 107: 703–711, 2007

Key words: reduced density matrices; cumulants; reconstruction functionals; contracted Schrödinger equation

1. Introduction

Recently, several groups [1–16] have presented ab initio electronic structure calculations based on direct solution of the contracted Schrödinger equation (CSE) [16–18] for the two-electron reduced density matrix (2-RDM). To decouple the 2-, 3-, and 4-RDMs appearing in the CSE, these groups introduce so-called "reconstruction functionals" [7–9, 14, 19–21], which amount to approximate expressions for the 3- and 4-RDMs in terms of the 2-RDM. Each of these proposed reconstruction schemes relies, tacitly if not explicitly, on an assumption that the p-electron RDM cumulant (p-

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RDMC) is negligible beyond a certain value of *p*. In particular, the functionals proposed by Valdemoro and coworkers [19, 20] neglect both the 3- and 4-RDMCs, whereas various reconstruction schemes proposed by Nakatsuji and Yasuda [7–9, 12] neglect the 4-RDMC, as does the prescription suggested by Mazziotti [14, 21]. Motivating these approximations is an assumption that these higher-order RDMCs are negligible relative to products of lower-order RDMs, an assumption that is viewed skeptically by some investigators [22, 23]. The purpose of this work is to examine this assumption using both formal arguments and numerical calculations.

So far there has been little serious effort to examine the accuracy of the reconstruction functionals themselves (as distinct from the accuracy of the final, iterative solution of the CSE) using realistic atomic or molecular wave functions. What few studies have appeared [14, 20] are limited to minimal or near-minimal basis sets, which we shall demonstrate can artificially suppress the magnitude of the RDMCs. In this work, we generate RDMs and RDMCs from full configuration interaction (FCI) wave functions using triple-ζ and polarized double-ζ basis sets, in addition to minimal basis sets. We choose Be atom as a representative example of strong correlation effects (owing to the quasi-degeneracy of the 2*s* and 2*p* manifolds [24]) and LiH as an example of a weakly correlated system with the same number of electrons.

2. Notation

The RDMC formalism has been reviewed recently [25, 26]; therefore, the present work simply summarizes the salient points in order to establish our notation. We denote the *p*-RDM as $\mathbf{D}_p$, whose matrix elements are

$$\mathbf{D}_{i_1,\ldots,i_p;j_1,\ldots,j_p} = \frac{1}{p!}\langle \hat{a}^\dagger_{i_1} \quad \cdots \quad \hat{a}^\dagger_{i_p}\hat{a}_{j_p} \quad \cdots \quad \hat{a}_{j_1}\rangle. \tag{1}$$

(According to this notation, the number of indices implicitly identifies the rank of the matrix.) This definition establishes the normalization

$$\operatorname{tr}\, \mathbf{D}_p = \binom{N}{p}, \tag{2}$$

where N is the number of electrons.

Indices in Eq. (1) refer to spin orbitals; in cases where we wish to specify the spins explicitly, we will use spin components of the RDMs [27, 28]. For example, the matrix $\mathbf{D}_3^{\alpha\alpha\beta}$ refers to that part of $\mathbf{D}_3$ in which the first two row and column indices [i_1, i_2, j_1, and j_2 in Eq. (1)] have α spin, while the final row and column indices (i_3 and j_3) possess β spin. We consider only closed-shell singlet states, for which there is one independent 1-RDM spin component (since $\mathbf{D}_1^{\alpha} \equiv \mathbf{D}_1^{\beta}$), two independent 2-RDM spin components (because $\mathbf{D}_2^{\alpha\alpha} \equiv \mathbf{D}_2^{\beta\beta}$), and also two independent 3-RDM spin components (since $\mathbf{D}_3^{\alpha\alpha\beta}$ is related by permutational symmetry to $\mathbf{D}_3^{\alpha\beta\alpha}$, $\mathbf{D}_3^{\alpha\beta\beta}$, etc.).

To define the RDMCs, partition the *p*-RDM according to

$$\mathbf{D}_p = \boldsymbol{\Delta}_p + \boldsymbol{\Sigma}_p, \tag{3}$$

where $\boldsymbol{\Delta}_p$ is the *p*-RDMC and $\boldsymbol{\Sigma}_p$ represents the "unconnected" contribution, which consists of an antisymmetrized product of lower-order RDMs. The first few such unconnected matrices are defined as [21, 25, 26]:

$$\boldsymbol{\Sigma}_1 = \mathbf{0}, \tag{4a}$$

$$\boldsymbol{\Sigma}_2 = \boldsymbol{\Delta}_1 \wedge \boldsymbol{\Delta}_1, \tag{4b}$$

$$\boldsymbol{\Sigma}_3 = \boldsymbol{\Delta}_1 \wedge \boldsymbol{\Delta}_1 \wedge \boldsymbol{\Delta}_1 + 3\boldsymbol{\Delta}_2 \wedge \boldsymbol{\Delta}_1, \tag{4c}$$

$$\boldsymbol{\Sigma}_4 = \boldsymbol{\Delta}_1 \wedge \boldsymbol{\Delta}_1 \wedge \boldsymbol{\Delta}_1 \wedge \boldsymbol{\Delta}_1 + 6\boldsymbol{\Delta}_2 \wedge \boldsymbol{\Delta}_1 \wedge \boldsymbol{\Delta}_1 + 3\boldsymbol{\Delta}_2 \wedge \boldsymbol{\Delta}_2 + 4\boldsymbol{\Delta}_3 \wedge \boldsymbol{\Delta}_1. \tag{4d}$$

The symbol "$\wedge$" represents an antisymmetrized (Grassmann) product [16, 26, 27]. Equations (3) and (4) together define the RDMCs $\boldsymbol{\Delta}_p$.

