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密度泛函活性理论中的Rényi 熵, Tsallis 熵和Onicescu 信息能

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摘要: 根据密度泛函理论, 分子的电子密度确定了该体系基态下的所有性质, 其中包括结构和反应活性. 如何运用电子密度泛函有效地预测分子反应活性仍然是一个有待解决的难题. 密度泛函活性理论(DFRT)倾力打造这样一个理论和概念架构, 使得运用电子密度以及相关变量准确地预测分子的反应特性成为可能. 信息理论方法的香农熵和费舍尔信息就是这样的密度泛函, 研究表明, 它们均可作为反应活性的有效描述符. 本文将在DFRT框架中介绍和引进三个密切相关的描述符, Rényi熵、Tsallis熵和Onicescu信息能. 我们准确地计算了它们在一些中性原子和分子中的数值并讨论了它们随电子数量和电子总能量的变化规律. 此外, 以第二阶Onicescu信息能为例, 在分子和分子中的原子两个层面上, 系统地考察了其随乙烷二面角旋转的变化模式. 这些新概念的引入将为我们深入洞察和预测分子的结构和反应活性提供额外的描述工具.

关键词: Rényi熵; Tsallis熵; Onicescu信息能; 香农熵; 密度泛函活性理论

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Rényi Entropy, Tsallis Entropy and Onicescu Information Energy in Density Functional Reactivity Theory

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Abstract: Density functional theory dictates that the electron density determines everything in a molecular system's ground state, including its structure and reactivity properties. However, little is known about how to use density functionals to predict molecular reactivity. Density functional reactivity theory is an effort to fill this gap: it is a theoretical and conceptual framework through which electron-related functionals can be used to accurately predict structure and reactivity. Such density functionals include quantities from the information-theoretic approach, such as Shannon entropy and Fisher information, which have shown great potential as reactivity descriptors. In this work, we introduce three closely related quantities: Rényi entropy, Tsallis entropy, and Onicescu information energy. We evaluated these quantities for a number of neutral atoms and molecules, revealing their scaling properties with respect to electronic energy and the total number of electrons. In addition, using the example of second-order Onicescu information

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energy, we examined how its patterns change with the angle of dihedral rotation of an ethane molecule at both the molecular level and atoms-in-molecules level. Using these quantities as additional reactivity descriptors, researchers can more accurately predict the structure and reactivity of molecular systems.

Key Words: Rényi entropy; Tsallis entropy; Onicescu information energy; Shannon entropy, Density functional reactivity theory

1 Introduction

According to density functional theory,¹ any property of a molecule in the ground state is determined by its electron density. These properties could be structure, reactivity, and many others. While in the past few decades, focuses have been paid to search for better behaved density functionals to approximate energy components such as kinetic and exchange-correlation energies, there is an integral piece of information that is still missing. That is, we still do not know much about how to employ density functionals to predict molecular reactivity. The endeavor to employ quantities directly related to the electron density and its associated quantities as descriptors to establish a conceptual framework so that quantitative predictions of chemical reactivity are possible is called density functional reactivity theory (DFRT).¹⁻⁴ Since quantities from information theory involve probability functions such as the electron density, they are natural choices as reactivity descriptors in DFRT. These quantities include Shannon entropy,⁵ Fisher information,⁶ Ghosh-Berkowitz-Parr entropy,⁷ and information gain.⁸⁻¹⁰ The effort to make use of these quantities in molecular reactivity study in DFRT is called the information-theoretic approach. Very recently, we have intensively investigated the properties of these quantities for atoms and molecules and applied them to quantify reactivity for a number of systems.¹¹⁻¹⁸

In this contribution, we expand the scope of the DFRT study by exploring three closely related quantities in the information-theoretic approach. They are Rényi entropy,¹⁹ Tsallis entropy,²⁰ and Onicescu information energy.²¹ The purpose of the present work is to formally introduce these quantities into DFRT and set the stage for their further applications in reactivity predictions in the future.

2 Theoretical framework

Given an electron density distribution $\rho(\mathbf{r})$ and density gradient $\nabla\rho(\mathbf{r})$ in the ground state of an N -electron system, which satisfies the normalization condition, $\int\rho(\mathbf{r})d\mathbf{r} = N$, according to the information-theoretic approach, Shannon entropy and Fisher information are, respectively, defined,^{5,6}

$$S_S = -\int\rho(\mathbf{r})\ln\rho(\mathbf{r})d\mathbf{r} \quad (1)$$

and

$$I_F = \int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} \quad (2)$$

The Ghosh-Berkowitz-Parr entropy and information gain can be defined accordingly, as detailed elsewhere.⁷⁻¹⁰ These quantities

were the recent focus of our extensive studies.¹¹⁻¹⁸ Three other quantities, Rényi entropy, Tsallis entropy, and Onicescu information energy, are closely related, whose definitions are as follows.

