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Interpretation of 'π Energy' and Its Linear Additivity in Polyenes

Hiroshi Ichikawa,* Atsushi Yoshida, Hirotaka Kagawa, and Jun'ichi Aihara†

Hoshi College of Pharmacy, Shinagawa, Tokyo 142-8501

†Faculty of Science, Shizuoka University, Ohya, Shizuoka 422-8529

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The kinetic energy of electrons in a one-dimensional box has the property of a linear additivity with respect to the unit length. This property coincides with that of the π electrons of linear polyenes. Both properties lead to an understanding of why the 'π energy' or the Hückel energy includes information about the nuclear configuration based on the molecular virial theorem. This article shows that the linear additivity is a property of the kinetic energy of particles that move in a one-dimensional box, and thus assures that the Hückel energy is another expression of the kinetic energy of π electrons. The reason for the coincidence of both methods is interpreted as meaning that they seek the same stationary wave functions. Thus, we may fairly say that the so-called Hückel energy, 'π energy', or the empirical π energy is a quantitative quantity of the kinetic energy of π electrons.

If the interpretation that the 'π energy' is the kinetic energy of π electrons is adopted, the explanation for a regular hexagon structure of benzene made by Shaik et al. is reversed.

In spite of the fact that the importance of the 'π energy' cannot be overemphasized in organic chemistry, the 'π energy', itself, is hardly said to be explicitly defined or understood. Namely, each researcher figures out the 'π energy' based on his idea. This seems to create confusion, as can be seen in the discussions concerning the role of π electrons in benzene,[1—9] where each author discusses the stability of the π electrons based on some ambiguous definition of the 'π energy'.

There seems to be two kinds of 'π energy' : the energy obtained by such an empirical or semi-empirical π-molecular orbital (MO) method as Hückel[10,11] or Pariser–Parr–Pople (PPP) (and the related) theory[12—14] and that analytically derived by partitioning the total energy obtained by ab initio Hartree–Fock[15—17] MO theories. Here, we call the former 'empirical π energy' and the latter 'analytical π energy'.

The empirical π-energy appeared when the Hückel MO theory was proposed.[10] Then, considerations of two-electron integrals and the anti-symmetric nature of the total wave function have been carried out to produce the PPP and its related theories.[12—14] However, the concept of an empirical π energy, like that of π electrons that move in potential fields from σ as well as other π electrons and nuclei (this literally means the π-electronic energy (E_π^{el}) as will soon be mentioned), still remains.

Any MO theory depends on the Born–Oppenheimer approximation.[18] Namely, the electronic energy (E^{el}) is first obtained and the total energy (E) is obtained by adding the nuclear repulsion energy as a classical quantity to E^{el}. This procedure is not performed in Hückel or PPP theories. This makes us believe that the 'π energy' is the π electronic energy. Here, we specify the Hückel energy for the empirical π energy in order to avoid any methodological confusion.

A notable characteristic of the empirical π energy is that it has linear additivity in linear polyenes.[14,19—22] This fact has been used as a measure of aromaticity: The Hückel energy of a cyclic polyene is compared with that of the corresponding linear polyene.[22] A question is : *The fact that the Hückel energy has the property of linear additivity means that the Hückel energy must include information about the nuclear repulsion in spite of the above-mentioned concept of the empirical π energy.*

The analytical π energy appeared quite recently with an energy-partitioning method in ab initio MO theories.[1—3,6—9,24,25] Energy components that have inherent physical meanings have been classified to either a σ or π group. The interpretation of 'π energy' in terms of such energy components has been carried out. The analytical π energy (E_π^{anal}) may be defined by the following equation:

$$E_\pi^{anal} = E_\pi^{el} = \langle T\rangle_\pi + \langle V_{eN}\rangle_\pi + \langle V_{ee}\rangle_\pi + \langle V_{ee}\rangle_{\pi-\sigma}, \quad (1)$$

where $\langle T\rangle_\pi$, $\langle V_{eN}\rangle_\pi$, $\langle V_{ee}\rangle_\pi$, and $\langle V_{ee}\rangle_{\pi-\sigma}$ are the kinetic energy, one-, two-electron potential energies of π electrons, and the two-electron potential energy of π electrons that receive from σ electrons. The mathematical expressions have been shown elsewhere.[9b,c]