The combinatorial nature of the coefficients in Eq. (4) has been discussed [22, 26], and up to the use of an antisymmetrized product, these relationships for the unconnected part of the *p*-RDM are the same as the corresponding classical expressions for the unconnected part of a *p*-particle distribution function. However, the need to obtain a spin eigenstate introduces important differences between the classical and quantum mechanical cumulant formalisms, as discussed in Section 3.1.

The normalization introduced in Eq. (2) is the most convenient choice for calculating expectation values, for in this case $\langle \hat{H} \rangle = \operatorname{tr}(\mathbf{H}_2\mathbf{D}_2)$, where $\hat{H}$ is the *N*-electron Hamiltonian, and $\mathbf{H}_2$ is the matrix of the two-electron reduced Hamiltonian, whose matrix elements in an orthonormal spin-orbital basis are

$$\mathbf{H}_{ij;rs} = \frac{\mathbf{h}_{ir} + \mathbf{h}_{js}}{N-1} + \mathbf{g}_{ij;rs}, \tag{5}$$

where **h** and **g** represent the one- and two-electron integrals, respectively; for example, $\mathbf{g}_{ij;rs} = \langle \phi_i \phi_j | r_{12}^{-1} | \phi_r \phi_s \rangle$.

Although the 2-RDM suffices for calculating $\langle \hat{H} \rangle$, in order to examine the importance of 3-RDM elements it is useful to generalize the two-electron reduced Hamiltonian to a three-electron matrix $\mathbf{H_3}$ whose elements

$$\mathbf{H}_{ijk;rst} = 2\,\frac{\mathbf{h}_{ir} + \mathbf{h}_{js} + \mathbf{h}_{kt}}{(N-1)(N-2)} + \frac{\mathbf{g}_{ij;rs} + \mathbf{g}_{ik;rt} + \mathbf{g}_{jk;st}}{N-2} \tag{6}$$

are defined such that $\langle \hat{H} \rangle = \mathrm{tr}(\mathbf{H_3 D_3})$. This concept can, of course, be generalized to $p > 3$, and the matrix elements of $\mathbf{H}_p$ provide an element-by-element weighting of how each p-RDM matrix element contributes to $\langle \hat{H} \rangle$.

3. Results and Discussion

3.1. FORMAL ARGUMENTS

Before presenting the numerical results, some formal reasoning is first presented that appears to favor a skeptical point of view with regard to the validity of truncating the cumulant hierarchy. These arguments are extensions and generalizations of a point regarding atomic Be (see below) that was first raised by Nooijen et al. [23].

Consider the matrix $\mathbf{\Delta_1} \wedge \mathbf{\Delta_1} \wedge \cdots \wedge \mathbf{\Delta_1}$ expressed in the natural spin orbital basis, in which all off-diagonal matrix elements vanish, save for those that can be generated as permutations of diagonal matrix elements. (In other words, the matrix is diagonal in a basis of determinants.) Up to an overall constant, the nonzero matrix elements are simply products of natural spin-orbital occupation numbers:

$$(\mathbf{\Delta_1} \wedge \mathbf{\Delta_1} \wedge \cdots \wedge \mathbf{\Delta_1})_{i_1,i_2,\ldots,i_p;i_1,i_2,\ldots,i_p} \propto n_{i_1} \quad n_{i_2} \quad \cdots \quad n_{i_p}. \tag{7}$$

Consider Be atom as a concrete example. For this system, the matrix $\mathbf{\Sigma_3}$ will contain terms like

$$(\mathbf{\Delta_1} \wedge \mathbf{\Delta_1} \wedge \mathbf{\Delta_1})_{1s,2p,\overline{2p};1s,2p,\overline{2p}} \propto n_{1s} n_{2p}^2, \tag{8}$$

where the index "1*s*," for example, indicates a $1s\alpha$ spin orbital and "$\overline{1s}$" indicates $1s\beta$. Similarly, the matrix $\mathbf{\Sigma_4}$ will contain terms such as

$$(\mathbf{\Delta_1} \wedge \mathbf{\Delta_1} \wedge \mathbf{\Delta_1} \wedge \mathbf{\Delta_1})_{2s,2p,\overline{2s},\overline{2p};2s,2p,\overline{2s},\overline{2p}} \propto n_{2s}^2 n_{2p}^2. \tag{9}$$

