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Information-Scattering Perspective on Orbital Hybridization

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Within the communication theory of the chemical bond, the transformation of atomic orbitals (AO) into molecular orbitals (MO) generates the information system for the associated electronic promotion of AOs in a molecule. It consists of the two orbital-mixing stages involving AOs and MOs, and one MO-occupation subchannel. The conditional-entropy and mutual-information descriptors of this resultant "communication" system, which measure the average "noise" and the amount of information in the molecular channel, provide novel information-theoretic measures of the system bond covalency and ionicity, respectively. This information-theoretic approach to the *many*-center probability-scattering in AO resolution is now applied to the *one*-center orbital transformations to examine the entropic indices of an effective promotion of the canonical AO in alternative valence states of an atom, identified by different occupations of hybrid orbitals (HO). This phenomenon is first illustrated and tested using the simplest scheme of mixing two atomic orbitals in a generalized sp hybridization. The conditions for the maximum of the AO-promotion covalency are examined, and the shape independence of the orbital channels and their entropy/information desciptors for the equalized probability weights of HO in the specified atomic valence state is commented upon. Entropic indices are then generated for selected valence states of the carbon atom, resulting from different hybridization schemes, in order to characterize their complementary aspects of the system electron polarization (*one*-center ionicity) and electron delocalization (*one*-cenetr covalency). The interpretation of these components as measures of a degree of the accqired *"order"* and surviving *"disorder"* (electron uncertainty) in the valence state is also given. These results are found to generally agree with intuitive expectations. The exact HO-occupation subchannel is derived, which reproduces the average AO occupations in the valence state. This approach is also proposed for the multicenter probability scattering in molecules, via the system occupied MO, in probing the system chemical bonds.

1. Introduction

The information theory (IT)[1−4] has been shown to generate a novel class of the entropy/information descriptors of chemical bonds in molecular systems within the communication-system approach using either atomic[5−16] or orbital[17−20] resolutions of electron probabilities. These molecular information channels generate the adequate entropy/information indices of the system bond covalency and ionicity, the valence numbers of bonded atoms, the overall IT bond multiplicities for both the ground- and excited-state molecular configurations, the molecular-fragment descriptors, and so forth. This IT approach provides an information-scattering (flow) perspective on chemical bonds, which was shown to be in general accord with the chemical intuition and the molecular orbital (MO) description.[9,14,16] The IT description gives a transparent account of the competition between the covalent and ionic bond components, which is also in accord with intuitive chemical expectations.

In this approach, a molecule is interpreted as an information channel of IT[2,4] in which the molecular or "promolecular"[21] electron probabilities are "scattered" *via* the network of chemical bonds connecting the constituent atoms[5−16] or the information system for the effective AO-promotion in the molecule, via the system occupied MO.[17−20] The *conditional entropy* (entropy-covalency) descriptor of such a "communication" network measures its average "noise", which reflects the extra uncertainty in the distribution of the valence electrons due to their delocalization in a molecule. The complementary index, called the *mutual information* (information-ionicity) of the channel input and output probabilities, measures the amount of information flowing through the molecular communication system.

The MO description, against which one ultimately compares the alternative treatments of chemical bonds in molecules and their fragments, generates the standard interpretation of the bond origin and provides useful measures of its multiplicity ("order"), for example, the "quadratic" valence indices.[22−30] This standard perspective usually refers to the AOs of constituent atoms, which form the basis functions for the majority of the quantum mechanical calculations determining the system electronic structure, as the starting point (source) of the bond-formation process. They define the associated "promolecule", consisting of the "frozen" (ground-state) atoms placed in their respective positions in the molecule, which constitutes the standard reference for extracting effects due to the chemical bonds, for example, in the familiar density-difference diagrams and the Hirshfeld[21] partition of the molecular electron density into pieces attributed to bonded atoms. These "stockholder" atoms-in-molecules (AIM) were recently shown to also have a strong basis in IT.[14,31−37]

In view of the importance of this orbital description in the theory of electronic structure, the molecular information channels in AO resolution have been introduced.[17−20] These *many*-center communication systems reflect the bonded-atom promotion due to the presence of the remaining AIM. Indeed, as a

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result of the electron delocalization throughout the system chemical bonds the AO occupations are effectively “promoted” to their effective, fractional values characterizing their valence state in the molecule. In the so-called *physical* channel, the chemical bonds are probed using the information cascade of the AO-probability scattering through the system occupied MO (eq 1)

$$[\mathrm{AO} \rightarrow \mathrm{AO}^*]^{\mathrm{MO}} = [\mathrm{AO} \rightarrow \mathrm{MO}] \rightarrow [\mathrm{MO} \rightarrow \mathrm{MO}^*] \rightarrow [\mathrm{MO}^* \rightarrow \mathrm{AO}^*] \quad (1)$$

It is seen to include the middle subchannel [MO → MO*] of MO occupations (stage 2) in the molecular electron configuration under consideration and the two orbital-mixing subchannels, [AO → MO] (stage 1) and [MO* → AO*] (stage 3). The sequential arrangement of these three elementary information-propagation networks generates the resultant channel [AO → AO*]$^{\mathrm{MO}}$ of the physical promotion of the AO basis in the molecular environment.[18−20] The two subchannels of the orbital transformations involve the conditional probabilities of AO, given MO (stage 3), or of MO, given AO (stage 1), which follow from the quantum-mechanical superposition principle as squares of the relevant expansion coefficients of one (dependent) set of orbitals in terms of the other (independent) set.

