

改进的三维分离变量表象方法计算振动光谱

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摘要: 用改进的三维分离变量表象(DVR3D)方法研究了基态电子态 H_2S 和 H_2O 的振动光谱. 哈密顿形式在 Jacobi 坐标下给出, 每个坐标都用一组 DVR 基函数表示. 角度部分的 DVR 基组选择勒让德多项式形式, 而径向坐标采用正弦函数形式. 为了降低需要对角化的最终哈密顿矩阵的维数, 采用连续对角化截断方法. 用 H_2S 和 H_2O 振动能级的计算验证算法的正确性.

关键词: 三维分离变量表象; 勒让德多项式; 正弦函数; 连续对角化截断方法; 振动光谱

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Modified DVR3D for Calculation of Vibrational Spectra

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Abstract The modified discrete variable representation for three-dimension (DVR3D) method was applied to the determination of the vibrational energy levels of the fundamental electronic state of H_2S and H_2O . The Hamiltonian was expressed in Jacobi coordinates and developed on a DVR basis for each internal coordinate. The angular coordinate used a DVR based on Legendre polynomials and the radial coordinates utilized a DVR based on sine basis functions. Successive diagonalization and truncation technique was used to reduce the size of the final Hamiltonian matrix to be diagonalized. Calculations were presented for H_2S and H_2O to demonstrate the accuracy of these algorithms.

Key words Discrete variable representation, Legendre polynomials, Sine basis functions, Successive diagonalization and truncation technique, Vibrational spectra

1 Introduction

The development of discrete variable representations (DVR) has significantly improved the numerical treatment of various quantum mechanical problems^[1-4]. Using such methods to determine the spectra of triatomic molecules is now a well-known strategy and it has been applied successfully to a number of cases^[5-7]. Probably the most important advantage of DVR is its simplicity. The DVR potential

energy matrix is constructed directly from the potential function without evaluating integrals.

Since 1993 Tennyson and co-workers have published several program suites for calculating triatomic ro-vibrational spectra^[8-10]. In their works, three coordinates are all treated in DVR (DVR3D). The angular coordinate uses a DVR based on (associated) Legendre polynomials and the radial coordinates utilize a DVR based on either Morse oscillator-like or spherical oscillator functions.

Intermediate diagonalization and truncation is performed on the hierarchical expression of the Hamiltonian operator to yield the final secular problem. These calculations are necessary to obtain the observed spectra, but also need some additional information. In fact, the parameters r_e , ω_e and D_e which are associated with equilibrium separation, fundamental frequency and dissociation energy of the relevant radial coordinate, must be found in some spectra books, and optimized accordingly.

In this work we choose the sine basis functions to define a DVR for the radial coordinates. The parameters M , R_{\min} and R_{\max} , which are associated with the number of grids, the lower and upper bounds chosen for the relevant radial coordinate, are easy to be provided. We use such a method to calculate the $J=0$ vibrational bound states of the fundamental electronic state of the H_2O and H_2S .

2 Theory

The calculations are performed in Jacobi coordinates. For a triatomic molecule ABC: R is the distance from A to the mass center of BC, r is the distance between B and C, and θ is the angle between