Recall that in Be, quasi-degeneracy of the 2*s* and 2*p* manifolds [24] results in 2*p* occupation numbers that are unusually large, relative to typical occupancies outside the formal electron configuration of a closed-shell atom [29]. This means that n_{2p} is large relative to n_{3s}, n_{3p}, etc., and consequently the matrix elements in Eqs. (8) and (9) are large, relative to other three- and four-electron matrix elements in which half (or more than one-half) of the indices fall outside of the formal electron configuration. Certainly, these matrix elements are small relative to those in which all indices refer to core spin orbitals; however, the element in Eq. (9), for example, is much larger than the corresponding 4-RDM element $\mathbf{D}_{2s,2p,\overline{2s},\overline{2p};\,2s,2p,\overline{2s},\overline{2p}}$. The dominant contribution to the latter comes from excitation of two core 1*s* electrons into the 2*p* shell, and such excitations will have extremely small amplitudes in the wave function. In contrast, the corresponding matrix element of $\mathbf{\Delta_1} \wedge \mathbf{\Delta_1} \wedge \mathbf{\Delta_1} \wedge \mathbf{\Delta_1}$ in Eq. (9) derives its magnitude from configurations involving only a single excitation into the 2*p* manifold.

Reasoning similarly, one may anticipate inequalities such as

$$\left|(\mathbf{\Delta_2} \wedge \mathbf{\Delta_1} \wedge \mathbf{\Delta_1})_{2s,2p,\overline{2s},\overline{2p};\,2s,2p,\overline{2s},\overline{2p}}\right| \gg \left|\mathbf{D}_{2s,2p,\overline{2s},\overline{2p};\,2s,2p,\overline{2s},\overline{2p}}\right| \tag{10}$$

involving the 2-RDM and the 2-RDMC, since the quantity on the left consists of terms such as n_{2p}^2 $\mathbf{D}_{2s,\overline{2s};\,2s,\overline{2s}}$ that involve only the core part of the 2-RDM, whereas the quantity on the right garners magnitude primarily from configurations involving excitation of two core electrons. In light of this discussion, it is reasonable to anticipate that

$$\left|\mathbf{\Delta}_{2s,2p,\overline{2s},\overline{2p};\,2s,2p,\overline{2s},\overline{2p}}\right| \gg \left|\mathbf{D}_{2s,2p,\overline{2s},\overline{2p};\,2s,2p,\overline{2s},\overline{2p}}\right|, \tag{11}$$

since the quantity on the left requires only single excitations out of the core.

This problem with atomic Be was first pointed out by Nooijen et al. [23] and, while Be may be especially pathological, owing to the anomalous 2*p* occupation numbers, this line of reasoning is likely to be valid more generally. Indeed, one may anticipate that in general

$$|\mathbf{\Delta}_{o_1,v_1,v_2;o_1,v_1,v_2}| \gg |\mathbf{D}_{o_1,v_1,v_2;o_1,v_1,v_2}|, \qquad (12)$$

and

$$|\mathbf{\Delta}_{o_1,o_2,v_1,v_2;o_1,o_2,v_1,v_2}| \gg |\mathbf{D}_{o_1,o_2,v_1,v_2;o_1,o_2,v_1,v_2}|, \qquad (13)$$

where the o_i and the v_i are indices for occupied and virtual (or strongly and weakly occupied) spin-orbitals, respectively. Equations (12) and (13) have obvious generalizations to the p-electron case, and these results arouse suspicion regarding whether it is ever reasonable to neglect $\mathbf{\Delta}_p$ in an attempt to approximate $\mathbf{D}_p$.

Next consider any four-electron singlet state, such as the ground states of Be and LiH. The wave function for such a system consists of determinants with two α electrons and two β electrons, which implies that $\mathbf{D}_3^{\alpha\alpha\alpha} \equiv \mathbf{0}$ and $\mathbf{D}_4^{\alpha\alpha\alpha\alpha} \equiv \mathbf{0}$. In contrast, $\mathbf{D}_1^{\alpha}$, $\mathbf{D}_2^{\alpha\alpha}$, and $\mathbf{\Delta}_2^{\alpha\alpha}$ are each nonzero, as are Grassmann products of these matrices. To cancel such unconnected products, it must be that $\mathbf{\Delta}_3^{\alpha\alpha\alpha} = -\mathbf{D}_3^{\alpha\alpha\alpha} \neq \mathbf{0}$ and $\mathbf{\Delta}_4^{\alpha\alpha\alpha\alpha} = -\mathbf{D}_4^{\alpha\alpha\alpha\alpha} \neq \mathbf{0}$. In such cases, it is misleading to consider either the cumulant or the unconnected part as separate quantities, since the sum of the two must be zero.

This is potentially a serious indictment of the current crop of reconstruction functionals. The basic shortcoming, with regard to the problem outlined in the preceding paragraph, is that the cumulants know nothing about $\langle \hat{S}^2 \rangle$ or spin coupling in general. This coupling implies a type of long-range order that arises because the individual electron spins must couple to an angular momentum eigenstate, and this type of correlation persists even though one expects that p-tuples of electrons must be uncorrelated, in a dynamical sense, for sufficiently large p. While dynamical correlation is expected to be unimportant beyond some value of p, nondynamical correlation persists, even in the higher-order cumulants. A way around the difficulties related to spin coupling is not obvious, although the spin-free RDMC formalism introduced recently by Kutzelnigg and Mukherjee [30] (see also Lain et al. [31]), wherein the definition of the cumulants depends on the spin quantum numbers S and M_S, merits investigation in this regard.