The *one*-center orbital-mixing into hybrid orbitals (HO), giving rise to diverse valence states of atoms, must similarly create an extra information noise (covalency) and a diminished amount of information (ionicity) flowing through the associated AO-promotion cascade due to the orbital hybridization:

$$[\mathrm{AO} \rightarrow \mathrm{AO}^*] = [\mathrm{AO} \rightarrow \mathrm{HO}] \rightarrow [\mathrm{HO} \rightarrow \mathrm{HO}^*] \rightarrow [\mathrm{HO}^* \rightarrow \mathrm{AO}^*] \equiv [\mathrm{AO} \rightarrow \mathrm{AO}^*] \quad (2)$$

For example, $N_v = 4$ valence electrons of the carbon atom, giving rise to the overall ground-state electron configuration [$2s^2 2p^2$], may be redistributed in the atom valence state among the hybrid orbitals (HO) resulting from the familiar sp^3, sp^2, or sp schemes. Moreover, for the selected shapes of the directed orbitals such valence states may involve several occupation patterns of HO. The information systems representing the effective AO promotion in transitions from the ground state of an atom to its valence state thus involve both the one-center transformation of AO into HO (stage 1 in eq 2) or HO into AO (stage 3 in eq 2), and the middle subchannel reflecting the occupations/probabilities of HO in the valence state under consideration (stage 2 in eq 2).

We shall generate the entropy/information indices describing this hybridization promotion of AO in several valence states resulting from the generalized $s^x p^{1-x}$ scheme and in selected promoted states of the carbon atom. It is the main purpose of the present work to investigate these phenomena using the illustrative orbital mixing schemes and alternative HO-occupations, which determine the probability weights of HO, and hence the [HO → HO*] subchannel, and specify the valence state in question. Our goal is to extract the entropy/information descriptors of such one-center IT covalency and IT ionicity for these illustrative hybridization promotions of AO. We shall examine a competition between these complementary aspects of the “bond” phenomena in atoms and how they reflect a changing polarization and an extra uncertainty in the distribution of valence electrons, when the ground-state atoms are promoted to alternative electron configurations of their directed orbitals.

Throughout the paper, the entropic quantities are reported in bits, which correspond to the base 2 in the logarithmic measure of information.[2−4]

2. Information Channels for AO Promotion in sp Hybridization

Consider first the simplest mixing of two canonical AO, $\chi = (2s, 2p) \equiv \{\chi_k\}$, into two directed HO

$$\boldsymbol{\lambda} = \{\lambda_m\} = \boldsymbol{\chi}\mathbf{T}, \quad \mathbf{T} = \begin{bmatrix} \sqrt{x} & -\sqrt{y} \\ \sqrt{y} & \sqrt{x} \end{bmatrix}, \quad x + y = 1, \quad \mathbf{T}\mathbf{T}^{\mathrm{T}} = \mathbf{I} \quad (3)$$

affected by the orthogonal transformation, **T**, which has been expressed in terms of the AO probability, *x*, reflecting the polarization (shape) of HO. It should be observed that these general (nonequivalent) hybrids $\lambda_1 = s^x p^y$ and $\lambda_2 = s^y p^x$ become symmetry-related only for the *equivalent* sp scheme, when $x = y = {}^1/_2$.

By the superposition principle of quantum mechanics, the squares of the expansion coefficients in this linear transformation of AO generate the conditional probabilities of HO, given AO, $\mathbf{P}(\mathrm{HO}|\mathrm{AO}) \equiv \mathbf{P}(\boldsymbol{\lambda}|\boldsymbol{\chi})$, or of AO, given HO, $\mathbf{P}(\mathrm{AO}|\mathrm{HO}) \equiv \mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\lambda})$, of χ_k in λ_m, and so forth.

$$\mathbf{P}(\mathrm{AO}|\mathrm{HO}) = \{P(k|m)\} = \begin{bmatrix} x & y \\ y & x \end{bmatrix} \equiv \mathbf{A} = \mathbf{P}(\mathrm{HO}|\mathrm{AO})^{\mathrm{T}}, \quad \Sigma_k P(k|m) = x + y = 1 \quad (4)$$

Here $P(k|m)$ stands for the conditional probability of observing. It satisfies the relevant normalization condition specified in the second part of eq 4.[38]

We first assume the conserved, equal occupations in such orbital transformation, for example, the transition [$2s^2 2p_i^2$] → [$\lambda_1^2 \lambda_2^2$] in the carbon valence shell, when both HO exhibit the same electron probabilities $\boldsymbol{P}_\lambda = ({}^1/_2, {}^1/_2)$, thus being equally weighed in the valence state. In the approximate, *non*diagonal representation of the HO-occupation subchannel [$\boldsymbol{\lambda} \rightarrow \boldsymbol{\lambda}^*$],[20] each row of the conditional probability matrix $\mathbf{P}(\mathrm{HO}^*|\mathrm{HO}) \equiv \mathbf{P}(\boldsymbol{\lambda}^*|\boldsymbol{\lambda}) \equiv \{P(n^*|m)\}$, where $P(n^*|m)$ stands for probability of λ_{n^*}, given λ_m, is determined by the row vector $\boldsymbol{P}_\lambda = \{P_m\}$ of the HO probabilities in the specific valence-state configuration:

$$\mathbf{P}(\mathrm{HO}^*|\mathrm{HO}) \equiv \mathbf{P}(\boldsymbol{\lambda}^*|\boldsymbol{\lambda}) = \begin{bmatrix} \boldsymbol{P}_\lambda \\ \boldsymbol{P}_\lambda \\ \cdots \\ \boldsymbol{P}_\lambda \end{bmatrix} = \{P(n^*|m) = P_{n^*}\} \equiv \mathbf{B} \quad (5)$$

