Irreducible Charge Density Matrices for Analysis of Many-Electron Wave Functions

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Received 26 July 2004; accepted 1 September 2004
Published online 7 January 2005 in Wiley InterScience (www.interscience.wiley.com).
DOI 10.1002/qua.20438

ABSTRACT: A novel procedure for deriving multicenter bond indices on the basis of irreducible spinless charge density matrices that are naturally introduced as in the Ursell–Mayer theory is presented. Unlike earlier schemes using central moments of the charge operator, the procedure presented here leads to a proper definition of multicenter bond indices for an arbitrary number of atoms. Formal relationships and numerical techniques for the typical configuration interaction (CI) approaches, up to full CI, are given and illustrated with simple molecular systems. Comparison of the molecular orbital and full CI results indicates strong electron correlation effects, especially for the 3-center and 4-center bond indices. Excited state multicenter bond indices are described within the CI singles approach. The problem of proper definition of atomic valence and bond indices for electronic states with nonzero spin is raised. © 2005 Wiley Periodicals, Inc. Int J Quantum Chem 102: 582–601, 2005

Key words: cumulant densities; contracted Schrödinger equation; multicenter bond indices; atomic valence; CI excited states; full CI

1. Introduction

Conventional methods of molecular wave function analysis are based on the reduced density matrix (RDM) theory [1–7]. Attention is concentrated primarily on the one-particle density matrix (1-RDM), which determines one-electron charge and spin distributions, and provides intuitive, pictorial interpretations of quantum chemical data [8, 9]. Other useful tools [10–20] for electronic structure analysis can be reduced to the 1-RDM representation as well. Yet, one-electron distribution functions alone are not sufficient for description of molecular systems, especially those undergoing chemical reactions and many-electron rearrangements, such as formation and breaking of bonds. The higher-order density matrices and relevant
many-particle operators are used in numerous works [21–41].

John Pople in particular was the first to analyze the two-electron distribution functions within the Hartree–Fock method [21], giving us an excellent motivation to devote this work to his memory.

Among many papers [22–41] employing higher-order RDMs for characterization of molecular electronic structure, references [22, 23, 25, 26] were of major importance in deriving the generalized two-center bond indices for many-electron state vectors. A measure of correlation in the fluctuations of localized atomic charges, the corresponding three-center bond index and more general multicenter indices were developed by analogy with the generalized two-center index [27, 28]. These indices were studied in detail at the Hartree–Fock level as described in the reviews [29, 38].

In probability theory, the high-order correlation functions correspond to the usual central moments. In contrast, the high-order central moments are not used in statistical physics for lack of the physically important asymptotic additivity, or size-consistency in quantum chemical terms. The so-called irreducible moments, or cumulants, appear instead [42–44]. Only the second- and third-order central moments coincide with the corresponding cumulants. To be consistent for any order, the analysis of charge fluctuations should be duly refined by use of the irreducible moments. The present work suggests a general way for treating this problem.

The article is organized as follows. Section 2 introduces the irreducible charge density matrix (ICDM) of an arbitrary order and derives formally exact equations for low-order ICDMs. Section 3 gives a proper definition of multicenter indices for any number of atomic centers. Sections 4 and 5 present computational schemes and illustrations with typical quantum chemical approaches, ranging from the molecular orbital (MO) model to the full configuration interaction (FCI) approach.

### 2. Irreducible Charge Densities

The densities required for the analysis of the many-electron wave functions are closely related to the Ursell cluster distribution functions in statistical physics. The difference stems from the fact that the classical distribution functions are replaced in quantum mechanics with the appropriate operators that are, in fact, RDMs. At present, we will use the most important spinless RDM component, usually called the charge density matrix, or charge RDM [2]. A general consideration of the high-order charge density matrices can be found in our work [45]. The current study uses this work’s notation and some of the results.

Let \( |\Psi\rangle = |\Psi(1\ldots N)\rangle \) be an \( N \)-electron wave function of an electronic state, and

\[
\rho^\Psi_k = \rho^\Psi(1\ldots k)
\]

be a \( k \)-th order RDM with Löwdin’s binomial coefficient scaling [1]. Contracting \( \rho^\Psi_k \) over all spin variables, or spin indices produces a \( k \)-electron charge density matrix denoted by \( R_k = R_k(1\ldots k) \). Explicitly,

\[
R_k(1\ldots k) = \text{Tr} \rho^\Psi(1\ldots k), \quad (1)
\]

where \( \text{Tr}_{(1\ldots k)}^{(\sigma)} \) symbolizes the spin contraction operation, i.e., integration over the spin variables of electrons 1, \ldots, \( k \). The main formal properties of \( R_k \) are same as of \( \rho^\Psi_k \), e.g.,

\[
\text{Tr}_{(k+1)} R_{k+1}(1\ldots k) = \frac{N-k}{k+1} R_k(1\ldots k), \quad (2)
\]

\[
\text{Tr}_{(1\ldots k)} R_k(1\ldots k) = \binom{N}{k}, \quad (3)
\]

with \( \text{Tr}_{(i)} \) being the spinless contraction operation, i.e., summation over the spinless indices of the \( i \)-th electron.

We introduce ICDMs in exactly the same manner as in the Ursell–Mayer theory for classical distribution functions [46, 47]. The \( k \)-th order ICDM is denoted by \( \pi_k(1\ldots k) = \pi_k \). In the first order, \( \pi_1 \) is identical to \( R_1 \), and

\[
\text{Tr} \pi_1 = N. \quad (4)
\]

One can write the following interrelations between the usual charge RDMs and the ICDMs:

\[
R_1(1) = \pi_1(1), \quad (5)
\]

\[
2!R_2(12) = \pi_1(1)\pi_1(2) + \pi_2(12), \quad (6)
\]

\[
3!R_3(123) = \pi_1(1)\pi_1(2)\pi_1(3)
+ \{ \pi_2(12)\pi_1(3) \} \text{symm} + \pi_3(123), \quad (7)
\]
4!\(R_4(1234) = \pi_1(1)\pi_1(2)\pi_1(3)\pi_1(4)\)
+ \(\{\pi_2(12)\pi_1(3)\pi_1(4)\}_{\text{symm}} + \{\pi_2(12)\pi_2(34)\}_{\text{symm}}\)
+ \(\{\pi_3(123)\pi_1(4)\}_{\text{symm}} + \pi_3(1234)\). \(\text{(8)}\)
and so on. Here \(\{\}_\text{symm}\) designates symmetrization over all nonequivalent arrangements of electron numbers,
\[
\{\pi_2(12)\pi_2(34)\}_{\text{symm}} = \pi_2(12)\pi_2(34)
+ \pi_2(13)\pi_2(24) + \pi_2(14)\pi_2(23). \quad \text{(9)}
\]
A general formula precisely reproduces the corresponding relation in [46]. Relations (5)–(7) can be rewritten as
\[
\pi_2(12) = 2!R_2(12) - \pi_1(1)\pi_1(2), \quad \text{(10)}
\]
\[
\pi_3(123) = 3!R_3(123) - \pi_1(1)\pi_1(2)\pi_1(3)
- \{\pi_2(12)\pi_1(3)\}_{\text{symm}}, \quad \text{(11)}
\]
and so on. In a general case, the following representation can be realized
\[
\pi_k(1...k) = k!R_k(1...k)
- \{\pi_{k-1}(1...k-1)\pi_1(k)\}_{\text{symm}}
- \{\pi_{k-2}(1...k-2)\pi_1(k-1)\pi_1(k)\}_{\text{symm}}... \quad \text{(12)}
\]
These equations may be used for computation of the high-order ICDMs from the low-order ones.
A useful recurrence,
\[
\text{Tr} \frac{1}{N-k} \{\text{Tr} \pi_{k+1}(1...k + 1) + N\pi_1(1...k)\} = k!R_k(1...k) + ... \quad \text{(15)}
\]
All terms in the right-hand side of Eq. (15) must form the irreducible construction (12), giving
\[
\frac{1}{N-k} \{\alpha \pi_k + N\pi_1\} = \pi_k. \quad \text{(16)}
\]
Hence, in Eq. (12), \(\alpha = -k\), q.e.d. Section 4.1 gives a less formal proof of Eq. (13).
The normalization condition follows immediately from Eq. (13):
\[
\text{Tr} \pi_k(1...k) = (-1)^{k-1}(k-1)!N. \quad \text{(16)}
\]
For example, in the special case of \(\pi_2\) discussed in Section 3.5 of Ref. [47],
\[
\text{Tr} \pi_2(12) = -N. \quad \text{(17)}
\]
Interestingly, in quantum chemistry, the quantity \(\pi_2(12)\) with the opposite sign was already introduced in Ref. [48] and introduced within the RDM theory for treating the so-called contraction Schrödinger equations (CSEs) derived in Ref. [49] (see also Refs. [4, 50–56]). Indeed, full RDMs involving spatial and spin degrees of freedom must be antisymmetrized, for instance, by applying the Grassmann wedge product to the counterparts of Eqs. (5)–(7). To avoid confusion, the corresponding quantities from [53, 54] are referred to as Grassmann irreducible RDMs. Even the spin-free counterparts of the Grassmann irreducible RDMs investigated in Ref. [54] have no direct relation to our ICDMs. For instance, ICDMs cannot disappear in any proper approximation, as indicated, for example, by the normalization equation (3), whereas the Grassmann irreducible RDMs vanish in the Hartree–Fock approximation.
The CSE theory is formulated using ICDMs starting with the CSEs [49, 50] and replacing \( \rho_0 \) with \( R_k \). The following spin-free CSEs result with low-order ICDMs