TABLE I

Total electronic energies and correlation energies from FCI wave functions.

System	E/E_h	$E_{\text{corr}}/10^{-3}E_h$
Be/STO-6G	−14.556092	−52.731
Be/6-31G	−14.613547	−46.783
Be/6-31G*	−14.616634	−49.690
Be/6-311G	−14.632870	−60.996
LiH/STO-6G[a]	−8.967459	−20.629
LiH/6-31G[a]	−8.993411	−19.253
LiH/6-311G[a]	−9.014652	−35.128

[a] Energies do not include internuclear repulsion.

3.2. NUMERICAL RESULTS

The arguments in Section 3.1 raise suspicion regarding the validity of truncating the cumulant expansion at finite order, although in the absence of concrete, numerical evidence, one must concede the possibility of a miraculous cancellation that rescues such a procedure. In formal analysis of a model wave function, Harris has searched for, and failed to detect, such a miracle [22]. Harris's model consists of a one-parameter wave function to describe an 8-fermion system, and the broader implications of this result are therefore unclear.

Less questionable are FCI results, so long as extended basis sets are employed. We have computed FCI wave functions for Be and LiH (the latter at its experimental bond length, 1.5957 Å [32]) using several different basis sets. These calculations were performed using GAMESS [33], and the electronic energy and correlation energy for each calculation are listed in Table I. (All energies in this work are reported in hartree atomic units, E_h.) These correlation energies confirm that correlation effects are indeed more important in Be than in LiH. From the FCI wave functions we have computed the 1-, 2-, and 3-RDMs, which we decompose into connected and unconnected parts according to Eqs. (3) and (4). Storage and manipulation of the p-RDM beyond $p = 1$ is a serious practical challenge; see Ref. [28] for the details of an indexing scheme that assigns a unique index to each permutationally distinct element of the p-RDM.

A direct comparison of the elements of $\mathbf{\Sigma}_3$ to those of $\mathbf{\Delta}_3$ confirms our suspicion that matrix elements of these two matrices are comparable in magnitude. This must be the case for the $\alpha\alpha\alpha$ spin component, as explained above, but it is also true of the $\alpha\alpha\beta$ component. Figure 1 shows a histogram of the quantities $\log|\mathbf{\Delta}_{ijk;rst}^{\alpha\alpha\beta}/\Sigma_{ijk;rst}^{\alpha\alpha\beta}|$ from two different extended-basis FCI wave functions for Be. (Only permutationally-distinct matrix elements are in-

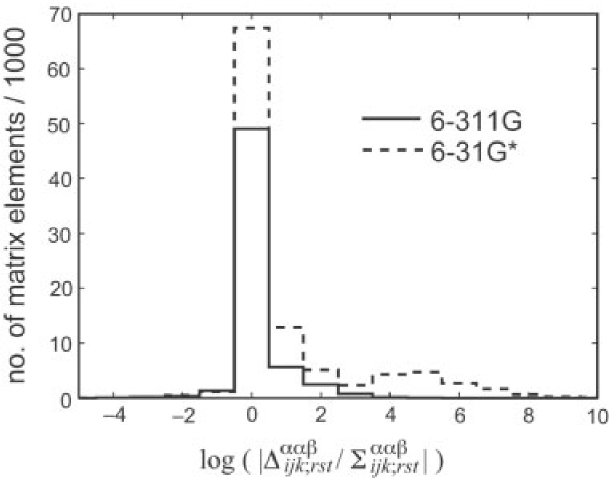

FIGURE 1. Histogram of the ratio of $\boldsymbol{\Delta}_3^{\alpha\alpha\beta}$ matrix elements to the corresponding elements of $\boldsymbol{\Sigma}_3^{\alpha\alpha\beta}$, from FCI wave functions for Be.

cluded in this histogram.) In both basis sets, the distribution of logarithmic ratios is strongly peaked around zero, indicating that the ratio is typically of order unity. In addition, both distributions are skewed toward positive values of the logarithmic ratio, indicating many cases in which the RDMC element is one or more orders of magnitude larger than the corresponding element of $\boldsymbol{\Sigma}_3$. This is especially true in the 6-31G* basis, which includes *d* functions.

Some selected matrix elements of $\boldsymbol{\Delta}_3$ and $\boldsymbol{\Sigma}_3$ are listed in Table II. Each row of this table represents a unique matrix element; the apparent degeneracies are accidental, and would disappear if additional significant figures were tabulated. It is a difficult task, if not a hopeless one, to summarize the information content of the 3-RDM in only a few selected pieces of data, nevertheless we have tried to provide representative examples of the major trends among elements of $\boldsymbol{\Delta}_3$ and $\boldsymbol{\Sigma}_3$. For the benefit of the following discussion, we have arranged the matrix elements in Table II into four groups labeled I–IV, each of which illustrates an important facet of the cumulant decomposition.

