Practical version of the Asymptotic Linearity Theorem with applications to the additivity problems of thermodynamic quantities

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Received 23 December 1991; in final form 22 July 1992

By using fundamental notions and theorems of the Lesbesgue integral, a practical version of the Asymptotic Linearity Theorem has been derived. From this new version of the theorem, it easily follows that the theorem is also applicable to the additivity problems of thermodynamic quantities of molecules having many identical moieties, as well as to those of the zero-point vibrational energy of hydrocarbons and the total pi-electron energies of alternant hydrocarbons.

1. Introduction

The Asymptotic Linearity Theorem (ALT) [1,2] involves an auxiliary function space through which one can handle a variety of additivity problems in a unifying manner. The extensiveness of this auxiliary space reflects the strength of the theorem and the degree of its applicability to studies of the correlation between structure and properties in molecules having many identical moieties.

It has already been shown that the auxiliary space denoted by $\overline{P(I)}$ (cf. section 2 for its definition) is wide enough for the theorem to be applicable to the additivity problems of the zero-point vibrational energies (ZPVEs) of hydrocarbons [1–15], and the total pi-electron energies (TPEEs) of alternant hydrocarbons [12–26]. However, since the above space was defined implicitly as the closure of

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a set in a normed space, we have been concerned whether it is possible to make a more concise characterization of $\overline{P(I)}$ in the ALT, which would clarify and simplify the applications of the theorem.

In the present paper, we show that $\overline{P(I)}$ in the ALT or the α space ALT [15] coincides with the space of real-valued absolutely continuous functions defined on a closed interval, and give some examples of functions associated with thermodynamic properties of molecules to which the ALT can be applied.

2. Practical versions of the Asymptotic Linearity Theorem and the α Space Asymptotic Linearity Theorem

By I, unless otherwise specified, we shall throughout denote a closed interval $I = [a, b]$ with $a, b \in \mathbb{R}$, $a < b$. Let AC(I) denote the set of all real-valued absolutely continuous functions defined on I (cf. section 3 for the definition of absolutely continuous functions).

The following theorem 1 and theorem 2 are practical versions of the ALT and X_αALT (α space ALT), respectively, which we wish to establish in this section.

THEOREM 1

Let $\{M_N\} \in X_r(q)$ be a fixed repeat sequence, let I be a fixed closed interval compatible with $\{M_N\}$. Then, for any element $\varphi \in \mathrm{AC}(I)$, there exist $\alpha(\varphi), \beta(\varphi) \in \mathbb{R}$ such that

$$\mathrm{Tr}\ \varphi(M_N) = \alpha(\varphi)N + \beta(\varphi) + o(1) \tag{2.1}$$

as $N \to \infty$.

THEOREM 2

Let $\{M_N\} \in X_\alpha(q)$ be a fixed α sequence, let I be a fixed closed interval compatible with $\{M_N\}$. Then, for any element $\varphi \in \mathrm{AC}(I)$, there exists an $\alpha(\varphi) \in \mathbb{R}$ such that

$$\mathrm{Tr}\ \varphi(M_N) = \alpha(\varphi)N + o(1) \tag{2.2}$$

as $N \to \infty$.

The theorems ALT and X_αALT can be reproduced by replacing the symbol "AC(I)" in theorems 1 and 2, respectively, with the phrase "$\overline{P(I)}$ in the normed space CBV(I)". Here and hereafter, $P(I)$ denotes the set of all polynomial functions with real coefficients defined on I, and CBV(I) denotes the normed space of all real-valued continuous functions of bounded variation defined on I equipped with the norm given by

$$\| \varphi \|_{\mathrm{CBV}} = \sup_{t \in I} | \varphi(t) | + V_I(\varphi), \tag{2.3}$$

where $V_I(\varphi)$ denotes the total variation of φ on I.