\[
h R_1 + 2 \text{Tr} [h(2) + g(12)] R_2 + 3 \text{Tr} g(23) R_3 = E R_1, \tag{18}
\]

\[
[h(1) + h(2)] R_2 + 3 \text{Tr} [h(3) + g(13) + g(23)] R_3 + 6 \text{Tr} g(34) R_4 = E R_2, \tag{19}
\]

where \( E \) is the total energy and \( h(1) \) and \( g(12) \) are the one- and two-electron operators in the usual \( N \)-electron space. Substituting Eqs. (5)–(8) into Eqs. (18) and (19) leads to the coupled equations

\[
f \sigma \sigma_1 + \text{Tr} [f \sigma(2) + g(12)] \sigma_2 + \frac{1}{2} \text{Tr} g(23) \sigma_3 = 0, \tag{20}
\]

\[
[f \sigma(1) + f \sigma(2)] \sigma_2 + \text{Tr} [f \sigma(3) + g(13) + g(23)] \sigma_3 + \{\text{Tr} g(13) \sigma_2(23) \sigma_3(1) \}_{\text{symm}} + \text{Tr} g(34) \{\sigma_2(13) \sigma_3(24) + \frac{1}{2} \sigma_3\} + g(12) \sigma_2(1) \sigma_1(2) = 0, \tag{21}
\]

where \( \{\} \) symm extends over 1 and 2, and

\[
f \sigma = h + \text{Tr} g(12) \sigma_1(2). \tag{22}
\]

In the corresponding term of Eq. (21), 3 is a dummy particle disappearing under the trace. The derivation of Eqs. (20) and (21) uses the known representation [2]

\[
E = \text{Tr} h(1) R_1 + \text{Tr} g(12) R_2, \tag{23}
\]

which reads in terms of ICDMs as

\[
E = \frac{1}{2} \{\text{Tr} [h + f \sigma] \sigma_1 + \text{Tr} g(12) \sigma_3\}.
\]

Equation (20) is applied while transforming Eq. (19). Equations (20) and (21) have no disconnected (factorized) terms, similar to the spin-free CSEs for the Grassmann irreducible RDMs [54].

Equations (20) and (21) are of a more simple form than their Grassmann counterparts. As in the original CSE theory, they cannot be used directly, since they require a procedure for replacing \( \sigma_3 \) and \( \sigma_4 \) with approximations invoking unknown functionals of \( \sigma_1 \) and \( \sigma_2 \). A critical analysis of the problem is given in Refs. [51, 55, 56].

The spin purity conditions for singlet states deserve special attention. They were first obtained in terms of charge RDMs of arbitrary order in Ref. [45] (see also Refs. [23, 57, 58]) and take the form

\[
2 \text{Tr} R_2(12) P_{12} = (2 - N/2) R_1, \tag{24}
\]

\[
3 \text{Tr} R_3(123) P_{123} = (2 - N/2 - P_{12}) R_2, \tag{25}
\]

and so on. In these equations, \( P_{ij} \) denotes the spinless transposition operator for electrons \( i \) and \( j \). Here and below, the simple contraction rule is used [41, 59]:

\[
\text{Tr} P_{ij} X(j) = X(i), \tag{26}
\]

with \( i \neq j \). Taking into account Eqs. (5)–(7), the contraction rule applied to Eqs. (24) and (25) gives the ICDM spin purity conditions

\[
\text{Tr} P_{12} \sigma_1(12) P_{12} = (2 - N/2) \sigma_1 - \bar{\sigma}_1, \tag{27}
\]

and so on. A full contraction of Eq. (27) produces

\[
\text{Tr} \sigma_2(12) P_{12} = -N^2/2 + 2N - \text{Tr} \bar{\sigma}_1. \tag{28}
\]

Equations (27) and (28) contain terms such as \( N^2/2 \), that are not size-consistent. The size-consistent contribution to Eq. (28) may be written as

\[
N_{\text{eff}} = 2N - \text{Tr} \bar{\sigma}_1; \tag{29}
\]

In fact, it is just the quantity introduced in Refs. [11, 19] for the effective number of unpaired electrons. A more detailed comparison of \( N_{\text{eff}} \) with other approaches to the open electron shell problem will be given elsewhere [60]. An alternative way for connecting Eq. (29) with the \( \bar{\sigma}_1 \) ICDM, or exchange density matrix in Ruedenberg terminology [48], is presented in Ref. [61].
3. Multicenter Indices

To formulate a scheme for generating multicenter bond orders that are closely related to IC-DMs, we follow the classic approach of Coulson and Longuet-Higgins [62] and apply perturbation theory (PT) to obtain the atom–atom interactions in terms of mutual polarizabilities within the Unsöld scheme [63]. The original Unsöld approximation is applicable up to the third order. The fourth- and higher-order Unsöld approximations are not size-consistent. Size-consistent higher-order expressions are proposed here on the basis of the irreducible electron structure unitary group theory [65]. These operators form a special type of generators known in the electronic structure unitary group theory [65].

The approach adopted here brings up novel points concerning the higher-order corrections. The second-order PT correction to energy \( E_{AB}^2 \) due to two concurrent perturbations \( U_A \) and \( U_B \) \((A \neq B)\) takes the form

\[
E_{AB}^2 = \langle \Psi | U_A | \Psi \rangle + \langle \Psi | U_B | \Psi \rangle = 2 \langle \Psi | U_A | U_B \rangle.
\]

Here and below, all quantities are assumed real. \( [\Psi_A] \) is the first-order correction to the unperturbed state vector \( \Psi \) due to \( U_A \). Note that related objects are considered in Ref. [66] when constructing the atomic softness matrix.

In the Unsöld approximation [63],

\[
[\Psi_A] = -\lambda^{-1} \Delta U_A |\Psi\rangle,
\]

\[
\Delta U_A = U_A - \langle U_A \rangle,
\]

where \( \lambda \) is the average excitation energy, Eq. (37) becomes

\[
-2^{-1} \lambda^{-1} E_{AB}^2 = \langle \Delta U_A \Delta U_B \rangle.
\]

The third-order relation \((A < B < C)\) is established the same way:

\[
(3!)^{-1} \lambda^{-2} E_{ABC}^3 = \langle \Delta U_A \Delta U_B \Delta U_C \rangle.
\]

Thus, the second- and third-order energy corrections in the Unsöld approximation are mixed central moments of the given order and are identical to the corresponding cumulants, namely,

\[
\langle \langle U_A U_B \rangle \rangle = \langle \Delta U_A \Delta U_B \rangle.
\]
where the cumulants of random variables $U_1, \ldots, W$ are designated by $\langle \langle (U, \ldots, W) \rangle \rangle$ as in Ref. [43].

Calculations of the fourth- and higher-order corrections according to the same Unsöld-like scheme do not produce size-consistent quantities. A useful, but not entirely satisfactory, expression is given in Ref. [67] for the related estimates of the second-order hyperpolarizabilities. Under these circumstances we propose to apply cumulants for any number of atoms. For instance, the cumulant

$$\langle \langle \Delta U_A \Delta U_B \Delta U_C \Delta U_D \rangle \rangle = \langle \langle \Delta U_A \Delta U_B \Delta U_C \Delta U_D \rangle \rangle - \langle \langle \Delta U_A \Delta U_B \rangle \langle \Delta U_C \Delta U_D \rangle \rangle_{\text{symm}}$$

(44)

is used as a proper correlator describing interaction of four atoms. In general, the $k$-order cumulant

$$\langle \langle U_{A_1} \ldots U_{A_k} \rangle \rangle$$

(45)

is used for the ordered atomic set

$$A_1 < \ldots < A_k.$$  

(46)

Having defined the mutual influence of several atoms, we can naturally define the high-order bond indices. The following properties of generators $U_A$

$$U_A U_B = \sum_{1 \leq i < j \leq N} u^{AB}(i, j),$$

(47)

$$u^{AB}(1, 2) = u^A(1)u^B(2) + u^B(1)u^A(2),$$

(47')

$$U_A U_B U_C = \sum_{1 \leq i < j < k \leq N} u^{ABC}(i, j, k),$$

(48)

$$u^{ABC}(123) = \{u^A(1)u^B(2)u^C(3)\}_{\text{symm}},$$

(48')

and so on, are taken into account, and condition (46) is implied. The following interrelations between the cumulants and ICDMs are obtained

$$\langle \langle U_A U_B \rangle \rangle = \langle \langle U_A \rangle \rangle \langle \langle U_B \rangle \rangle = \Tr u^A(1)u^B(2)\pi_2 = \pi_{(A, B)},$$

