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A variational algebraic method used to study the full vibrational spectra and dissociation energies of some specific diatomic systems

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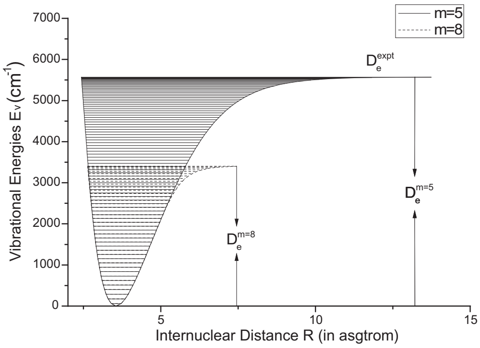
HIGHLIGHTS

- We modify our algebraic method (AM) to be a variational AM (VAM).
- The VAM can adapt to individual physical nature of different diatomic systems.
- The VAM can offset the possible errors that may exist in experimental data.
- The VAM can predict the full vibrational spectra for some specific diatomic systems.

GRAPHICAL ABSTRACT

The results of the Na_2–$C^1\Pi_u$ state have shown that the new VAM (variational algebraic method) energies $E_\upsilon^{VAM}(5)$ beautifully reproduce the experimental data and converge to the correct dissociation limit, while the original AM energies $E_\upsilon^{AM}(8)$ converge to a wrong dissociation limit that is 2159.066 cm^{-1} lower than the experimental dissociation energy! Their RKR curves are shown in Fig 1.



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ABSTRACT

The algebraic method (AM) proposed by Sun et al. is improved to be a variational AM (VAM) to offset the possible experimental errors and to adapt to the individual energy expansion nature of different molecular systems. The VAM is used to study the full vibrational spectra $\{E_\upsilon\}$ and the dissociation energies D_e of $^4HeH^+$–$X^1\Sigma^+$, $^7Li_2$–$1^3\Delta_g$, Na_2–$C^1\Pi_u$, NaK–$7^1\Pi$, Cs_2–$B^1\Pi_u$ and $^{79}Br_2$–$\beta1_g(^3P_2)$ diatomic electronic states. The results not only precisely reproduce all known experimental vibrational energies, but also predict correct dissociation energies and all unknown high-lying levels that may not be given by the original AM or other numerical methods or experimental methods. The analyses and the skill suggested here might be useful for other numerical simulations and theoretical fittings using known data that may carry inevitable errors.

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Introduction

Molecular high-lying vibrational levels, especially the ones near dissociation limits, are very important in the studies of molecular

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long-range interactions, chemical reactions, molecular scattering, near dissociation molecular dynamics, and so on [1–3]. However, due to the limitations in experimental measurements, it is usually quite difficult to obtain accurate high-lying vibrational levels for many molecular electronic states; on the other hand, extensive computations and complicated techniques are often needed to study vibrational energies and molecular dissociation energies using *ab initio* based theoretical methods [4–7]. As an alternative, one may use the algebraic method (AM) [8] proposed by Sun et al. to study the full vibrational spectra and molecular dissociation energies of diatomic systems economically and efficiently. The AM has generated correct full vibrational spectra $\{E_\upsilon\}$ and molecular dissociation energies D_e for more than one hundred diatomic states recently [8–16].

However, the original AM did not give accurate vibrational spectra and dissociation energies for some specific diatomic states such as the $^4HeH^+$–$X^1\Sigma^+$, $^7Li_2$–$1^3\Delta_g$, Na_2–$C^1\Pi_u$, NaK–$7^1\Pi$ and Cs_2–$B^1\Pi_u$ states. In this study, the original AM is improved to be a nodal variational algebraic method (VAM) to study the vibrational spectra of the specific diatomic states like those above. Section 2 briefly outlines the original AM, analyzes the error amplification effect, and presents the VAM. Section 3 studies the full vibrational spectra $\{E_\upsilon\}$ and dissociation energies of the above specific states using the VAM. Section 4 concludes this study.

Variational algebraic method

Outline of the AM

The algebraic method started from the physical law of vibrational energies of a stable diatomic molecular electronic state [8]

$$E_\upsilon = \omega_0 + (\omega_e + \omega_{e0})\left(\upsilon+\frac{1}{2}\right) - \omega_e x_e\left(\upsilon+\frac{1}{2}\right)^2 + \omega_e y_e\left(\upsilon+\frac{1}{2}\right)^3 + \omega_e z_e\left(\upsilon+\frac{1}{2}\right)^4 + \omega_e t_e\left(\upsilon+\frac{1}{2}\right)^5 + \omega_e s_e\left(\upsilon+\frac{1}{2}\right)^6 + \omega_e r_e\left(\upsilon+\frac{1}{2}\right)^7 + \cdots\cdots \quad (1)$$