For the first two elements, denoted group I in Table II, we note that $\boldsymbol{\Delta}_3^{\alpha\alpha\alpha} = -\boldsymbol{\Sigma}_3^{\alpha\alpha\alpha}$, as required, although the individual matrix elements are in some cases as large as $\sim 10^{-4}$ in magnitude. This is arguably the most troubling feature of the whole cumulant decomposition, for we will discover that $\boldsymbol{\Sigma}_3^{\alpha\alpha\alpha}$ contributes a chemically significant amount to the total electronic energy, which must then be annihilated by $\boldsymbol{\Delta}_3^{\alpha\alpha\alpha}$.

Group II in Table II consists of diagonal $\alpha\alpha\beta$ elements for which at least one index refers to a core 1*s* orbital. The largest of these core-indexed matrix elements have values of about 0.15, and these are the largest elements of the 3-RDM. For these group II matrix elements, $|\boldsymbol{\Sigma}^{\alpha\alpha\beta}_{ijk;ijk}| \gg |\boldsymbol{\Delta}^{\alpha\alpha\beta}_{ijk;ijk}|$, which can be understood as follows. First, note that any spin orbital ϕ_{j_0} with *exact* unit occupancy separates from the *N*-electron wave function [34], so that $\Psi_N = \hat{\mathcal{A}}(\Psi_{N-1}\phi_{j_0})$, where $\hat{\mathcal{A}}$ is an antisymmetrizer. This separable wave function has the form of two noninteracting subsystems, one of which contains only a single electron, and consequently all

TABLE II

Selected elements of various three-electron matrices and their contributions to the total electronic energy, taken from a FCI/6-31G* wave function for Be.

Group	Matrix element	Matrix element[a]			Energy/E_h[a]	
		$\mathbf{D}_{ijk;rst}$	$\boldsymbol{\Sigma}_{ijk;rst}$	$\boldsymbol{\Delta}_{ijk;rst}$	$\boldsymbol{\Sigma}_{ijk;rst} \times \mathbf{H}_{rst;ijk}$	$\boldsymbol{\Delta}_{ijk;rst} \times \mathbf{H}_{rst;ijk}$
I	$1s, 2s, 2p; 1s, 2s, 2p$	0.00	−1.48 (−7)	1.48 (−7)	4.43 (−7)	−4.43 (−7)
I	$2s, 2p, \overline{2p'}; 2s, 2p, \overline{2p'}$	0.00	−2.48 (−4)	2.48 (−4)	2.23 (−4)	−2.23 (−4)
II	$1s, 2s, \overline{1s}; 1s, 2s, \overline{1s}$	1.50 (−1)	1.50 (−1)	−5.47 (−7)	−6.32 (−1)	2.30 (−6)
II	$1s, 2s, \overline{2s}; 1s, 2s, \overline{2s}$	1.50 (−1)	1.50 (−1)	8.03 (−7)	−5.13 (−3)	−2.74 (−8)
II	$1s, 2p, \overline{2p}; 1s, 2p, \overline{2p}$	4.32 (−3)	4.32 (−3)	−8.01 (−8)	−1.26 (−2)	2.35 (−7)
III	$2s, 2p, \overline{2s}; 2s, 2p, \overline{2s}$	1.01 (−7)	−3.48 (−3)	3.48 (−3)	3.46 (−3)	−3.46 (−3)
III	$2s, 2p, \overline{2p}; 2s, 2p, \overline{2p}$	3.30 (−7)	3.65 (−3)	−3.65 (−3)	−3.22 (−3)	3.22 (−3)
IV	$1s, 2s, \overline{1s}; 2s, 2p, \overline{2p}$	−1.96 (−5)	−1.86 (−6)	−1.77 (−5)	−1.86 (−6)	−1.77 (−6)
IV	$1s, 2s, \overline{2s}; 3p, 2p, \overline{3d}$	−8.64 (−5)	3.11 (−15)	−8.64 (−5)	0.00	0.00

[a] Numbers in parentheses indicate powers of 10.

matrix elements of $\mathbf{\Delta}_p$ ($p > 1$) that contain the index j_0 must be zero [35]. Because core spin orbitals have *nearly* unit occupancy, it is reasonable to expect that p-RDMC matrix elements ($p > 1$) containing a core index will be small in magnitude.

For the Be wave functions used in the present study, the 3-RDMC matrix elements in group II have typical magnitudes of $\sim 10^{-7}$–10^{-8}. This is consistent with the high accuracy reported by Colmenero and Valdemoro [20] for most elements of the reconstructed 3-RDMs for Be and H_2O, since their 3-RDM reconstruction functional [19] amounts to the approximation $\mathbf{D_3} \approx \mathbf{\Sigma_3}$. However, the analysis above demonstrates that minimal-basis wave functions, in which a relatively large fraction of the basis functions represent core orbitals, artificially exaggerate the accuracy of such reconstruction functionals by artificially reducing the importance of the cumulants. This fact is important to consider when evaluating benchmark CSE calculations in the literature, since all these calculations to date employ minimal or near-minimal basis sets. Table II clearly shows that this level of accuracy cannot be expected for all matrix elements in extended basis sets.