It should be observed that for this *independent-event* approximation[20] of the HO-occupation channel each row of the effective conditional probability matrix determining the AO promotion due to hybridization, defined by the product of conditional probabilities of the three elementary subchannels involved in the probability cascade of eq 2

$$\mathbf{P}(\mathrm{AO}^*|\mathrm{AO}) \equiv \mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\lambda}|\boldsymbol{\chi})\, \mathbf{P}(\boldsymbol{\lambda}^*|\boldsymbol{\lambda})\, \mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\lambda}^*) = \mathbf{A}\mathbf{B}\mathbf{A}^{\mathrm{T}} = \begin{bmatrix} \boldsymbol{P}^*_\chi \\ \boldsymbol{P}^*_\chi \\ \cdots \\ \boldsymbol{P}^*_\chi \end{bmatrix} = \{P(l^*|k) = P_{l^*}\} \quad (6)$$

represents the row vector of the promoted AO probabilities $\boldsymbol{P}^*_\chi = \{P_{l^*}\}$:

$$P(l^*|k) = \sum_{m}^{\mathrm{HO}}\sum_{n^*}^{\mathrm{HO}} P(m|k)P(n^*|m)P(l^*|n^*) = \sum_{m}^{\mathrm{HO}}\sum_{n^*}^{\mathrm{HO}} P(m|k)[P_{n^*}P(l^*|n^*)] = \sum_{m}^{\mathrm{HO}} P(m|k)\sum_{n^*}^{\mathrm{HO}} P(l^*,n^*) = P_{l^*} \tag{7}$$

In the preceding equation, we have used the normalization of *conditional* probabilities (eq 4) and that for the *simultaneous* two-orbital probabilities $\mathbf{P}(\mathrm{AO}^*, \mathrm{HO}^*) \equiv \mathbf{P}(\boldsymbol{\chi}^*,\boldsymbol{\lambda}^*) = \{P(l^*,n^*) = P_{n^*}\, P(l^*|n^*)\}$ of the joint AO-HO events: $\Sigma_{n^*} P(l^*,n^*) = P_{l^*}$.

Hence, for equal weights of HO in the atomic valence state $[\lambda_1{}^2\lambda_2{}^2]$, $\mathbf{P}(\mathrm{HO}^*|\mathrm{HO}) = \{P(n^*|m) = {}^1/_2\}$. The resultant conditional probabilities in the probability-propagation cascade $\boldsymbol{\chi} \to (\boldsymbol{\lambda} \to \boldsymbol{\lambda}^*) \to \boldsymbol{\chi}^*$, of the promoted AO $\boldsymbol{\chi}^*$, given the ground-state AO $\boldsymbol{\chi}$, which determine the effective channel of the AO promotion due to the orbital hybridization shown in Scheme 1, are then independent of the HO polarization (shape) controlled by the probability parameter x:

$$\mathbf{P}(\mathrm{AO}^*|\mathrm{AO}) = \{P(l^*|k) = {}^1/_2\} \tag{8}$$

Thus, for equal input probabilities of AO, for example, in the $[2s^22p_i{}^2]$ configuration of carbon or $[2s^12p_i{}^1]$ configuration of the promoted berylium, $\boldsymbol{P}_\chi{}^0 = \{P_k\} = ({}^1/_2, {}^1/_2) = \boldsymbol{P}_\chi{}^*$.

Hence, the average communication noise (IT covalency) in this AO-promotion channel, measuring the conditional entropy of the promoted AO output given the initial AO input

$$S(\mathrm{AO}^*|\mathrm{AO}) = S(\mathrm{AO}|\mathrm{AO}^*) = -\Sigma_k\, \Sigma_l\, P_k\, P(l^*|k) \log_2 P(l^*|k) = S(\mathrm{AO}) = 1 \tag{9}$$

where the Shannon entropy of the AO-input probabilities $S(\mathrm{AO}) = -\Sigma_k\, P_k \log_2 P_k$.

The channel complementary descriptor of the mutual information (IT ionicity) in the initial AO input and the promoted AO output, which measures the amount of information flowing through the communication system, is seen to identically vanish, when the probability weights of the two sp HOs in the atomic valence state are equal

$$I(\mathrm{AO{:}AO}^*) = S(\mathrm{AO}) - S(\mathrm{AO}|\mathrm{AO}^*) = 0 \tag{10}$$

because for the equalized input/output probabilities of Scheme 1

$$S(\mathrm{AO}) = H({}^1/_2) = 1 \tag{11}$$

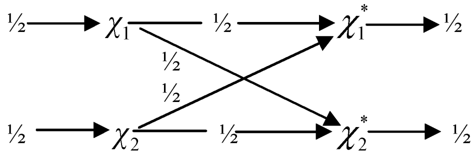
Here, the binary-entropy function (in bits), $H(x) = -x \log_2 x - (1 - x) \log_2(1 - x)$, assumes values in the range $H({}^1/_2) = 1 \geq H(x) \geq 0 = H(0) = H(1)$.