For a continuous probability distribution like $\rho(\mathbf{r})$, the Rényi entropy of order n , where $n \geq 0$ and $n \neq 1$, is defined as¹⁹

$$R_n = \frac{1}{1-n} \log \left[\int \rho(\mathbf{r})^n d\mathbf{r} \right] \quad (3)$$

when n approaches to 1, the Rényi entropy, Eq.(3), reduces to the Shannon entropy, Eq.(1). The Tsallis entropy of order n is defined as follows,²⁰

$$T_n = \frac{1}{n-1} \left[1 - \int \rho(\mathbf{r})^n d\mathbf{r} \right] \quad (4)$$

It is a generalization of the standard Boltzmann-Gibbs entropy. The common term in Eqs.(3) and (4) is the integral of the n -th power of the electron density, which can indeed be regarded as a separate definition in its own right. It is called the Onicescu information energy of order n :²¹

$$E_n = \frac{1}{n-1} \int \rho(\mathbf{r})^n d\mathbf{r} \quad (5)$$

Onicescu introduced this quantity in an attempt to define a finer measure of dispersion distribution than that of Shannon entropy.

These three quantities can similarly be re-defined with the shape function $\sigma(\mathbf{r})$, which is related to the electron density via $\rho(\mathbf{r}) \equiv N\sigma(\mathbf{r})$. Eqs.(3-5) become¹⁶

$$R_n^\sigma = \frac{1}{1-n} \log \left[\int \sigma(\mathbf{r})^n d\mathbf{r} \right] \quad (6)$$

$$T_n^\sigma = \frac{1}{n-1} \left[1 - \int \sigma(\mathbf{r})^n d\mathbf{r} \right] \quad (7)$$

and

$$E_n^\sigma = \frac{1}{n-1} \int \sigma(\mathbf{r})^n d\mathbf{r} \quad (8)$$

Using the explicit relationship between $\rho(\mathbf{r})$ and $\sigma(\mathbf{r})$, we can readily prove that

$$R_n - R_n^\sigma = \frac{n}{1-n} \log N \quad (9)$$

$$T_n - N^n T_n^\sigma = \frac{1-N^n}{n-1} \quad (10)$$

and

$$E_n = N^n E_n^\sigma \quad (11)$$

Again, N is the total number of electrons in the system, and n is the order of the quantities studied. In the special case of $n = 1$, Rényi entropy and Tsallis entropy are both reduced to the

Shannon entropy, and Onicescu information energy is ill-defined because $1/(n-1)$ diverges. In this work, we consider the cases of $n \geq 2$.

Same as the Shannon entropy and Fisher information, these quantities can also be decomposed into atomic contributions through three distinct atom partition schemes, Bader's zero-flux,²² Becke's fuzzy atom,²³ and Hirshfeld's stockholder²⁴ approaches. As have been shown recently, these three approaches yield similar results.¹⁶ In this work, we investigate atoms-in-molecules behavior using Hirshfeld's stockholder partition scheme. For any quantity above $Q[\rho]$, the evaluation of the total molecular value can be rewritten as the sum of atomic contributions,

$$Q[\rho] = \sum_A Q_A[\rho] = \sum_A \int_{\Omega_A} q(\mathbf{r}) d\mathbf{r} \quad (12)$$

where $Q_A[\rho]$ is the atomic contribution from atom A and Ω_A as

the atomic basin of atom A in the molecule.

3 Computational details

In this work, we consider the cases $n = 2$ and $n = 3$ in Eqs. (3–11). That is, we only examine the behavior of Rényi entropy, Tsallis entropy, and Onicescu information energy of orders 2 and 3. Higher orders of these quantities can be investigated similarly. All of these formulas have been successfully implemented in the Multiwfn 3.3 package developed by one of the present authors,²⁵ whose reliability and applicability have extensively been tested before. As illustrative examples, we present below results of these new information-theoretic quantities for a number of atomic and molecular systems.