$$\begin{aligned} {}^{(3D)}H_{\alpha,\alpha',\beta,\beta',\gamma,\gamma'} &= \left(\sum_{m,m'} T_m^\alpha \langle m \left| -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} \right| m' \rangle T_{m'}^{\alpha'} \right) \delta_{\beta,\beta'} \delta_{\gamma,\gamma'} + \left(\sum_{n,n'} T_n^\beta \langle n \left| -\frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} \right| n' \rangle T_{n'}^{\beta'} \right) \delta_{\alpha,\alpha'} \delta_{\gamma,\gamma'} + \\ &\left(\sum_{m,m'} T_m^\alpha \langle m \left| -\frac{1}{2\mu_R R^2} \right| m' \rangle T_{m'}^{\alpha'} \right) \left(\sum_j T_j^\gamma j(j+1) T_j^\gamma \right) \delta_{\beta,\beta'} + \left(\sum_{n,n'} T_n^\beta \langle n \left| -\frac{1}{2\mu_r r^2} \right| n' \rangle T_{n'}^{\beta'} \right) \times \\ &\left(\sum_j T_j^\gamma j(j+1) T_j^\gamma \right) \delta_{\alpha,\alpha'} + \sum_{m,n,j} \sum_{m',n',j'} T_{m,n,j}^{\alpha,\beta,\gamma} \langle m,n,j | V(R,r,\theta) | m',n',j' \rangle T_{m',n',j'}^{\alpha',\beta',\gamma'} \\ &= K_{\alpha,\alpha'}^{(1)} \delta_{\beta,\beta'} \delta_{\gamma,\gamma'} + K_{\beta,\beta'}^{(2)} \delta_{\alpha,\alpha'} \delta_{\gamma,\gamma'} + L_{\alpha,\alpha',\gamma,\gamma'}^{(1)} \delta_{\beta,\beta'} + L_{\beta,\beta',\gamma,\gamma'}^{(2)} \delta_{\alpha,\alpha'} + V(R_\alpha, r_\beta, \theta_\gamma) \delta_{\alpha,\alpha'} \delta_{\beta,\beta'} \delta_{\gamma,\gamma'} \quad (4) \end{aligned}$$

In Eq. (4), the potential energy operator is diagonal because of the quadrature approximation^[1], where $(R_\alpha, r_\beta, \theta_\gamma)$ is the value (R, r, θ) at (α, β, γ) .

We choose the sine basis functions to define a DVR for the radial coordinate^[12],

$$\begin{aligned} T_m^\alpha &= \langle R | m \rangle \\ &= \sqrt{\frac{2}{L}} \sin\left(\frac{m\pi R_\alpha'}{L}\right) \\ &= \sqrt{\frac{2}{L}} \sin\left(\frac{\alpha m \pi}{M+1}\right) \quad (5) \end{aligned}$$

where $L = R_{\max} - R_{\min}$, $R_\alpha' = R_\alpha - R_{\min} = \alpha \Delta R$, $\alpha = 1$,

R and r . Using a finite basis representation (FBR), the Hamiltonian matrix for the zero rotational angular momentum ($J=0$) can be written as (we use atomic units throughout)^[11]

$$\begin{aligned} \langle m, n, j | \hat{H} | m', n', j' \rangle &= \langle m \left| -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} \right| m' \rangle \delta_{n,n'} \delta_{j,j'} + \langle n \left| -\frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} \right| n' \rangle \delta_{m,m'} \delta_{j,j'} + \\ &\left(\langle m \left| \frac{1}{2\mu_R R^2} \right| m' \rangle \delta_{n,n'} + \langle n \left| \frac{1}{2\mu_r r^2} \right| n' \rangle \delta_{m,m'} \right) \times \\ &j(j+1) \delta_{j,j'} + \langle m, n, j | V(R, r, \theta) | m', n', j' \rangle \quad (1) \end{aligned}$$

where it has been assumed that the angular basis functions $|j\rangle$ are Legendre polynomials, and $|m\rangle$, $|n\rangle$ are the appropriate radial basis functions.

A three-dimensional DVR is obtained by apply the transformation

$$\begin{aligned} H_{\alpha,\alpha',\beta,\beta',\gamma,\gamma'} &= \sum_{m,n,j} \sum_{m',n',j'} T_{m,n,j}^{\alpha,\beta,\gamma} \langle m, n, j | H | m', n', j' \rangle T_{m',n',j'}^{\alpha',\beta',\gamma'} \quad (2) \end{aligned}$$

The 3D transformation is written as a product of 1D transformations:

$$T_{m,n,j}^{\alpha,\beta,\gamma} = T_m^\alpha T_n^\beta T_j^\gamma \quad (3)$$

The transformed Hamiltonian can be written at the DVR grid points as

$2, \dots, M$, and $\Delta R = L/(M+1)$. The corresponding DVR basis $|\bar{R}_\alpha\rangle$ is defined as

$$\langle \bar{R}_\alpha | m \rangle = \sqrt{\Delta R} \langle R_\alpha | m \rangle \quad (6)$$