To summarize, the complementary IT descriptors of the AO promotion to the valence state of the equally weighted generalized sp hybrids give 1 bit of the overall entropic index, independent of the actual shapes of the two directed orbitals of eq 3:

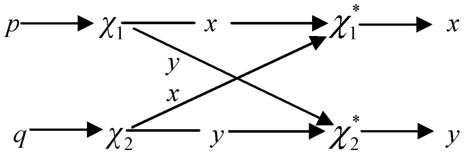
$$N(\mathrm{AO};\, \mathrm{AO}^*) = S(\mathrm{AO}^*|\mathrm{AO}) + I(\mathrm{AO{:}AO}^*) = S(\mathrm{AO}^*|\mathrm{AO}) = S(\mathrm{AO}) = 1 \tag{12}$$

This shape invariance should indeed be expected.[19] Namely, the transformation of the system fully occupied AO $\boldsymbol{\chi} = (2s, 2p)$ into the physically equivalent set $\boldsymbol{\lambda} = \{\lambda_1, \lambda_2\}$, also doubly occupied, cannot affect the (probability-based) information channels and the predicted entropy/information descriptors of the system IT ionicity and IT covalency. This is because such orbital transformations affect only the shapes of the (normalized) orbitals, thus having no effect on their occupations, the integral properties of the associated orbital densities, which solely determine the orbital probabilities. Hence, the communication connections for the orbital promotion, say in the carbon atom, are determined by electron probabilities, which are invariant with respect to arbitrary choices of the specific representation of the system equivalent occupied orbitals, be it canonical or directed.

SCHEME 1: Physical AO Promotion Channel for the sp Hybridization Promotion $[2s^22p^2] \to [\lambda_1{}^2\lambda_2{}^2]$ in the Carbon Atom



SCHEME 2: AO Promotion Channel for the sp Hybridization Promotion $[2s^22p^0] \to [\lambda_1{}^2\lambda_2{}^0]$, for example, in the Berylium Atom, for a General Input Probability Vector $\boldsymbol{P}_\chi = (p, q)$, $p + q = 1$



Next, let us examine the associated AO promotion due to the sp hybridization of eq 3, which corresponds to *non*equal weights of HO in the valence state. For example, in the valence shell of beryllium atom the AO-hybridization cascade $[2s^22p^0] \to [\lambda_1{}^2, \lambda_2{}^0] \to [2s^{2x}2p^{2y}]$, with only one sp hybrid being fully occupied in the promoted, valence state the other being empty, should generate a *directed* cylindrical polarization of the initially spherical atom. The input electron probabilities of AO in the beryllium ground-state, $\boldsymbol{P}_\chi{}^0 = \{P_k\} = (1, 0)$, can be extended into more general, fractional values $\boldsymbol{P}_\chi = (p, q)$, $p + q = 1$ (see Scheme 2). The physical AO promotion due to such hybridization is again defined by the product of eq 6:

$$\mathbf{P}(\mathrm{AO}^*|\mathrm{AO}) = \begin{bmatrix} x & y \\ y & x \end{bmatrix}\begin{bmatrix} 1 & 0 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} x & y \\ y & x \end{bmatrix} = \mathbf{P}(\mathrm{AO}|\mathrm{AO}^*) = \begin{bmatrix} x & y \\ x & y \end{bmatrix} \tag{13}$$

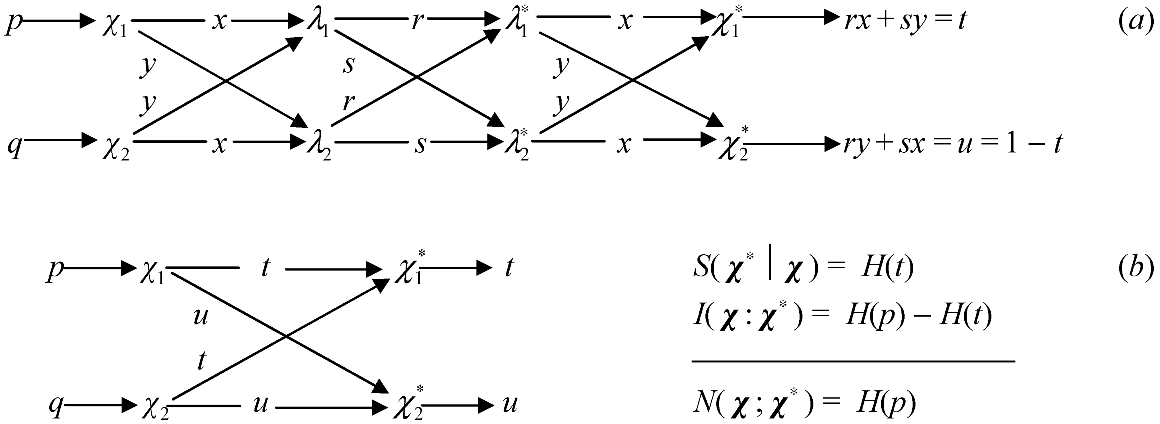
These conditional probabilities determine the effective communication network shown in Scheme 2. The relevant IT indices of this information system read:

$$S(\mathrm{AO}^*|\mathrm{AO}) = S(\mathrm{AO}|\mathrm{AO}^*) = H(x) \equiv S, \quad I(\mathrm{AO{:}AO}^*) = H(p) - H(x) \equiv I, \quad N(\mathrm{AO};\, \mathrm{AO}^*) = H(p) \equiv N \tag{14}$$

Therefore, the Shannon entropy of the input probabilities determines the overall index $N(\mathrm{AO};\, \mathrm{AO}^*) = S(\mathrm{AO}) = H(p)$ for this hybridization promotion of AO. For example, for $p = q = {}^1/_2$, when $H(p) = H({}^1/_2) = 1$, for example, in the excited configuration $[2s^12p^1]$ of beryllium

$$S = H(x) \geq 0, \quad I = 1 - H(x) \geq 0, \quad \text{and } N = 1 \tag{15}$$

SCHEME 3: Communication Channel of the AO Promotion due to the Generalized sp Hybridization and Fractional Weights of HO in the Atomic Valence State



$$S(\boldsymbol{\chi}^* \mid \boldsymbol{\chi}) = H(t)$$

$$I(\boldsymbol{\chi} : \boldsymbol{\chi}^*) = H(p) - H(t)$$

$$N(\boldsymbol{\chi} ; \boldsymbol{\chi}^*) = H(p)$$

The increase in the IT-covalency descriptor is thus counterbalanced by the decrease in the IT-ionicity index, in order to keep the overall IT multiplicity at the conserved 1-bit level.