All electronic wave functions were obtained from the Gaussian 09 package, version D01.²⁶ For all atoms and molecules invest-

Table 1 Atomic values of new information-theoretic quantities (units are in atomic unit) obtained with the total electron density

Atom	N^a	E_2	E_3	R_2	R_3	T_2	T_3	E^a
H	1	0.039	0.002	1.41	1.21	0.96	0.50	-0.50
He	2	0.763	0.389	0.12	0.05	0.24	0.11	-2.90
Li	3	3.139	6.170	-0.50	-0.55	-2.14	-5.67	-7.48
Be	4	8.40	42.76	-0.92	-0.97	-7.40	-42.26	-14.66
C	6	31.87	580.9	-1.50	-1.53	-30.87	-580.37	-37.84
N	7	52.69	1538.8	-1.72	-1.74	-51.69	-1538.28	-54.58
O	8	81.65	3567.3	-1.91	-1.93	-80.65	-3566.82	-75.06
F	9	120.3	7455.5	-2.08	-2.09	-119.3	-7455.0	-99.72
Ne	10	170.5	14377.0	-2.23	-2.23	-169.5	-14376.5	-128.92
Na	11	234.0	26194.0	-2.37	-2.36	-233.0	-26193.5	-162.24
Mg	12	313.0	45493.0	-2.50	-2.48	-312.0	-45492.5	-200.05
Si	14	523.3	120384.6	-2.72	-2.69	-522.3	-120384.1	-289.35
P	15	658.1	185814.7	-2.82	-2.79	-657.1	-185814.2	-341.24
S	16	815.3	278831.0	-2.91	-2.87	-814.3	-278830.5	-398.10
Cl	17	996.0	407976.6	-3.00	-2.96	-995.0	-407976.1	-460.13
Ar	18	1203.0	583504.5	-3.08	-3.03	-1202.0	-583504.0	-527.52
K	19	1440.9	820114.8	-3.16	-3.11	-1439.9	-820114.3	-599.90
Ca	20	1708.0	1132761	-3.23	-3.18	-1707.0	-1132761	-677.56
Cr	24	3094.7	3531757	-3.49	-3.42	-3093.7	-3531757	-1044.32
Mn	25	3530.3	4544622	-3.55	-3.48	-3529.3	-4544622	-1150.77
Co	27	4533.3	7324860	-3.66	-3.58	-4532.3	-7324860	-1382.53
Ni	28	5105.7	9187318	-3.71	-3.63	-5104.7	-9187318	-1508.14
Zn	30	6386.7	14073009	-3.81	-3.72	-6385.7	-14073009	-1779.26
Ge	32	7889.8	20976835	-3.90	-3.81	-7888.8	-20976835	-2076.90
As	33	8725.5	25385817	-3.94	-3.85	-8724.5	-25385816	-2235.80
Se	34	9621.0	30546397	-3.98	-3.89	-9620.0	-30546397	-2401.50
Br	35	10577.7	36545294	-4.02	-3.93	-10576.7	-36545293	-2574.13
Kr	36	11603.3	43529405	-4.06	-3.97	-11602.3	-43529404	-2753.80
$R^2(N)^b$		0.834	0.653	0.806	0.806	0.834	0.653	
$R^2(E)^b$		0.986	0.874	0.558	0.558	0.986	0.874	

Onicescu information energy of orders 2 and 3, E_2 and E_3 ; Rényi entropy of orders 2 and 3, R_2 and R_3 ; and Tsallis entropy of orders 2 and 3, T_2 and T_3 , for a list of neutral atoms. ^a N is the total number of atoms; E is the total electronic energy. ^b R^2 is the correlation coefficients of these quantities with respect to both N and E .

igated in this work, the M062X density functional was employed.²⁷ For the choice of basis sets, in atomic calculations, where neutral species from H to Kr were considered, the standard Pople's 6-311G(3df, 3pd) basis set²⁸ was used. In molecular calculations, we made use of the augmented version of correlation consistent basis set with added diffuse functions, aug-cc-pVDZ,²⁹ for all the systems examined. A total of 21 molecular systems were investigated in this work with the general formula of $R_1R_2R_3CF$ with R_1 , R_2 , and R_3 representing alkyl groups such as $-H$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, and $-C_4H_9$, which were previously considered elsewhere. We denote these molecular species in terms of three substituting groups in the format of $(R_1R_2R_3)$. The molecular values of the Shannon entropy, Fisher information, as well as quantities in Eqs.(3–11) for the orders of 2 and 3 were calculated for these systems. We also calculated the profile of these quantities as a function of the $\angle HCCCH$ dihedral angle rotation for the ethane molecule. The $\angle HCCCH$ dihedral angle is changed from 0° (staggered conformer) to 360° with the step size of 5° .³⁰ The purpose of

this profiling study is to examine the change patterns of these quantities with respect to the change of this dihedral angle at both molecular and atoms-in-molecules levels. All molecules were fully optimized. The tight self-consistent field convergence criterion and ultrafine integration grids were employed. Checkpoint files obtained from these Gaussian calculations were used as the input file to obtain these and other information-theoretic quantities.

