

The total π -electron energy as a problem of moments: application of the Backus–Gilbert method

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The total π -electron energy problem can be formulated as a classical problem of moments. This observation allows us to apply general methodologies developed in the field of moment's theory to solve the total π -electron energy problem. In the present article, we apply the Backus–Gilbert method to obtain analytical expressions for the total π -electron energy in terms of its spectral moments.

KEY WORDS: total π -electron energy, problem of moments, chemical graph theory, spectral moments, Backus–Gilbert method

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1. Introduction

The classical problem of moments can be formulated as follows: given an infinite sequence $M_n (n = 0, 1, 2, \dots)$ find a distribution F on the interval $[a, b]$ such that

$$M_n = \int_a^b x^n dF(x), \quad n = 0, 1, 2, \dots \quad (1)$$

The Stieltjes moment problem searches for a distribution on $[0, \infty]$ [1,2]; the Hamburger moment problem searches for a distribution on $[-\infty, \infty]$ and the Hausdorff moment problem searches for a distribution on a finite interval [2]. In particular, the moment problem that Stieltjes formulated was to find the necessary and/or sufficient conditions for the existence of a solution $F(x)$ on $[0, \infty]$, and for this solution to be unique on $[0, \infty]$. Stieltjes himself gave the solution to his problem and in the interim introduced his well known Stieltjes integral [1]. Other moment problems and their solutions are associated with the names of Chebyshev, Markov, Nevanlinna, and Riesz, among others [2].

Because many applied problems can be formulated as problems of moments, several methods have been developed to find approximately the distribution function associated with a given problem when some of its moments are known. One technique particularly useful is the Backus–Gilbert (BG) method. This technique has been widely used in geophysics to analyze the internal structure of the Earth from information such as frequencies of oscillation, and seismic travel times [3–9]. In abstract, the BG method is used for estimating values of an unknown function on the basis of scarce information.

On the other hand, in chemical graph theory an important line of research has been the search for approximate expressions or bounds for the total π -electron energy (E) [10,11]. E is an important chemical quantity related to the thermodynamic stability of conjugated molecules [11]. The E function of a molecular graph G is defined by [12]

$$E = \int_{-\infty}^{\infty} |x| \Gamma(x) dx \quad (2)$$

and its spectral moments by

$$M_k = \int_{-\infty}^{\infty} x^k \Gamma(x) dx. \quad (3)$$

The spectral-density function $\Gamma(x)$ is defined as

$$\Gamma(x) = \sum_{k=1}^n \delta(x - \lambda_k) \quad (4)$$

with $\delta(x)$ being the Dirac delta function and the λ_k , $k = 1, 2, \dots, n$, being the eigenvalues of the adjacency matrix of G .

From equations (2–4) we obtain

$$E = \sum_{k=1}^n |\lambda_k|, \quad (5)$$

$$M_i = \sum_{k=1}^n \lambda_k^i. \quad (6)$$

The total π -electron energy problem can be formulated as a classical problem of moments. Indeed, given a model and a set of spectral moments $\{M_2, M_4, \dots, M_{2j}\}$, in general an incomplete information, we try to construct an approximate distribution function $\hat{\Gamma}(x)$ from which E can be found.

Since the known number of spectral moments is finite, the problem of the existence of a given density function $\Gamma(x)$ does not arise. The question we try to answer in this paper is to what extent can the density function $\Gamma(x)$ be recovered from the set $M = \{M_2, M_4, \dots, M_{2j}\}$ of spectral moments and used to calculate E . In this case the problem is reduced to one of “regularization”, this is,

to the problem of fitting the function $\Gamma(x)$ as closely as possible to the known moments. To accomplish this fit, we use the BG method in this paper.

2. The Backus–Gilbert method [3–9]

The BG method tries to map as accurate as possible the approximate solution $\hat{\Gamma}(x)$ to the true solution $\Gamma(x)$ through the relationship

$$\hat{\Gamma}(x) = \int \hat{\delta}(x', x) \Gamma(x') dx', \quad (7)$$

where $\hat{\delta}(x', x)$ is the resolution function or averaging kernel. The BG method tries to minimize the spread of $\hat{\delta}(x', x)$ or, in other words, to maximize the resolving power. Observe that when $\hat{\delta}(x', x)$ is equal to the Dirac delta function the resolution is maximal.