(49)

$$\langle \langle U_A U_B U_C \rangle \rangle = \langle \langle U_A \rangle \rangle \langle \langle U_B \rangle \rangle \langle \langle U_C \rangle \rangle = \Tr u^A(1)u^B(2)u^C(3)\pi_3 = \pi_{(A, B, C)},$$

(50)

$$\langle \langle U_A U_B U_C U_D \rangle \rangle = \Tr u^A(1)u^B(2)u^C(3)u^D(4)\pi_4 = \pi_{(A, B, C, D)}.$$  

(51)

The general expression is quite evident:

$$\langle \langle U_{A_1} \ldots U_{A_k} \rangle \rangle = \Tr u^{A_1}(1) \ldots u^{A_k}(k)\pi_k = \pi_{(A_1, \ldots, A_k)},$$

(52)

The cumulants (49)–(52) defined above are the main quantities of our approach and are directly proportional to the multicenter indices. The existing definitions [26–28] of the two-center bond index $\kappa_{AB}$ differs from Eq. (49) by a factor of $-2$, and the three-center bond index $\kappa_{ABC}$ differs from Eq. (50) by a factor of three:

$$\kappa_{AB} = -2 \pi_{(A, B)},$$

(53)

$$\kappa_{ABC} = 3 \pi_{(A, B, C)}.$$  

(54)

The difference is due to the normalization condition (16). To clarify this point and eliminate the discrepancy, consider Eq. (16) written in the form

$$N = (-1)^{k-1} \frac{1}{(k-1)!} \Tr \pi_k(1 \ldots k)l(1) \ldots l(k).$$

(55)

Substituting the resolution of identity (32) into Eq. (55), the contribution of (52) into (55) may be presented as

$$(-1)^{k-1} \sum_{1 \leq A_1 < \ldots < A_k \leq M} \pi_{(A_1, \ldots, A_k)}$$

(56)

suggesting the following definition of the $k$-order $(k$-center) bond index:

$$\kappa_{A_1 \ldots A_k} = (-1)^{k-1}k \pi_{(A_1, \ldots, A_k)}.$$  

(57)

For $k = 2$ and $k = 3$, this expression reproduces the previous definitions of $\kappa_{AB}$ and $\kappa_{ABC}$ [26–28]. At the same time, Eq. (57) defines proper multicenter indices for $k > 3$. For example, the four-center index is given by the formula

$$\kappa_{ABCD} = -4 \pi_{(A, B, C, D)}.$$  

(58)

The matrix elements of $\pi_k$ in (52) and (57) can be computed in the same manner as in (36):
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\[ \pi((A_1, \ldots, A_i)) = \sum_{\mu_1}^{A_1} \cdots \sum_{\mu_i}^{A_i} \pi((\mu_1, \ldots, \mu_i)_r) \]

\[ \pi((\mu_1, \ldots, \mu_i)) = \langle \chi_{\mu_1} \cdots \chi_{\mu_i} | \pi_k | \chi_{\mu_1} \cdots \chi_{\mu_i} \rangle \]  

(59)

in particular,

\[ \pi((A,B)) = \sum_{\mu}^A \sum_{\nu}^B \pi((\mu, \nu)) r. \]  

(60)

4. Bond Indices for Many-Electron Wave Functions

4.1. MO BOND INDICES

First consider the single-determinant state \( |\Phi\rangle \), for which RDMs are well known [1]. Focusing on singlet states for simplicity, the one-electron RDM \( \rho^o \) is identified with the Dirac–Fock density matrix \( \rho \) of the form

\[ \rho = \rho^o (|\alpha\rangle \langle \alpha | + |\beta\rangle \langle \beta |). \]  

(61)

Here, \( \rho^o \) is the spin-free Dirac–Fock density matrix, which is the projector on the occupied MOs with the idempotency relation \( \rho^o = (\rho^o)^2 \). The functions \( |\alpha\rangle, |\beta\rangle \) are the standard spin eigenkets for spin-up and spin-down electrons.

Given \( \rho \), the \( k \)-RDM is calculated via the expression [1]

\[ \rho^o = A_k \rho(1) \cdots \rho(k), \]  

(62)

where \( A_k \) is the total \( k \)-electron antisymmetrizer. Application of the full spin contraction as prescribed by (1) to Eqs. (61) and (62) yields the charge densities \( R^o_k \) expressed in the MO approximation with \( |\Psi\rangle = |\Phi\rangle \) as

\[ R^o_k = \left( \sum_{j=0}^{k-1} (-1)^j 2^{k-j} \hat{P}^{(j)} \right) \rho(1) \cdots \rho(k), \]  

(63)

where \( \hat{P}^{(j)} \) denotes the sum over all spin-free permutations containing precisely \( j \) cycles for the given \( k \)-value. The \( k \)-ICDM in the MO approximation (63) is denoted by \( \pi^o_k \). Then,

\[ \pi^o_k = R^o_k = 2 \rho^o. \]  

(64)

It is convenient to employ the shorthand notation

\[ X(1) Y(2) \cdots Z(k) = X |Y| \cdots |Z| \]  

(65)

The following known formula [2] can be obtained from Eq. (63):

\[ R^o_k = 2(2 - P_{12}) \rho^o |\rho^o| \]  

(66)

giving 2-ICDM

\[ \pi^o_2 = -P_{12} \rho^o |\rho^o| = \frac{1}{2} P_{12} \rho^o |\rho^o|. \]  

(67)

Similarly, the three-electron case of Eq. (63)

\[ R^o_k = [8 - 4(P_{12} + P_{13} + P_{23}) + 2P_{12}(P_{13} + P_{23})] \rho^o |\rho^o| |\rho^o| \]  

(68)

A general relation is obtained from Eq. (63) by retaining in the formula the linked component that occurs in (63) due to \( \hat{P}^{(k-1)} \):

\[ \pi^o_k = (-1)^k 2^{k-1} \hat{P}^{(k-1)} \rho^o |\rho^o| |\rho^o|. \]  

(69)

One of the possible representations for \( \hat{P}^{(k-1)} \) is of the form

\[ \hat{P}^{(k-1)} = \{P_{12} P_{23} \cdots P_{k-1 k}\}_{\text{symm}(1,2,3,\ldots,k)}, \]  

(70)

where \( \text{symm}(1,2,3,\ldots,k) \) symmetrizes the set \( \{1,2,3,\ldots,k\} \) over all \( (k-1)! \) permutations. The normalization condition (16) for \( \pi^o_k \) follows immediately from Eq. (69) by use of the reduction rule (26) and idempotency of \( \rho^o \). Analogously, Eq. (13) can be derived directly for ICDMs (69). The derivation may be viewed as a general proof of (13), since interrelations of that kind are universal and cannot depend on a specific choice of wave function.

Equation (64) gives the following MO approximation for 4-ICDM:

\[ \pi^o_4 = -2^{-3} \hat{P}^{(3)} \rho^o |\rho^o| \rho^o |\rho^o| \]  

(71)

\[ P_{12}^{(4)} = P_{12} \{P_{13} + P_{23} + P_{14} + P_{24}\} P_{34} + P_{14} P_{23} + P_{13} P_{24}. \]  

(72)
The main cases of \( k \)-ICDM in the MO approximation are:

\[
\pi^i_{\langle \mu, \nu \rangle} = -2^{-1}(\pi^i_{\mu \nu})^2, \quad (72)
\]

\[
\pi^\sigma_{\langle \mu, \nu, \rho \rangle} = 2^{-1}\pi^i_{\mu \nu} \pi^\sigma_{\nu \rho} \pi^i_{\rho \mu}, \quad (73)
\]

\[
\pi^\sigma_{\langle \mu, \nu, \rho, \sigma \rangle} = -2^{-2}[\{\mu, \nu, \rho, \sigma\} + [\mu, \nu, \sigma, \rho]
+ [\mu, \rho, \nu, \sigma]], \quad (74)
\]

\[
[\mu, \nu, \rho, \sigma] = \pi^i_{\nu \mu} \pi^\sigma_{\nu \rho} \pi^i_{\rho \mu}. \quad (75)
\]

The expressions for the bond indices (53) and (54) that follow from Eqs. (72) and (73) are the same as in the previous MO theory studies [26–29]. The four-center bond indices require additional remarks. While Refs. [31, 37] use chain formulas of the type (75), such expressions cannot be strictly derived from the four-order fluctuation directly as suggested in Ref. [31], but only through irreducible moments (cumulants). The correctly inferred MO four-center bond index given in the cited papers is excellent guesswork. It is, however, very difficult to guess correctly in models that are more complex than the Hartree–Fock scheme.