According to the conventional idea of the empirical π energy, it should be equal to E_π^{el}. A comparison of the Hückel energy and the energy components or their combination has been carried out. An unexpected result is that *the empirical π energy or the Hückel energy in polyenes is not proportional to E_π^{el} but to the kinetic energy of π electrons ($\langle T\rangle_\pi$) and that the ratio of $\langle T\rangle_\pi$ to the total kinetic energy ($\langle T\rangle$) is constant.*[24,25] This also indicates that the empirical π energy includes information about the nuclear configuration.

A preceding paper discussed the reason why the empirical π energy includes the nuclear repulsion energy, and found that it explainable based on the molecular virial theorem[26] and the fact that the ratio of the kinetic energy of π electron ($\langle T\rangle_\pi$) to that of total electrons ($\langle T\rangle$) is constant.[27] The last question is that the constancy of the ratio $\langle T\rangle_\pi/\langle T\rangle$ is not easily acceptable, since $\langle T\rangle$ is homogeneous of degree −2 to the coordinate. Thus, we examined the kinetic energy of electrons in a one-dimensional box by comparing the Hückel energy in linear polyenes.

Linear Additivity in the Hückel Method and Particles-in-A-Box Model

A resemblance of the Hückel results with the particles-in-a-box model has been pointed out.[28—30] This also assures that the Hückel energy may represent $\langle T\rangle_\pi$, since the particles-in-a-box model treats only the kinetic energy of the particles, and since Hückel MO method treats only the π electrons. Hobey showed that the particles-in-a-box model reproduces the results of the Hückel aromaticity measurement.[29] This gives additional confidence that the Hückel energy is a quantitative expression of $\langle T\rangle_\pi$.

As stated in the introduction, one of the characteristics of the empirical π energy is its linear additivity. Here, we examine whether such linearity is reproducible in the particles-in-a-box model. Let us consider a linear polyene with $2(n+2)$ π electrons, as shown in Fig. 1. The Hückel energy is expressed by

$$E_n^{\text{Hückel}} = 2\alpha(N+2)+2\beta\left\{\left(\sin\frac{\pi}{2(2n+5)}\right)^{-1}-1\right\}. \quad (2)$$

By increasing one ethylene unit, the difference ($\Delta E = E(n+1)-E(n)$) is given by

$$\Delta E^{\text{Hückel}} = 2\alpha+2\beta\left\{(\sin(\pi/2(2n+7))^{-1}-(\sin(\pi/2(2n+5))^{-1}\right\}. \quad (3)$$

Equation 3 shows that the so-called linear additivity of the Hückel energy is not perfect. However, $\Delta E^{\text{Hückel}}$ rapidly converges on $2\alpha+8\beta/\pi$ as n increases. (This has already been shown by one of the present authors (J. A.)[21])

In the case of the one-dimensional particles-in-a-box model, the kinetic energy for the linear $(n+2)L$ unit with $2(n+2)$ particles (electrons) is obtained as

$$E_n^{\text{Particle}} = \frac{h^2}{8mL^2}\frac{(n+2)(n+3)(2n+5)}{3(2n+1)^2}. \quad (4)$$

Due to an increase of one unit of length L, the displacement is given by

$$\Delta E^{\text{particle}} = \frac{h^2}{48mL^2}\left(1-\frac{44n^2+200n+213}{(2n+3)^2(2n+5)^2}\right). \quad (5)$$

Again, the linear additivity in the particles-in-a-box model is not perfect, but it is easily understood that as n increases, $\Delta E^{\text{Particle}}$ approaches $h^2/(48mL^2)$. Equations 2 and 4 are plotted against n in Fig. 2.