In the BG method the function $\hat{\Gamma}(x)$ is expressed as a linear combination of the data, in our case the moments M_i ,

$$\hat{\Gamma}(x) = \sum_{i=1}^N c_i(x) M_i, \quad (8)$$

where $\hat{\Gamma}(x)$ is an estimate of the density function at some value x , and the coefficients c_i depend on the value of x at which the density is estimated. The BG method is then a method to determine the best set of coefficients $c_i(x)$.

Since, from equations (3) and (8), $\hat{\Gamma}(x)$ can be written as

$$\hat{\Gamma}(x) = \sum_{i=1}^N c_i(x) \int x'^i \Gamma(x') dx', \quad (9)$$

equation (7) gives

$$\hat{\delta}(x', x) = \sum_{i=1}^N c_i(x) x'^i. \quad (10)$$

In the BG method the coefficients are to be chosen such that the spread $\hat{\delta}(x, x')$ resembles as much as possible a Dirac delta function centered in around x .

The BG method requires that

$$\int \hat{\delta}(x', x) dx' = \sum_{i=1}^N c_i(x) \int x'^i dx' = 1. \quad (11)$$

The BG method defines the spread of the resolution function by

$$A(x) = \int (x' - x)^2 \left[\hat{\delta}(x', x) \right]^2 dx'. \quad (12)$$

The aim is then to minimize the spread $A(x)$ subject to the constraint (11). Based on functional analysis techniques, Backus and Gilbert have shown rigorously that this method produces a spread function that gives the most localized estimate of $\Gamma(x)$ [4]. This means that $\hat{\Gamma}(x)$ will be close to $\Gamma(x)$ only if $A(x)$ is small. The reason for choosing the mathematical form of $A(x)$ is that it leads to linear equations for the coefficients c_i when searching for the smallest $A(x)$.

3. The total π -electron energy

We now apply the BG method to find the optimal formulas for E in terms of two arbitrary moments M_a and M_b , with M_b being the lowest of the two. We model our approximate density function as a linear combination of the two moments

$$\hat{\Gamma}(x') \simeq c_a(x')M_a + c_b(x')M_b. \quad (13)$$

As stated in section (2), we obtain the following integral equation

$$\hat{\Gamma}(x) \simeq \int_{-\infty}^{\infty} (c_a x'^a + c_b x'^b) \Gamma(x') dx'. \quad (14)$$

Here we suppose that the function $(c_a x'^a + c_b x'^b) \Gamma(x')$ is concentrated about the point $x = 0$ and that $\Gamma(x') = \Gamma(-x')$. This last consideration implies that all odd moments are zero. Thus, we concentrate the support of the function in the interval $[-s, s]$, where s is a small positive number. In this way, we substitute equation (14) by the model density

$$\hat{\Gamma}(x) \simeq \int_{-s}^s (c_a x'^a + c_b x'^b) \Gamma(x') dx'. \quad (15)$$

The parameter s is a free parameter in our model and it will be fixed by requiring that $\Gamma(x)$ reproduces a known moment.

Now impose the normalization condition by assuming $\Gamma(x') = 1$,

$$1 = \int_{-s}^s (c_a x'^a + c_b x'^b) dx' \quad (16)$$

$$= 2s \left\{ \frac{c_a}{(1+a)} s^a + \frac{c_b}{(1+b)} s^b \right\}. \quad (17)$$

Our restriction is then

$$g(c_a, c_b, s) = 2s \left\{ \frac{c_a}{(1+a)} s^a + \frac{c_b}{(1+b)} s^b \right\} - 1 = 0. \tag{18}$$

We next shape the function $c_a x'^a + c_b x'^b$ by penalizing values at points x' that are distant from 0. Following the BG method, we minimize the integral

$$f(c_a, c_b, s) = \int_{-s}^s (c_a x'^a + c_b x'^b)^2 x'^2 dx', \tag{19}$$

subject to the constraint (17). This is a problem of constrained quadratic minimization and can be solved by the method of Lagrange’s multipliers. A necessary condition for a solution is the existence of a number λ satisfying [8]

$$\nabla_{c_i} f(c_a, c_b, s) + \lambda \nabla_{c_i} g(c_a, c_b, s) = 0, \tag{20}$$

where ∇_{c_i} are gradients with respect to the c_i .