The strongly orthogonal group functions introduced by McWeeny [2] form an important special case. Consider a system composed of subsystems I and II. Then, in the one-determinant approximation

\[
\rho^i = \rho^i_1 + \rho^i_2 \quad (76)
\]

\[
\rho^i_1 \rho^i_2 = 0. \quad (77)
\]

The last condition reflects the strong orthogonality of the subsystems. Substitution of Eq. (76) into Eq. (66) gives a representation for \( \pi^{1+2}_{2} \), which determines 2-ICDM of the whole I + II system. In general, beyond a single-determinant scheme,

\[
\pi^{1+2}_{2} = \pi^i_{2} + \pi^i_{2} - \frac{1}{2} P_{12}(\pi^i_{1} \pi^i_{2} + \pi^i_{1} \pi^i_{2}), \quad (78)
\]

which is valid for any wave function constructed with two strongly orthogonal group functions. The general proof of Eq. (78) is provided in Ref. [2] using RDMs. Equation (78) is an asymptotic representation of 2-ICDM describing dissociation of a molecule into two singlet subsystems.

### 4.2. CIS and SF-CIS

Configuration interaction with single excitations (CIS) is widely used as a simple theory of excited states [68]. The recent spin-flip (SF) CIS [69, 70] describes simple quasi-degenerate electronic states and is considered here along with the usual CIS. The current presentation rather closely follows that of Refs. [30, 59].

Starting with a single-determinate ground-state reference state-vector \( |\Phi\rangle \), the CIS state-vector is expressed as

\[
|\Psi^{\text{CIS}}\rangle = \sum_{i \in \pi \subseteq N} \tau(i)|\Phi\rangle, \quad (79)
\]

where the excitation operator \( \tau \) has the form

\[
\tau = \sum_{i \in \pi \subseteq N} \tau_{\pi} |\varphi_i\rangle \langle \varphi_i|, \quad (80)
\]

In the conventional notation, \( |\varphi_i\rangle \) and \( |\varphi_o\rangle \) are the occupied and vacant spin-MOs, respectively. The configuration coefficient \( \tau_{\pi} \) is normalized to 1. In these terms, the RDMs for (79) are cast in the form

\[
\rho_{\pi}^{\text{CIS}} = \rho_{\pi}^{\Phi} + A_{\Delta}(\rho(2) \cdot \rho(k))
+ k(k-1)\tau(1)\tau(2)\rho(3) \cdot \rho(k)]A_{\Delta}
\Delta = [\tau, \tau^T]. \quad (81)
\]

In particular,

\[
\rho_{\pi}^{\text{CIS}} = \rho + \Delta, \quad (82)
\]

\[
\rho_{\pi}^{\text{CIS}} = \rho_{\pi}^{\Phi} + A_{\Delta}(\rho(2) + \rho(1)\Delta(2)
+ \tau(1)\tau(2) + \tau(1)\tau(2)]. \quad (83)
\]

The charge 2-RDM calculated from Eq. (83) coincides with the expression given in Ref. [71], as expected.

Excitations from singlet ground states to singlet \((s = 0)\) and triplet \((s = 1)\) excited states are described with the following excitation operators:

\[
s = 0: \quad \tau = \tau'(|\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta|)/\sqrt{2},
\]

\[
s = 1: \quad \tau = \tau'(|\alpha\rangle\langle\alpha| - |\beta\rangle\langle\beta|)/\sqrt{2},
\]

where the spin-free operator \( \tau' \) is normalized to 1. With the above formulas the two-center bond indi-
ces are computed via (60) by application of the following CIS relationships derived from Eq. (83):

$$\pi_{\langle \mu \nu \rangle}^{\text{CIS}} = \pi_{\langle \mu \nu \rangle}^\alpha + \Delta \pi_{\langle \mu \nu \rangle}^\text{r}$$

(84)

$$\Delta \pi_{\langle \mu \nu \rangle} = 4(1 - s)\tau_{\mu \nu}^\alpha + \Delta_{\mu \nu}^\alpha \Delta_{\nu \nu}^\alpha + \Delta_{\nu \nu}^\alpha \Delta_{\nu \nu}^\text{r}$$

(85)

$$l_{\mu \nu} = (\tau_{\mu \nu}^\alpha)^2.$$ (86)

Here, the conventional AO representation for the spin-free matrices is used. In particular,

$$\tau^\alpha = ||\tau_{\mu \nu}^\alpha||, \quad \tau_{\nu \nu}^\alpha = \langle \chi_{\nu} | \tau^\alpha | \chi_{\nu} \rangle,$$

and

$$\Delta^\alpha = [\tau^\alpha, (\tau^\alpha)^T].$$

Equation (86) defines the charge transfer orbital indices used below in Section 5.4. Similarly, the high-order indices may be produced from Eq. (78), but the results are too cumbersome to be given here.

We now proceed to study the SF-CIS model [69, 70]. This approximation can be viewed as an important case of a general approach proposed in Ref. [72] and based on the many-electron SF operators generating a given molecular spin state from a high-spin reference determinant. Following Refs. [72, 73] consider the matrix formulation of SF-CIS, cf. Eq. (79),

$$\Psi_{(s)}^{\text{SF-CIS}} = \sum_{i \in \mathbb{N}} \tau(i) |\Phi_{(s+1)}\rangle,$$ (87)

where subscripts (s) and (s + 1) refer to the spin projection values of the states under study. The excitation operator takes the form

$$\tau = t|\beta\rangle\langle\alpha|.$$ (88)

To ensure representability of operator (88) in the form (80), the spin-free matrix t should satisfy the condition

$$t = (1 - \rho^\beta)t \rho^\alpha,$$ (89)

$$\rho^\alpha, \rho^\beta$$ being the usual spin-free components in the representation

$$\rho = \rho^\alpha |\alpha\rangle\langle\alpha| + \rho^\beta |\beta\rangle\langle\beta|$$ (90)

that is valid for \( s \neq 0 \). Computation of \( \pi^\alpha \) for the state-vector (87) using the general formulas (80) and (81) gives

$$\pi_{\langle \mu \nu \rangle}^{\text{SF-CIS}} = \pi_{\langle \mu \nu \rangle}^{\text{ROHF}} + \Delta \pi_{\langle \mu \nu \rangle}^\text{r}$$

(91)

$$\pi_{\langle \mu \nu \rangle}^{\text{ROHF}} = -[(\rho_{\mu \nu}^\alpha)^2 + (\rho_{\mu \nu}^\beta)^2]$$

(92)

$$\Delta \pi_{\langle \mu \nu \rangle} = -[(t_{\mu \nu}^\alpha + t_{\mu \nu}^\beta + \Delta_{\mu \nu}^\alpha \Delta_{\nu \nu}^\alpha + 2(\Delta_{\mu \nu}^\alpha \rho_{\mu \nu}^\alpha + \Delta_{\mu \nu}^\beta \rho_{\mu \nu}^\beta)]$$

(93)

where

$$\Delta^\alpha = -tt^T, \quad \Delta^\beta = t^Tt, \quad \Delta^\text{r} = \Delta^\alpha + \Delta^\beta.$$ (94)

Note that at the ROHF level, the \( \alpha \) and \( \beta \) shells contribute simultaneously to the high-order IC-DMs, similarly to Eq. (92).

4.3. FCI

We derive the bond indices at the full CI using the determinant-based method developed in Refs. [74, 75]. The details can be found in review [76]. For simplicity, we consider systems with even numbers of electrons

$$N = 2n,$$

where \( n \) is an integer. Recall that John Pople was among the first developers of the general spin-free formulation of the many-electron theory [77].

The FCI matrix representation used in this section was proposed in Ref. [78] (see also Refs. [30, 79]). The following decomposition of the spin-free wave function holds:

$$|\Psi(1 \ldots 2n)\rangle = \sum_{i,j} X_{ij} |\psi_i(1 \ldots n)\rangle |\psi_j^{\text{full}}\rangle \times (n + 1 \ldots 2n),$$ (95)

where \( |\psi_i(1 \ldots n)\rangle \) is an \( n \)-electron determinant wave function constructed from spin-free orthonormal AOs \( |\chi_{\mu}\rangle \) taken from the list

$$I = \mu_1 < \mu_2 < \ldots < \mu_n.$$ (96)

The expansion coefficients \( X_{ij} \) are treated as the matrix elements of the following wave function operator:
IRREDUCIBLE CHARGE DENSITY MATRIX AND MANY-ELECTRON WAVE FUNCTIONS

\[ X(1 \ldots n) = \|X\|_r \] (97)

which is Hermitian for the even spin states considered below. The correspondence rule

\[ \sum_{1 \leq i \leq 2n} u(i) |\Psi(1 \ldots 2n)\rangle = \left[ \sum_{1 \leq i \leq n} u(i), X(1 \ldots n) \right]_+ \] (98)

is easily verified. Equation (98) leads to the algorithm for calculation of \( \pi_{\text{FCI}}^2 \). Defining the spin-free operators

\[ U_A(1 \ldots n) = \sum_{1 \leq i \leq n} u^A(i), \] (99)

\[ X_A(1 \ldots n) = [U_A(1 \ldots n), X(1 \ldots n)]_+ \] (100)

the FCI electron population on atoms is computed as

\[ \pi_{\text{FCI}}^{(A)} = \text{Tr} \ X_A(1 \ldots n) X(1 \ldots n). \] (101)

