Bull. Chem. Soc. Jpn., 72, 955—961 (1999)

A Reason of Linear Additivity of 'π Energy' in Polyenes

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(Received November 19, 1998)

The Hückel molecular orbital theory stands on the approximation that a π electron moves in the average field of potentials from other (σ and π) electrons and nuclei, where the nuclear–nuclear repulsion energies are not taken into consideration. A strange property of the Hückel energy is that it has a linear additivity with respect to the ethylene unit in polyenes. Based on the molecular virial theorem and a previous finding that the Hückel energy represents the kinetic energy of π electrons ($\langle T\rangle_\pi$), the linearity problem is reduced to two points: (1) why the ratio of $\langle T\rangle_\pi$ to the total kinetic energy ($\langle T\rangle$) is constant in linear polyenes and (2) why $\langle T\rangle$ is linear with respect to the ethylene unit.

We treated the second problem using a newly developed energy-partitioning technique, and found that the *total atomic interactions* are well localized around the region between neighboring atoms in spite of strong long-range interactions of the individual potential-energy terms. If we adopt the fact that $\langle T\rangle_\pi/\langle T\rangle$ is constant, the riddle of why $\langle T\rangle_\pi$ or Hückel energy includes the information on the nuclear configuration is also understood through the virial theorem.

We use 'empirical π energy' for the so-called 'π energy' which is calculated by the Hückel molecular orbital theory.[1] A notable characteristic of the empirical π energy is that it has a linear additivity with respect to the ethylene unit in linear polyenes. This has served as the measure in the modern definition of aromaticity.[2—7]

The Hückel molecular orbital theory stands on the approximation that a π electron moves in the average field of potentials from other (σ and π) electrons and nuclei, where the nuclear–nuclear repulsion energies are not taken into consideration.[1] Here a strange point is that although the kinetic-energy and potential-energy operators are homogeneous of degrees −2 and −1 to the coordinate, the sum is, somehow, homogeneous of degree +1. Thus, the property of the linear additivity is a strange outcome.

In the preceding papers,[8,9] we have compared the Hückel energy with the partitioned ab initio total energies (E) to give this result: (1) the empirical π energy does not correspond to the π-electronic energy (E_π^{el}), the energy of π electrons that move in the fields of other π as well as σ electrons and nuclear charges as the Hückel energy was expected to represent. Instead, (2) it represents a relative amount of the kinetic energy of π electrons ($\langle T\rangle_\pi$) in a quantitative manner and (3) the $\langle T\rangle_\pi/\langle T\rangle$ is a constant in linear polyenes.[9]

Thus, although the reason has not been given, the empirical π energy is understood to express a relative amount of $\langle T\rangle$ of a polyene. Besides, since the simple virial theorem[10] holds in a molecular system, the empirical π energy is also supposed to express E, or the relative potential energy ($\langle V\rangle$). Therefore, the linearity problem of the empirical π energy comes to two points: (1) why $\langle T\rangle_\pi/\langle T\rangle$ is a constant in linear polyenes and (2) why E, $\langle T\rangle$, or $\langle V\rangle$ is linear with respect to the ethylene unit. This article treats the latter problem.

Method

The procedure must begin to inspect the manners in which atoms interact with each other in a molecular system. To this end, it is necessary to express, in an explicit way, the total and partitioned energies as a sum of the energies of atomic parts and of the interactions between all pairs of atoms (Eq. 1). Kollmar[11] has proposed this for the ab initio Hartree–Fock–Roothaan theory.[12—14] However, since he used the Fock matrix, the one-center term (E_A) inevitably includes a large amount of two-center energies and vice versa.

The explicit partitioning has recently been carried by us and the resultant expressions are:[15]

$$E = \sum_A E_A + \sum_{A>B} E_{AB}, \tag{1}$$

$$E_A = \langle T\rangle_A + \langle V_{eN}\rangle_A + \langle V_{ee}\rangle_A, \tag{2}$$

$$E_{AB} = \langle T\rangle_{AB} + \langle V_{eN}\rangle_{AB} + \langle V_{ee}\rangle_{AB} + V_{AB}^N \tag{3}$$

where, E_A and E_{AB} are the total one- and two-center energies while $\langle T\rangle$, $\langle V_{eN}\rangle$, $\langle V_{ee}\rangle$, and V^N are the kinetic energy of electrons, one-electron potential energy, two-electron potential energy, and nuclear–nuclear repulsion energy. They are obtained by the following formulae. 1) The kinetic energy,

$$\langle T\rangle_A = \sum_{r\in A}\sum_{s\in A} P_{rs}\int \chi_r^*(1)\left(-\frac{1}{2}\nabla^2(1)\right)\chi_s(1)\mathrm{d}\tau_1, \tag{4}$$

$$\langle T\rangle_{AB} = 2\sum_{r\in A}\sum_{s\in B} P_{rs}\int \chi_r^*(1)\left(-\frac{1}{2}\nabla^2(1)\right)\chi_s(1)\mathrm{d}\tau_1. \tag{5}$$