There are two classes of matrix elements for which the 3-RDMC is actually larger than the 3-RDM. In particular, the group III matrix elements in Table II consist of elements that do not contain any core indices, and in such cases it is frequently found that $|\mathbf{\Delta}_{ijk;rst}| \gg |\mathbf{D}_{ijk;rst}|$. This appears to be a general feature of the 3-RDMC, as similar matrix elements can be found in the case of LiH. Group IV matrix elements are off-diagonal and, while the two examples listed in Table II should not be construed as indicative of the entire off-diagonal structure of $\mathbf{D_3}$, these examples do make the point that off-diagonal elements of $\mathbf{\Delta_3}$ can be comparable to, or even significantly larger than, the corresponding elements of $\mathbf{\Sigma_3}$.

The actual values of the dimensionless quantities $\mathbf{\Delta_3}$, $\mathbf{\Sigma_3}$, and $\mathbf{D_3}$ are only part of the story; arguably, a more important criterion for judging the importance of $\mathbf{\Delta_3}$ is its impact on expectation values, especially the electronic energy. The contribution of any particular three-electron matrix element $\mathbf{M}_{ijk;rst}$ ($\mathbf{M} = \mathbf{D}, \mathbf{\Sigma}, \mathbf{\Delta}$) to the total electronic energy is given by the product $\mathbf{M}_{ijk;rst}\mathbf{H}_{rst;ijk}$. For the selected matrix elements in Table II, we also list the value of this product, for $\mathbf{M} = \mathbf{\Sigma}$ and $\mathbf{M} = \mathbf{\Delta}$. (All energies in this study are reported in hartree atomic units, E_h.) Based on this tiny sample of matrix elements, the energy associated with any one particular $\mathbf{\Delta_3}$ matrix element appears to be small (a few millihartree or less), although not chemically insignificant in all cases. For the diagonal matrix elements in group III, where $|\mathbf{\Delta}_{ijk;ijk}|$ is comparable to $|\mathbf{\Sigma}_{ijk;ijk}|$, both quantities contribute $\sim 10^{-3}$ hartree to the electronic energy, with opposite signs. Importantly, those matrix elements for which neglect of the 3-RDMC is most justified, i.e., those in which all indices refer to core spin orbitals, are also the matrix elements that contribute the most to the electronic energy.

Let us consider the total electronic energy associated with $\mathbf{\Delta_3}$, a quantity that we shall further decompose into spin components. Define

$$E^{\mathrm{C}}_{\sigma\tau\mu} = \mathrm{tr}(\mathbf{H_3}\mathbf{\Delta}_3^{\boldsymbol{\sigma\tau\mu}}) = \sum_{ijkrst} \mathbf{H}_{rst;ijk}\mathbf{\Delta}^{\boldsymbol{\sigma\tau\mu}}_{ijk;rst} \tag{14}$$

to be a "connected contribution" to the electronic energy, where $\sigma, \tau, \mu \in \{\alpha, \beta\}$ are spin indices, and let

$$E^{\mathrm{U}}_{\sigma\tau\mu} = \mathrm{tr}(\mathbf{H_3}\mathbf{\Sigma}_3^{\boldsymbol{\sigma\tau\mu}}) \tag{15}$$

be an "unconnected contribution" to the energy. The total electronic energy is given by

$$E = \sum_{\sigma\tau\mu} (E^{\mathrm{C}}_{\sigma\tau\mu} + E^{\mathrm{U}}_{\sigma\tau\mu}). \tag{16}$$

For any singlet state, this reduces to $E = E^{\mathrm{C}}_3 + E^{\mathrm{U}}_3$ with

$$E^{\mathrm{C}}_3 = 2E^{\mathrm{C}}_{\alpha\alpha\alpha} + 6E^{\mathrm{C}}_{\alpha\alpha\beta} \tag{17a}$$

$$E^{\mathrm{U}}_3 = 2E^{\mathrm{U}}_{\alpha\alpha\alpha} + 6E^{\mathrm{U}}_{\alpha\alpha\beta}, \tag{17b}$$

and for a four-electron singlet, we have the additional simplification that $E^{\mathrm{C}}_{\alpha\alpha\alpha} = -E^{\mathrm{U}}_{\alpha\alpha\alpha}$ so $E = 6(E^{\mathrm{C}}_{\alpha\alpha\beta} + E^{\mathrm{U}}_{\alpha\alpha\beta})$.

This energy decomposition for our Be and LiH calculations is summarized in Table III. For both systems, the total connected contribution to the electronic energy is relatively small, roughly 1000 times smaller than the unconnected contribution. The ratio $E^{\mathrm{C}}_3/E^{\mathrm{U}}_3$ for each calculation is given in Table III and, because the $\alpha\alpha\alpha$ energy component is small (for reasons discussed below), this ratio is nearly equal to E^{C}_3/E, the fraction of the total energy that comes from $\mathbf{\Delta_3}$. In an absolute sense, $E^{\mathrm{C}}_3 = 0.022$–$0.026\ E_h$ in Be and 0.006–$0.010\ E_h$ in LiH. These values are about an order of magnitude larger than those reported by Colmenero and Val-

TABLE III

Decomposition of the total electronic energies obtained from FCI wave functions.