Hence, one has

$$\frac{\partial f}{\partial c_a} + \lambda \frac{\partial g}{\partial c_a} = 2 \int_{-s}^s (c_a x'^a + c_b x'^b) x'^{2+a} dx' + 2\lambda \frac{s^{1+a}}{1+a} \tag{21}$$

$$= 4s^3 \left\{ \frac{c_a}{(3+2a)} s^{2a} + \frac{c_b}{(3+a+b)} s^{a+b} \right\} + 2\lambda \frac{s^{1+a}}{1+a} \tag{22}$$

$$= 0 \tag{23}$$

$$\frac{\partial f}{\partial c_b} + \lambda \frac{\partial g}{\partial c_b} = 2 \int_{-s}^s (c_a x'^a + c_b x'^b) x'^{2+b} dx' + 2\lambda \frac{s^{1+b}}{1+b} \tag{24}$$

$$= 4s^3 \left\{ \frac{c_b}{(3+2b)} s^{2b} + \frac{c_a}{(3+a+b)} s^{a+b} \right\} + 2\lambda \frac{s^{1+b}}{1+b} \tag{25}$$

$$= 0. \tag{26}$$

The set of equations to be solved is then given by equations (18), (22) and (25), with solution

$$c_a = -\frac{(1+a)(3+2a)(1+b)(2+b)}{2(a-b)(5+3a+3b+2ab)} s^{-1-a}, \tag{27}$$

$$c_b = \frac{(1+a)(2+a)(1+b)(3+2b)}{2(a-b)(5+3a+3b+2ab)} s^{-1-b}, \tag{28}$$

while the expression for λ is no needed for constructing $\Gamma(x)$.

The optimal value for s is selected by requiring that $\Gamma(x')$ satisfies exactly the lowest-order moment M_b

$$\int_{-s}^s x'^b \hat{\Gamma}(x') dx' = M_b, \tag{29}$$

giving, from equations (13), (27), and (28),

$$s = \left[\frac{(1+a)M_a}{(1+b)M_b} \right]^{1/(a-b)}. \quad (30)$$

The expression for the total π -electron energy is obtained by integration, see equation (2),

$$E = \int_{-s}^s |x'| \hat{\Gamma}(x') dx' \quad (31)$$

$$= s^2 \hat{\Gamma}(x) \quad (32)$$

$$= \frac{(1+a)(1+b) [(2+a)(3+2b)M_b s^{1-b} - (3+2a)(2+b)M_a s^{1-a}]}{2(a-b)(5+3a+3b+2ab)}, \quad (33)$$

with s given by equation (30).

For the case of a density function expressed as a linear combination of the moments M_0 and M_2 , equations (30) and (33) give $E = \frac{\sqrt{3}}{2} \sqrt{M_2 M_0} \simeq 0.87 \sqrt{M_2 M_0}$, which is McClelland's approximation [13].

We have found that the BG method is able to reproduce the best formulas already obtained in [12] and it is also able to produce new explicit and accurate formulas for the total π -electron energy. In Appendix A we show that the expressions obtained in [12] can be obtained by applying a particular approximation to the BG method. We can use the BG method to include more than two moments, however, when doing so, the expressions obtained become more and more complex and eventually no analytical expression can be found for s . The parameter s is found through the solution of an algebraic equation whose degree depends on the order of the moments included in the spectral density function. Thus, there are combinations of spectral moments that do not lead to analytically soluble equations. Although the procedure of the BG method can all be carried out numerically, and that is the way it is usually done in applications in other fields, the tacit philosophy in the present field is to obtain analytical expressions for E and we will follow that philosophy here.

When the density function is expressed as a linear combination of three moments

$$\hat{\Gamma}(x') \simeq c_a(x')M_a + c_b(x')M_b + c_c(x')M_c, \quad (34)$$

and the BG method is employed, the two best analytical expressions for the total π -electron energy are given by

$$E = \frac{21(99M_6 - 154M_2s^4 + 72M_0s^6)}{1462s^5}, \quad (35)$$

where

$$s = \frac{1}{\sqrt{142}} \left[\frac{1}{M_0} \left(196M_2 + \frac{2^{1/3}7^{2/3}2744M_2^2}{q} + 2^{2/3}7^{1/3}q \right) \right]^{1/2}, \quad (36)$$

with

$$q = \left[268912M_2^3 + 213 \left(-639M_0^2M_6 \right. \right. \quad (37)$$

$$\left. \left. + \sqrt{3M_0^2M_6 \left(-537824M_2^3 + 136107M_0^2M_6 \right)} \right) \right]^{1/3}, \quad (38)$$

and

$$E = M_0 \frac{\left(75M_2 + (5625M_2^2 - 3080M_0M_4)^{1/2} M_0 \right)^{1/2}}{4\sqrt{7}}. \quad (39)$$

We believe that equation (35) is up to now the best analytical expression for the total π -electron energy in terms of three spectral moments.