Here, P_{rs}, χ_r, and ∇^2 are the element of the bond order matrix between atomic orbitals, χ_r and χ_s, and the Laplacian operator. And $\sum_{r\in A}$ indicates the summation of r that belongs to atom A. 2) The one-electron potential energy,

$$\langle V_{eN}\rangle_A = \sum_{r\in A}\sum_s P_{rs}\int \chi_r^*(1)\left(\frac{-Z_A}{r_{1A}}\right)\chi_s(1)\mathrm{d}\tau_1, \tag{6}$$

$$\langle V_{eN}\rangle_{AB}=\sum_{r\in A}\sum_{s}P_{rs}\int\chi_r^*(1)\left(\frac{-Z_B}{r_{1B}}\right)\chi_s(1)\mathrm{d}\tau_1 + \sum_{r\in B}\sum_{s}P_{rs}\int\chi_r^*(1)\left(\frac{-Z_A}{r_{1A}}\right)\chi_s(1)\mathrm{d}\tau_1, \quad (7)$$

where, Z_A and r_{1A} are the nuclear charge of atom A and the distance between nucleus A and electron 1. And indicates the $\sum_s$ summation concerning all AOs. 3) The two-electron potential energy,

$$\langle V_{ee}\rangle_A=\frac{1}{2}\sum_{r\in A}\sum_{s}P_{rs}\sum_{t\in A}\sum_{u}P_{tu}(rs/tu) - \frac{1}{4}\sum_{r\in A}\sum_{s\in A}P_{rs}\sum_{t}\sum_{u}P_{tu}(rt/su), \quad (8)$$

$$\langle V_{ee}\rangle_{AB}=\sum_{r\in A}\sum_{s}P_{rs}\sum_{t\in B}\sum_{u}P_{tu}(rs/tu) - \frac{1}{2}\sum_{r\in A}\sum_{s\in B}P_{rs}\sum_{t}\sum_{u}P_{tu}(rt/su). \quad (9)$$

In the above equation, two-electron integrals ((rs/tu)) are,

$$(rs/tu)=\int\int\chi_r^*(1)\chi_s(1)\left(\frac{1}{r_{12}}\right)\chi_t^*(2)\chi_u(2)\mathrm{d}\tau_1\mathrm{d}\tau_2. \quad (10)$$

The rationalization of these formulae has been given in the preceding paper and results calculated by the above scheme satisfy all the theoretical requirements.[15]

The calculation for the following results has been carried out on an IBM RS/6000-590 computer using GAUSSIAN-90 program package[16] with additional subroutines for the above energy-partitioning.

Results and Discussion

To know the characteristics of σ system concerning the linear additivity, we first inspect the case of linear saturated hydrocarbons; then we discuss the polyenes. We have adopted the STO-6G basis set[17] and all the molecular geometries have been optimized.

Additivity in Linear Saturated Hydrocarbons. Table 1 shows the partitioned energies as a function of n in CH_3–$(CH_2)_n$–CH_3. The molecular system is required to satisfy the simple virial theorem: $\langle V\rangle = -2\langle T\rangle$. Most LCAO-MO wave functions are far from this requirement. Besides, the expectation values are greatly dependent on the scale factor of the wave function.[18] We used both the usual unscaled wave function and the wave function so scaled as to satisfy the simple virial ratio ($\langle V\rangle = -2\langle T\rangle$) to see the effect of scaling: This is a way to see the basis set dependency.

A near-perfect linear additivity is found in E and $\langle T\rangle$ in the linear saturated hydrocarbons. The linearity holds within a deviation of 0.004% in both E and $\langle T\rangle$. When the wave function is scaled, such a deviation is further reduced, i. e., if a more sophisticated basis set is adopted, the linearity is expected to be much more improved. Let us seek the reason of the linearity.

Since E, $\langle T\rangle$, and $\langle V\rangle$ are linked by the virial theorem, examining one term of them would be enough to understand the additive nature. Here we take $\langle V\rangle$ for this purpose. Let us consider a general case as one atomic group (–CH_2–) is added to molecule P to give its homologue Q (Scheme 1). For the process from P to Q, if the potential energy is shown to increase proportionally to n, the number of units, or if the energy difference between n and n+1 homologues gives a constant,

$$2\Delta E=-2\Delta\langle T\rangle=\Delta\langle V\rangle=const, \quad (11)$$

we may get an answer to why E and $\langle T\rangle$ have the character of a linear additivity.

