Theoret. Chim. Acta (Berl.) 66, 183-192 (1984)

THEORETICA CHIMICA ACTA

Evaluation of moments and their application in Hückel molecular orbital theory

Yuansheng Jiang*, **Aoqing Tang***

Institute of Theoretical Chemistry Jilin University, Changchun, China

Roald Hoffmann*

Department of Chemistry, Cornell University, Ithaca, NY 14853, USA

Moments of acyclic carbon chains are treated in a systematic way. Explicit formulas in terms of connectivities are tabulated up to μ_{14}. This facilitates the evaluation of moments by simply counting the numbers of various fragments involved. The total π electron energy is analyzed by means of moments and the meaning of additivity is interpreted. An approximate formula for E_π is parametrized by truncation, preserving only five bond parameters. Based on these, we attempt to better rationalize and reformulte the concept of aromaticity.

Key words: Hückel theory—Graph theory—moments—aromaticity

1. Introduction

The traditional way for dealing with MO (abbreviation of "molecular orbital") calculations is to solve a secular equation [1]

$$|ES-H|=0. \tag{1}$$

This equation depends on the basis set $\{\phi_i\}$ selected, because the overlap and Hamiltonian matrices S and H are defined in terms of $\{\phi_i\}$

$$\begin{aligned} S&=(S_{ij}) \qquad S_{ij}=\langle\phi_i|\phi_j\rangle \\ H&=(H_{ij}) \qquad H_{ij}=\langle\phi_j|\hat{H}|\phi_j\rangle. \end{aligned} \tag{2}$$

---

* Formerly used names: Kiang, Yuan-sun; Tang, Au-chin

Usually, energy levels are obtained first, and wave functions and other observable calculations follow. If $\boldsymbol{S}$ is approximated by the unit matrix

$$\boldsymbol{S}=\boldsymbol{I}, \qquad S_{ij}=\delta_{ij} \tag{3}$$

then Eq. (1) is easily expanded into a polynomial characterized by powers of E [2-4]

$$E^N+a_1E^{N-1}+a_2E^{N-2}+\cdots+a_N=0. \tag{4}$$

The coefficients a_1, $a_2, \ldots, a_N$ are related to the energy eigenvalues E_1, $E_2, \ldots, E_N$, thus they can be equally well utilized for handling MO problems. Still other possibilities exist. Among them, moments are a useful analytical tool. They are defined as

$$\mu_l=E_1^l+E_2^l+\cdots+E_N^l \qquad (l=0,1,2,\ldots) \tag{5}$$

and are equal to the trace of l-th power of the matrix H

$$\mu_l=\text{trace}\,\boldsymbol{H}^l \tag{6}$$

Obviously, only the lower N members constitute an independent set, since all of the higher moments with $l \geq N$ are equal to a linear combination of preceding N members, according to Eq. (4). Namely

$$\mu_{N+m}=a_1\mu_{N+m-1}+a_2\mu_{N+m-2}+\cdots+a_N\mu_m \qquad (m=0,1,2,\ldots). \tag{7}$$

The importance and advantage of utilizing moments rests upon their topological meaning in relationship to the connectivity of a molecule. The situation is particularly simple and elegant for the Hückel theory. After putting

$$\alpha=0, \qquad \beta=1. \tag{8}$$

$\boldsymbol{H}$ becomes an adjacency matrix $\boldsymbol{A}$, with its entries satisfying

$$\begin{aligned} A_{ij}&=1 \quad \text{when } i,j \text{ connected}\\ &=0 \quad \text{otherwise.}\end{aligned}$$

In this case, each non-zero term in μ_l is exactly equal to unity

$$\mu_l=\sum_{i=1}^{N}(\boldsymbol{A}^l)_{ii}=\sum_{i=1}^{N}\sum_{\alpha,\beta,\ldots,\delta}A_{i\alpha}A_{\alpha\beta}\cdots A_{\delta i}=\sum_{i=1}^{N}\sum_{\alpha,\beta,\ldots,\delta}(1) \tag{10}$$