4 Results and discussion

Shown in Table 1 are atomic values of the new information-theoretic quantities obtained for the total electron density, including Onicescu information energy of orders 2 and 3, E_2 and E_3 , Rényi entropy of orders 2 and 3, R_2 and R_3 , and Tsallis entropy of orders 2 and 3, T_2 and T_3 , respectively, for neutral atoms up to krypton. Also shown in the Table are the total number of electrons N , the total electronic energy E at the M062X/6-311G(3df, 3pd) level of theory, and correlation coefficients of these new quantities with respect to both N and E . As can be

Table 2 Atomic values of new information-theoretic quantities (units are in atomic unit) obtained with the shape density for neutral atoms up to Kr

Atom	N	E_2^s	E_3^s	R_2^s	R_3^s	T_2^s	T_3^s	E
H	1	0.04	0.00	1.41	1.21	0.96	0.50	-0.50
He	2	0.19	0.10	0.72	0.51	0.81	0.31	-2.90
Li	3	0.35	0.46	0.46	0.17	0.65	0.11	-7.48
Be	4	0.53	1.34	0.28	-0.06	0.47	-0.33	-14.66
C	6	0.89	5.38	0.05	-0.37	0.11	-2.36	-37.84
N	7	1.08	8.97	-0.03	-0.48	-0.08	-4.15	-54.58
O	8	1.28	13.93	-0.11	-0.57	-0.28	-6.63	-75.06
F	9	1.49	20.45	-0.17	-0.66	-0.49	-9.89	-99.72
Ne	10	1.70	28.75	-0.23	-0.73	-0.70	-14.04	-128.92
Na	11	1.93	39.36	-0.29	-0.80	-0.93	-19.35	-162.24
Mg	12	2.17	52.65	-0.34	-0.86	-1.17	-25.99	-200.05
Si	14	2.67	87.74	-0.43	-0.97	-1.67	-43.54	-289.35
P	15	2.92	110.11	-0.47	-1.02	-1.92	-54.72	-341.24
S	16	3.18	136.15	-0.50	-1.07	-2.18	-67.74	-398.10
Cl	17	3.45	166.08	-0.54	-1.11	-2.45	-82.71	-460.13
Ar	18	3.71	200.10	-0.57	-1.15	-2.71	-99.72	-527.52
K	19	3.99	239.14	-0.60	-1.19	-2.99	-119.23	-599.90
Ca	20	4.27	283.19	-0.63	-1.23	-3.27	-141.26	-677.56
Cr	24	5.37	510.96	-0.73	-1.35	-4.37	-255.15	-1044.32
Mn	25	5.65	581.71	-0.75	-1.38	-4.65	-290.52	-1150.77
Co	27	6.22	744.28	-0.79	-1.44	-5.22	-371.81	-1382.53
Ni	28	6.51	837.04	-0.81	-1.46	-5.51	-418.19	-1508.14
Zn	30	7.10	1042.45	-0.85	-1.51	-6.10	-520.89	-1779.26
Ge	32	7.70	1280.32	-0.89	-1.55	-6.70	-639.83	-2076.90
As	33	8.01	1412.80	-0.90	-1.58	-7.01	-706.06	-2235.80
Se	34	8.32	1554.37	-0.92	-1.60	-7.32	-776.85	-2401.50
Br	35	8.63	1704.74	-0.94	-1.62	-7.63	-852.04	-2574.13
Kr	36	8.95	1865.97	-0.95	-1.64	-7.95	-932.65	-2753.80
$R^2(N)$		0.994	0.838	0.773	0.788	0.994	0.838	
$R^2(E)$		0.946	0.988	0.526	0.539	0.946	0.988	

seen from the Table, E_2 and E_3 are always positive and monotonically increasing, but R_2 , R_3 , T_2 , and T_3 are not always positive or negative, even though they appear to be monotonically decreasing with respect to the total number of electrons. From the values of correlation coefficients R^2 , we can see that E_2 and T_2 have the largest R^2 value with respect to the total electronic energy. For others, the correlations are also reasonably strong. This particularly strong linear correlation between E_2 and E could partially explain why E_2 has been called information energy. Another explanation is to make use of the following identity³¹⁻³³

$$q(\mathbf{r}) = -\frac{1}{4\pi} \int \frac{\nabla^2 q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (13)$$

for any local strongly decaying quantity $q(\mathbf{r})$. With $q(\mathbf{r}) \equiv \rho^2(\mathbf{r})$ and after some manipulations, we have

$$E_2 = -\frac{1}{2\pi} \left[\iint \frac{\nabla \rho(\mathbf{r}') \cdot \nabla \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \iint \frac{\rho(\mathbf{r}') \nabla^2 \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \right] \quad (14)$$