System	tr $\mathbf{\Delta}_3^{\alpha\alpha\alpha}$	2 $E^{\mathrm{C}}_{\alpha\alpha\alpha}/10^{-3}E_h$	6 $E^{\mathrm{C}}_{\alpha\alpha\beta}/10^{-3}E_h$	6 $E^{\mathrm{U}}_{\alpha\alpha\beta}/E_h$	$E^{\mathrm{C}}_3/E^{\mathrm{U}}_3 \times 1{,}000$	$E^{\mathrm{C}}_3/E_{\mathrm{corr}}$
Be/STO-6G	0.006993	−16.330	−9.223	−14.546869	1.76	0.485
Be/6-31G	0.006082	−13.334	−8.616	−14.604931	1.50	0.469
Be/6-31G*	0.005798	−12.722	−10.389	−14.606245	1.58	0.465
Be/6-311G	0.005663	−12.255	−13.732	−14.619138	1.78	0.426
LiH/STO-6G[a]	0.000060	−0.099	−6.037	−8.961422	0.68	0.297
LiH/6-31G[a]	0.000085	−0.125	−6.181	−8.987230	0.70	0.328
LiH/6-311G[a]	0.000126	−0.223	−10.783	−9.003869	1.22	0.313

[a] Total energy does not include internuclear repulsion.

demoro [20] in minimal-basis calculations, but are comparable to the errors (relative to FCI) that Mazziotti [14] reports following self-consistent solution of the CSE.

The smallness of the ratio $E_3^{\mathrm{C}}/E_3^{\mathrm{U}}$ is a consequence of the fact that the approximation $\mathbf{D_3} \approx \mathbf{\Sigma_3}$ is most accurate for exactly those 3-RDM elements that are largest in magnitude, namely, the core-indexed ones. Of the remaining 3-RDM elements, the vast majority each contribute only a tiny amount to the electronic energy. Figure 2 presents histograms of the quantities $\log|\mathbf{H}_{rst;ijk}\mathbf{M}_{ijk;rst}/E_h|$, for $\mathbf{M} = \mathbf{\Sigma}_3^{\alpha\alpha\alpha}$, $\mathbf{\Sigma}_3^{\alpha\alpha\beta}$, and $\mathbf{\Delta}_3^{\alpha\alpha\beta}$. Although certain individual elements of $\mathbf{\Sigma}_3^{\alpha\alpha\beta}$ contribute as much as 0.632 hartree to the electronic energy (see Table II), the number of matrix elements this large is tiny in comparison with the total number of matrix elements.

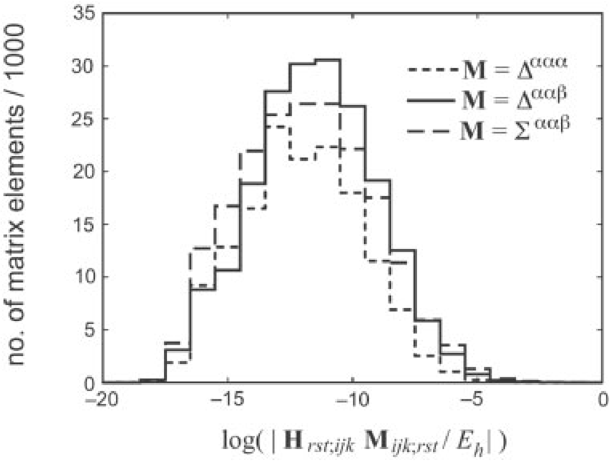

FIGURE 2. Histogram of absolute magnitudes of the energy contributions from the connected and unconnected parts of the 3-RDM spin components, from a FCI/6-31G* wave function for Be.

Another circumstance that conspires to keep $E_3^{\mathrm{C}}/E_3^{\mathrm{U}}$ small is the fact that the reduced Hamiltonian matrices $\mathbf{H}_p$ are diagonally dominant for $p > 2$, by virtue of the two-electron nature of $\hat{H}$. To obtain a nonzero value for $\mathbf{H}_{i_1,\ldots,i_p;j_1,\ldots,j_p}$, at most two of the row indices may differ from the corresponding column index. This implies that $\mathbf{H_2}$ is dense while the higher-order reduced Hamiltonian matrices are rather sparse, thus diminishing the energetic significance of individual p-RDM and p-RDMC matrix elements, for $p > 2$.