The conditional-entropy index, S, characterizes the atomic (*one*-center) IT-covalency, which has been acquired due to the orbital hybridization. Its positive sign signifies an extra uncertainty in electron probabilities in the promoted AO configuration $[2s^{2x}2p^{2y}]$ compared to the original configuration $[2s^2 2p^0]$. This extra noise in the communication channel of the sp hybridization also implies that only a fraction $I = 1 - H(x)$ of the input information content of 1 bit survives in the channel output. It measures the *one*-center information-ionicity of the promoted atom.

Accordingly, for the ground state of beryllium, that is, $p = 1$ $(q = 0)$ and hence $H(p) = H(1) = 0$

$$S = H(x) \geq 0, \quad I = -H(x) \leq 0, \quad \text{and } N = 0 \qquad (16)$$

In this case, the 2s orbital acts as a “donor” of both electrons, which ultimately occupy a single sp hybrid in the valence state. Such information channels are seen to give rise to the vanishing overall index N and a negative mutual-information descriptor. A similar property has been detected in the molecular information channels representing “communications” between bonded atoms in the donor−acceptor systems.[17]

In model considerations, one could also examine the continuously changing complementary weights (r, $s = 1 - r$) of two sp hybrids, reflecting their electron occupations in the atomic valence state. The resulting AO-promotion cascade and its entropy/information descriptors are summarized in Scheme 3. This general communication system reproduces that shown in Scheme 1, for $r = s = 1/2$ and hence also $t = u = 1/2$. It also gives rise to the effective channel of Scheme 2, when $r = 1$ and $s = 0$, that is, $t = x$ and $u = y$.

This general sp channel allows one to search for the HO probability weights (r, s), which maximize the IT-covalency index $S(\mathrm{AO}^*|\mathrm{AO}) = S(\mathrm{AO}|\mathrm{AO}^*) = H(t(r))$. The condition for the extremum of this quantity

$$\frac{\partial H(t(r))}{\partial r} = (x - y) \ln\left(\frac{1 - t}{t}\right) = 0 \qquad (17)$$

indicates that it occurs either for the equivalent sp hybrids, when $x = y = 1/2$ and hence also $t = u = 1/2$, or for general, symmetry-unrelated hybrids, that is, $x \neq y$, when the probability weights of both HO are equalized, $r = s = 1/2$, which further implies $t = u = 1/2$ (see, e.g., Scheme 1).

3. Entropic Effects of Alternative Hybridizations of the Carbon Atom

Next, let us compare the IT indices for different hybridizations, for example, the familiar sp^3 (tetrahedral, $\{h_m\}$), sp^2 (trigonal, $\{t_m\}$), or sp (linear, $\{\lambda_m\}$), symmetry-equivalent schemes for the carbon atom. Sould one assume equal (single) occupations of all four AO/HO in the valence state, that is, equal probability weights for all occupied orbitals, $\boldsymbol{P}_{\mathrm{AO/HO}} = (1/4, 1/4, 1/4, 1/4)$, one finds slightly higher Shannon entropy of the promoted orbitals, $S_{\mathrm{AO^*/HO^*}} = 2$, compared to those obtained for admissible electron distributions among 2p orbitals, which give rise to the overall ground-state configuration $[2s^2 2p^2]$ of the carbon atom:

$$[2s^2 2p_z^{\ 2}]:\ S_{\mathrm{AO/HO}} = 1; \quad [2s^2 2p_x^{\ 1} 2p_y^{\ 1}]:\ S_{\mathrm{AO/HO}} = 1.5;$$
$$[2s^2 2p_x^{\ 2/3} 2p_y^{\ 2/3} 2p_z^{\ 2/3}]:\ S_{\mathrm{AO/HO}} = 1.79$$

Indeed, the electron uncertainty measured by this quantity must increase with a growing degree of uniformization of the orbital electron occupations.

It should be observed that the equalized weights $\boldsymbol{P}_{\mathrm{AO/HO}}$ in the atomic valence state generate the IT indices, which do not distinguish between different hybridization schemes. Indeed, in this case different AO-mixing procedures produce different sets of the physically equivalent orbitals, with no effect on the occupation/probability-based information channels and the entropy/informations indices they generate. For the specified input probability vector of the valence electrons, for example, $\boldsymbol{P}_\chi^{\ 0} = (1/2, 1/6, 1/6, 1/6)$, they all correspond to the same AO-promotion channel defined by the equalized effective conditional probabilities:

$$\begin{aligned}\mathbf{P}(\mathrm{AO}^*|\mathrm{AO}) &= \mathbf{P}(\mathrm{sp}|\mathrm{AO})\, \mathbf{P}(\mathrm{sp}^*|\mathrm{sp})\, \mathbf{P}(\mathrm{AO}^*|\mathrm{sp}^*) \\ &= \mathbf{P}(\mathrm{sp}^2|\mathrm{AO})\, \mathbf{P}(\mathrm{sp}^{2*}|\mathrm{sp}^2)\, \mathbf{P}(\mathrm{AO}^*|\mathrm{sp}^{2*}) \\ &= \mathbf{P}(\mathrm{sp}^3|\mathrm{AO})\, \mathbf{P}(\mathrm{sp}^{3*}|\mathrm{sp}^3)\, \mathbf{P}(\mathrm{AO}^*|\mathrm{sp}^{3*}) = \{P(l^*|k) = 1/4\}\end{aligned} \qquad (18)$$

This resultant channel generates the following IT indices describing the electron probability scattering of the AO promotion due to orbital hybridization: $S = N = 2$, and $I = 0$. Therefore, the amount of information I (IT ionicity) that flows through this channel exactly vanishes and the whole output entropy $S(\mathrm{AO}^*/\mathrm{HO}^*) = 2$ is being dissipated as the average information noise, S.