The matrix elements of \( U_A \) are obtained via the conventional Slater rules, namely,

\[ (U_A)_{ij} = (U_A)_{\delta_{ij}}, \] (102)

\[ (U_A)_I = \langle \Phi_I(1 \ldots n) | U_A | \Phi_I(1 \ldots n) \rangle = \sum_{i=1}^{n} \sum_{\mu} \delta_{\mu,\mu} \] (103)

Then, the FCI two-center bond indices \( \pi_{\text{FCI}}^{(A,B)} \) are

\[ \pi_{\text{FCI}}^{(A,B)} = 2 \text{Tr} \ U_A(1 \ldots n) X_B(1 \ldots n) - \pi_{\text{FCI}}^{(A)} \pi_{\text{FCI}}^{(B)}, \] (104)

The scheme calculates the two-center indices as cumulants (49) related to Eq. (10). By the same token, the FCI three-center bond indices \( \pi_{\text{FCI}}^{(A,B,C)} \) are calculated from Eqs. (7) and (50):

\[ \pi_{\text{FCI}}^{(A,B,C)} = 2 \text{Tr} \ U_A(1 \ldots n) X_B(1 \ldots n) X_C(1 \ldots n) \]

\[ - \pi_{\text{FCI}}^{(A)} \pi_{\text{FCI}}^{(B)} \pi_{\text{FCI}}^{(C)} - \pi_{\text{FCI}}^{(A,B)} \pi_{\text{FCI}}^{(C)} - \pi_{\text{FCI}}^{(A,C)} \pi_{\text{FCI}}^{(B)} - \pi_{\text{FCI}}^{(B,C)} \pi_{\text{FCI}}^{(A)} \]

\[ - \pi_{\text{FCI}}^{(A)} \pi_{\text{FCI}}^{(B,C)} - \pi_{\text{FCI}}^{(A,B)} \pi_{\text{FCI}}^{(C)} - \pi_{\text{FCI}}^{(A,C)} \pi_{\text{FCI}}^{(B)} - \pi_{\text{FCI}}^{(B,C)} \pi_{\text{FCI}}^{(A)} \] (105)

The corresponding expressions for the four-center indices have the form

\[ \pi_{\text{FCI}}^{(A,B,C,D)} = 2 \text{Tr} \ U_A(1 \ldots n) X_B(1 \ldots n) \]

\[ \times [U_C(1 \ldots n), X_D(1 \ldots n)]_+ - \{\pi_{\text{FCI}}^{(A,B,C,D)}\}_{\text{symm}}^{} \]

\[ - \{\pi_{\text{FCI}}^{(A,B,C)}\}_{\text{symm}}^{} - \{\pi_{\text{FCI}}^{(A,B,D)}\}_{\text{symm}}^{} - \{\pi_{\text{FCI}}^{(A,C,D)}\}_{\text{symm}}^{} - \{\pi_{\text{FCI}}^{(B,C,D)}\}_{\text{symm}}^{} \] (106)

With minor modifications, the above relations can be used for complete active space self-consistent field (CASSCF) as well.

An analogous calculation of bond indices as cumulants may be carried out directly for arbitrary wave functions. For instance, the calculation of \( \pi_{\text{FCI}}^{(A)} \) and \( \pi_{\text{FCI}}^{(A,B)} \) requires only a redefinition of the one- and two-electron Hamiltonian matrix elements \( \hat{h}_{\mu \nu} \) and \( g_{\mu \nu \rho \sigma} \), respectively, in an orthonormal AO basis. Namely,

\[ h(1) = \|h_{\mu \nu}\| \rightarrow u^A(1) = \|u^A_{\mu \nu}\|, \] (107)

\[ g(12) = \|g_{\mu \nu \rho \sigma}\| \rightarrow u^{AB}(12) = \|u^{AB}_{\mu \nu \rho \sigma}\|, \] (108)

where

\[ u^A_{\mu \nu} = \delta_{\mu,\nu} \sum_{\alpha} u^A_{\alpha \mu} \] (109)

\[ u^{AB}_{\mu \nu \rho \sigma} = u^A_{\mu \rho} u^B_{\nu \sigma} + u^B_{\mu \rho} u^A_{\nu \sigma}. \] (110)

Then

\[ \pi_{\text{FCI}}^{(A)} = \left\langle \Psi \sum_{1 \leq i \leq N} u^A(i) \right\rangle \Psi \right\rangle, \] (111)

\[ \pi_{\text{FCI}}^{(A,B)} = \left\langle \Psi \sum_{1 \leq i < j \leq N} u^{AB}(ij) \right\rangle \Psi \right\rangle - \pi_{\text{FCI}}^{(A)} \pi_{\text{FCI}}^{(B)}. \] (112)

Equations (111) and (112) can easily be used to compute the needed combination of the 1-RDM and 2-RDM directly with the existing quantum chemistry codes. In addition to MO, CIS, and FCI, we applied the method based on Eqs. (107)–(112) to the conventional CID and CISD models, where the use
of the explicit formulae for the corresponding RDMs leads to more cumbersome algorithms.

5. Numerical Results and Discussion

5.1. Technical Details

The multicenter bond indices (53), (54), and (58) were computed for singlet molecular ground states, unless explicitly stated otherwise. In addition to the bond index, the realized atomic valence was calculated according to the definition

$$ V_A = \sum_{B} \kappa_{ABr} $$

(113)
given in the original papers considering quantum chemical description of atomic valences in molecules [80, 81]. In all cases, the bond index generators (33) were constructed using the local projectors (31) onto Löwdin’s orthonormal AO basis set.

Small molecules and atomic clusters were investigated in the standard 6-31G basis, and only the Li4 and Li5 clusters were studied in the minimal s-AO basis taken from the STO-6G basis set. The modest basis sets were used for numerical illustrations and elucidation of the electron correlation effects on the \( \kappa_{ABr} \), \( \kappa_{ABCD} \) indices. For this purpose, it was essential to apply FCI, which is computationally very expensive and limited to modest basis sets. The \( \pi \)-electron systems were investigated with the semi-empirical Pariser–Parr–Pople (PPP) approach (see Ref. [23]), yet another tribute to John Pople. Apart from geometry optimization, all electronic structure calculations were performed with a code written in Mathematica-5 [82].

Molecular geometries for the ab initio calculations were taken from Refs. [83, 84]. The geometries not available in [83, 84] were optimized with MP2/6-31G(d, p) using GAMESS [85]. The neutral H4 and H6 clusters were studied in the model geometry where all H—H bond lengths were equal to 1 Å. The atoms in the linear H4 and H6 clusters are numbered sequentially starting from the terminal atoms. The numbering of atoms in the more complicated systems is listed below. Namely, for atomic clusters,

5.2. Two-Center Bond Indices and Realized Atomic Valences

First, consider the multicenter bond indices for a series of simple hydrides obtained by several quantum chemical approaches (Table I). The calculations show that electron correlation systematically de-

<table>
<thead>
<tr>
<th>Molecule</th>
<th>RHF</th>
<th>CID</th>
<th>CISD</th>
<th>FCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.805</td>
<td>0.751</td>
<td>0.706</td>
<td>0.706</td>
</tr>
<tr>
<td>LiH</td>
<td>0.980</td>
<td>0.794</td>
<td>0.783</td>
<td>0.783</td>
</tr>
<tr>
<td>BH</td>
<td>1.032</td>
<td>0.901</td>
<td>0.898</td>
<td>0.883</td>
</tr>
<tr>
<td>BeH2</td>
<td>0.995</td>
<td>0.851</td>
<td>0.852</td>
<td>0.864</td>
</tr>
<tr>
<td>HF</td>
<td>0.888</td>
<td>0.797</td>
<td>0.804</td>
<td>0.798</td>
</tr>
<tr>
<td>CH2</td>
<td>1.015</td>
<td>0.875</td>
<td>0.873</td>
<td>0.857</td>
</tr>
<tr>
<td>H2O</td>
<td>0.929</td>
<td>0.815</td>
<td>0.816</td>
<td>—</td>
</tr>
</tbody>
</table>
increases the magnitudes of the bond indices, in some contrast to the literature data [29, 38], as discussed in more detail in Section 5.3. It is our general experience that proper treatment of electron correlation results in substantially smaller atomic valences \( V_A \) in molecular ground states compared with the atomic valences derived from the traditional chemical structure formulas. At the same time, the values of the \( V_A \) index computed at the RHF MO level are very close to the chemical valences of atoms, implying that the MO approach prescribes weak free atomic valences in contradiction to the experimentally observed chemical activities. Incorporation of electron correlation lifts the contradiction between experiment and theory. Even the simple CID is adequate for most systems, including the highly nontrivial singlet methylene. Further data illustrating the point are presented in Table II, which shows only the CID and CISD results, due to computational limitations. Our data should be compared with the CISD data obtained in Ref. [36] for the \( \text{N}_2 \), \( \text{F}_2 \), and \( \text{CO} \) molecules in a different basis and with a somewhat different bond index methodology, the so-called delocalization index \( \delta(AB) \), Table I, in Ref. [36]. The two sets of data are qualitatively very similar. Note that the CO bond index is small in both Ref. [36] and our calculations, although the \( \text{CO} \) and \( \text{N}_2 \) molecules are isoelectronic and may be expected to have similar bond indices.

