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(n, m)-TYPE APPROXIMATIONS FOR TOTAL π-ELECTRON ENERGY OF BENZENOID HYDROCARBONS

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Dedicated to Professor
Alexandru T. Balaban
founder of Chemical Graph Theory on the occasion of his 70th birthday

Abstract. In the half-century long research of the structure-dependency of the total π-electron energy (E) of benzenoid hydrocarbons (as calculated within the Hückel molecular orbital model) a large number (over 40) of (n, m)-type approximate formulas for E were put forward. These formulas (denoted here by E^*) depend on only two parameters: n - the number of carbon atoms (= number of vertices of the molecular graph) and m - the number of carbon-carbon bonds (= number of edges of the molecular graph). We provide here a complete list thereof (published until the middle of 2000) and report statistical data indicating the accuracy of the approximation $E \approx a\,E^* + b$, with coefficients a and b determined by least-squares fitting. The best (n, m)-type formulas of this kind are capable of reproducing E with an average relative error of 0.30%. There are several such formulas, the McClelland expression $E^* = \sqrt{2mn}$ (designed already in 1971) having the simplest algebraic form. It seems that 0.30% is the limit of the accuracy for the (n, m)-type approximations for total π-electron energy.

INTRODUCTION

In this paper we are concerned with the total π-electron energy as calculated within the simple tight-binding Hückel molecular-orbital (HMO) approximation, expressed - as usual - in units of the resonance integral β [1]-[3]. We denote this quantity by E The problem of the structure-dependency of E attracts the attention of theoretical chemists longer than half a century and numerous results in this area have been obtained [4, 5]. The theory of E is nowadays reasonably well elaborated, mainly due to the application of various methods of algebra and graph spectral theory [4, 5].

The fact that the gross part of the total π-electron energy is determined by two simple topological parameters: the number n of vertices of the molecular graph (equal to the number of carbon atoms in the underlying conjugated hydrocarbon) and the number m of edges of the molecular graph (equal to the number of carbon-carbon bonds) was certainly noticed by the pioneers in this area - Charles Coulson [6] and especially George Hall [7]; see also [8]-[11] However the real breakthrough came with the seminal 1971 article of Bernard McClellan [12], who first arrived at the famous approximation $E \approx a\sqrt{2mn}$.

It may be that McClelland opened a Pandora's box, because his work was followed b a flood of publications by other authors and by well over 40 distinct (n, m)-type approximat formulas for E. The references [12]-[30] cited here are just those in which novel (n, m)-typ formulas for E were put forward; we did not intend (and did not dare) to compile a complet bibliography of the many hundreds of papers concerned with research of the (n, m)-typ formulas for E.

The (n, m)-*type* formulas for E have three main sources: 1° some of them wer obtained by using mathematically and/or physically justified approximations in HMO theor 2° some were obtained without any theory, by a clever guess. 3° A significant number formulas are in fact lower or upper bounds for E, supplied by a pertinent empirical multiplier.

A limited number of the formulas reported in the literature applies to all conjugate hydrocarbons, a few more to all alternant hydrocarbons. The majority of them have bee designed for benzenoid systems, using the distinguished topological properties of this class conjugated molecules [31].

Concerning class 3° of (n, m)-type formulas for E recall that McClelland [12] prove the inequality $E \le \sqrt{2mn}$ (which is a mathematically correct result), and then observed th between E and the upper bound $\sqrt{2mn}$ there is a remarkably good linear correlation, leadi to $E \approx a\sqrt{2mn}$. The same procedure may be, and has been, repeated (with good or less goo success) with any other (n, m)-type lower and upper bound for E.

Comparative studies of (n, m)-type approximate formulas for the total π-electr energy of benzenoid hydrocarbons were earlier undertaken [5, 32]. However, because of the appearance of a multitude of novel such formulas, the papers [5, 32] are nowadays outdated; for instance, in [5] only 24 formulas were examined (because only 24 formulas existed in that time). The aim of the present work is to provide a *fin de siècle* report on this topic.