Thus, to prove theorems 1 and 2, we have only to prove the following

PROPOSITION 1

The closure of $P(I)$ in the normed space CBV(I) is the set AC(I), i.e.

$$\overline{P(I)} = \mathrm{AC}(I). \tag{2.4}$$

Henceforth, let AC(I) denote the normed space (as well as its underlying set) of all real-valued absolutely continuous functions defined on $I = [a, b]$ equipped with the norm given by

$$\| \varphi \| \mathrm{AC} = \sup_{t \in I} | \varphi(t) | + \int_a^b | \varphi'(t) | \, \mathrm{d}t. \tag{2.5}$$

Let $L^1(I)$ denote the linear space of all real-valued Lebesgue integrable functions defined on $I = [a, b]$ equipped with the semi-norm given by

$$\| \varphi \|_{L^1} = \int_a^b | \varphi(t) | \, \mathrm{d}t. \tag{2.6}$$

Before proceeding to the proof of proposition 1, we shall recall well-known fundamental properties of AC(I) and $L^1(I)$.

PROPOSITION 2

Let $I = [a, b]$, where $a, b \in \mathbb{R}$, $a < b$; then the following statements are true:

(i) $P(I) \subset \mathrm{AC}(I) \subset \mathrm{CBV}(I) \subset L^1(I)$. (2.7)

(ii) If $\varphi \in \mathrm{AC}(I)$, then $\varphi'(t)$ exists a.e. and is Lebesgue integrable on I. Moreover,

$$\varphi(t) - \varphi(a) = \int_a^t \varphi'(s) \, \mathrm{d}s \tag{2.8}$$

for all $t \in I$.

(iii) If $f \in L^1(I)$ and $\varphi\colon I \to \mathbb{R}$ is the function defined by $\varphi(t) = \int_a^t f(s) \, \mathrm{d}s +$ constant, then $\varphi \in \mathrm{AC}(I)$. Moreover,

$$\varphi'(t) = f(t) \text{ (a.e.)}. \tag{2.9}$$

(iv) If $\varphi \in \mathrm{AC}(I)$, then

$$V_I(\varphi) = \int_a^b |\varphi'(t)|\,dt, \tag{2.10}$$

where $V_I(\varphi)$ denotes the total variation of φ on I.

(v) For any $f \in L^1(I)$ and $\varepsilon > 0$, there exists a polynomial function $p \in P(I)$ such that

$$\int_a^b |f(t) - p(t)|\,dt < \varepsilon, \tag{2..11}$$

(vi) The quotient space $\mathbf{L}^1(I) = L^1(I)/\{f \in L^1(I) : f(t) = 0 \text{ (a.e.)}\}$ equipped with the $\mathbf{L}^1$ norm is a complete normed space, i.e. a Banach space.

Proof of proposition 1

(i) $\overline{P(I)} \supset \mathrm{AC}(I)$: By proposition 2(i), (iv), we may regard $X_1 = (\mathrm{AC}(I), \|\cdot\|_{\mathrm{AC}})$ as a subspace of the normed space $X_2 = (\mathrm{CBV}(I), \|\cdot\|_{\mathrm{CBV}})$. Hence, it suffices to show that $P(I)$ is dense in X_1.

Let $\varphi \in \mathrm{AC}(I)$, $\varepsilon > 0$ be arbitrary. By proposition 2(v), there exists a $p \in P(I)$ such that

$$\varphi(a) = p(a) \tag{2.12}$$

and

$$\int_a^b |\varphi'(t) - p'(t)|\,dt < \varepsilon/2. \tag{2.13}$$

On the other hand, since $\varphi, p \in \mathrm{AC}(I)$, by proposition 2(ii), (2.12), and (2.13), we obtain

$$|\varphi(t) - p(t)| = \left|\int_a^t \varphi'(s) - p'(s)\,ds\right| \le \int_a^b |\varphi'(s) - p'(s)|\,ds < \varepsilon/2 \tag{2.14}$$

for all $t \in I$, so that

$$\sup_{t \in I} |\varphi(t) - p(t)| \le \varepsilon/2. \tag{2.15}$$

By (2.13) and (2.15), it then immediately follows that

$$\|\varphi - p\|_{AC} < \varepsilon, \tag{2.16}$$

proving that $P(I)$ is dense in X_1.