The matrix elements of the kinetic energy operator in DVR have already been given by Colbert and Miller in Ref. [13]

$$\begin{aligned} K_{\alpha,\alpha'}^{(1)} &= \sum_{m,m'} T_m^\alpha \langle m \left| -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} \right| m' \rangle T_{m'}^{\alpha'} \\ &= \frac{1}{2\mu_R} \frac{(-1)^{\alpha-\alpha'}}{L^2} \frac{\pi^2}{2} \left(\frac{1}{\sin^2[\pi(\alpha-\alpha')/2(M+1)]} - \frac{1}{\sin^2[\pi(\alpha+\alpha')/2(M+1)]} \right), \quad (\alpha \neq \alpha') \quad (7a) \end{aligned}$$

$$K_{\alpha,\alpha}^{(1)} = \frac{1}{2\mu_R} \frac{(-1)^{\alpha-\alpha'}}{L^2} \frac{\pi^2}{2} \left(\frac{2(M+1)^2 + 1}{3} - \frac{1}{\sin^2[\pi\alpha(M+1)]} \right), \quad (\alpha = \alpha') \quad (7b)$$

the other kinetic energy term in Eq. (4) is represented by applying the quadrature approximation^[9]

$$L_{\alpha,\alpha',\gamma,\gamma'}^{(1)} = \sum_{m,m'} T_m^\alpha \langle m | \frac{1}{2\mu_R R^2} | m' \rangle T_{m'}^{\alpha'} \sum_j T_j^\gamma (j+1) T_j^{\gamma'} \equiv \frac{J_{\gamma,\gamma'}}{2\mu_R R_\alpha^2} \delta_{\alpha,\alpha'} \quad (8)$$

where

$$J_{\gamma,\gamma'} = \sum_j T_j^\gamma (j+1) T_j^{\gamma'} \quad (9)$$

the other radical coordinate r should be treated as the same way. If $\chi_\gamma (= \cos\theta_\gamma)$ and ω_γ are the points and weights of N-point Gauss-associated Legendre quadrature, then the transformation for the θ coordinate can be written^[14] as

$$T_j^\gamma = \left(\frac{2j+1}{2} \right)^{1/2} \omega_\gamma^{1/2} P_j(\chi_\gamma) \quad (10)$$

We use successive diagonalization and truncation techniques to generate efficient intermediate bases which reduce the size of the final Hamiltonian matrix to be diagonalized. The details can be found elsewhere^[5].

3 Application

The H₂S potential surface is issued from Senekowitsch *et al.*^[15]. The radial coordinate r is the length of the H-H internuclear vector, R is the length of the vector from the H-H mass center to the S nucleus. The parameters employed are as follows: the radial coordinate R extends from $R_{\min} = 0.5$ a. u. to $R_{\max} = 3.0$ a. u. with 32 grids. The coordinate r extends from $r_{\min} = 1.5$ a. u. to $r_{\max} = 6.0$ a. u. with 32 grids. 40 DVR points are taken to represent the wave packet in the θ coordinate. In Table 1 the vibrational band origins derived from the above method are compared with the previous DVR3D results^[9] and the observed values^[17]. The discrepancy of the vibrational level obtained with two calculational methods is within 1 cm^{-1} .

For H₂O, we use Polyansky-Jensen-Tennyson (PJT2) potential energy surface^[16]. The radial

coordinate r is the length of the O-H internuclear vector, R is the length of the vector from the OH mass center to the H nucleus. The parameters employed are as follows: the radial coordinate R extends from $R_{\min} = 0.5$ a. u. to $R_{\max} = 4.0$ a. u. with 32 grids. The coordinate r extends from $r_{\min} = 0.5$ a. u. to $r_{\max} = 6.0$ a. u. with 32 grids. 41 DVR points are taken to represent the wave packet in the θ coordinate. In Table 2 the vibrational band origins derived from above method are compared with the previous DVR3D results^[10] and the observed values^[18]. The maximal deviation between our results and the Ref. [10] is within 5 cm^{-1} .