THE FORMULAS

In this section we list the various (n, m)-type expressions, all denoted by E^*, that may be used to approximate the HMO total π-electron energy of benzenoid hydrocarbons by means of either

$$E \approx a\,E^* + b \tag{1}$$

or

$$E \approx a_1 E^* \tag{2}$$

with a, b and a_1 being empirically determined fitting parameters (see the subsequent section). For each formula (except nos. 1 and 2) we quote its source, where the interested reader can learn how the formula was actually deduced. The formulas are ordered chronologically.

Formula 1:

$$E^* = n$$

Formula 2:

$$E^* = m$$

Formula 3 [12]:

$$E^* = \sqrt{2mn}$$

Formula 4 [13]:

$$E^* = \sqrt{\frac{3n^2}{4(n^2-1)}}\sqrt{2mn}$$

Formula 5 [14]:

$$E^* = 2\sqrt{m + \frac{1}{2}\sqrt{n(n-2)(m^2-9m+6n)}}$$

Formula 6 [15]:

$$E^* = 2t\sqrt{\frac{2m}{n} + R\sqrt{\frac{n}{2t}-1}} + (n-2t)\sqrt{\frac{2m}{n} - \frac{R}{\sqrt{n/(2t)-1}}} \tag{3}$$

where

$$R = \frac{\sqrt{2(9mn - 6n^2 - 2m^2)}}{n} \tag{4}$$

and where $t = 1$.

Formula 7 [15,16]: E^* and R are same as in (3) and (4), whereas $t = 2$.

Formula 8 [15, 16]: E^* and R are same as in (3) and (4), whereas $t = (1/2)[m^2/(9m - 6$

Formula 9 [15, 16]: E^* and R are same as in (3) and (4), whereas $t = [m^2/(9m - 6n)]$

Formula 10 [17]:

$$E^* = 2\left[6\sqrt{\alpha a_6} + 3m\sqrt{\sqrt{4\beta a_4} + m} - \sqrt{\frac{8m^3}{n}}\right]^{1/3}$$

where

$$\alpha = \frac{n(n-2)(n-4)}{48}; \quad \beta = \frac{n(n-2)}{8}$$

$$a_4 = \frac{m^2 - 9m + 6n}{2}; \quad a_6 = \frac{m^3 - 27m^2 + 158m + 48}{6} + 3n(m-8)$$

Formula 11 [18]: E^* is the solution of the equation (5):

$$E^4 + 6(2mn - E^2)\,[E^2 + A\,E\sqrt{2mn - E^2} + B\,(2mn - E^2)] = 6n^3\,(3m - 2n) \tag{5}$$

for $A = 1.1360$, $B = -1.7600$.

Formula 12 [26]: E^* is the solution of the equation (5) for $A = 1.1360$, $B = -1.33$.

Formula 13 [26]: E^* is the solution of the equation (5) for $A = 1.1360$, $B = -1.97$.

Formula 14 [19]:

$$E^* = \sqrt{\frac{4m^3 9m - 6n}{}}$$

Formula 15 [19]:

$$E^* = (n\sqrt{P_0} + 2m)\sqrt{Q_0 + 2\sqrt{P_0}}$$

where

$$P_0 = \frac{72mn - 72n^2 - 4m^2 + 48}{9mn - 6n_2 - 2m^2}; \quad Q_0 = \frac{91mn - 72n^2 - 18m^2 + 24n}{9mn - 6n_2 - 2m^2}$$

Formula 16 [20]:

$$E^* = \frac{n}{4}\left(\sqrt{\frac{15m-10n}{m}}+\sqrt{\frac{25m^2-45mn+30n^2}{mn}}\right)$$

Formula 17 [20]:

$$E^* = \frac{n}{4}\left(Q+\sqrt{\frac{1080m^2-2379mn+1512n^2-504n}{45m-30n}}\right)$$

where

$$Q = \sqrt{\frac{553m-504n+168}{45m-30n}} \qquad (6)$$

Formula 18 [20]:

$$E^* = \frac{n}{4}\left(\frac{553m-504n+168}{3m}\right)^{1/4}+\sqrt{\frac{3mn}{2}-\frac{3n^2}{16}\sqrt{\frac{553m-504n+168}{3m}}}$$

Formula 19 [20]:

$$E^* = 3m\sqrt{\frac{m}{15m-10n}}$$

Formula 20 [20]:

$$E^* = \frac{3m}{Q}$$

where Q is given by (6).