In Eq. 11, $\Delta\langle V\rangle$ is partitioned as

$$\Delta\langle V\rangle=\Delta\langle V_{eN}\rangle+\Delta\langle V_{ee}\rangle+\Delta V^N. \quad (12)$$

To satisfy Eq. 11, $\langle V_{eN}\rangle_{AB}+\langle V_{ee}\rangle_{AB}+V_{AB}{}^N$ must be linear to n. Namely, the sum to be null or close to null in atoms A and B except for neighboring groups. Let us examine how the long-range interactions are cancelled.

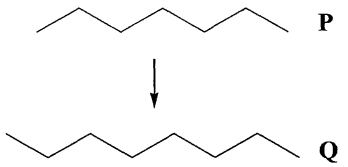
Tables 2, 3, and 4 show the group interaction energies between methyl and/or methylene groups in $CH_3(CH_2)_{11}CH_3$. Here the group interaction indicates the sum of the interactions between atomic groups. The interaction of the total energy (i. e., E_{AB}) between adjacent methylene groups (m and m+1 interaction) results in a value between −0.0990 and −0.1132 au. Noted is that m and m+1 interaction energy is almost fixed to be −0.1132 except 1-2 and 12-13 interactions. The exception is understandable because the first and 13th groups are methyl and the others are methylene groups.

The m and m+2 interactions appear to be a repulsive value between 0.0202 and 0.0216 au: except interactions including the first and last groups, they are constant at 0.0216 au. Other long-range interactions are found to be almost zero. Thus, the change of the total by adding one CH_2 group to such a system can be easily predicted. Thus, we may understand that the σ system has a potential-energy localizability.

However, such localizability is strange enough if one considers the nuclear–nuclear interaction energies that are given by Z_AZ_B/R_{AB}. Namely, they are long-range interactions. As a matter of fact, as Table 2 (lower triangle) shows, even that between 1 and 13 is more than 2.7 au. To have the energy localizability hold, the nuclear–nuclear interaction energy must be near-perfectly cancelled by other electrostatic interactions, i. e., by one- and two-electron potential energies.

One- and two-electron potential energies in Table 3 show that each value of the two-electron potential energy is almost equal to that of the nuclear–nuclear interaction energy and that the absolute value of one-electron potential energy is about double that of the two-electron potential energy. Namely, $\langle V_{eN}\rangle_{AB}\approx-2\langle V_{ee}\rangle_{AB}\approx-2V_{AB}{}^N$ holds in a long-range group interaction. Table 4 verifies that the nuclear–nuclear repulsion energy is almost cancelled by both one- and two-electron potential energies.

The above results show that the linear saturated hydrocarbons have the nature of a linear additivity. This indicates



Scheme 1.

Table 1. Verification of Linearity of the Kinetic ($\langle T\rangle$) and Total Energies (E) in CH_3–$(CH_2)_n$–CH_3[a]