The insertion reaction

\[
\text{Be} + \text{H}_2 \rightarrow \text{BeH}_2, \quad (114)
\]

presents an instructive example studied theoretically in a number of works, including [86, 87]. We use the reaction path developed in these references:

![Insertion Reaction Diagram](image)

The values of the \( \{y, R\} \) coordinates of the H atom along the reaction path are given in Table III, which shows that the decrease of the atomic valence due to electron correlation is particularly pronounced in the transition state (TS) region, points E and F. Naturally, near TS the MO approach fails, prescribing the hydrogen atom the values of the atomic valence that are close to 1, even in points E and F.

Metal clusters remain a nontrivial class of systems of active and continuous theoretical interest [88–92]. The simpler clusters consisting of \( \text{Li} \) and \( \text{H} \) atoms are presented in Table IV. In particular, note the \( \text{Li}_4 \) and \( \text{Li}_5 \) systems, where RHF gives a very rough description of bond orders, overestimating the valences of the weakly bound atoms by more than a factor of 2. The importance of the electron correlation effects in these systems is also indicated.

### TABLE II

<table>
<thead>
<tr>
<th>Molecule</th>
<th>RHF</th>
<th>CID</th>
<th>CISD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_2)</td>
<td>1.027</td>
<td>0.932</td>
<td>0.927</td>
</tr>
<tr>
<td>C(_2)</td>
<td>3.767</td>
<td>2.523</td>
<td>2.526</td>
</tr>
<tr>
<td>N(_2)</td>
<td>3.325</td>
<td>2.518</td>
<td>2.509</td>
</tr>
<tr>
<td>F(_2)</td>
<td>1.151</td>
<td>0.859</td>
<td>0.858</td>
</tr>
<tr>
<td>BeO</td>
<td>2.214</td>
<td>1.884</td>
<td>1.885</td>
</tr>
<tr>
<td>CO</td>
<td>2.869</td>
<td>2.234</td>
<td>2.242</td>
</tr>
</tbody>
</table>

### TABLE III

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Coordinates ((y, R)) (au)</th>
<th>(-E(\text{FCI}))</th>
<th>(\kappa_{\text{HH}})</th>
<th>(V_{\text{HH}})</th>
<th>(V_{\text{Be}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15.800544</td>
<td>0.014</td>
<td>1.010</td>
<td>1.991</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.766034</td>
<td>0.016</td>
<td>1.013</td>
<td>1.993</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.703556</td>
<td>0.010</td>
<td>1.008</td>
<td>1.966</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.652296</td>
<td>0.024</td>
<td>1.005</td>
<td>1.961</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.628593</td>
<td>0.054</td>
<td>1.003</td>
<td>1.888</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.637680</td>
<td>0.667</td>
<td>0.978</td>
<td>0.622</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.698434</td>
<td>0.893</td>
<td>1.000</td>
<td>0.413</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.739975</td>
<td>0.889</td>
<td>1.009</td>
<td>0.241</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.763325</td>
<td>0.983</td>
<td>1.001</td>
<td>0.040</td>
</tr>
</tbody>
</table>
by the invariant collectivity index $\kappa$ that characterizes the importance of configuration interaction [30, 60]. For reference, $\kappa = 1$ in the MO approach, $\kappa = 2$ in the two-determinant approximation for open-shell singlet states, and so on. We find that for Li$_4$ in the minimal basis the FCI approach gives 1.49. In comparison, the FCI $\kappa$-value for Li$_2$ is 1.15, which is much closer to the MO value of 1.

The $\pi$-electron systems presented in Table V exhibit similar features. Our focus is on alternant hydrocarbons, whose properties in the MO approximation have been investigated in many details starting from the classic work of Coulson using the Hückel approach [62]. One of the important contributions of John Pople to the problem was to show that the pairing theorem is valid in the PPP approximation [21]. As a corollary to John Pople’s result, the $\pi$-valences of all atoms $\mu$ of a neutral alternant hydrocarbon in the MO approach are the same and equal:

$$V_{\mu}^{\text{RHF}} = 1.$$  \hspace{1cm} (115)

In other words, the atomic valence indices predict that the $\pi$-bonds of any alternant system are saturated in the MO approach (see also Ref. [80]). We find that incorporation of electron correlation eliminates this inconsistency, resulting in a non-trivial distribution of the $\pi$-valence indices (Table V). The rule (115) does not apply to $\pi$-ions. Even in this case, though, the FCI values of $\pi$-valences are clearly smaller than the RHF values, Table VI.

### TABLE IV
Atomic valence indices for atomic clusters.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atom ($\mu$)</th>
<th>$V_{\mu}^{\text{RHF}}$</th>
<th>$V_{\mu}^{\text{FCI}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$ ($D_3h$)</td>
<td>1</td>
<td>0.762</td>
<td>0.715</td>
</tr>
<tr>
<td>H$_5$ ($C_2v$)</td>
<td>1</td>
<td>0.921</td>
<td>0.819</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.933</td>
<td>0.795</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.995</td>
<td>0.823</td>
</tr>
<tr>
<td>H$_6$ ($D_6h$)</td>
<td>1</td>
<td>—</td>
<td>0.528</td>
</tr>
<tr>
<td>H$_8$ ($D_8h$)</td>
<td>1</td>
<td>1.000</td>
<td>0.710</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.000</td>
<td>0.820</td>
</tr>
<tr>
<td>H$_9$ ($D_9h$)</td>
<td>1</td>
<td>1.005</td>
<td>0.851</td>
</tr>
<tr>
<td>Li$_2$ ($D_2h$)</td>
<td>1</td>
<td>0.899</td>
<td>0.593</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.899</td>
<td>0.416</td>
</tr>
<tr>
<td>Li$<em>3$ ($D</em>{3h}$)</td>
<td>1</td>
<td>0.784</td>
<td>0.637</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.961</td>
<td>0.332</td>
</tr>
</tbody>
</table>

### TABLE V
Atomic $\pi$-valence indices for neutral alternant hydrocarbons in the FCI/PPP scheme.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Carbon atom ($\mu$)</th>
<th>$V_{\mu}^{\text{FCI}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butadiene</td>
<td>1</td>
<td>0.622</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.725</td>
</tr>
<tr>
<td>Cyclobutadiene</td>
<td>1</td>
<td>0.483</td>
</tr>
<tr>
<td>Cyclobutadiene (Möbius)</td>
<td>1</td>
<td>0.824</td>
</tr>
<tr>
<td>Hexatriene</td>
<td>1</td>
<td>0.615</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.735</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.710</td>
</tr>
<tr>
<td>Benzene</td>
<td>1</td>
<td>0.811</td>
</tr>
<tr>
<td>Benzene (Möbius)</td>
<td>1</td>
<td>0.607</td>
</tr>
<tr>
<td>Decapentaene</td>
<td>1</td>
<td>0.611</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.740</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.706</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.728</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.722</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1</td>
<td>0.788</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.874</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.805</td>
</tr>
<tr>
<td>Diphenylene</td>
<td>1</td>
<td>0.808</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.805</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.822</td>
</tr>
</tbody>
</table>

* See text for atom numbering.

### TABLE VI
Atomic $\pi$-valence indices for alternant hydrocarbon ions in the RHF/PPP and FCI/PPP schemes.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Carbon atom ($\mu$)</th>
<th>$V_{\mu}^{\text{RHF}}$</th>
<th>$V_{\mu}^{\text{FCI}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$H$_5^-$</td>
<td>1</td>
<td>0.840</td>
<td>0.638</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.991</td>
<td>0.836</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.849</td>
<td>0.796</td>
</tr>
<tr>
<td>C$_7$H$_7^-$</td>
<td>1</td>
<td>0.898</td>
<td>0.644</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.992</td>
<td>0.836</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.896</td>
<td>0.809</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.988</td>
<td>0.878</td>
</tr>
<tr>
<td>Naphthalene$^{2+}$</td>
<td>1</td>
<td>0.830</td>
<td>0.706</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.977</td>
<td>0.792</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.983</td>
<td>0.898</td>
</tr>
</tbody>
</table>
tigate the effects of electron correlation on $\kappa_{ABC}$ as reviewed, for instance, in Ref. [37]. The approaches cited in Ref. [37] are approximate and do not compute, explicitly or implicitly, correlators (50) or their analogues invoking 3-RDMs. Perhaps for this reason, only minor electron correlation effects were detected, Table IV of Ref. [38]. The density functional theory (DFT) results reported in Table III of Ref. [38] remain open to the extent that the high-order RDMs are not clearly defined within the DFT theory. More rigorously defined three-center bond indices were suggested recently [93]. This section presents the results of the FCI calculations for the three- and four-center bond indices.