Formula 21 [20]:

$$E^* = 3m\left(\frac{3m}{553m-504n+168}\right)^{1/4}$$

Formula 22 [20]:

$$E^* = \frac{45m-30n}{Q^3}$$

where Q is given by (6).

Formula 23 [20]:

$$E^* = \frac{nQ}{4}+\frac{\sqrt{8n(45m-30n)Q^2-3n^2Q^6}}{4Q^2}$$

where Q is given by (6).

Formula 24 [21]:

$$E^* = m^p n^{1-p} \quad ; \quad p = 0.35$$

Formula 25 [21]:

$$E^* = m^p n^{1-p} \quad ; \quad p = \frac{1}{3}$$

Formula 26 [22]:

$$E^* = \sqrt[4]{18}\left[\left(m - \frac{2n}{3}\right)n^3\right]^{1/4}$$

Formula 27 [22]:

$$E^* = \sqrt[6]{158}\left[\left(m - \frac{72n}{79} + \frac{24}{79}\right)n^5\right]^{1/6}$$

Formula 28 [22]:

$$E^* = \sqrt[8]{1330}\left[\left(m - \frac{682n}{665} + \frac{352}{665}\right)n^7\right]^{1/8}$$

Formula 29 [22]:

$$E^* = \sqrt[10]{10762}\left[\left(m - \frac{5855n}{5381} + \frac{3690}{5381}\right)n^9\right]^{1/10}$$

Formula 30 [23]:

$$E^* = \sqrt{4m + \sqrt{32\left(m^2 - 9m + 6n\right)}} \equiv E_L$$

Formula 31 [23]:

$$E^* = \sqrt{4m + \sqrt{4n(n-2)\left(m^2 - 9m + 6n\right)}} \equiv E_U$$

Formula 32 [23]:

$$E^* = \sqrt{4m + \sqrt{32\left(m^2 = 9m + 6n\right) + n(n-2)\left(n^2 - 2n - 8\right)}} \equiv E_{LB}$$

Formula 33 [23]:

$$E^* = \alpha E_L + (1-\alpha)E_U \quad ; \quad \alpha = \frac{1}{8}$$

Formula 34 [24]:

$$E^* = \alpha E_L + (1-\alpha)E_U \quad ; \quad \alpha = 0.1197$$

Formula 35 [24]:

$$E^{*} = \alpha E_{LB} + (1-\alpha)E_{U} \quad ; \quad \alpha = 0.306$$

Formula 36 [25]:

$$E^{*} = 2\sqrt{m + \frac{1}{2}\frac{n-2}{m}\sqrt{n(n-2)(m^{2}-9m+6n)}}$$

Formula 37 [25]:

$$E^{*} = 2\sqrt{m + \frac{1}{2}\frac{n-1}{m}\sqrt{n(n-2)(m^{2}-9m+6n)}}$$

Formula 38 [27]:

$$E^{*} = \frac{2mn}{m+n/2}$$

Formula 39 [27]:

$$E^{*} = \frac{2mn}{m+1.19n}$$

Formula 40 [28, 30]:

$$E^{*} = \frac{2m}{n} + \sqrt{(n-1)\left[2m - \left(\frac{2m}{n}\right)^{2}\right]}$$

Formula 41 [28]:

$$E^{*} = 2\left(\frac{2m}{n}\right) + \sqrt{(n-2)\left[2m - 2\left(\frac{2m}{n}\right)^{2}\right]}$$

Formula 42 [29]:

$$E^{*} = 0.1\left(\frac{2m}{n}\right) + \sqrt{(n-0.1)\left[2m - 0.1\left(\frac{2m}{n}\right)^{2}\right]}$$

Formula 43 [29]:

$$E^{*} = \sqrt{(n+3)\left(2m + \frac{12m^{2}}{n^{2}}\right)} - \frac{6m}{n}$$

Formula 44 [29]:

$$E^{*} = \sqrt{(n+2.9)\left(2m + \frac{11.6m^{2}}{n^{2}}\right)} - \frac{5.8m}{n}$$

QUALITY OF THE FORMULAS - A COMPARATIVE STUDY

The approximations (1) and (2) were tested on the standard set of 105 Kekule a benzenoid hydrocarbons, from the book of Zaliradnik and Pancir [33]. The statistical data indicating the quality of the formulas considered are given in Table 1. The coefficients of Eqs. (1) and (2) is found in Table 2.