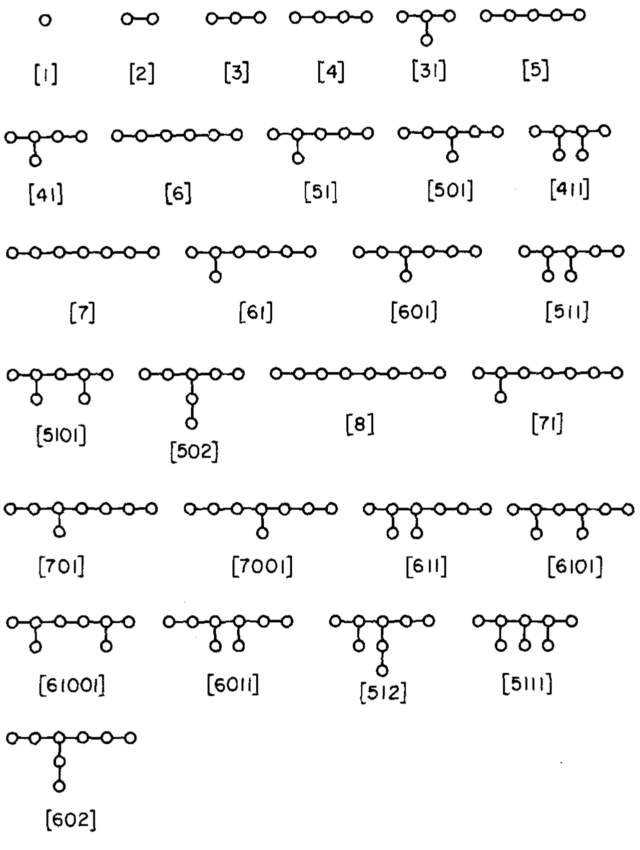
representing a cyclic walk of length l starting from vertex i and passing through vertices α, $\beta, \ldots, \delta$ irrespective of the repeated appearance of some vertices. The sum of such walks with respect to each vertex is the value of μ_l, namely the number of random closed walks of length l.

Directly enumerating moments is feasible for small molecules but becomes tedious when the molecule is large. In this paper, we present a procedure for evaluating moments and list formulas for the convenience of enumerating the moments of acyclic chains. It is proposed that the total π electron energy be expanded in terms of moments. A better interpretation of additivity may thus be achieved.

We reformulate a previous theory of aromaticity by parametrization of the total energy in terms of five branching types of bonds.

2. Moments of acyclic systems

We limit our attention to acyclic conjugated skeletons with a maximum atom valency of three. Nevertheless, the method proposed is general. First of all, it seems worthwhile to discuss how to characterize these skeletons or fragments. Let us present the smaller members up to $N=8$ by diagrams and symbols



The symbol $[N-n; a, b, c, \ldots, n-a-b-c-\cdots]$ temporarily used here signifies the topology of the fragment, $N-n$ representing the length of the main chain and a, b, $c, \ldots$ signifying lengths of the first, second, ... straight side chains respectively. For higher members, where branching side chains exist, this symbol should be modified, but we omit doing that for simplicity. These diagrams can represent real molecules as their carbon skeletons or they can represent fragments that a real molecule includes.

Because an acyclic chain is alternant, with vanishing odd moments, we concentrate on even moments only. Obviously for any molecule G we have its moments satisfying

$$\mu_{2n}^{G} = \sum_{G'} C_{2n}^{G'} N_{G'} \tag{11}$$

where G' represents a fragment of G involving bonds equal to or less than n, $N_{G'}$ signifies the appearances of G' and $C_{2n}^{G'}$ counts the random closed walks of length $2n$ spanned by G'. All of these are well illustrated by a simple example shown below.

G = butadiene

$n = 3$	possible G'	[4]	[3]	[2]
	$N_{G'}$	1	2	3
$n = 2$	G'	[3]	[2]	
	$N_{G'}$	2	3	.