First, consider $H_3^+$ that is the simplest three-center system. The basic symmetry and idempotency of $\rho_{cc}$ in the minimal basis immediately give $\kappa_{123}^{\text{RHF}} = 4/9$ [32]. This MO value is decreased by nearly a factor of 2 with inclusion of the electron correlation effects in a realistic 6-31G basis (Table VII). Electron correlation is even stronger in the $Li_4$ cluster, in contrast to the RHF results.

Analysis of the insertion reaction (114) in terms of the three-center bond indices gives quite interesting results (Table VIII). The indices are maximized near, but not at the TS, although the largest charge transfer is observed exactly at the TS saddle point. As before, RHF overestimates all these effects, but gives a qualitatively correct picture with deep changes in the electronic structure near the TS region and unusually large values of the three-center indices.

The $\pi$-electron systems of neutral alternant hydrocarbons obey the selection rule ($A < B < C$):

$$\kappa_{ABC} = 0,$$

which holds in any proper approximation, including $\pi$-FCI. Characteristic results for $\pi$-electron ions are presented in Table IX.

Consider the four-center indices of the $\pi$-systems. Butadiene, the simplest four-center $\pi$-electron

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$ABC$</th>
<th>$\kappa_{ABC}^{\text{RHF}}$</th>
<th>$\kappa_{ABC}^{\text{FCI}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_3^+$</td>
<td>123</td>
<td>0.444</td>
<td>0.255</td>
</tr>
<tr>
<td>$H_4^+$</td>
<td>123</td>
<td>0.397</td>
<td>0.221</td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>−0.040</td>
<td>−0.030</td>
</tr>
<tr>
<td></td>
<td>145</td>
<td>0.161</td>
<td>0.113</td>
</tr>
<tr>
<td></td>
<td>234</td>
<td>0.024</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>245</td>
<td>0.030</td>
<td>0.019</td>
</tr>
<tr>
<td>$Li_4^+$</td>
<td>123</td>
<td>10^{-4}</td>
<td>0.0</td>
</tr>
<tr>
<td>$Li_4^-$</td>
<td>123</td>
<td>0.005</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>−0.030</td>
<td>0.005</td>
</tr>
<tr>
<td>$Li_5^+$</td>
<td>123</td>
<td>0.222</td>
<td>0.086</td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>−0.222</td>
<td>−0.039</td>
</tr>
<tr>
<td>$C_6H_5^+$</td>
<td>123</td>
<td>0.230</td>
<td>0.043</td>
</tr>
<tr>
<td></td>
<td>145</td>
<td>−0.127</td>
<td>−0.019</td>
</tr>
<tr>
<td></td>
<td>234</td>
<td>0.085</td>
<td>0.042</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$ABC$</th>
<th>$\kappa_{ABC}^{\text{RHF}}$</th>
<th>$\kappa_{ABC}^{\text{FCI}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_5^-$</td>
<td>123</td>
<td>0.223</td>
<td>0.104</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>0.054</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>134</td>
<td>−0.053</td>
<td>−0.040</td>
</tr>
<tr>
<td></td>
<td>135</td>
<td>−0.040</td>
<td>−0.017</td>
</tr>
<tr>
<td></td>
<td>234</td>
<td>−0.032</td>
<td>0.008</td>
</tr>
<tr>
<td>$C_7H_7^+$</td>
<td>123</td>
<td>0.170</td>
<td>0.090</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>0.0037</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>134</td>
<td>−0.063</td>
<td>−0.027</td>
</tr>
<tr>
<td></td>
<td>145</td>
<td>0.046</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>234</td>
<td>−0.035</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>235</td>
<td>−0.031</td>
<td>−0.029</td>
</tr>
<tr>
<td></td>
<td>345</td>
<td>0.181</td>
<td>0.071</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Geometrya</th>
<th>Charge transferb</th>
<th>$\kappa_{HBeH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.135 0.100</td>
<td>0.015 0.012</td>
</tr>
<tr>
<td>B</td>
<td>0.141 0.103</td>
<td>0.019 0.020</td>
</tr>
<tr>
<td>C</td>
<td>0.108 0.069</td>
<td>0.010 0.024</td>
</tr>
<tr>
<td>D</td>
<td>0.077 0.024</td>
<td>0.003 0.003</td>
</tr>
<tr>
<td>E</td>
<td>0.052 −0.091</td>
<td>−0.001 0.015</td>
</tr>
<tr>
<td>F</td>
<td>−0.355 −0.281</td>
<td>0.367 0.116</td>
</tr>
<tr>
<td>G</td>
<td>−0.207 −0.193</td>
<td>0.261 0.152</td>
</tr>
<tr>
<td>H</td>
<td>−0.102 −0.099</td>
<td>0.153 0.109</td>
</tr>
<tr>
<td>I</td>
<td>−0.014 −0.014</td>
<td>0.025 0.019</td>
</tr>
</tbody>
</table>

a See Table III.

b Charge transfer is quantified by the Löwdin net charge value $q_{\text{net}}$.
The four-indices in the MO approximation exhibit the typical behavior of the four-indices already at the RHF level. The four-indices take on negative values for any four strongly interacting, usually nearest-neighbor, atoms in a molecule. For instance, using the known \( \pi \)-electron bond orders in butadiene [94], we find

\[
\kappa_{1234}^{\text{RHF}} = -(\pi_{12}^2)^2 \left( 1 - (\pi_{12}^2)^2 \right) \leq 0, \quad (117)
\]

where \( \pi_{12}^2 \) is the \( \pi \)-electron order of the first and third bonds in the butadiene molecule. In addition, it is easy to prove for neutral alternant hydrocarbons that the four-indices in the MO approximation obey

\[
\kappa_{1234}^{\text{RHF}} = 0 \quad (118)
\]

in the cases where the numbers of atoms in the \( \{A, B, C, D\} \) set from each of the two alternant, starred and not-starred subsystems are not equal. \( \pi \)-electron correlation introduces substantial corrections. The (118) rule does not hold. Weak interactions become stronger, while strong interactions weaken. All these features are illustrated by the calculated data presented in Table X. Note the Möbius \( \pi \)-system of cyclobutadiene, which models the TS of an electrocyclic reaction [95]. In this case, the value of the four-index is particularly great, indicating a very large change in the electronic structure of the reaction system around the TS region.

The atomic clusters behave similarly to the isovalent \( \pi \)-electron systems (Table XI). The four-center index is negative for any four closely located atoms. The correlation effects are also quite pronounced with the atomic clusters, particularly for Li4 and H6.

It is worth noting that an alternative description of the four-center interactions exists in the literature. The so-called covariant analysis was developed in Ref. [34] at the RHF level. The technique developed in Section 4 of the present work can be adjusted for the covariant analysis, although this task extends beyond the scope of this discussion.

### 5.4. ANALYSIS OF EXCITED STATES

A number of works are devoted to illustration and interpretation of molecular excited states, for instance [24, 96–101]. Here, we discuss the utility of the bond index approach in describing the distribution of excitation over individual atoms in molecules. First, consider the results of the FCI/6-31G calculations for the low lying excited states of the BeH2 molecule. Table XII shows the excitation induced changes in atomic valences

\[
\Delta V_A = V_A \text{ (excited state)} - V_A \text{ (ground state)},
\]

and atomic charges

\[
\Delta q_A = \pi_{(A)} \text{ (excited state)} - \pi_{(A)} \text{ (ground state)}.
\]
TABLE XII

| Electronic structure of BeH₂ low-energy excited states within the CIS and FCI schemes. |
|---------------------------------|-----------------|---------------|---------------|---------------|---------------|---------------|
| Excited state | Method | λ_{exc} (in eV) | ∆q_{Be} | ∆V_{Be} | ∆V_{H} | κ_{BeH} | κ_{HBeH} |
| ¹Π_g  | CIS  | 7.24 | -0.503 | -0.500 | -0.099 | 0.165 | 0.215 |
| ¹Π_u  | CIS  | 9.52 | -0.559 | -0.486 | -0.125 | 0.133 | 0.193 |
| ¹Σ_u⁺  | CIS  | 11.77 | -0.094 | -0.926 | 0.224 | 0.711 | 0.048 |
| ¹Σ_u⁻  | CIS  | 11.32 | -0.046 | -0.660 | 0.171 | 0.522 | 0.030 |
|                    | FCI  |              |          |          |          |          |          |
|                    | FCI  |              |          |          |          |          |          |

*Geometry of ground and excited states corresponds to point A in Table III.*

The calculations show no simple correlation between the magnitude of the excitation induced charge transfer (CT) and the change in the atomic valences. For instance with the ¹Σ_u⁻ term, the valence index of the Be atom drops considerably and the valence indices of the H atoms increase, while the charge distribution remains nearly the same as in the ground state. Also note the anomalous increase in the κ_{BeH} bond index. At the same time, the considerable amount of CT induced by the excitation correlates with a substantial growth of the κ_{HBeH} three-center index. It is not accidental that these observations resemble the properties of the TS region for the insertion reaction (114) considered above. As shown in Table XII, CIS qualitatively reproduces the FCI data, although in a relatively rough form.