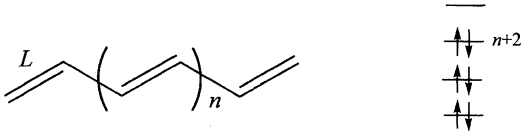

Fig. 1. Linear polyene with $2(n+2)$ π electrons.

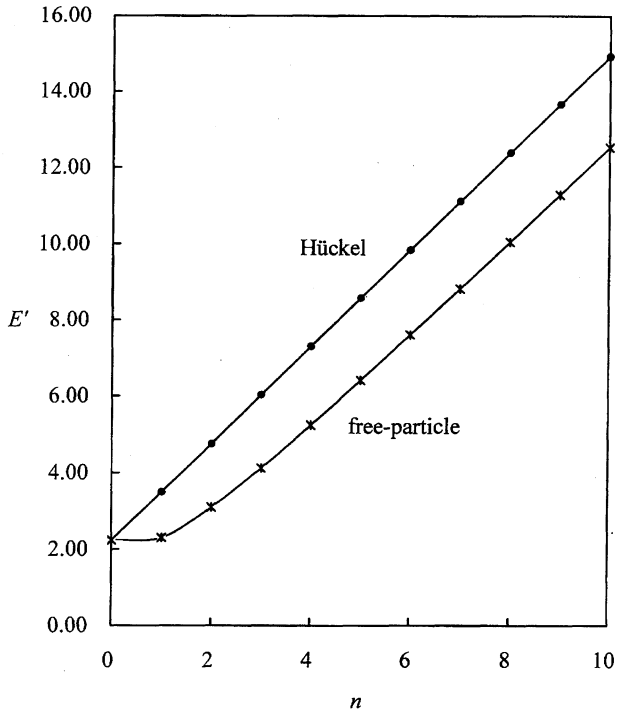

Fig. 2. Linear energy additivities of the Hückel and particles-in-a-box models. The scale for the Hückel energy is 2β, while that for the particles-in-a-box model is $12h^2/(\pi mL^2)$, where h and m are the Planck's constant and the mass of the particle (electron).

The figure shows that both the Hückel and particles-in-a-box model methods arrive at linear additivity within a small number of length units. Here, it is suggested that *the linear additivity is a nature of the kinetic energy in one-dimensional movement of electrons. This may be the reason why* $\langle T\rangle_\pi/\langle T\rangle$ *is constant,* since E, $\langle T\rangle$, or $\langle V\rangle$ has the nature of linear additivity, as shown in a preceding paper.[27]

Why Results by Hückel Method and Particles-in-A-Box Model Coincide

The Hückel calculation for cyclic conjugate hydrocarbons results in a double-degenerate solutions, except for the lowest and highest ones. This double-degeneracy problem can be correlated with the direction of electron movement, and the linear additivity is a property of the kinetic energy of a particle that moves in a one-dimensional box. It was also shown that the three-dimensional Hückel method, an extension of the ordinary Hückel theory to free-moving electrons by allowing free movement of particles to adjacent nodes by setting β between them, reproduced the patterns of the degeneration and wave functions of particles in a three-dimensional box.[32] Both the Hückel method and particles-in-a-box model give the same results concerning the shapes of the wave functions. Such a coincidence may be interpreted in terms of the fact that they both obtain the wave functions of stationary waves in the similar systems.

The wave function for the particles-in-a-box model is determined by imposing boundary conditions, while that of the Hückel method is obtained by imposing variational condi-

tions. The boundary conditions, for example, for a one-dimensional box with length L are

$$\psi(0) = 0 \text{ and } \psi(L) = 0. \quad (6)$$

Apparently such procedures give stationary waves.