An expression for the coefficient C_{2n}^{G} in terms of $\mu_{2n}^{G'}$ can be derived from Eq. (10) by induction. It takes the following form

$$C_{2n}^{G} = \mu_{2n}^{G} - \sum_{t} N_{G-t} \mu_{2n}^{G-t} + \sum_{t,t'} N_{G-t-t'} \mu_{2n}^{G-t-t'} - \sum_{t,t',t''} N_{G-t-t'-t''} \mu_{2n}^{G-t-t'-t''} + \cdots \tag{12}$$

where t, t', t'', ... represent terminal atoms in molecule G; $G-t$, $G-t-t'$, ... mean fragments generated by deleting one, two, ... or more terminals from G respectively. If we still take butadiene as an example, Eq. (12) is reduced to

$$C_{2n}^{[4]} = \mu_{2n}^{[4]} - 2\mu_{2n}^{[3]} + \mu_{2n}^{[2]}. \tag{13}$$

3. Analytical C_{2n}^{G}'s

Generally speaking, coefficients C_{2n}^{G} are too complicated to be given analytically except for some special G or special n. If no more than three terms are involved in the characteristic polynomial of G, namely

$$\mathrm{P}_G = X^m (X^4 - a_1 X^2 + a_2) \tag{14}$$

then by utilizing Eq. (7) recursively, an analytical form for μ_{2n}^{G} will be obtained:

$$\mu_{2n}^{G} = g_{n-1}(a_1, a_2)\mu_2^G - g_{n-2}(a_1, a_2) a_2 \mu_0^G \tag{15}$$

where

$$g_{n-1}(a_1, a_2) = \sum_r \binom{n-r}{r} (-1)^r a_1^{n-2r} a_2^r. \tag{16}$$

The symbol $\binom{n-r}{r}$ means the binomial coefficient and $g_n(a_1, a_2)$, a polynomial of a_1 and a_2, is further reduced to a Tchebiecheff polynomial when a_2 equals unity. In Eq. (15), μ_2^G and μ_0^G are simply analytical (see Eq. (19)). As a corollary, analytical C_{2n}^{G} are also deduced from Eq. (12). Some of them are listed below

$$
\begin{aligned}
&C_{2n}^{[0]}=1\\
&C_{2n}^{[2]}=2\\
&C_{2n}^{[3]}=2^{n+1}-2^{2}\\
&C_{2n}^{[4]}=6g_{n-1}(3,1)-4g_{n-2}(3,1)-2(2^{n}-1)\\
&C_{2n}^{[31]}=6(3^{n-1}-2^{n}+1)\\
&\ldots.
\end{aligned}
\tag{17}
$$

If the fragment G has its number of bonds equal to n, the coefficient C_{2n}^{G} is also given analytically, namely

$$C_{2n}^{G}=(2n)2^{N_3} \tag{18}$$

where N_3 is the number of trivalent atoms. Eq. (18) originates from the fact that the fragment G is exactly spanned by random closed walks of length $2n$.

4. Formulas for computing moments

Based on results given above, moments of acyclic chains can be derived one by one by proceeding from the lowest member to higher ones. We list formulas with n up to 7 below

$$
\begin{aligned}
\mu_0^G&=N_{[1]}\\
\mu_2^G&=2N_{[2]}\\
\mu_4^G&=2N_{[2]}+4N_{[3]}\\
\mu_6^G&=2N_{[2]}+12N_{[3]}+6N_{[4]}+12N_{[31]}\\
\mu_8^G&=2N_{[2]}+28N_{[3]}+32N_{[4]}+72N_{[31]}+8N_{[5]}+16N_{[41]}\\
\mu_{10}^G&=2N_{[2]}+60N_{[3]}+120N_{[4]}+300N_{[31]}+60N_{[5]}+140N_{[41]}\\
&\quad+10N_{[6]}+20N_{[51]}+20N_{[501]}+40N_{[411]}\\
\mu_{12}^G&=2N_{[2]}+124N_{[3]}+390N_{[4]}+1080N_{[31]}+300N_{[5]}+804N_{[41]}\\
&\quad+96N_{[6]}+216N_{[51]}+228N_{[501]}+504N_{[411]}\\
&\quad+12N_{[7]}+24N_{[61]}+24N_{[601]}+48N_{[511]}+48N_{[5101]}+24N_{[502]}\\
\mu_{14}^G&=2N_{[2]}+252N_{[3]}+1176N_{[4]}+3612N_{[31]}+1260N_{[5]}+3836N_{[41]}\\
&\quad+588N_{[6]}+1484N_{[51]}+1652N_{[501]}+3976N_{[411]}\\
&\quad+140N_{[7]}+308N_{[61]}+322N_{[601]}+728N_{[511]}+672N_{[5101]}\\
&\quad+366N_{[502]}\\
&\quad+14N_{[8]}+28N_{[71]}+28N_{[701]}+28N_{[7001]}+28N_{[602]}\\
&\quad+56N_{[611]}+56N_{[6101]}+56N_{[61001]}+56N_{[6011]}+56N_{[512]}\\
&\quad+112N_{[5111]}.
\end{aligned}
\tag{19}
$$