The expressions for the known moments of benzenoid hydrocarbons are the following [14]

$$M_0 = n,$$

$$M_2 = 2m,$$

$$M_4 = 18m - 12n,$$

$$M_6 = 158m - 144n + 48 + 6b_6,$$

$$M_8 = 1330m - 1364n + 704 + 8b_8,$$

$$M_{10} = 10762m - 11710n + 7380 + 10b_{10},$$

where n and m are the number of vertices and the number edges of the graph G , respectively, and b_6 , b_8 , and b_{10} are the number of certain elements of structure, which are very small with respect to the other terms and, following [12], they will be neglected here. In this way our formulas for E are expressed in terms of n and m only.

In table 1 we give the total π -electron energy for a sample of benzenoid compounds using the found formulas. As shown there, formula (35) gives the best agreement with the numerical results. If we set $a = r$, $b = r - t$ in equation (33) and set $s = r$ or $s = r - t$ in equation (14) of [12] (our equation (A.4)), equation (33) becomes the same as the best obtained in [12] (equation (A.4) of the present article) when two moments are equal.

Table 1

Total π -electron energy for a sample of benzenoid hydrocarbons, calculated with the formulae developed by the Backus-Gilbert method. The notation (a, b, c) indicates the order of the moments which give the best results.

Name	n	m	$(4, 2, -)^a$	$(4, 2, 0)^b$	$(6, 2, 0)^c$	Exact ^d
Benzene	6	6	8.0498	8.28215	8.0104	8.0000
Naphthalene	10	11	13.5754	14.0655	13.6480	13.6832
Anthracene	14	16	19.2000	19.8911	19.3498	19.3137
Phenanthrene	14	16	19.2000	19.8911	19.3498	19.4483
Pyrene	16	19	22.2227	23.0053	22.3262	22.5055
Tetracene	18	21	24.8475	25.7327	25.0746	24.9308
Chrysene	18	21	24.8475	25.7327	25.0746	25.1922
Perylene	20	24	27.8855	28.8603	28.0724	28.2453
Benzo[a]pyrene	20	24	27.8855	28.8603	28.0724	28.2220
Benzo[e]pyrene	20	24	30.7222	30.7019	28.0724	28.3361
Picene	22	26	30.5040	31.5817	30.8098	30.9452
Anthanthrene	22	27	30.9443	32.0092	31.1011	31.2529
Coronene	24	30	34.0168	35.1740	34.1542	34.5718

^aEquation (33) with $a = 4$, $b = 2$, ^bequation (39), ^cequation (35), ^dsolving the corresponding eigenvalue problem.

4. Concluding remarks

We have shown that the observation that the total π -electron energy problem can be framed as a problem of moments allows one the application of techniques that have been developed to solve the latter problem. In particular, in the present paper, we have applied the Backus-Gilbert method to the derivation of new explicit analytical formulas for the total π -electron energy. The Backus-Gilbert method is based on variational principles and thus gives the best possible results from the assumed form of the spectral density function. Furthermore, we have shown that a recent method applied to the total π -electron energy problem can be considered as a particular approximation within the Backus-Gilbert method.

Appendix A

Here we show that the formulas for the total π -electron energy obtained in [12] can be found as an approximation to the BG method applied to this problem.

Consider the following model which approximates the spectral density function $\hat{\Gamma}(x')$ as a linear combination of two moments M_a and M_b

$$\hat{\Gamma}(x') = c_a(x')M_a + c_b(x')M_b. \quad (\text{A.1})$$

Following the procedure of the BG method explained in section 2, the coefficients $c_a(x')$ and $c_b(x')$ are given by equations (27) and (28), together with equation (30).

A simple analytical expression for the total π -electron energy is obtained by expressing the spectral density in terms of only one moment

$$\hat{\Gamma}(x') \simeq c_c(x')M_c. \quad (\text{A.2})$$

Following the BG method, the optimum coefficient c_c is giving by

$$c_c = \frac{1}{2}(1 + c)s^{-1-c}. \quad (\text{A.3})$$

The analytical expression for E then follows from equations (2), (A.2) and (A.3)

$$E = \int_{-s}^s |x'| \hat{\Gamma}(x') dx' \quad (\text{A.4})$$

$$= \frac{1}{2}(1 + c)M_c s^{1-c}, \quad (\text{A.5})$$

where s is given by equation (30).

If we make the substitutions $a = r$, $b = r - t$, and $c = s$ then equation (A.5), together with equation (30), becomes the best formula for E obtained in [12] (equation (14) of that reference).

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