	Unscaled[b]			Scaled[c]		
n	$\langle T\rangle$	$\Delta\langle T\rangle$	$\Delta^2\langle T\rangle$	$\langle T\rangle$	$\Delta\langle T\rangle$	$\Delta^2\langle T\rangle$
1	117.919216[d]			118.02199		
2	156.816367	38.897151		156.978671	38.956681	
3	195.713737	38.897370	0.000219	195.935124	38.956453	−0.000228
4	234.610987	38.897250	−0.000120	234.891750	38.956626	0.000173
5	273.506749	38.895762	−0.001488	273.847963	38.956213	−0.000413
6	312.403681	38.896932	0.001170	312.804019	38.956056	−0.000157
n	$\Sigma\langle T\rangle_{AB}$	$\Delta\Sigma\langle T\rangle_{AB}$	$\Delta^2\Sigma\langle T\rangle_{AB}$	$\Sigma\langle T\rangle_{AB}$	$\Delta\Sigma\langle T\rangle_{AB}$	$\Delta^2\Sigma\langle T\rangle_{AB}$
1	3.761691			3.763663		
2	4.896471	1.134780		4.899340	1.135677	
3	6.031630	1.135159	0.000379	6.034926	1.135586	−9.1E−05
4	7.166756	1.135126	−3.3E−05	7.170487	1.135561	−2.5E−05
5	8.30040	1.133644	−0.001482	8.306031	1.135544	−1.7E−05
6	9.435082	1.134682	0.001038	9.441554	1.135523	−2.1E−05
n	$\Sigma\langle T\rangle_A$	$\Delta\Sigma\langle T\rangle_A$	$\Delta^2\Sigma\langle T\rangle_A$	$\Sigma\langle T\rangle_A$	$\Delta\Sigma\langle T\rangle_A$	$\Delta^2\Sigma\langle T\rangle_A$
1	114.157525			114.258327		
2	151.919896	37.762371		152.079331	37.821004	
3	189.682106	37.762210	−0.000161	189.900198	37.820867	−0.000137
4	227.444232	37.762126	−8.4E−05	227.721264	37.821066	0.000199
5	265.206349	37.762117	−9E−06	265.541932	37.820668	−0.000398
6	302.968599	37.762250	0.000133	303.362465	37.820533	−0.000135
n	E	ΔE	Δ^2E	E	ΔE	Δ^2E
1	−118.022349			−118.022379		
2	−156.978684	−38.956335		−156.978737	−38.956358	
3	−195.934999	−38.956315	2E−05	−195.935077	−38.956340	1.8E−05
4	−234.891317	−38.956318	−3E−06	−234.891422	−38.956345	−5E−06
5	−273.847636	−38.956319	−1E−06	−273.847768	−38.956346	−1E−06
6	−312.803955	−38.956319	8.52651E−14	−312.804113	−38.956345	1E−06
n	ΣE_{AB}	$\Delta\Sigma E_{AB}$	$\Delta^2\Sigma E_{AB}$	ΣE_{AB}	$\Delta\Sigma E_{AB}$	$\Delta^2\Sigma E_{AB}$
1	−1.213209			−1.211362		
2	−1.571989	−0.35878		−1.56924	−0.357878	
3	−1.930508	−0.358519	0.000261	−1.927134	−0.357894	−1.6E−05
4	−2.288994	−0.358486	3.3E−05	−2.285049	−0.357915	−2.1E−05
5	−2.648424	−0.35943	−0.000944	−2.642975	−0.357926	−1.1E−05
6	−3.007228	−0.358804	0.000626	−3.000916	−0.357941	−1.5E−05
n	ΣE_A	$\Delta\Sigma E_A$	$\Delta^2\Sigma E_A$	ΣE_A	$\Delta\Sigma E_A$	$\Delta^2\Sigma E_{AB}$
1	−116.80914			−116.811017		
2	−155.406695	−38.597555		−155.409497	−38.59848	
3	−194.004490	−38.597795	−0.00024	−194.007944	−38.598447	3.3E−05
4	−232.602323	−38.597833	−3.8E−05	−232.606373	−38.598429	1.8E−05
5	−271.199212	−38.596889	0.000944	−271.204793	−38.598420	9E−06
6	−309.796727	−38.597515	−0.000626	−309.803198	−38.598405	1.5E−05

a) STO-6G. b) Results by the unscaled wave function. c) Results by the scaled wave function. d) In au.

that the σ skeleton of linear polyenes has a similar character and may be interpreted as if the σ electrons are localized to shield nuclear charges.

Energy Additivity in Linear Polyenes. Tables 5, 6, and 7 show the atomic group (CH_2 or CH) interactions in CH_2=CH–(CH=CH)$_5$–CH=CH_2. The interaction of the total energy is characteristic: except the first and last units, neighboring interactions are found to be −0.144 (C–C) or −0.150 au (C=C). The one-three interactions are greatly reduced to be a small constant of 0.025 au (the exception for including the first or last groups can be understood as following from the fact that the numbers of the hydrogen atoms attached to the carbon atom are different from other groups).

One-four interactions and further long-range interactions are negligible. Thus it is easily understood that addition of the one unit of (CH=CH) to a polyethylenic system produces a regular lowering of the total energy. The lower triangle of Table 5 shows the nuclear–nuclear interactions (V_{AB}^{N}). They are long-range according to the classical electrostatic interaction. The interactions in the one-electron potential energy

Table 2. Interaction Energy between Two Methyl and/or Methine Groups in CH_3^{1}–CH_2^{2}---CH_3^{13} (E_{AB} and V_{AB}^{N})[a]

Total energy[b]