TABLE 1: Entropy-Covalency (*S*) and Information-Ionicity (*I*) Descriptors, Conserving the Overall Index $N = 1.79$, for Selected Valence-State Configurations of the Carbon Atom

hybridization	valence state	configuration from HO composition	output configuration in AO promotion	$S(\chi^*\|\chi) \equiv S$	$I(\chi:\chi^*) \equiv I$
$sp^3(s, p_x, p_y, p_z)$	$h_1^2h_2^1h_3^1,h_1^2h_2^2$	$s^1p_x^1p_y^1p_z^1$	$s^1p_x^1p_y^1p_z^1$	2.00	−0.21
$sp^2(s, p_x, p_y)$	$t_1^1t_2^1p_z^2$	$s^{2/3}p_x^{5/6}p_y^{1/2}p_z^2$	$s^1p_x^{1/2}p_y^{1/2}p_z^2$	1.75	0.04
	$t_1^1t_2^1t_3^2$	$s^{4/3}p_x^{7/6}p_y^{3/2}$	$s^1p_x^{3/2}p_y^{3/2}$	1.56	0.23
	$t_1^2p_z^2$	$s^{2/3}p_x^{4/3}p_z^2$	$s^{2/3}p_x^{2/3}p_y^{2/3}p_z^2$	1.79	0.00
	$t_2^2p_z^2$	$s^{2/3}p_x^{1/3}p_y^1p_z^2$	$s^{4/3}p_x^{1/3}p_y^{1/3}p_z^2$	1.26	0.53
	$t_1^2t_2^2$	$s^{4/3}p_x^{5/3}p_y^1$	$s^2p_x^1p_y^1$	1.50	0.29
$sp(s, p_z)$	$\lambda_1^2p_x^1p_y^1$	$s^1p_x^1p_y^1p_z^1$	$s^1p_x^1p_y^1p_z^1$	2.00	−0.21
	$\lambda_1^2p_x^2$	$s^1p_x^1p_y^1p_z^1$	$s^1p_x^2p_z^1$	1.50	0.29
	$\lambda_1^2\lambda_2^2$	$s^2p_z^2$	$s^2p_z^2$	1.00	0.79

Finally, let us selectively explore the role played by *non*equal weights of AO/HO in the valence state of the carbon atom. For the given hybridization scheme in Table 1, the valence-state electron configurations have been ordered in accordance with the increasing modulus of their IT-ionicity index, reflecting a growing atom deformation (polarization). The calculated IT indices of the carbon atom, which conserve the overall entropic multiplicity $N = 1.79$, equal to the Shannon entropy of the ground-state configuration $[2s^22p_x^{2/3}2p_y^{2/3}2p_z^{2/3}]$ of the spherical atom, are listed in the last two columns of the table. It also compares the average electron configurations (third column) in the valence state specified in the second column

$$\boldsymbol{N}^{\mathrm{val}} \equiv N_v \boldsymbol{P}_\chi^{\mathrm{val}} = N_v \boldsymbol{P}_\lambda \mathbf{P}(\mathrm{AO}|\mathrm{HO}) \equiv \boldsymbol{N}_\lambda \mathbf{A}^{\mathrm{T}} = \{N_k^{\mathrm{val}} = N_v \sum_m^{\mathrm{HO}} P_m P(k|m) = \sum_m^{\mathrm{HO}} N_m P(k|m) \equiv N_v P_k^{\mathrm{val}}\} \tag{19}$$

with that resulting from the probability propagation using the approximate occupation channel of eq 5 (fourth column):

$$\boldsymbol{N}^* = (N_v \boldsymbol{P}_\chi^0) \mathbf{P}(\mathrm{AO}^*|\mathrm{AO}) = \boldsymbol{N}^0 \mathbf{P}(\mathrm{AO}^*|\mathrm{AO}) = \{N_{k^*} = N_v P_{k^*}\} \tag{20}$$

The IT-ionic descriptor indeed reflects the intuitively expected differences in deformation of the initially spherical distribution of electrons in the assumed ground-state configuration. Namely, the highest IT-ionicity index, reflecting the maximum "structure" (order) in the angular distribution of valence electrons, compared to the spherical atom, is predicted in the *delocalized* cylindrical distortion of the valence shell around the *z* axis, when the two equivalent sp hybrids are doubly occupied. The completely occupied pair of sp^2 hybrids or the singly occupied sp hybrid supplemented by a doubly occupied $2p_x$ orbital generate less than a half of this exceptionally high mutual-ionicity index generated by the two (doubly occupied) sp hybrids, thus diagnosing less polarizational distortion of the promoted carbon. The lowest, marginal value of the positive mutual-information index is found in the sp^2 hybridization case, when a pair of singly occupied hybrids is combined with the doubly occupied $2p_z$ orbital. Indeed, one would intuitively associate with this valence-state configuration only a minor deformation of the carbon atom.