From a practitioner's point of view the most important indicator of the quality of an approximation is its average relative error *(ARE)*. Namely, if the respective formula is applied to a conjugated system whose F-value is not known, then it may be expected that the error committed will be round *ARE*. In the worst case, this error may be around *MRE*.

In view of this, we assume that the quality of the approximations increases with decreasing ARE-values. In case when two formulas have equal *ARE*, the one with smaller *MRE* is declared to be better.

Formulas of the form (2) were often considered in the earlier works on *(n,* m)-type approximations for F, following McClelland's original approach [12]. However, in our opinion it is more justified to use approximations of the form (1). These, of course, have smaller ARE-values than the analogous formulas of the form (2), but this is not the decisive advantage of (1) over (2). The real problem with (2) is that it would give different results for (linearly dependent) expressions F^* and $E^* + c$, *for C* being a non-zero constant.

TABLE 1. Statistical data indicating the quality of the approximation (1): ARE =average relative error (in %), MER = maximal relative error observed (in %), ft =correlation coefficient (1 one standard deviation), ASD = average square deviation, F = F-ratio

E*	*ARE*	*MRE*	*R*	*ASD*	*F*
1	0.58	2.6	0.99925 ± 0.00015	0.0926	16193.4
2	0.58	2.5	0.99926 ± 0.00014	0.0916	16367.2
3	0.30	1.0	0.99982 ± 0.00003	0.0219	68396.4
4	0-30	1.0	0.99982 ± 0.00003	0.0220	68154.0
5	0.30	1.1	0.99982 ± 0.00003	0.0220	68191.1
6	0.31	1.3	0.99982 ± 0.00004	0.0226	66247.9
7	0.31	1.1	0.99982 ± 0.00004	0.0226	66420.6
8	0.32	1.2	0.99981 ± 0.00004	0.0240	62456.6
9	2.76	8.8	0.98473 ± 0.00296	1.8754	799.4
10	0.32	1.6	0.99982 ± 0.00004	0.0228	65849.6

TABLE 1. (continued)

11	0.30	1.1	0.99982 ± 0.00003	0.0221	67937.0
12	0.31	1.1	0.99982 ± 0.00004	0.0227	65986.0
13	0.36	1.3	0.99973 ± 0.00005	0.0335	44753.8
14	0.32	1.2	0.99980 ± 0.00004	0.0247	60614.8
15	2.04	8.3	0.99103 ± 0.00174	1.1057	1355.9
16	0.31	1.1	0.99981 ± 0.00004	0.0235	63889.0
17	0.43	1.4	0.99966 ± 0.00007	0.0422	35497.3
18	0.35	1.3	0.99976 ± 0.00005	0.0295	50784.8
19	0.32	1.2	0.99980 ± 0.00004	0.0247	60614.8
20	0.46	1.6	0.99961 ± 0.00008	0.0483	31022.3
21	0.38	1.3	0.99973 ± 0.00005	0.0335	44717.4
22	0.88	2.8	0.99867 ± 0.00026	0.1650	9087.4
23	0.89	3.0	0.99861 ± 0.00027	0.1720	8715.0
24	0.33	1.2	0.99978 ± 0.00004	0.0277	54199.4
25	0.34	1.2	0.99976 ± 0.00005	0.0291	51524.9
26	0.31	1.0	0.99982 ± 0.00004	0.0227	66063.8
27	0.35	1.0	0.99978 ± 0.00004	0.0274	54709.1
28	0.40	1.2	0.99971 ± 0.00006	0.0355	42263.8
29	0.45	1.4	0.99963 ± 0.00007	0.0452	33193.1
30	1.73	33.8	0.99459 ± 0.00105	0.6674	2246.3
31	0.30	1.1	0.99982 ± 0.00003	0.0220	68191.1
32	0.47	2.1	0.99948 ± 0.00010	0.0647	23184.3
33	0.30	1.0	0.99982 ± 0.00003	0.0219	68432.1
34	0.30	1.0	0.99982 ± 0.00003	0.0219	68516.6
35	0.31	1.2	0.99980 ± 0.00004	0.0241	62117.3
36	0.30	1.1	0.99982 ± 0.00003	0.0221	67937.0
37	0.30	1.1	0.99982 ± 0.00003	0.0221	67937.0
38	0.36	1.3	0.99973 ± 0.00005	0.0335	44692.6
39	0.30	1.0	0.99982 ± 0.00003	0.0219	68597.0
40	0.30	1.1	0.99982 ± 0.00003	0.0220	68186.3
41	0.30	1.1	0.99982 ± 0.00004	0.0222	67405.6
42	0.30	1.0	0.99982 ± 0.00003	0.0219	68401.1
43	0.31	1.0	0.99982 ± 0.00004	0.0226	66251.6
44	0.31	1.0	0.99982 ± 0.00004	0.0226	66365.8