The first two equalities are obvious, following the definitions of zero- and second-moments. The derivation of other members is also straightforward. We illustrate μ_4^G and μ_6^G for instance, for which coefficients in Eq. (11) are readily obtained from Eqs. (17) and (18). Eq. (17) gives

$$C_4^{[2]}=2, \qquad C_6^{[2]}=2, \qquad C_6^{[3]}=12$$

and Eq. (18) gives

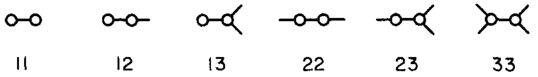
$$C_4^{[3]}=2\times 2=4, \qquad C_6^{[4]}=2\times 3=6, \qquad C_6^{[31]}=2\times 3\times 2=12.$$

Eq. (19) shows how moments are dependent on connectivities in detail, where not only bonds but also multi-atom fragments play roles. Notice also that smaller fragments appear more frequently than larger ones, which seems to imply the nearer neighbor interactions are more important.

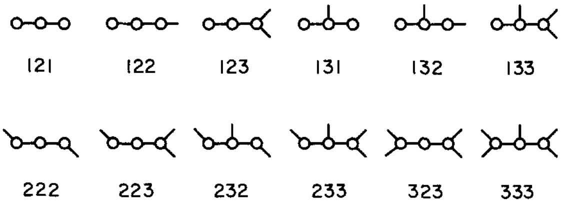
5. Alternative description

The fragment set used to characterize connectivity is not unique. Various choices are possible. An alternative scheme [15] which is useful in practice is based on the characterization of each atom by its valency (or degree) in detail. Thus, there are four species of atoms, specified by zero-, mono-, bi- and tri-valencies shown diagrammatically below

Similarly, we have six types of bonds characterized by a pair of atomic valencies



and twelve tri-atomic fragments with a set of triple atomic valencies



and so on.

If we deal with one component systems other than free atoms and ethylene, we are able to ignore the trivial fragments 0 and 11, and write down the relations holding for numbers of various fragments in the same set as well as between different sets. These include

$$\begin{aligned}
&N_1+N_2+N_3=N_{[1]}\\
&N_1+2N_2+3N_3=2[N_{12}+N_{13}+N_{22}+N_{23}+N_{33}]=2N_{[2]}\\
&2N_2+6N_3=N_{12}+2N_{13}+2N_{22}+3N_{23}+4N_{33}\\
&\qquad\qquad=2\{N_{121}+N_{123}+N_{131}+N_{132}+N_{133}\\
&\qquad\qquad+N_{222}+N_{223}+N_{232}+N_{233}+N_{323}+N_{333}\}=2N_{[3]}\\
&\ldots
\end{aligned}\tag{20}$$

and others which we omit for simplicity. By means of Eq. (20) moments in Eq. (19) can be transformed in terms of the new set as follows

$$\begin{aligned}
&\mu_0^G=\tfrac{1}{6}\{9N_{12}+8N_{13}+6N_{22}+5N_{23}+4N_{33}\}\\
&\mu_2^G=2N_{12}+2N_{13}+2N_{22}+2N_{23}+2N_{33}\\
&\mu_4^G=4N_{12}+6N_{13}+6N_{22}+8N_{23}+10N_{33}\\
&\mu_6^G=8N_{12}+18N_{13}+20N_{22}+36N_{23}+58N_{33}\\
&\mu_8^G=16N_{12}+54N_{13}+62N_{22}+148N_{23}+298N_{33}\\
&\qquad+8N_{222}+16N_{223}+32N_{323}+8N_{232}+16N_{233}+32N_{333}\\
&\ldots
\end{aligned}\tag{21}$$

where we omit moments higher than μ_8^G.