As can be seen from Eq.(14), the double integral form of E_2 resembles the classical Coulombic repulsion between electrons,

$$J = \frac{1}{2} \iint \frac{\rho(\mathbf{r}') \cdot \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (15)$$

except that Eq.(14) involves interactions among $\rho(\mathbf{r})$, $\nabla \rho(\mathbf{r})$, and $\nabla^2 \rho(\mathbf{r})$.

Table 2 exhibits the numerical results of these information-theoretic quantities obtained for the shape density, Eqs.(6–8), of orders 2 and 3, respectively, for neutral atoms from H to Kr. Their correlation coefficients with both E and N are also appended in the Table. It becomes clear that the shape function version of these new information-theoretic quantities possesses different correlations with E and N . Strong linear correlations between E_2^σ and N , and between T_2^σ and N are seen, so are correlations of E_2^σ , E_3^σ , T_2^σ , T_3^σ and with respect to the total electronic energy E . These linear relationships can be harnessed to predict properties for atoms and ions.

For molecules, Table 3 illustrates numerical results for 21 species of the same category with the general molecular formula of $R_1R_2R_3C-F$. To save space, we do not show their counterparts in terms of the shape function. Their correlation coefficients with N and E are also shown, which, as can be seen from the Table, are remarkable. Since the electron density determines everything in the ground state, it is not surprising that strong correlations among different quantities in different sys-

Table 3 Molecular values of new information-theoretic quantities (units are in atomic unit) obtained with the total electron density

$R_1R_2R_3$	N^a	E_2	E_3	R_2	R_3	T_2	T_3	E
HHH	28	270.90	15285.70	-2.433	-2.243	-269.90	-15285.20	-239.55
CH ₃ HH	36	302.58	15846.16	-2.481	-2.250	-301.58	-15845.66	-278.85
C ₂ H ₅ HH	44	334.23	16404.65	-2.524	-2.258	-333.23	-16404.15	-318.15
CH ₃ CH ₃ H	44	334.26	16407.22	-2.524	-2.258	-333.26	-16406.72	-318.16
C ₂ H ₅ CH ₃ H	52	365.92	16965.94	-2.563	-2.265	-364.92	-16965.44	-357.46
C ₃ H ₇ HH	52	365.90	16963.84	-2.563	-2.265	-364.90	-16963.34	-357.45
CH ₃ CH ₂ CH ₃	52	365.94	16966.97	-2.563	-2.265	-364.94	-16966.47	-357.47
C ₂ H ₅ C ₂ H ₅ H	60	397.58	17524.38	-2.599	-2.272	-396.58	-17523.88	-396.76
C ₂ H ₅ CH ₂ CH ₃	60	397.60	17525.81	-2.599	-2.272	-396.60	-17525.31	-396.77
C ₃ H ₇ CH ₃ H	60	397.58	17525.07	-2.599	-2.272	-396.58	-17524.57	-396.76
C ₄ H ₉ HH	60	397.57	17524.58	-2.599	-2.272	-396.57	-17524.08	-396.75
C ₂ H ₅ C ₂ H ₅ CH ₃	68	429.26	18084.94	-2.633	-2.279	-428.26	-18084.44	-436.07
C ₃ H ₇ C ₂ H ₅ H	68	429.25	18084.21	-2.633	-2.279	-428.25	-18083.71	-436.06
C ₃ H ₇ CH ₂ CH ₃	68	429.27	18085.16	-2.633	-2.279	-428.27	-18084.66	-436.07
C ₂ H ₅ C ₂ H ₅ C ₂ H ₅	76	460.92	18643.97	-2.664	-2.286	-459.92	-18643.47	-475.36
C ₃ H ₇ C ₂ H ₅ CH ₃	76	460.93	18644.35	-2.664	-2.286	-459.93	-18643.85	-475.36
C ₃ H ₇ C ₃ H ₇ H	76	460.92	18643.53	-2.664	-2.286	-459.92	-18643.03	-475.35
C ₃ H ₇ C ₂ H ₅ C ₂ H ₅	84	492.60	19203.48	-2.692	-2.292	-491.60	-19202.98	-514.66
C ₃ H ₇ C ₃ H ₇ CH ₃	84	492.60	19203.53	-2.692	-2.292	-491.60	-19203.03	-514.66
C ₃ H ₇ C ₃ H ₇ C ₂ H ₅	92	524.27	19762.76	-2.720	-2.298	-523.27	-19762.26	-553.96
C ₃ H ₇ C ₃ H ₇ C ₃ H ₇	100	555.94	20322.10	-2.745	-2.304	-554.94	-20321.60	-593.26
$R^2(E)$		1.000	1.000	0.988	0.998	1.000	1.000	
$R^2(N)$		1.000	1.000	0.988	0.998	1.000	1.000	