On the other hand, the expressions E^* and $E^* + C$ describe the very same structure-dependency. When Eq. (1) is employed, then all linearly dependent functions E~ yield one and the same approximate formula for E.

TABLE 2. The coefficients in approximations (1) and (2);
the uncertainties represent one estimated standard deviation

E^*	a	b	a_1
1	1.431 ± 0.005	-0.50 ± 0.15	1.413 ± 0.006
2	1.126 ± 0.004	1.40 ± 0.14	1.167 ± 0.006
3	0.898 ± 0.002	0.441 ± 0.07	0.908 ± 0.002
4	1.038 ± 0.002	0.38 ± 0.07	1.0481 ± 0.002
5	0.8991 ± 0.002	0.88 ± 0.07	0.9201 ± 0.003
6	0.926 ± 0.002	0.89 ± 0.07	0.9481 ± 0.003
7	0.932 ± 1 0.002	1.111 ± 0.07	0.959 ± 0.00:3
8	0.970 1 ± 0.002	0.29 ± 0.07	0.978 ± 0.002
9	1.067 ± 0.019	0.37 ± 0.67	1.0771 ± 0.019
10	0.903 ± 0.002	1.101 ± 0.07	0.928 ± 0.003
11	0.635 ± 0.001	2.341 ± 0.07	0.675 ± 0.004
12	0.977 ± 0.002	0.301 ± 0.07	0.985 ± 0.002
13	1.0141 ± 0.002	0.02 ± 0.09	1.014 ± 0.002
14	1.1681 ± 0.002	0.181 ± 0.08	1.1741 ± 0.002
15	0.083 ± 0.001	1.92 ± 0.49	0.0871 ± 0.001
16	1.009 ± 0.002	0.25 ± 0.07	1.0151 ± 0.002
17	1.020 ± 0.003	0.41 ± 0.10	1.031 ± 0.003
18	1.014 ± 0.002	0.321 ± 0.08	1.023 ± 0.002
19	1.005 ± 0.002	0.18 ± 0.08	1.0101 ± 0.002
20	1.0191 ± 0.003	0.41 ± 0.11	1.030 ± 0.003
21	1.012 ± 0.002	0.29 ± 0.09	1.0201 ± 0.002
22	1.045 ± 0.005	0.89 ± 0.19	1.0691 ± 0.006
23	1.0451 ± 0.005	0.90 ± 0.20	1.070 ± 0.006
24	1.317±0.003	0.15 ± 0.08	1.322 ± 0.003
25	1.322 ± 0.003	0.121 ± 0.08	1.3261 ± 0.003
26	0.7881 ± 0.001	0.56 ± 0.07	0.799 ± 0.002
27	0.729 ± 0.002	0.54 ± 0.08	0.739 ± 0.002
28	0.693 1 ± 0.002	0.51 ± 0.09	0.702 ± 0.002
29	0.669 ± 0.002	0.49 ± 0.10	0.677 ± 0.002
30	3.856 ± 0.040	-28.57 ± 0.69	2.2221 ± 0.166
31	0.899 ± 0.002	0.88 ± 0.07	0.9201 ± 0.003
32	1.434 ± 0.005	-3.01 ± 0.13	1.333 ± 0.011
33	0.995 ± 0.002	-0.08 ± 0.07	0.993 ± 0.002
34	0.990 ± 0.002	-0.03 ± 0.07	0.989 ± 0.002
35	1.015 ± 0.002	0.04 ± 0.08	1.016 ± 0.002
36	0.635 ± 0.001	2.34 ± 0.07	0.675 ± 0.004
37	0.6351 ± 0.001	2.34 ± 0.07	0.675 ± 0.004
38	0.997 ± 0.002	0.05 ± 0.09	0.999 ± 0.002
39	1.386 ± 0.003	0.43 ± 0.07	1.401 ± 0.003
40	0.899 ± 0.002	0.63 ± 0.07	0.914 ± 0.002
41	0.899 ± 0.002	0.90 ± 0.07	0.920 ± 0.003
42	0.8981 ± 0.002	0.45 ± 0.07	0.909 ± 0.002
43	0.894 ± 0.002	0.10 ± 0.07	0.8961 ± 0.002
44	0.894 ± 0.002	0.11 ± 0.07	0.896 ± 0.002