Finally, the two configurations in the sp^3 scheme and one in the sp case exhibit a medium size, negative IT-ionicity, a clear sign of a substantial donor−acceptor deformation relative to the initial ground-state configuration. A closer examination of these configurations indeed reveals that they all give rise to the single effective occupations of all valence AOs, which signify the 2s → 2p transfer of a single electron relative to the assumed initial distribution of electrons.

The complementary, conditional-entropy entries in the table, which reflect the *one*-center covalency of the valence state, reach the maximum value of 2 bits for the uniform distribution of electrons among AO in the promoted state. They are seen to diminish gradually with increasing inhomogeneity of the AO occupations, reaching the lowest level of 1 bit for the double occupations of two AOs.

These IT results directly demonstrate a competition between the acquired *one*-center ionicity and covalency in the promoted atom. This observation accords with intuitive chemical expectations. More specifically, the strong scattering ("sharing") of the valence electrons among AO increases the entropy-covalency due to AO hybridization. It also implies a lower degree of the electron AO-localization, which favors the IT ionicity. Indeed, the latter effect signifies an increasing displacement of the promoted atom from the initial, spherical distribution of electrons, for the equalized occupations of the open-shell orbitals, which is ultimately responsible for the atomic deformation indexed by the *one*-center information-ionicity.

It follows from a comparison of the two sets of the effective AO-configurations in Table 1 that in the sp^2 hybridization the average AO configurations of the specified valence states (eq 19) may differ slightly from the promoted (output) AO occupations (eq 20) resulting from the approximate HO occupational channel of eq 5, formulated using the independent-orbital approximation.[20] A reference to these entries in the table shows that the probability propagation equalizes the occupations of orbitals p_x and p_y, which are used in this hybridization, thus effectively removing a possible dependence of IT indices on the adopted reference frame. This property makes the communication theory predictions more objective.

At this point the following question natuarally arises: what is the exact form of the HO occupation channel, $\tilde{\mathbf{B}} \equiv \tilde{\mathbf{P}}(\mathrm{HO}^*|\mathrm{HO})$, the promoted AO probabililities of which (seen in eq 20)

$$\boldsymbol{P}_\chi^* = \boldsymbol{P}_\chi^0 \mathbf{P}(\mathrm{AO}^*|\mathrm{AO}) = \boldsymbol{P}_\chi^0 \mathbf{A} \tilde{\mathbf{B}} \mathbf{A}^{\mathrm{T}} \tag{21}$$

reproduce the average valence-state probabilities (see eq 19)

$$\boldsymbol{P}_\chi^{\mathrm{val}} = \boldsymbol{P}_\lambda \mathbf{P}(\mathrm{AO}|\mathrm{HO}) = \boldsymbol{P}_\lambda \mathbf{A}^{\mathrm{T}} \tag{22}$$

at the end of the probability-propagation cascade of eq 2? The equation $\boldsymbol{P}_\chi^* = \boldsymbol{P}_\chi^{\mathrm{val}}$ can be solved for the unknown conditional-probability matrix $\tilde{\mathbf{B}}$:

$$\tilde{\mathbf{B}} = (\mathbf{F}\mathbf{A})^{-1} \mathbf{G} = \mathbf{A}^{-1} \mathbf{F}^{-1} \mathbf{G}, \ \mathbf{F} = \boldsymbol{P}_\lambda^{\mathrm{T}} \boldsymbol{P}_\chi^0 \ \mathbf{G} = \boldsymbol{P}_\lambda^{\mathrm{T}} \boldsymbol{P}_\lambda \tag{23}$$

Clearly, the same approach can be adopted in the *multi*center AO-promotion cascades of eq 1, which probe the chemical bonds in molecules. Here we want to determine the exact MO-occupation channel $\tilde{\mathbf{B}}^{\mathrm{MO}} = \tilde{\mathbf{P}}(\phi^*|\phi) \equiv \tilde{\mathbf{P}}(\mathrm{MO}^*|\mathrm{MO})$, which gives rise to the promoted probabilities of AO

$$\begin{aligned} \boldsymbol{P}_\chi^{\ \mathrm{MO}} &\equiv \boldsymbol{P}_\chi^{\ 0}\, \mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\chi})^{\mathrm{MO}} = \boldsymbol{P}_\chi^{\ 0}\, \mathbf{P}(\phi|\boldsymbol{\chi})\, \tilde{\mathbf{P}}(\phi^*|\phi)\, \mathbf{P}(\boldsymbol{\chi}^*|\phi^*) \\ &= \boldsymbol{P}_\chi^{\ 0}\, \mathbf{P}(\mathrm{MO}|\mathrm{AO})\, \mathbf{P}(\mathrm{MO}^*|\mathrm{MO})\, \mathbf{P}(\mathrm{AO}^*|\mathrm{MO}^*) \\ &\equiv \boldsymbol{P}_\chi^{\ 0} \mathbf{A}^{\mathrm{MO}}\, \tilde{\mathbf{B}}^{\mathrm{MO}} \mathbf{A}^{\mathrm{MO,T}} \end{aligned} \qquad (24)$$

which have to reproduce the effective probabilities of the valence-shell AO obtained from the SCF LCAO MO calculations:

$$\boldsymbol{P}_\chi^{\ \mathrm{SCF}} = \{\gamma_{k,k}^{\mathrm{AO}}/N_v\} = \boldsymbol{P}_\varphi\, \mathbf{P}(\mathrm{AO}|\mathrm{MO}) = \boldsymbol{P}_\varphi\, \mathbf{A}^{\mathrm{MO,T}} \qquad (25)$$