(ii) $\overline{P(I)} \subset AC(I)$: By proposition 2(i) and the fundamental properties of the closure operation, it is enough to prove that the set $AC(I)$ is a closed set in the normed space $X_2 = (CBV(I), \|\cdot\|_{CBV})$.

Consider $X_1 = (AC(I), \|\cdot\|_{AC})$ as a subspace of the normed space $X_2 = (CBV(I), \|\cdot\|_{CBV})$ as in (i), and note that if X_1 is a complete space, then $AC(I)$ is a closed set in X_2. Thus, it remains to show that X_1 is complete.

Let $C(I)$ denote the Banach space of all real-valued continuous functions defined on I equipped with the norm given by

$$\|\varphi\|_\infty = \sup_{t \in I} |\varphi(t)|. \tag{2.17}$$

Recall the definitions of $\|\cdot\|_{AC}$ and $\|\cdot\|_{L^1}$ and note that for all $\varphi \in AC(I)$ the equality

$$\|\varphi\|_{AC} = \|\varphi\|_\infty + \|\varphi'\|_{L^1} \tag{2.18}$$

holds.

Let $\varphi_n \in X_1$ be any Cauchy sequence. Then by the completeness of $C(I)$ and $L^1(I)$ (proposition 2(vi)), we infer that there exist $f \in C(I)$, $g \in L^1(I)$ such that

$$\|\varphi_n - f\|_\infty \to 0, \tag{2.19}$$

$$\|\varphi_n' - g\|_{L^1} \to 0, \tag{2.20}$$

as $n \to \infty$.

By proposition 2(iii), it is easy to verify the following inequalities valid for any $t \in I$:

$$\begin{aligned} &|f(t) - f(a) - \int_a^t g(s)\,ds| \\ &\quad \le |f(t) - \varphi_n(t)| + |\varphi_n(a) - f(a)| + |\varphi_n(t) - \varphi_n(a) - \int_a^t g(s)\,ds| \\ &\quad \le 2\|\varphi_n - f\|_\infty + \|\varphi_n' - g\|_{L^1}. \end{aligned} \tag{2.21}$$

Letting $n \to \infty$ in (2.21), and using (2.19) together with (2.20), we see that the smallest side of (2.21) vanishes so that f can be expressed as an indefinite integral of the Lebesgue integrable function g:

$$f(t) = f(a) + \int_a^t g(s)\,\mathrm{d}s\,, \quad t \in I. \tag{2.22}$$

Hence, by proposition 2(iii), we have

$$f \in \mathrm{AC}(I), \tag{2.23}$$

$$f'(t) = g(t) \quad \text{(a.e.)}, \tag{2.24}$$

from which it readily follows that

$$\|\varphi_n - f\|_{\mathrm{AC}} \to 0 \tag{2.25}$$

as $n \to \infty$. Therefore, we conclude that φ_n is a convergent sequence in X_1 and that X_1 is complete. □

Remark

In Dunford and Schwartz [27], AC(I) is equipped with the norm

$$\|\varphi\|_0 = |\varphi(a)| + \int_a^b |\varphi'(t)|\,\mathrm{d}t\,. \tag{2.26}$$

It is easy to check that $\|\cdot\|_0$ and $\|\cdot\|_{\mathrm{AC}}$ are equivalent norms, so the completeness of X_1 could also be derived from the fact that $(\mathrm{AC}(I), \|\cdot\|_0)$ is a Banach space, Theorem IV.12.3 [27].