These formulas emphasize the role of atomic valency characteristic of each fragment, in addition to that of fragment length. This is well known as the branching effect by chemists. Eq. (21) emphasizes again the dominant role of bonds. They appear uniquely before μ_6^G and play a major role in the subsequent moments.

6. Total π electron energy

Because the pairing theorem holds for alternants, the total π electron energy of the ground state of acyclic systems may be written as

$$E_\pi=2\sum_{i=\mathrm{occ}}E_i=\sum_{i=1}^{N}|E_i| \tag{22}$$

where the latter summation runs through the entire orbital set. The quantity $|E|$ means the absolute value of E, which is an even behaved function of E and can be expanded in terms of even powers of E [6]

$$|E|=a_0+a_2E^2+a_4E^4+\cdots \tag{23}$$

provided the point $E=0$ is excluded (which actually has no effect on the evaluation of E_π), or empirically approximated by a polynomial of E^2 [7].

On substituting Eq. (23) into Eq. (22) and utilizing the expression for moments, we have

$$E_\pi = a_0\mu_0 + a_2\mu_2 + a_4\mu_4 + \cdots. \tag{24}$$

On further substituting either Eq. (19) or (21) into Eq. (24), E_π is transformed to

$$E_\pi = \sum_K a_{[K]} N_{[K]} \tag{25}$$

$$E_\pi = \sum_{i,j,k\cdots} E_{ijk} \cdots N_{[ijk\cdots]} \tag{26}$$

where the numbers of various fragments are used as variables. Thus the coefficient $a_{[K]}$ or $E_{ijk\cdots}$ means the energy component contributed by fragment $[K]$ or $ijk\cdots$. These formulas display the desired feature of additivity of the total energy in terms of the constituents of a molecule.

One should be able, in principle, to determine a coefficient set $\{a_{[K]}\}$ or $\{E_{ijk}\cdots\}$. A set of known values of E_π can be used for fitting Eq. (25) or (26) if they are truncated. For example, the following approximate formula comes from Eq. (26)

$$E_\pi = E_{12}N_{12} + E_{13}N_{13} + E_{22}N_{22} + E_{23}N_{23} + E_{33}N_{33} \tag{27}$$

by eliminating higher terms than numbers of bonds. Known E_π values of 42 acyclic conjugated molecules have been used for fitting Eq. (27) by a least squares procedure. In this way, the coefficients E_{ij} are determined, as tabulated in the following table.

Table 1. Five E_{ij} determined by least square procedure

E_{12}	E_{13}	E_{22}	E_{23}	E_{33}
1.5898	1.4145	1.2691	1.1328	1.0221

A significant trend is shown by this Table in that the bond energy decreases with branching.

7. Aromaticity analysis

Based on Eq. (27) and Table 1, a similar analysis of aromaticity of cyclic conjugated systems can be carried out by utilizing the criterion proposed by Dewar [8, 9] as well as by Hess and Schaad [10]. Values of E_π of real systems are available from Tables [11] and E_π of their corresponding references are calculated from Eq. (27) by enumerating the numbers of the five types of bonds. Then the resonance energy per electron (REPE) is calculated according to