Here $\gamma_{k,k}^{\mathrm{AO}}$ represents the kth diagonal element of the familiar *charge-and-bond-order* matrix of the MO theory, which provides the AO representation of the projection operator onto the occupied-MO subspace. The orbital-mixing matrix $\mathbf{A}^{\mathrm{MO}}$ is uniquely determined by the LCAO MO coefficients and AO-overlap matrix[20] so that the only unknown matrix $\tilde{\mathbf{B}}^{\mathrm{MO}}$can be straightforwardly extracted from the equation $\boldsymbol{P}_\chi^{\ \mathrm{MO}} = \boldsymbol{P}_\chi^{\ \mathrm{SCF}}$:

$$\tilde{\mathbf{B}}^{\mathrm{MO}} = (\mathbf{F}^{\mathrm{MO}}\mathbf{A}^{\mathrm{MO}})^{-1}\mathbf{G}^{\mathrm{MO}} = (\mathbf{A}^{\mathrm{MO}})^{-1}(\mathbf{F}^{\mathrm{MO}})^{-1}\mathbf{G}^{\mathrm{MO}}, \qquad \mathbf{F}^{\mathrm{MO}} = \boldsymbol{P}_\varphi^{\ \mathrm{T}}\boldsymbol{P}_\chi^{\ 0}, \quad \mathbf{G}^{\mathrm{MO}} = \boldsymbol{P}_\varphi^{\ \mathrm{T}}\boldsymbol{P}_\varphi \qquad (26)$$

In the future, this exact MO-occupation channel should facilitate a better comparison between the IT and MO bond indices.

4. Conclusions

In this work, we have applied the orbitally resolved communication theory, which has previously been used to probe the chemical bonds in molecular systems, to explore the *one*-center covalency and ionicity accqired in the atom promotion to its valence state. The latter concept has been widely used by chemists to characterize the prospective atom polarizations in the bond-forming processes as preparations for the most effective chemical interaction between the two partners of the localized-bond in a molecule. This promotion involves mixing the atomic valence orbitals into the relevant directed hybrids, similar to the multicenter AO-mixing into MO, which is responsible for the system chemical bonds. The nonuniform electron occupations of HO give rise to deformations of free atoms, that is, their displacements from the initial spherical character.

In this IT approach in orbital resolution, the covalent and ionic descriptors describe the complementary aspects in the effective communication system of the AO-promotion, viz., the average noise and the amount of the passing information, respectively. This information channel is generated by the sequential cascade of three elementary subchannels describing the orbital-mixing and orbital-occupation displacements in the system electronic structure. Although the chemical bonds involve both the *one*- and *multi*center information scattering, the atom hybridization phenomenona are limited to the probability scattering within a single atom. Otherwise, the essence of the communication theory description remains the same.

We have examined in some detail the entropic consequences of alternative AO transformations into directed orbitals and the role played by the HO electron occupations (probability weights) in the atomic valence state. In the generalized sp-type hybridization, the maximum of the one-center IT-covalency has been attained for either the symmetry-equivalent hybrids, irrelevant of their occupations, or for the equally weighted (occupied) hybrids, which are not related by symmetry.

The equally weighted hybrids were shown to give rise to the shape invariance of the information systems for the AO-promotion, that is, their independence of the particular hybridization scheme applied. This is because the AO and all admissible HO sets then represent the physically equivalent sets of orbitals, which generate the same Slater-determinant.

The nonequalized weights of HO in the atomic valence state reveal differences due to the shapes of directed orbitals, that is, the sensitivity of the orbital channels and their entropic descriptors with respect to the specific orbital-mixing scheme applied. The increasing deviations of the promoted atom from the initial spherical distribution of electrons were shown to give rise to increasing IT-ionic descriptor, which competes with the IT-covalent component for a fraction of the initial information content of the AO probabilities. Both components were shown to conserve the overall IT index of the AO promotion relative to the free-atom input.

It should be emphasized that the spherical atom, corresponding to the equalized occupations of the open-shell canonical orbitals, represents the highest degree of the *angular* (directional) uncertainty of the position vector of an electron because for the specified distance from the nucleus each direction is equally probable. The only structure (order) is then detected in the electronic *radial* distribution, manifested by the atomic shell structure.

Breaking the atom spherical symmetry in the valence state thus diminishes the degree of this directional uncertainty, relative to this maximum, spherical-atom level. The removal of a fraction of this directional uncertainty implies gaining some information about the angular distribution of electrons, to the amount of the diminished entropy (uncertainty). Therefore, the distorted atom in the valence state, by corresponding to more information about the system angular distribution, represents an increased degree of structure (order) in electron probabilities. For example, the promoted carbon in preparation for forming four CH bonds in methane exhibits the tetrahedral angular structure and hence a lower level of the electron angular uncertainty. Because the atomic IT-ionicity reflects this atomic polarization, this index can be also used as a measure of the extra information accquired about the atom angular distribution in the valence state. The complementary index of the IT covalency similarly signifies the degree of the original, directional uncertainty (“disorder”) of the spherical atom, which still survives in the valence state.

In the present analysis, we have also compared the average and IT-promoted electron configurations of selected valence states of the carbon atom. The observed differences, due to the approximate character of the adopted independent-event representation of the HO-occupation subchannel, indicate that the exit probabilities resulting from the probability-propagation cascade exhibit a higher degree of equalization of AO occupations. The exact HO-occupation subchannel has also been formulated, which reproduces the average configurations at the exit of the one-center probability propagation of eq 2. A similar approach to the MO-occupation subchannel can be adopted in the multicenter information scattering of eq 1, which probes chemical bonds in molecular systems.

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(38) Note: throughout the paper P denotes a *scalar* quantity, $\boldsymbol{P}$ stands for a *row* vector, and $\mathbf{P}$ represents a square or rectangular *matrix*.