	1	2	3	4	5	6	7	8	9	10	11	12	13	
	−39.48923	−0.09907	0.02022	−0.00149	0.00001	−0.00001	0.00000	0.00000	0.00000	0.00000	−0.00001	0.00000	0.00000	1
		−38.86373	−0.11317	0.02159	−0.00149	0.00001	−0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	2
1	9.71413		−38.86339	−0.11312	0.02155	−0.00148	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	−0.00001	3
2	20.91051	6.16139		−38.86331	−0.11314	0.02155	−0.00148	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	4
3	13.90806	19.00342	6.16251		−38.86325	−0.11319	0.02155	−0.00148	0.00001	0.00000	0.00000	0.00000	0.00000	5
4	9.18842	12.74521	19.00444	6.16251		−38.86324	−0.11312	0.02156	−0.00148	0.00001	0.00000	0.00000	0.00000	6
5	7.22758	8.30710	12.74482	19.00385	6.16251		−38.86327	−0.11311	0.02155	−0.00148	0.00001	0.00000	0.00000	7
6	5.74032	6.53898	8.30672	12.74427	19.00245	6.16251		−38.86324	−0.11320	0.02155	−0.00148	0.00001	−0.00001	8
7	4.87008	5.16566	6.53890	8.30689	12.74450	19.00391	6.16249		−38.86325	−0.11314	0.02155	−0.00149	0.00001	9
8	4.15612	4.38287	5.16565	6.53906	8.30700	12.74560	19.00404	6.16251		−38.86331	−0.11312	0.02159	−0.00149	10
9	3.67014	3.72958	4.38271	5.16556	6.53886	8.30700	12.74464	19.00245	6.16251		−38.86339	−0.11317	0.02022	11
10	3.25304	3.29345	3.72955	4.38274	5.16556	6.53906	8.30695	12.74427	19.00385	6.16251		−38.86373	−0.09907	12
11	2.94404	2.91403	3.29339	3.72955	4.38271	5.16565	6.53894	8.30672	12.74482	19.00444	6.16251		−39.48923	13
12	2.67110	2.63715	2.91403	3.29345	3.72958	4.38287	5.16568	6.53898	8.30710	12.74521	19.00342	6.16139		
13	2.74719	2.67110	2.94404	3.25304	3.67014	4.15612	4.87010	5.74032	7.22758	9.18842	13.90806	20.91051	9.71413	
	1	2	3	4	5	6	7	8	9	10	11	12	13	

Nuclear repulsion energy[b]

a) STO-6G. b) In au.

Table 3. Interaction Energy between Two Methyl and/or Methine Groups in CH_3^{1}–CH_2^{2}---CH_3^{13} ($\langle V_{eN}\rangle_{AB}$ and $\langle V_{ee}\rangle_{AB}$)[a]

One electron potential energy[b]

	1	2	3	4	5	6	7	8	9	10	11	12	13	
	−111.23422	−42.04039	−27.83820	−18.38901	−14.46452	−11.48755	−9.74588	−8.31696	−7.34435	−6.50967	−5.89101	−5.34243	−5.50021	1
		−102.75881	−38.20008	−25.48528	−16.60660	−13.07293	−10.32659	−8.76184	−7.45560	−6.58382	−5.82496	−5.26916	−5.34243	2
1	22.69739		−102.82226	−38.21966	−25.49487	−16.61311	−13.07849	−10.33112	−8.76536	−7.45890	−6.58630	−5.82496	−5.89101	3
2	20.63430	19.25727		−102.82632	−38.21988	−25.49515	−16.61428	−13.07946	−10.33143	−8.76594	−7.45890	−6.58382	−6.50967	4
3	13.94203	18.69394	19.29806		−102.82528	−38.21711	−25.49540	−16.61433	−13.07890	−10.33143	−8.76536	−7.45560	−7.34434	5
4	9.20010	12.75232	18.71269	19.30122		−102.82569	−38.21996	-25.49755	−16.61433	−13.07945	−10.33112	−8.76184	−8.31696	6
5	7.23692	8.29903	12.76228	18.71361	19.30045		−102.82594	−38.22021	−25.49567	−16.61440	−13.07857	−10.32664	−9.74592	7
6	5.74723	6.53394	8.30594	12.76310	18.71229	19.30074		−102.82576	−38.21713	−25.49517	−16.61312	−13.07293	−11.48756	8
7	4.87580	5.16093	6.53958	8.30693	12.76312	18.71366	19.30090		−102.82530	−38.21988	−25.49487	−16.60661	−14.46452	9
8	4.16083	4.37896	5.16547	6.54037	8.30687	12.76418	18.71378	19.30078		−102.82632	−38.21966	−25.48528	−18.38900	10
9	3.67421	3.72602	4.38265	5.16587	6.54002	8.30687	12.76324	18.71231	19.30046		−102.82226	−38.20008	−27.83820	11
10	3.25663	3.29038	3.72935	4.38320	5.16587	6.54037	8.30698	12.76312	18.71362	19.30122		−102.75881	−42.04039	12
11	2.94697	2.91093	3.29291	3.72935	4.38264	5.16547	6.53961	8.30594	12.76228	18.71269	19.29806		−111.23422	13
12	2.67134	2.63201	2.91093	3.29038	3.72602	4.37896	5.16096	6.53394	8.29903	12.75232	18.69394	19.25727		
13	2.75304	2.67134	2.94697	3.25663	3.67421	4.16083	4.87582	5.74723	7.23692	9.20010	13.94203	20.63430	22.69739	
	1	2	3	4	5	6	7	8	9	10	11	12	13	

Two electron potential energy[b]

a) STO-6G. b) In au.