3. Absolutely continuous functions and the applications of the practical version of the Asymptotic Linearity Theorem

A function $\varphi: I = [a, b] \to \mathbb{R}$ is said to be absolutely continuous on I if, given any $\varepsilon > 0$, there exists a $\delta > 0$ such that for every finite system of pairwise disjoint subintervals $(a_1, b_1), (a_2, b_2), \ldots, (a_n, b_n) \subset [a, b]$,

$$\sum_{k=1}^{n} (b_k - a_k) < \delta \tag{3.1}$$

implies

$$\sum_{k=1}^{n} |\varphi(b_k) - \varphi(a_k)| < \varepsilon\,. \tag{3.2}$$

The function $\varphi_1: I \to \mathbb{R}$ defined by $\varphi_1(t) = |t|$ is obviously absolutely continuous on I, and $\varphi_{1/2}: I \to \mathbb{R}$ defined by $\varphi_{1/2}(t) = |t|^{1/2}$ is easily shown to be absolutely continuous on I by setting $\delta = \varepsilon^2/2$ for any given $\varepsilon > 0$ in the above argument. Thus, the applicability of the ALT to the additivity problems of the TPEEs (φ_1) and the ZPVEs ($\varphi_{1/2}$) becomes more easily checked (cf. ref. [2] for the proof of φ_1, $\varphi_{1/2} \in \overline{P(I)} \subset \mathrm{CBV}(I)$).

With the criteria of the absolute continuity in mind, we may find other additivity problems to which the ALT can be applied.

Let $\mathrm{Ch}'_N(m, k)$ denote a linear chain with fixed ends consisting of N particles each of mass m and separation 1 which can vibrate harmonically under a restoring force due to the first neighbour interaction k [12]. Assume that $\mathrm{Ch}'_N(m, k)$ is in thermal equilibrium with the heat bath at absolute temperature $T > 0$. Let M'_N with $N \geq 2$ denote the mass-weighted Hessian matrix associated with $\mathrm{Ch}'_N(m, k)$, which is an $N \times N$ positive definite real symmetric matrix [12] and put $M'_0 = c > 0$ as a dummy term.

Then by a similar argument as in the expression of ZPVEs of $\mathrm{Ch}'_N(m, k)$ [12], one can express the internal energy U_N of $\mathrm{Ch}'_N(m, k)$ in terms of the trace of the matrix,

$$U_N = \mathrm{Tr}\ \varphi_U(M'_N). \tag{3.3}$$

Here, φ_U is defined as follows on a closed interval $I = [0, b]$ compatible with the repeat sequence $\{M'_N\}$:

$$\varphi_U = g_U \circ f, \tag{3.4}$$

where $f\colon I \to [0, \sqrt{b}]$ and $g_U\colon [0, \sqrt{b}] \to \mathbb{R}$ are functions defined by

$$f(t) = \sqrt{t} \tag{3.5}$$

and

$$g_U(\omega) = (\hbar/2)\omega + \hbar\,\omega/[\exp(\hbar\omega/kT) - 1], \tag{3.6}$$

where $\hbar$ is the Planck constant, k is the Boltzmann constant.

Similarly, the vibrational heat capacity at constant volume C_{vN} of $\mathrm{Ch}'_N(m, k)$ can be expressed by

$$C_{vN} = \mathrm{Tr}\ \varphi_C(M'_N). \tag{3.7}$$

Here, φ_C is defined as follows on a closed interval $I = [0, b]$ compatible with the repeat sequence $\{M'_N\}$:

$$\varphi_C = g_C \circ f, \tag{3.8}$$

where $f\colon I \to [0, \sqrt{b}]$ and $g_C\colon [0, \sqrt{b}] \to \mathbb{R}$ are functions defined by (3.5) and

$$g_C(\omega) = k(\hbar\,\omega/(2kT))^2/\sinh^2(\hbar\omega/2kT). \tag{3.9}$$

(See, e.g. refs. [28,29] for the usual expressions of U and C_v which do not use the trace of the matrix.)