This fact is relevant because our numerical analysis reveals that off-diagonal 3-RDMC matrix elements are often significantly larger in magnitude than the corresponding off-diagonal elements of $\mathbf{\Sigma_3}$, as for example in the case of the $(1s, 2s, \overline{2s}; 3p, 2p, \overline{3d})$ element listed in Table II. Despite the fact that $|\mathbf{\Delta}_{ijk;rst}| \gg |\mathbf{\Sigma}_{ijk;rst}|$ for these elements, the off-diagonal $\mathbf{H}_{rst;ijk}$ are frequently so small that the cumulant cannot run up E_3^{C} too much relative to E_3^{U}. In contrast, as noted above, the largest (absolute) values of $\mathbf{H}_{rst;ijk}$ coincide with precisely those matrix elements for which $\mathbf{\Delta}_{ijk;rst}$ is smallest.

In total, the 3-RDMC accounts for no more than 0.2% of the total electronic energy in any of the examples considered in this study, but this is only part of the story. Arguably, a more important observation is that E_3^{C} represents a substantial fraction of the correlation energy. Table III shows that the ratio $E_3^{\mathrm{C}}/E_{\mathrm{corr}}$ varies between 0.43–0.48 in Be, and 0.30−0.33 in LiH, depending on which basis set is employed. Thus, if the 3-RDMC is neglected and the energy is calculated using $\mathbf{\Sigma_3}$, one may recover as little as 30% of the correlation energy, even when exact 1- and 2-RDMs are used to construct $\mathbf{\Sigma_3}$. In comparison, even a low-level treatment of electron correlation such as second-order Møller–Plesset perturbation theory (MP2) often recovers 80% or more of the FCI correlation energy [36]. Even in an absolute sense, the total energy associated with the 3-RDMC is chemically significant, amounting to as much as 0.026 E_h (16 kcal/mol) for Be and 0.011 E_h (7 kcal/mol) for LiH.

4. Summary and Conclusions

Analysis of the 3-RDMs and 3-RDMCs for Be and LiH, using FCI wave functions in extended basis sets, demonstrates that the cumulant matrix elements are generally not small relative to those of the RDM; in some cases they are even considerably larger. By neglecting $\mathbf{\Delta}_3$ (as in the RDM reconstruction scheme of Valdemoro and coworkers [19]), one is left with an abysmal off-diagonal structure for $\mathbf{D}_3$, but with fairly accurate values for the spin-orbital matrix elements corresponding to core electrons, which are far more important to the total electronic energy than are the valence or mixed core/valence matrix elements. Consequently, the total electronic energy suffers only slightly (0.01–0.03 E_h, or less than 0.2%) when $\mathbf{\Delta}_3$ is neglected. This does suggest, however, that it is important to examine the performance of CSE-based electronic structure methods in systems containing more than two non-hydrogen atoms, because the RDMs for these systems possess a smaller fraction of matrix elements involving only core orbitals, as compared with molecules of the form AH_n. To the author's knowledge, no such calculations have been reported to date.

Although neglect of $\mathbf{\Delta}_3$ has a relatively small impact on the total energy, this approximation does neglect 50–70% of the correlation energy, the very quantity that solution of the CSE is intended to recover. This is the case, even when correlated (in fact, exact) 1- and 2-RDMs are used to reconstructed the unconnected part of the 3-RDM.

While Valdemoro's reconstruction scheme [19] neglects both $\mathbf{\Delta}_3$ and $\mathbf{\Delta}_4$, the reconstruction schemes of Mazziotti [21], as well as those of Nakatsuji and Yasuda [7–9], only neglect $\mathbf{\Delta}_4$. For reasons of computational convenience, we have not performed a numerical analysis of 4-RDMs and 4-RDMCs, nor have we considered systems with more than four electrons. In systems with $N > 4$ (or high-spin systems with $N = 4$), $\mathbf{D}_3^{\alpha\alpha\alpha}$ is nonzero, so our results regarding the $\alpha\alpha\alpha$ spin components of Be and LiH 3-RDMs cannot be extrapolated to more general systems. On the other hand, the analysis in Section 3.1 suggests that many out-of-core matrix elements of $\mathbf{\Delta}_4$ are likely to be significant, relative to the corresponding unconnected matrix elements, for the same reasons that these $\mathbf{\Delta}_3$ elements are significant. As such, for the mixed-spin (i.e., $\alpha\alpha\beta$) components, we suspect that the numerical results presented in the present work are probably indicative of the general structure of the RDMs and RDMCs.

Ultimately, the results of this study indicate that RDM reconstruction alone is of insufficient accuracy to serve as a useful electronic structure method. To the extent that CSE-based methods afford useful results, it must be that the aforementioned problems are somehow ameliorated by the process of self-consistent iteration [1, 5, 15, 23] that is used to solve the CSE. A further problem is the requirement that the RDMs be *N*-representable [34], as approximate, reconstructed RDMs need not be *N*-representable, even when *N*-representable 1- and 2-RDMs are used to carry out the reconstruction [27]. If the CSE is to yield useful results, it would seem that this problem also must be corrected or at least mitigated by the process of self-consistent iteration. Indeed, several investigators [6, 14, 16, 37, 38] have suggested that approximate *N*-representability conditions be applied as auxiliary constraints during the self-consistent iterations. Whether, and how, these procedures can correct the problems with reconstruction documented in this work remains an open question for future investigation.

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