Table 4. Interaction Energy between Two Methyl and/or Methine Groups in CH_3^1–CH_2^2---CH_3^{13} ($\langle V_{eN}\rangle_{AB}+\langle V_{ee}\rangle_{AB}+V_{AB}^{N}$ and $\langle T\rangle_{AB}$)[a]

Potential energy[b]

	1	2	3	4	5	6	7	8	9	10	11	12	13	
	−78.82271	−0.49558	0.01190	−0.00048	−0.00002	0.00000	0.00000	−0.00001	0.00000	0.00000	0.00000	0.00001	0.00001	1
		−77.34014	−0.50272	0.01225	−0.00047	−0.00002	−0.00001	−0.00001	0.00000	0.00001	0.00000	0.00000	0.00001	2
1	39.33348		−77.36169	−0.50253	0.01222	−0.00046	−0.00002	−0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	3
2	0.39651	38.47641		−77.36259	−0.50241	0.01222	−0.00046	−0.00002	0.00000	0.00000	0.00000	0.00001	0.00000	4
3	0.00831	0.38955	38.49830		−77.36232	−0.50237	0.01222	−0.00046	−0.00003	0.00000	0.00000	0.00000	0.00001	5
4	−0.00100	0.00935	0.38941	38.49928		−77.36244	−0.50239	0.01223	−0.00046	−0.00002	0.00000	−0.00001	−0.00001	6
5	0.00002	−0.00103	0.00933	0.38928	38.49908		−77.36255	−0.50238	0.01222	−0.00047	−0.00002	0.00000	0.00000	7
6	0.00000	0.00002	−0.00102	0.00933	0.38918	38.49920		−77.36247	−0.50237	0.01222	−0.00046	−0.00001	0.00000	8
7	0.00000	0.00000	0.00002	−0.00102	0.00934	0.38927	38.49928		−77.36233	−0.50241	0.01223	−0.00047	−0.00002	9
8	0.00000	0.00000	0.00000	0.00002	−0.00102	0.00934	0.38927	38.49923		−77.36259	−0.50253	0.01225	−0.00048	10
9	0.00000	0.00000	0.00000	0.00000	0.00002	−0.00102	0.00934	0.38918	38.49908		−77.36169	−0.50272	0.01190	11
10	0.00000	0.00000	0.00000	0.00000	0.00000	0.00002	−0.00102	0.00933	0.38928	38.49928		−77.34014	−0.49558	12
11	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00002	−0.00102	0.00933	0.38941	38.49830		−78.82271	13
12	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00002	−0.00103	0.00935	0.38955	38.47641		
13	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00002	−0.00100	0.00831	0.39651	39.33348	
	1	2	3	4	5	6	7	8	9	10	11	12	13	

Kinetic energy[b]

a) STO-6G. b) In au.

Table 5. Atomic Group Interactions in CH_2^1=CH^2–CH^3=CH^4–CH^5=CH^6–CH^7=CH^8–CH^9=CH^{10}–CH^{11}=CH^{12}–CH^{13}=CH_2^{14} (E_{AB} and V_{AB}^{N})[a]

Total energy[b]

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
	−38.84405	−0.13447	0.02289	−0.00341	0.00002	−0.00022	0.00000	−0.00003	0.00000	0.00000	0.00000	0.00000	−0.00001	0.00000	1
		−38.23139	−0.14404	0.02492	−0.00190	0.00003	−0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	−0.00001	2
1	6.18523		−38.22051	−0.15032	0.02496	−0.00346	0.00004	−0.00023	0.00000	−0.00003	0.00000	−0.00001	0.00000	0.00000	3
2	19.45335	2.93879		−38.22384	−0.14456	0.02501	−0.00191	0.00003	−0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	4
3	11.31228	15.92811	2.93987		−38.22190	−0.15021	0.02501	−0.00346	0.00004	−0.00023	0.00000	−0.00003	0.00000	0.00000	5
4	7.67524	10.25515	17.62181	2.93960		−38.22254	−0.14462	0.02502	−0.00191	0.00004	−0.00001	0.00000	0.00000	0.00000	6
5	5.82940	6.56969	10.26328	15.97753	2.93987		−38.22223	−0.15015	0.02502	−0.00346	0.00003	−0.00023	0.00000	−0.00003	7
6	4.70893	5.20717	6.86497	10.26278	17.60590	2.93987		−38.22223	−0.14462	0.02501	−0.00191	0.00004	−0.00001	0.00000	8
7	3.92301	4.07164	5.20938	6.57626	10.26406	15.98618	2.93987		−38.22254	−0.15021	0.02501	−0.00346	0.00003	−0.00022	9
8	3.38751	3.48275	4.18438	5.20931	6.86399	10.26396	17.60370	2.93987		−38.22190	−0.14456	0.02496	−0.00190	0.00002	10
9	2.95561	2.94073	3.48371	4.07370	5.20961	6.57719	10.26396	15.98618	2.93987		−38.22384	−0.15032	0.02492	−0.00341	11
10	2.64320	2.61516	2.99926	3.48370	4.18426	5.20961	6.86399	10.26406	17.60590	2.93987		−38.22051	−0.14404	0.02289	12
11	2.37074	2.29921	2.61563	2.94155	3.48370	4.07370	5.20931	6.57626	10.26278	15.97753	2.93960		−38.23139	−0.13447	13
12	2.16640	2.09327	2.33495	2.61563	2.99926	3.48371	4.18438	5.20938	6.86497	10.26328	17.62181	2.93987		−38.84405	14
13	1.97880	1.88646	2.09327	2.29921	2.61516	2.94073	3.48275	4.07164	5.20717	6.56969	10.25515	15.92811	2.93879		
14	2.08290	1.97880	2.16640	2.37074	2.64320	2.95561	3.38751	3.92301	4.70893	5.82940	7.67524	11.31228	19.45335	6.18523	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	