Table XIII presents the atomic excitation index L_{A}^{CIS} computed at the CIS level. The atomic excitation index gives an alternative account of localization of electronic excitation. It was originally introduced within our covariant approach [99, 100] and was often used in the past; see for instance [100, 102, 103]. L_{A}^{CIS} can be expressed directly in terms of the orbital CT indices defined by Eq. (87), namely,

\[
L_{A}^{CIS} = \frac{1}{2} \sum_{\mu} \sum_{\nu} (l_{\mu-\nu} + l_{\nu-\mu}),
\]

\[
\sum_{A} L_{A}^{CIS} = 1. \quad (121)
\]

In addition, the following representation

\[
q_{A}^{CIS} = \sum_{B} (l_{A-B}^{CIS} - l_{B-A}^{CIS}), \quad (122)
\]

holds true for ∆q_{A} of Eq. (120). The so-called CT numbers l_{A-B}^{CIS} are defined as

\[
l_{A-B}^{CIS} = \sum_{\mu} \sum_{\nu} l_{\mu-\nu}. \quad (123)
\]

Relationship (122) provides a good justification of the CT number terminology. Reference [103] gives an example of a spectral chemical application of the CT numbers.

The data presented in Table XIII indicate that CT does not systematically correlate with the excitation-induced changes in the three-center index. It may be expected in the cases in which dynamic electron correlation is insignificant that CIS should adequately reproduce changes in the two- and three-center indices. The CIS/6-31G calculations of the lowest nπ* excitations in the small molecules containing the carbonyl group provide one more illustration of the excited state analysis (Table XIV). The CIS model unmistakably reproduces the strong localization of the nπ* excitation on the carbonyl group, accompanied by the corresponding CT from the oxygen to the carbon. The valences of the O and...
C atoms decrease considerably only in the compounds with a single carbonyl group.

6. Concluding Remarks

Within the past 20 years, a whole new direction in quantum chemistry has emerged focusing on the development of the generalized Wiberg indices for the evaluation of two-center bond orders in arbitrary molecular electronic states [20, 26]. At the MO level, the Wiberg approach was powerfully expanded to multicenter bond indices for an arbitrary number of atomic centers [27–29, 32]. With the development came the appreciation for the need in the high-order RDMs [31, 33]. At the same time, a systematic procedure for extracting the relevant components of RDMs for proper analysis of the bond indices was not clearly formulated for a general case. The current investigation presents and clarifies such a procedure, where the relevant RDM components are computed in general, by way of irreducible charge density matrices. These ICDMs emerge simply as particular cases of the well-known Ursell–Mayer distribution functions, whose appearance in the analysis of many-electron systems is quite natural from the viewpoint of general many-particle theory.

The matrix technique version of FCI [78] allowed us to derive a rather simple algorithm shown in Eqs. (99)–(106) for computation of the key bond indices $k_{AB}$, $k_{ABC}$ and $k_{ABCD}$. It is emphasized that the calculation of $k_{AB}$ for a pair of atoms $A$ and $B$ presents the same level of difficulty as a single calculation of the full molecular electronic energy. Hence, the computation of $k_{AB}$ can be easily implemented within any quantum chemical approach with a variational wave function. Nonvariational approaches such as Møller–Plesset PT may run into the problem of non-N-representative RDMs, resulting in practice in violation of the ICDM normalization. For this reason, we did not consider the multicenter bond indices for the nonvariational MP-2 model. The calculations of the $k_{ABC}$ and $k_{ABCD}$ indices for the CID and CISD variational approximations are rather lengthy, although possible. In particular, for the CISD approach, RDM expressions are available at any order [104]. Approximate schemes for the evaluation of the multicenter indices in the CID and CISD models are desirable. It should be kept in mind that the three- and four-center indices computed in the low-order CI ap-

---

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atom (A)(^a)</th>
<th>$V_{A}^{RHF}$</th>
<th>$\Delta V_{A}^{CIS}$</th>
<th>$\Delta q_{A}^{CIS}$</th>
<th>$L_{A}^{CIS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>1</td>
<td>2.380</td>
<td>-0.308</td>
<td>0.502</td>
<td>0.556</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.270</td>
<td>-0.423</td>
<td>-0.595</td>
<td>0.320</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.329</td>
<td>-0.078</td>
<td>0.115</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>10004</td>
<td>-0.029</td>
<td>0.074</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.928</td>
<td>-0.010</td>
<td>0.075</td>
<td>0.004</td>
</tr>
<tr>
<td>Acroleine</td>
<td>1</td>
<td>2.348</td>
<td>-0.207</td>
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<td>0.553</td>
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<tr>
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<td>4.215</td>
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<td></td>
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<td>0.002</td>
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<tr>
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<td>-0.001</td>
<td>0.003</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.005</td>
<td>-0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Glyoxal</td>
<td>1</td>
<td>2.390</td>
<td>0.004</td>
<td>0.134</td>
<td>0.301</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.194</td>
<td>-0.004</td>
<td>-0.188</td>
<td>0.172</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.983</td>
<td>0.020</td>
<td>0.054</td>
<td>0.027</td>
</tr>
</tbody>
</table>

\(^{a}\) See text for atom numbering.
proaches are of a significantly lower accuracy than the two-center indices, since the variational calculation of the electronic energy in the simple versions of CI produces good estimates only for the second-order RDMs. Our analysis of the three-center indices for CIS excited states, as well as MO ground states, emphasizes this issue.

A number of fundamental problems remain in the multicenter index theory. One problem concerns normalization of the multicenter indices, reflected within the ICDM formulation by the normalization conditions (16) and (17). These conditions suggest that all \( N \) electrons are involved in formation of chemical bonds, in contrast to the simple Lewis valence point of view, advocating that the number of active electron pairs cannot be greater than \( N/2 - s \), where \( s \) is total spin. For this reason, we avoided the use of ICDM-derived bond indices in cases with \( s > 0 \). It can be expected that for \( s \geq 0 \), the so far unspecified irreducible densities of the valence electronic shell subsystem will be normalized to the total number of closed-shell electrons \( N - 2s \) rather than \( N \). In Ref. [30], we introduced the relevant component of such two-particle density matrix and established the relationship between the valence spin-pairing indices \( \sigma_{\mu\nu} \) and spin-correlators \( \langle \hat{S}_\mu \cdot \hat{S}_\nu \rangle \). The latter are well known in quantum theory of magnetism and quantum chemistry as Penney–Dirac bond orders [23, 105, 106]. Notably, the spin-pairing indices in the MO approach with \( s = 0 \) are directly related to the Wiberg indices. Specifically with the notation of Eq. (72), \( \sigma^{\text{RHF}}_{\mu\nu} = -\pi_{\mu\nu}^{\text{RHF}} \) [30]. Subsequently, the analogy between \( \sigma_{\mu\nu} \) and \( \langle \hat{S}_\mu \cdot \hat{S}_\nu \rangle \) was independently studied by a number of investigators [107–109], initiating a new direction in the two-center bond index theory. It is desirable to extend the developed methodology to extract irreducible (cumulant) components of spin density matrices at arbitrary order \( k \). As shown in Ref. [59], fundamental difficulties exist for an unambiguous determination of high-order \( (k > 2) \) spin density matrices. Additional work is required to find the many-electron spin distributions suitable for the analysis of many-electron wave functions with non-zero spin.

In conclusion, we would like to stress one more time that quantum chemical description of molecules and molecular processes greatly benefits from a careful and transparent analysis of the many-electron wave function and its relationship to molecular structure. The multicenter bond indices determined in this work provide useful tools for such analysis. Elucidating the relationship between the fine features of the molecular electronic structure reflected by the multicenter indices to the observable physico-chemical characteristics of molecular systems is essential for successful applications of the multicenter indices in chemistry. For example, it is important to understand what aspects of chemical reactivity within a four-atom molecular fragment are reflected in large values of the corresponding four-center bond index. Nontrivial relationships between the magnitudes of the multicenter bond indices and chemical reactivity merit further investigation.

**ACKNOWLEDGMENTS**

O. V. P. is a Camille and Henry Dreyfus New Faculty and an Alfred P. Sloan Fellow. O. V. P. is grateful to Professor Daniel Borgis at the Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, Paris, France, for hospitality during manuscript preparation.

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