Onicescu information energy of orders 2 and 3, E_2 and E_3 ; Rényi entropy of orders 2 and 3, R_2 and R_3 ; and Tsallis entropy of orders 2 and 3, T_2 and T_3 , for a total of 21 molecular systems of the same kind with the general formula of $R_1R_2R_3C-F$

Fig.1 Profiles of information-theoretic quantities as a function of the $\angle$ HCCH dihedral angle for the ethane molecule

- (a) the Onicescu information energy of orders 2 (E_2) of C_2H_6 ; (b) the Shannon entropy of C_2H_6 ; (c) atomic E_2 values for carbon atoms in C_2H_6 ; (d) atomic E_2 values for hydrogen atoms in C_2H_6

tems can be obtained in some cases. These amazingly strong correlations likely originate from the fact that this set of molecules is similar in nature. Whether or not these linear relationships persist in other systems remains to be validated, but based on the results from our previous studies, the answer to above question is likely no.¹⁵

To demonstrate different behaviors of these quantities at the level of atoms in molecules, as an illustrative example, shown in Fig.1 are the profiles of the second-order Onicescu information energy E_2 as a function of the $\angle$ HCCH dihedral angle for the ethane molecule at both molecular and atoms-in-molecules levels. Fig.1a is the second-order Onicescu information energy at the molecular level, Fig.1b is the molecular value of the Shannon entropy, Fig.1c denotes the atomic E_2 value for the carbon atom in C_2H_6 , and Fig.1d represents the atomic E_2 value for the hydrogen atom in C_2H_6 . While in all the cases smoothly varying curves are observed as the dihedral angle increases from 0° (the staggered conformer) to 360° , we can clearly see that the changing patterns are markedly different. The second-order Onicescu information energy is the largest (Fig.1a) at $\angle$ HCCH = 0° , that is, when the conformer is staggered, so is the atomic value of E_2 on the carbon atom (Fig.1c). However, for its value on the hydrogen atom, it becomes the least, as shown in Fig.1d. This latter behavior is also true for the molecular value of the Shannon entropy exhibited in Fig.1b.¹¹ Overall, the profiling changing pattern of the molecular value of the second-order Onicescu information energy as well as its atomic value on the carbon atom in ethane is like a cosine curve, whereas for its atomic value on the hydrogen atom together with the molecular value of the Shannon entropy, the changing pattern resembles a sine curve. These different patterns on molecular and atomic levels were unveiled elsewhere for other information-theoretic quantities.^{11,16} These different behaviors will likely result in different reactivity properties for

different atoms in molecules.

5 Concluding remarks

As a continuation of our recent efforts to develop an information-theoretic approach in density functional reactivity theory, in this work, we have introduced three new quantities, Rényi entropy, Tsallis entropy, and Onicescu information energy, into the framework of DFRT. These quantities are all functionals of the electron density and they are closely related to each other as well. These quantities can be represented not only for the electron density, but also for the shape function, as have been shown in this work. We evaluated the second and third orders of these quantities for a number of neutral atomic and molecular systems under both the electron density and shape function representations. Their correlations with the total number of electrons and electronic energy have also been obtained and discussed. In addition, using the second-order Onicescu information energy as an example, we examined the changing pattern of this quantity as a function of the $\angle$ HCCH dihedral angle for the ethane molecule at both molecular and atoms-in-molecules levels, where different changing patterns have been observed. It is our belief that these new quantities can be used to serve as novel reactivity descriptors in DFRT to provide more in-depth insights for the accurate predictions of structure and reactivity properties for molecular systems. More studies along this line are in progress and will be reported elsewhere.

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