Nuclear repulsion energy[b]

a) STO-6G. b) In au.

Table 6. Atomic Group Interactions in $CH_2{}^1{=}CH^2{-}CH^3{=}CH^4{-}CH^5{=}CH^6{-}CH^7{=}CH^8{-}CH^9{=}CH^{10}{-}CH^{11}{=}CH^{12}{-}CH^{13}{=}CH_2{}^{14}$ ($\langle V_{eN}\rangle$ and $\langle V_{ee}\rangle$)[a]

One electron potential energy[b]

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
	−103.05538	−39.14121	−22.65410	−15.39928	−11.67081	−9.43681	−7.85250	−6.78533	−5.91546	−5.29302	−4.74454	−4.33747	−3.95827	−4.17233	1
		−95.17231	−31.98738	−20.50551	−13.12369	−10.41119	−8.13463	−6.96281	−5.87582	−5.22811	−4.59437	−4.18466	−3.76815	−3.95827	2
1	19.40046		−95.23197	−35.44589	−20.53297	−13.76207	−10.42093	−8.37948	−6.96801	−6.00353	−5.23139	−4.67268	−4.18466	−4.33747	3
2	18.82736	16.26920		−95.22832	−32.10285	−20.53158	−13.14366	−10.42068	−8.14261	−6.96796	−5.88013	−5.23139	−4.59437	−4.74454	4
3	11.35674	15.48366	16.30896		−95.22981	−35.41363	−20.53461	−13.76004	−10.42137	−8.37923	−6.96796	−6.00353	−5.22811	−5.29302	5
4	7.72150	10.26596	16.97042	16.30737		−95.22954	−32.12105	−20.53436	−13.14567	−10.42137	−8.14261	−6.96801	−5.87582	−5.91546	6
5	5.84139	6.55333	10.28533	15.54288	16.30855		−95.23002	−35.40927	−20.53436	−13.76004	−10.42068	−8.37948	−6.96281	−6.78533	7
6	4.72767	5.20402	6.89457	10.28446	16.95729	16.30843		−95.23002	−32.12105	−20.53461	−13.14366	−10.42093	−8.13463	−7.85250	8
7	3.92949	4.06298	5.21156	6.56672	10.28622	15.55119	16.30882		−95.22954	−35.41363	−20.53158	−13.76207	−10.41119	−9.43681	9
8	3.39780	3.48006	4.19487	5.21138	6.89353	10.28607	16.95567	16.30882		−95.22981	−32.10285	−20.53297	−13.12369	−11.67081	10
9	2.95985	2.93509	3.48430	4.06889	5.21176	6.56778	10.28607	15.55119	16.30843		−95.22832	−35.44589	−20.50551	−15.39928	11
10	2.64982	2.61294	3.00423	3.48426	4.19474	5.21176	6.89353	10.28622	16.95729	16.30855		−95.23197	−31.98738	−22.65410	12
11	2.37381	2.29516	2.61576	2.93858	3.48426	4.06889	5.21138	6.56672	10.28446	15.54288	16.30737		−95.17231	−39.14121	13
12	2.17107	2.09139	2.33772	2.61576	3.00423	3.48430	4.19487	5.21156	6.89457	10.28533	16.97042	16.30896		−103.05538	14
13	1.97946	1.88169	2.09139	2.29516	2.61294	2.93509	3.48006	4.06298	5.20402	6.55333	10.26596	15.48366	16.26920		
14	2.08944	1.97946	2.17107	2.37381	2.64982	2.95985	3.39780	3.92949	4.72767	5.84139	7.72150	11.35674	18.82736	19.40046	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	

Two electron potential energy[b]

a) STO-6G. b) In au.