The variation method is defined as

$$\psi \rightarrow \psi + \Delta\psi \Rightarrow E \rightarrow E + \Delta E$$
$$\text{where} \quad \Delta E = 0. \quad (7)$$

Namely, concerning the change in the wave function, its energy is not varied. In an LCAO approximation,

$$\psi = \sum_r C_r \chi_r. \quad (8)$$

Since χ_r are assumed to be fixed, the condition expressed by Eq. 7 is equivalent to

$$\frac{\partial E}{\partial C_r} = 0. \quad (9)$$

The condition expressed by Eq. 7 indicates that if the wave would not be stationary, it would shift to a different form with a lower energy as time passes. Therefore, it can be said that both procedures seek stationary points that give stationary wave functions. Since stationary waves are uniquely determined by the given topology, both methods may give the same phases.[33]

An Application of New Interpretation of π Energy:

Role of π Electrons in Benzene. "The role of π electrons in benzene" has created much confusion concerning the concept of the aromaticity of benzene. In 1961, Berry raised a doubt concerning the stability of uniformly distributed π electrons. Namely, the π electrons are not the major source of stability for the regular hexagon, and the π electrons might well have a lower energy if the ring approaches cyclohexatriene-like shapes.[34] More than twenty years later Shaik and Hiberty and their co-workers investigated this problem and supported the above idea.[1,2] There have appeared approval and opposite opinions to it.[3—9]

As already stated, the confusion is caused by the fact that the problem has been discussed without any consensus concerning the 'π energy'. Now that we have established that the 'π energy' is the kinetic energy of π electrons, we may obtain a new interpretation for the role of π electrons.

Benzene has a D_{6h} symmetry at the optimized geometry. At this geometry, it was shown that the partial derivatives of the total (E), π-electronic (E_π^{el}) π-kinetic energies ($\langle T\rangle_\pi$) with respect to bond order (P_{rs}) are all null.[9c] Namely, $\partial\langle T\rangle_\pi/\partial P_{rs}$ is null, indicating that 'the π energy' of benzene is lowest. In other words, π electrons are not the cause of bond alternation.

Benzene with a distorted geometry is not the same quantum-mechanical system as that of benzene.[35] However, since the discussion stems from an abnormal low frequency of the B_{2u} vibration, let us consider the case when the geometry is distorted along the B_{2u} coordinate. Figure 3 is a schematic expression of the behaviors of E, E_π^{el}, and $\langle T\rangle_\pi$ when the bond order (P_{rs}) is varied at a fixed geometry on a B_{2u} coordinate.

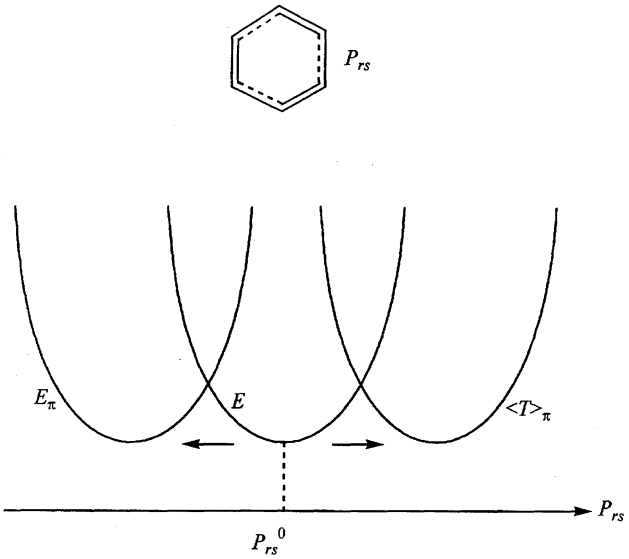

Fig. 3. Changes of E, E_π^{el}, and $\langle T\rangle_\pi$ with respect to P_{rs} at a D_{3h}-distorted benzene along the B_{2u} coordinate, where P_{rs}^0 is the optimized π-bond order at the given geometry. The bond alternation is expressed by using solid and dotted lines.

Such a relationship was obtained by solving the constrained Hartree–Fock equation and quoted from Ref. 9c.