By inspection of Table 1 we arrive at the following conclusions.

- The best formulas reproduce the total 'v-electron energy of benzenoid hydrocarbons with an average relative error of 0.30% and maximal observed error of 1.0%.

There are several such formulas, nos. 3, 4, 33, 34, 39 and 42. Besides, there are other formulas with *ARE* = 0.30% and an insignificantly greater *MRE* of 1.1%, nos. 11, 31, 36, 40 and 41. Further, quite a few other approximate formulas have *ARE* only slightly above 0.30%.

- Thus, the total π-electron energy of benzenoid hydrocarbons can be approximated by many, analytically quite different, approximate formulas, all of which have essentially the same accuracy. Among them the McClelland expression (no. 3) has certainly the simplest mathematical form and, therefore, it should be given advantage over the other - equally accurate - (n, m)-type approximations.

- Formulas that have greater *ARE* than the trivial approximations $E \sim a\,n + 6$ and $E \sim a\,m + 6$ must be characterized as fully unsatisfactory, they do not deserve to be considered any further and should be completely eliminated from the theory of total π-electron energy. These are the formulas no. 22, 23, 30 and especially 9 and 15.

- The high correlation coefficients (which, in almost all cases considered exceed 0.999) clearly indicate that the correlation between E and E^* is essentially linear. For not a single E^* was curvilinearity, modeled by $E \approx aE^* + b + c(E^*)^2$, found to be statistically significant.

CONCLUDING REMARKS

The McClelland formula [12], which according to our calculation assumes the form

$$E \approx 0.898\sqrt{2mn} + 0.44$$

is practically the first (n, m)-type approximation for total π-electron energy. It is capable of reproducing 99.7% of the total π-electron energy of benzenoid hydrocarbons (in average, of course). Since 1971 many other (n, m)-type approximations for E were designed, but - as the present comparative study shows - none of them is better than McClelland's. Remarkably, however, many of these later approximations have exactly the same accuracy as McClelland's.

This hints toward the conclusion that *ARE* = 0.30% is the lower limit which an (n, m)-

type formula can achieve in the case of benzenoid hydrocarbons. In other words, some 0.30% of the variation of the E-values of benzenoid hydrocarbons must be ascribed to structural factors other than n and m. Less than one third of a percent!!! Among these the variation in the Kekule structure count is usually considered as the most important [5, 34]. These "other" structural factors, having a seemingly very small influence on the value of E, are responsible for the differences in the thermodynamic stability of isomers and are therefore of major chemical importance. Their examination goes beyond the ambit of the present study.

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