Table 7. Atomic Group Interactions in $CH_2{}^1{=}CH^2{-}CH^3{=}CH^4{-}CH^5{=}CH^6{-}CH^7{=}CH^8{-}CH^9{=}CH^{10}{-}CH^{11}{=}CH^{12}{-}CH^{13}{=}CH_2{}^{14}$ ($\langle V_{eN}\rangle_{AB} + \langle V_{ee}\rangle_{AB} + V_{AB}{}^N$ and $\langle T\rangle_{AB}$)[a]

Potential energy[b]

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
	−77.46970	−0.86050	0.01491	−0.00254	−0.00001	−0.00021	0.00000	−0.00003	0.00000	0.00000	0.00000	0.00000	−0.00001	0.00001	1
		−75.96432	−0.57561	0.01560	−0.00068	−0.00001	−0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	−0.00001	2
1	38.62565		−75.98313	−0.85365	0.01564	−0.00253	0.00000	−0.00023	0.00000	−0.00003	0.00000	−0.00001	0.00000	0.00000	3
2	0.72603	37.73293		−75.98135	−0.58244	0.01566	−0.00069	0.00000	−0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	4
3	0.00797	0.43157	37.76263		−75.98139	−0.85043	0.01566	−0.00252	0.00000	−0.00023	0.00000	−0.00003	0.00000	0.00000	5
4	−0.00087	0.00932	0.70333	37.75751		−75.98123	−0.58368	0.01567	−0.00069	0.00000	−0.00001	0.00000	0.00000	0.00000	6
5	0.00004	−0.00122	0.00932	0.43788	37.75949		−75.98133	−0.84990	0.01567	−0.00252	0.00000	−0.00023	0.00000	−0.00003	7
6	0.00000	0.00004	−0.00093	0.00935	0.70022	37.75869		−75.98133	−0.58368	0.01566	−0.00069	0.00000	−0.00001	0.00000	8
7	0.00000	0.00000	0.00004	−0.00122	0.00935	0.43906	37.75910		−75.98123	−0.85043	0.01566	−0.00253	−0.00001	−0.00021	9
8	0.00000	0.00000	0.00000	0.00004	−0.00093	0.00935	0.69975	37.75910		−75.98139	−0.58244	0.01564	−0.00068	−0.00001	10
9	0.00000	0.00000	0.00000	0.00000	0.00004	−0.00122	0.00935	0.43906	37.75869		−75.98135	−0.85365	0.01560	−0.00254	11
10	0.00000	0.00000	0.00000	0.00000	0.00000	0.00004	−0.00093	0.00935	0.70022	37.75949		−75.98313	−0.57561	0.01491	12
11	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00004	−0.00122	0.00935	0.43788	37.75751		−75.96432	−0.86050	13
12	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00004	−0.00093	0.00932	0.70333	37.76263		−77.46970	14
13	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00004	−0.00122	0.00932	0.43157	37.73293		
14	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00004	−0.00087	0.00797	0.72603	38.62565	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	

Kinetic energy[b]

a) STO-6G. b) In au.

and two-electron potential energy are shown in Table 6. They are of course long-range. Similar to the former case, if all the potential energies are added (i. e. $\langle V_{eN}\rangle_{AB}+\langle V_{ee}\rangle_{AB}+V_{AB}{}^{N}$), the long-range interactions are beautifully cancelled as shown in the upper triangle of Table 7. The kinetic energy interactions ($\langle T\rangle_{AB}$) behave similarly to those of the total energy, although the sign is reversed. The differences in the neighboring interactions are seen to be much larger than those in the total energy.

Concluding Remarks

If we reviewed the works concerning the empirical π energy, the followings are shown. (1) The empirical π energy is a quantitative expression of the kinetic energy of free-moving electrons in a one-dimensional box given by CH=CH units.[19] (2) They are linearly additive with respect to the ethylenic units.[2–7] (3) The empirical π energy expresses the relative quantity of the kinetic energy of π electrons.[8,9] (4) The ratio of the kinetic energy of π electrons to the total kinetic energy in linear polyenes is constant.[9]

The present results lead to the ideas that (1) the empirical π energy reflects the total energy because of the virial theorem (2) and that the linear additive nature is caused by the fact that the atomic group interactions are localized to those around neighboring atoms.

The research was supported by the Ministry of Education, Science, Sports and Culture.

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