It is essentially of the form of Herzberg [17], and can be rewritten as a matrix form

$$\mathbf{AX} = \mathbf{E} \quad (2)$$

where

$$A_{\upsilon k} = \left(\upsilon+\frac{1}{2}\right)^k, X = \begin{pmatrix} \omega_0 \\ \omega'_e \\ -\omega_e x_e \\ \omega_e y_e \\ \vdots \end{pmatrix}_{m\times 1}, E = \begin{pmatrix} E_{\upsilon_1} \\ E_{\upsilon_2} \\ E_{\upsilon_3} \\ \vdots \\ E_{\upsilon_s} \end{pmatrix}_{m\times 1} \quad (3)$$

and $\omega'_e = \omega_e + \omega_{e0}$. In the original AM, eight ($m = 8$) of the $n(>m)$ known experimental vibrational energies are chosen in term of our experience to form the energy vector matrix E, and the vector matrix X that includes eight vibrational spectroscopic constants can be obtained by solving the Eq. (2) using standard algebraic method. The eight constants correspond to the eight expansion terms in the Eq. (1). Then the full vibrational spectra $\{E_\upsilon\}$ can be generated from these vibrational spectroscopic constants using the Eq. (1). Usually, there are C_n^8 groups of solutions X's for the Eq. (2) and the best physical spectroscopic representation X can be found from the C_n^8 vectors by satisfying the following physical criteria

$$\frac{dE_\upsilon}{d\upsilon}\Big|_{\upsilon=\upsilon_{\max}} = 0 \quad (4)$$

$$\Delta\bar{E}(e,c) = \sqrt{\frac{1}{m}\sum_{\upsilon=0}^{m-1}|E_{\upsilon,\exp} - E_{\upsilon,cal}|^2} \to 0 \quad (5)$$

$$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1} = E_{\upsilon_{\max}} - E_{\upsilon_{\max}-1} \to small \quad enough \quad (6)$$

$$D_e^{\text{expt}} - E_{\upsilon_{\max}} \to small \quad enough \quad (7)$$

$$D_e^{cal} \cong E_{\upsilon_{\max}} + \frac{\Delta E^2_{\upsilon_{\max},\upsilon_{\max}-1}}{\Delta E_{\upsilon_{\max},\upsilon_{\max}-2} - \Delta E_{\upsilon_{\max},\upsilon_{\max}-1}} \quad (8)$$

$$E_{\upsilon_{\max}} < D_e^{cal} \leqslant D_e^{\text{expt}} \quad (9)$$

$$0 < Error = \frac{D_e^{\text{expt}} - D_e^{cal}}{\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}} \leqslant 1 \quad (10)$$

where the sign "*expt*" denotes experimental data, the "*cal*" denotes the calculated data, and

$$\Delta E_{\upsilon_{\max},\upsilon_{\max}-2} = E_{\upsilon_{\max}} - E_{\upsilon_{\max}-2} \quad (11)$$

with $E_{\upsilon_{\max}}$ the highest vibrational energy.

Two improvements of computational process

Firstly as is well known that usually there are some errors hidden in different measured data due to experimental conditions. Comparing to the least square method that used all known data to fit physical constants, the advantage of the AM is that it could select the best eight vibrational levels containing the least experimental errors through the physical criteria from Eqs. (4)–(10) so that the spectrum generated by solving Eq. (2) can precisely reproduce all known experimental levels and accurately converge to the dissociation limit.

However, the error hidden in some of the eight vibrational levels may play a worse role and an error amplification effect may occur during the computational process of the spectrum studies in some specific electronic states. For example, if function $f(\upsilon) = E_\upsilon$ is used to denote Eq. (1) for short, it should satisfy

$$f(\upsilon_i) = \sum_{j=0}^{m-1} a_j\left(\upsilon_i + \frac{1}{2}\right)^j = E_{\upsilon_i} \quad (12)$$

where E_{υ_i} are the experimental levels and a_j correspond to vibrational spectroscopic constants in Eqs. (1) and (3). Suppose that there is a tiny experimental error ζ_{υ_p} in state υ_p of the eight selected experimental levels, so the Eq. (12) becomes

$$f'(\upsilon_i) = E_{\upsilon_i}, i{\neq}p; f'(\upsilon_p) = E_{\upsilon_p} + \zeta_{\upsilon_p} \quad (13)$$

where the f' denotes the new spectroscopic function in this case. Then a deviation function can be defined as $\Delta f(\upsilon) = f'(\upsilon) - f(\upsilon)$ and it should satisfy

$$\Delta f(\upsilon_i) = 0, i{\neq}p; \Delta f(\upsilon_p) = \zeta_{\upsilon_p} \quad (14)$$

Since the $(m - 1=)$ seven $\upsilon_i(i \neq p)$ are just the mathematical roots of the deviation functions $\Delta f(\upsilon_i)$, they can be rewritten as

$$\Delta f(\upsilon) = c\prod_{\substack{i=1\\ i\neq p}}^{m}(\upsilon - \upsilon_i) \quad (15)$$

One can obtain that $c = \zeta_{\upsilon_p}\Big/\cdot\prod_{\substack{i=1\\ i\neq p}}^{m}(\upsilon_p - \upsilon_i)$ by using the second half of the Eq. (14), and this can lead to an important deviation amplification formula

$$\Delta E_\upsilon = \Delta f(\upsilon) = \zeta_{\upsilon_p}\cdot\prod_{\substack{i=1\\ i\neq p}}^{m}\left(\frac{\upsilon - \upsilon_i}{\upsilon_p - \upsilon_i}\right) \quad (16)$$

It is obviously from this formula that the tiny error ζ_{υ_p} will be amplified in any other calculated vibrational level υ when the absolute

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