Table 1 Comparison of calculated and observed band origins for H₂S

| $\nu_1 \nu_2 \nu_3$ | Revised DVR3D/cm ⁻¹ | DVR3D/cm ⁻¹ | Obs. ^[17] /cm ⁻¹ |
|---------------------|--------------------------------|------------------------|--|
| 0 1 0 | 1190.4 | 1190.4 | 1182.6 |
| 0 2 0 | 2372.0 | 2372.0 | 2354.0 |
| 1 0 0 | 2620.5 | 2620.4 | 2614.4 |
| 0 0 1 | 2631.0 | 2631.0 | 2628.4 |
| 0 3 0 | 3543.5 | 3543.5 | |
| 1 1 0 | 3794.7 | 3794.6 | 3779.2 |
| 0 1 1 | 3799.8 | 3799.8 | 3789.1 |
| 0 4 0 | 4703.7 | 4703.7 | |
| 0 2 1 | 4960.0 | 4960.0 | 4939.2 |
| 1 2 0 | 4960.4 | 4960.1 | |
| 2 0 0 | 5155.0 | 5154.4 | 5145.1 |
| 1 0 1 | 5155.9 | 5155.5 | 5147.4 |
| 0 0 2 | 5251.7 | 5251.3 | |
| 0 5 0 | 5851.8 | 5851.6 | |
| 0 3 1 | 6110.4 | 6110.2 | |
| 1 3 0 | 6116.2 | 6115.7 | |
| 2 1 0 | 6308.5 | 6307.9 | 6288.3 |
| 1 1 1 | 6308.6 | 6307.9 | 6289.3 |
| 0 1 2 | 6403.8 | 6403.1 | |
| 0 6 0 | 6986.7 | 6986.4 | |

4 Summary

We use sine basis functions to define a DVR for the radial coordinates. Compared with the previous DVR3D program, the parameters in our method are given more easily. The results derived from our method

Table 2 Comparison of calculated and observed band origins for H₂O

| $\nu_1\nu_2\nu_3$ | Revised DVR3D/cm ⁻¹ | DVR3D/cm ⁻¹ | Obs. ^{[17] /cm⁻¹} |
|-------------------|--------------------------------|------------------------|---------------------------------------|
| 0 1 0 | 1594.5 | 1594.6 | 1594.7 |
| 0 2 0 | 3151.2 | 3151.5 | 3151.6 |
| 1 0 0 | 3659.7 | 3657.1 | 3657.1 |
| 0 0 1 | 3757.9 | 3755.8 | 3755.9 |
| 0 3 0 | 4666.6 | 4666.8 | 4666.8 |
| 1 1 0 | 5237.2 | 5234.9 | 5235.0 |
| 0 1 1 | 5333.2 | 5331.4 | 5331.2 |
| 0 4 0 | 6134.3 | 6133.1 | 6134.0 |
| 1 2 0 | 6777.5 | 6775.2 | 6755.1 |
| 0 2 1 | 6873.9 | 6871.5 | 6871.5 |
| 2 0 0 | 7194.8 | 7202.2 | 7201.5 |
| 1 0 1 | 7253.3 | 7249.9 | 7249.8 |
| 0 0 2 | 7448.0 | 7444.7 | 7445.1 |
| 0 5 0 | 7540.6 | 7536.7 | |
| 1 3 0 | 8276.5 | 8273.8 | 8274.0 |
| 0 3 1 | 8378.9 | 8373.9 | 8373.8 |
| 2 1 0 | 8757.9 | 8761.8 | 8761.6 |
| 1 1 1 | 8810.9 | 8806.8 | 8807.0 |
| 0 6 0 | 8854.9 | 8851.3 | |
| 0 1 2 | 9005.3 | 9000.0 | 9000.1 |

are similar to the previous one. We will use this method to deal with the ro-vibrational spectra of triatomic in the future work.

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