$$\mathrm{REPE} = \frac{1}{N}[E_\pi - E_\pi\,(\mathrm{ref.})]. \tag{27}$$

Table 2. REPE of some conjugated molecules

Molecule	E_π	E_π (Ref.)	REPE	REPE $(H-S)$
I	4.000	5.0764	−0.269	−0.268
II	8.000	7.6146	0.064	0.065
III	9.6569	10.1528	−0.062	
IV	13.6832	13.1679	0.052	0.055
V	19.3137	18.7212	0.042	0.047
VI	19.4531	18.7468	0.050	0.055
VII	7.2077	7.3858	−0.030	−0.028
VIII	9.6568	9.7464	−0.011	−0.010
IX	10.3812	10.6297	−0.031	−0.027
X	16.5055	16.2342	0.023	0.027
XI	15.9962	16.2086	−0.018	−0.012
XII	16.2010	16.1830	0.002	0.007
XIII	7.4659	7.4874	−0.004	−0.002
XIV	9.9943	10.0256	−0.004	−0.002
XV	10.4556	10.6297	−0.022	−0.018
XVI	13.3635	13.1679	0.020	0.023
XVIII	12.7992	13.1679	−0.037	−0.033
XIX	15.9306	15.7061	0.019	0.022
XX	18.0048	18.2443	−0.017	−0.014

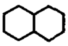
REPE's of acyclic systems calculated in this way vary from −0.005 to 0.005 (β), which gives the range of non-aromaticity. Compounds with their REPE outside this range should be aromatic (+) or antiaromatic (−).

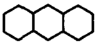
Dozens of compounds have been calculated, and the result seems parallel to that of Hess and Schaad [10]. Only part of our results is listed in Table 2, which includes the following compounds

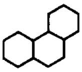

I


II


III

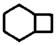

IV


V

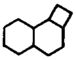

VI

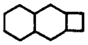

VII


VIII


IX

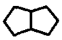

X

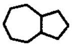

XI

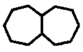

XII

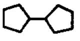

XIII

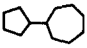

XIV

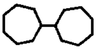

XV


XVI


XVII


XVIII


XIX


XX

A few points seem worthwhile emphasizing: (1) The number of parameters used here is limited to five possible bonds. They are uniquely determined, without arbitrariness, and the result (including a large number of compounds) may be refined upon including more parameters. (2) The numbers of various types of bonds are also uniquely enumerable, without averaging in terms of Kekule structures. So, it seems available for non-classical systems, too. We feel the moment analysis gives a sound basis for understanding additivity and aromaticity. It should be extendable to other chemical problems [12].

Acknowledgment. This work is an outcome of a joint USA-PRC research program supported by NSF Grant INT-8117267 and the Academia Sinica. Collaborating in this project are the groups of Lu Jiaxi, Tang Aoqing, James A. Ibers and Roald Hoffmann.

References

1. See, for example Dewar, M. J. S.: The molecular orbital theory of organic chemistry. New York: McGraw-Hill 1969
2. Graovac, A., Gutman, I, Trinajstic, N.: Topological approach to the chemistry of conjugated molecules. Berlin, Heidelberg, New York: Springer-Verlag 1977
3. Tang, Au-chin, Kiang, Yuan-sun: Sci. Sin. **19**, 208 (1976)
4. Kiang Yuan-sun: Int. J. Quantum Chem. **28**, 331 (1980); Int. J. Quantum Chem. **S15**, 293 (1981)
5. Cao, Wei-liang, Jiang, Yuan-sheng: Acta Chimica Sinica **40**, 880 (1982)
6. Gutman, I, Trinajstic, N.: Chem. Phys. Lett. **17**, 535 (1972)
7. Gutman, I, Trinajstic, N.: Chem. Phys. Lett. **20**, 257 (1973)
8. Dewar, M. J. S., Gleicher, G. J.: J. Am. Chem. Soc. **87**, 685, 692 (1965)
9. Dewar, M. J. S., and de Llano, C.: J. Am. Chem. Soc. **91**, 789 (1969)
10. Hess, Jr., B. A., Schaad, L. J.: J. Am. Chem. Soc. **93**, 305 (1971)
11. See, for example E. Heilbronner, P. A. Straub; "HMO" Hückel molecular orbitals. New York: Springer-Verlag, 1966
12. Burdett, J. K., Lee, S., Sha, W. C.: to be published in Croat. Chem. Acta.

Received April 11, 1984