By the definition of the absolutely continuous functions, one easily verifies that if f is both absolutely continuous and monotone increasing on $[a, b]$, and g is absolutely continuous on $[f(a), f(b)]$, then the composite function $g \circ f$ is absolutely continuous on $[a, b]$.

Since f defined by (3.5) is obviously both absolutely continuous and monotone increasing on $I = [0, b]$, to prove that $\varphi_U, \varphi_C \in \mathrm{AC}(I)$, it clearly suffices to show that g_U and g_C are absolutely continuous. Using the well-known fact that continuously differentiable functions on a compact interval are all absolutely continuous functions, we may easily verify that g_U and g_C are absolutely continuous. Therefore, $\varphi_U, \varphi_C \in \mathrm{AC}(I)$.

Thus, we see that one can apply the practical version of the Asymptotic Linearity Theorem also to the additivity problems of thermodynamic quantities, in addition to those of ZPVEs and TPEEs. A more detailed discussion will be published elsewhere.

References

[1] S. Arimoto, Phys. Lett. 113A(1985)126.
[2] S. Arimoto and M. Spivakovsky, J. Math. Chem. 13(1993)217.
[3] T.L. Cottrell, J. Chem. Soc. (1948) 1448.
[4] K.S. Pitzer and E. Catalano, J. Am. Chem. Soc. 78(1956)4844.
[5] H. Shingu and T. Fujimoto, J. Chem. Phys. 31(1959)556.
[6] H. Shingu and T. Fujimoto, Bull. Japan Petroleum Inst. 1(1959)11.
[7] T. Fujimoto and H. Shingu, Nippon Kagaku Zasshi 82(1961)789, 794, 945, 948.
[8] T. Fujimoto and H. Shingu, Nippon Kagaku Zasshi 83(1962)19.
[9] T. Fujimoto and H. Shingu, Nippon Kagaku Zasshi 83(1962)23, 359, 364.
[10] J.M. Schulman and R.L. Disch, Chem. Phys. Lett. 133(1985)291.
[11] M.C. Flanigan, A. Kormornicki and J.W. McIver, Jr., in: *Electronic Structure Calculation*, ed. G.A. Segel (Plenum Press, New York, 1977).
[12] S. Arimoto, Phys. Lett. 124A(1987)131.
[13] S. Arimoto, Phys. Lett. 124A(1987)275.
[14] S. Arimoto and G.G. Hall, Int. J. Quant. Chem. 41(1992)613.
[15] S. Arimoto and K. Taylor, J. Math. Chem. 13(1993)249.
[16] G.G. Hall, Proc. Roy. Soc. A229(1955)251.
[17] G.G. Hall, Int. J. Math. Educ. Sci. Technol. 4(1973)233.
[18] G.G. Hall, Bull. Inst. Math. Appl. 17(1981)70.
[19] J. Aihara, J. Am. Chem. Soc. 98(1976)2750.
[20] A. Graovac, I. Gutman and N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules* (Springer, Berlin, 1977).
[21] I. Gutman and N. Trinajstić, Chem. Phys. Lett. 20(1973)257.
[22] A.T. Balaban, *Chemical Applications of Graph Theory* (Academic Press, New York, 1976).
[23] A. Tang, Y. Kiang, G. Yan and S. Tai, *Graph Theoretical Molecular Orbitals* (Science Press, Beijing, 1986).
[24] Y. Jiang, A. Tang and R. Hoffmann, Theor. Chim. Acta 66(1984)183.
[25] A. Motoyama and H. Hosoya, J. Math. Phys. 18(1977)1485.
[26] H. Hosoya and A. Motoyama, J. Math. Phys. 26(1985)157.
[27] N. Dunford and J.T. Schwartz, *Linear Operators* (Interscience, New York, 1963).
[28] H. Tadokoro, *Structure of Crystalline Polymers* (Wiley, New York, 1979).
[29] P. Brüesch, *Phonons: Theory and Experiments*, Vol. 1 (Springer, Berlin, 1982).