At a distorted geometry, the minimum points of E, E_π^{el}, and $\langle T\rangle_\pi$ do not coincide: at the optimized bond order (P_{rs}^0: $\partial E/\partial P_{rs} = 0$), only the total energy takes the minima. The π electronic energy has its minima at a smaller P_{rs} while the π kinetic energy, which equals the 'π energy' or empirical π enegy, has its minimum at a larger P_{rs}. If one looks at the behavior of E_π^{el} or the conventional idea of the 'π energy', π electrons are in favor of being bond-alternative, the same conclusion as that by Shaik and Hiberty and their coworkers.[1,2] However, $\langle T\rangle_\pi$ has the minima at a larger P_{rs}, indicating that it dislikes bond alternation. The more distorted is the geometry, the more is this tendency prominent. This even means that the π electrons are the major forces which maintain keeping the D_{6h} symmetry of benzene.

Concluding Remarks

In this series of our papers,[24,25,27] we might establish the following: (1) The Hückel energy or 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. (2) Such kinetic energy is linear-additive with respect to the ethylenic unit. (3) The ratio of the kinetic energy of π electrons to the total kinetic energy in linear polyenes is constant. (4) Thus, the total energy includes information about the nuclear configuration through the virial theorem. Namely, the relationship $E^{Hückel} \propto \langle T\rangle_\pi \propto \langle T\rangle \propto E \propto \langle V\rangle$ holds. To understand this relationship, we must seek the reason for the constancy of the ratio $\langle T\rangle_\pi/\langle T\rangle$ or the linear property of the kinetic energy of free-moving electrons in a linear one-dimensional box.

The conclusion of this paper is that the Hückel energy as well as the kinetic energy of particles that move in a

one-dimensional box has the property of linear additivity with respect to the unit length, although the linearity is not perfect; the deviation from the perfect linearity was found to be limited within a small number of units. This quasi-linear property makes the constancy of $\langle T\rangle_\pi/\langle T\rangle$ understandable. Thus, we may fairly say that the so-called Hückel energy, 'π energy', or the empirical π energy is a quantitative quantity of the kinetic energy of free-moving electron as well as that of π electrons in polyene.

As an energetic expression of the uncertainty relationship, the kinetic energy of an electron appears when walls restrict its movement. Electrostatic potentials and/or atomic orbital orthogonalization in molecules give such walls. If an electron is packed in a cubic box with volume V, the ground-state kinetic energy (E) is calculated to be $E = h^2/(8mV^{2/3})$, where h is Planck's constant and m is the mass. When the box is 1 Å^3, E is more than 10^4 kJ mol^{-1}; the electron tends to spread out as widely as possible. This tendency is called kinetic-energy pressure.[36]

The concept of 'kinetic-energy pressure' seems to be very convenient, because the reason of conjugation between double bonds can be interpreted as 'relaxation' of the kinetic energy pressure.[37] Aromaticity is also given by the relaxation of the kinetic energy pressure of π electrons.[24] In this way, if we stand on this viewpoint, a number of riddles concerning 'π energy' seem to be solved.

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References

1 S. S. Shaik and R. Bar, *Nouv. J. Chim.*, **8**, 411 (1984); S. S. Shaik and P. C. Hiberty, *J. Am. Chem. Soc.*, **107**, 3089 (1985); P. C. Hiberty, S. S. Shaik, J. -M. Lefour, and G. Ohanessian, *J. Org. Chem.*, **50**, 4657 (1985); S. S. Shaik, P. C. Hiberty, J. -M. Lefour, and G. Ohanessian, *J. Am. Chem. Soc.*, **109**, 363 (1987); G. Ohanessian, P. C. Hiberty, J. -M. Lefour, J. -P. Flament, and S. S. Shaik, *Inorg. Chem.*, **27**, 2219 (1988); S. S. Shaik, P. C. Hiberty, G. Ohanessian, and J. -M. Lefour, *J. Phys. Chem.*, **92**, 5086 (1988); P. C. Hiberty, D. Danovich, A. Shurki, and S. Shaik, *J. Am. Chem. Soc.*, **117**, 7760 (1995).

2 P. C. Hiberty, *Top. Curr. Chem.*, **153**, 27 (1990).

3 K. Jug and A. Köster, *J. Am. Chem. Soc.*, **112**, 6772 (1990).

4 R. Janoschek, *J. Mol. Struct. (Theochem)*, **229**, 197 (1991).

5 T. Nakajima and M. Kataoka, *Theoret. Chim. Acta*, **84**, 27 (1992).

6 N. C. Baird, *J. Org. Chem.*, **51**, 3908 (1986).

7 H. Kollmar, *J. Am. Chem. Soc.*, **101**, 4832 (1979).

8 E. D. Glendenig, R. Faust, A. Streitwieser, K. P. C. Vollhardt, and F. Weinhold, *J. Am. Chem. Soc.*, **115**, 10952 (1993).

9 a) H. Ichikawa and H. Kagawa, *J. Phys. Chem.*, **99**, 2307 (1995). b) *Bull. Chem. Soc. Jpn.*, **70**, 61 (1997). c) *Bull. Chem. Soc. Jpn.*, **70**, 727 (1997).

10 E. Hückel, *Z. Phys.*, **70**, 204 (1931).

11 A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York (1966).

12 R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 and 767 (1953).

13 R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953); **24**, 250 (1956).

14 M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1969).

15 D. R. Hartree, *Proc. Camb. Philos. Soc.*, **24**, 89 (1928).

16 V. Fock, *Z. Phys.*, **61**, 126 (1930).

17 C. C. J. Roothann, *Rev. Mod. Phys.*, **23**, 69 (1951).

18 M. Born and J. R. Oppenheimer, *Ann. Phys.*, **84**, 457 (1927).

19 B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **93**, 305 and 2413 (1971); *J. Org. Chem.*, **36**, 3418 (1971); B. A. Hess, Jr., C. A. Ogle, and L. J. Schaad, *J. Am. Chem. Soc.*, **103**, 5052 (1981), and references therein.

20 A. Moyano and C. Paniagura, *J. Org. Chem.*, **51**, 2250 (1986).

21 J. Aihara, *Bull. Chem. Soc. Jpn.*, **47**, 3169 (1974).

22 J. Aihara, *Bull. Chem. Soc. Jpn.*, **48**, 517 (1975).

23 R. Breslow, *Chem. Eng. News*, **43**, 90 (1965); *Chem. Br.*, **4**, 100 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 565 (1968).

24 H. Ichikawa and Y. Ebisawa, *J. Am. Chem. Soc.*, **107**, 1161 (1985).

25 H. Ichikawa and K. Sameshima, *Bull. Chem. Soc. Jpn.*, **63**, 3248 (1990).

26 R. B. Parr and J. E. Brown, *J. Chem. Phys.*, **49**, 4849 (1968).

27 H. Ichikawa, A. Yoshida, H. Kagawa, and J. Aihara, *Bull. Chem. Soc. Jpn.*, **72**, 955 (1999).

28 N. S. Bayliss, *Q. Rev. Chem. Soc.*, **6**, 319 (1964).

29 W. B. Hobey, *J. Org. Chem.*, **37**, 1137 (1972).

30 G. Taubmann, *J. Chem. Educ.*, **69**, 96 (1992).

31 E. g. J. P. Lowe, "Quantum Chemistry," 2nd ed, Academic Press, San Diego, CA, USA (1978), Chap. 8.

32 H. Ichikawa, H. Kagawa, A. Yoshida, T. Sugiyama, S. Tokita, and J. Aihara, "27th Symposium on Structural Organic Chemistry," Osaka, Japan, 1997, Abstr., p. 83.

33 In the variation method, we should realize that we do not seek the lowest E by varying the coefficients since we never take care of the second derivatives. Namely, we never know whether we obtained the maximum or minimum extreme points. What we can say is that we only obtained the stationary wave functions.

34 R. S. Berry, *J. Chem. Phys.*, **35**, 2253 (1961).

35 This means that comparison of a partitioned energy (e.g. 'π energy') between different geometries is meaningless.

36 M. J. Feinberg, K. Ruedenberg, and E. L. Mehler, *Adv. Quantum Chem.*, **5**, 27 (1970).

37 H. Ichikawa and H. Kagawa, *Int. J. Quantum Chem.*, **52**, 575 (1994).