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Computing the pure vibrational and vibrational_rotational energy eigenvalues of $^7Li_2$ by difference method

YI Han_wei[1], ZHANG Feng_dong[1], SHI Ai_min[2], LIU Shu_qin[3], DING Pei_zhu[4]
(1. Optical Physics Department, Changchun Institute of Optics and Fine Mechanics, Changchun 130022, China;
2. Department of Physics, Dalian Railway College, Dalian 116028, China;
3. Department of Applied Mathematics, Jilin University, Changchun 130026, China;
4. Institute of Atomic and Molecular Physics, Jilin University, Changchun 130023, China)

Abstract: The difference method for solving pure vibrational energy level and vibration- rotational energy level is proposed in this paper. Vibratioanal and vibrational- rotatioonal energy eigenvalues of $^7Li_2$ were calculated by means of introducing a difference method, and the computed results were compared with the results calculated by Ley- Koo, et al. In the process of solving the vibrational energy levels, the difference method is distinguished from other methods, in which wave functions do not need finding out, and vibrational energy levels can be found directly. Therefore it has the advantage of simplicity over other methods. It can be used to accurately determine both analytical and numerical potential functions of biatomic molecules. Furthermore, it can be employed to solve radiation problems such as quasi- molecular radiation.

Key words: diatomic molecule; vibrational energe; vibradional_rotational energe; difference method
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I　Introduction

Morse potentials are analytical functions which describe the potentials of diatomic molecules. They have been widely used in computing energy levels. Solution of Schrödinger equation that contains potential should be found out for the domain $0< r < \infty$, where r is the distance between two nuclei of the diatomic molecule. Morse's "exact" solution of Schrödinger equation was obtained for domain $- < r < \infty$ of the internuclear separation. This solution includes the unphysical domain $- < r < 0$. In 1995, a method of confining the diatomic molecule in a spherical box was developed by Ley- Koo et al to obtain pure vibrational energy spectra and the eigenvectors of Schr(dinger equation for Morse Potential in the physical domain $0< r < \infty$. In the problem, N wave functions of a free particle with the same boundary conditions are overlapped to find out energy eigenvalues and eigenfunctions of pure vibration of diatomic molecule. At the same time Frank- Gondon factors of some diatomic molecules were found out by means of these eigenfunctions[1]. In 1996 vibrational - rotational energy levels and eigenfunctions as well as the corresponding Franck- Condon factors of Morse potentials of $^7Li_2$ and AlO were found out by the same method[2]. The difference method is also effective to solve radical equations of the diatomic molecule.

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In 1981, Cooney et al calculated eigenvalues of H_2 and $Ħ_2$ using difference method[3]. In 1994 Wu Lianao et al calculated eigenvalues of linear and non-linear harmonic oscillators[4]. Pure vibrational and vibrational-rotational energy eigenvalues of $^7Li_2$ are calculated in this paper by the difference method in physical region $0< r < \infty$. In the process of solving the vibrational energy levels the difference method is distinguished from other methods, in which wave functions do not need finding, vibrational energy levels can be found out directly. Therefore it has advantage of simplicity over other methods. It can be used to accurately determine both analytical and numerical potential functions of biatomic molecules. Furthermore, it can be used to solve radiation problems such as quasi-molecular radiation.

II Radical equation of nuclei of diagomic molecule in relative movement

In B-O approximate conditions, studying vibration and rotation of diatomic molecules is changed into finding the solution of the radical equation of the diatomic molecules

$$-\frac{\hbar^2}{2\mu}\frac{d^2\Psi(r)}{dr^2}+\left[\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}+V(r)\right]\Psi(r)=E\Psi(r), \qquad (1)$$

with boundary conditions.

$$\Psi(0)=0, \quad \Psi(\infty)=0, \qquad (2)$$

Where μ is reduced mass of two atoms. $V(r)$ is molecular potential energy. Analytical Morse potential energy

$$V(r)=D\{[\exp[-2a(r-r_e)]-2\exp[-a(r-r_e)]]\}, \qquad (3)$$

is used in formula (1), where r_e represents the relative balance position. If $l=0$, then equation (1) describes pure vibration.

III Solution of pure vibration and vibrational_rotational energy eigenvalues by difference method

The diatomic molecule is limited in region $(0, R)$, which means that we think approximately $\Psi(R)=0$. R is divided into N parts, $\Delta r = R/N$.

There is a small increase in radical variable Δr, $\Psi(r+\Delta r)$ and $\Psi(r-\Delta r)$ which when expanded, we obtained

$$\Psi(r+\Delta r) = \Psi(r)+\Delta r\frac{d}{dr}\Psi(r)+\frac{1}{2}\Delta r^2\frac{d^2}{dr^2}\Psi(r) + \frac{1}{3!}\Delta r^3\frac{d^3}{dr^3}\Psi(r)+O(\Delta r^4), \qquad (4)$$

and

$$\Psi(r-\Delta r) = \Psi(r)-\Delta r\frac{d}{dr}\Psi(r)+\frac{1}{2}\Delta r^2 \frac{d^2}{dr^2}\Psi(r)-\frac{1}{3!}\Delta r^3\frac{d^3}{dr^3}\Psi(r)+O(\Delta r^4), \qquad (5)$$

When formula (4) and formula (5) are added together, we obtained

$$\Psi(r+\Delta r)+\Psi(r-\Delta r)=2\Psi(r) + \Delta r^2\frac{d^2}{dr^2}\Psi(r)+O(\Delta r^4), \qquad (6)$$

From formula (6)

$$\frac{d^2}{dr^2}\Psi(r)=\frac{1}{\Delta r^2}[\Psi(r+\Delta r) - 2\Psi(r)+\Psi(r-\Delta r)]+O(\Delta r^2), \qquad (7)$$

is obtained.

With the help of formula (7), formula (1) is changed into a difference equation

$$-\frac{\hbar^2}{2\mu(\Delta r)^2}[\Psi_{j+1}-2\Psi_j+\Psi_{i-1}] + \left[\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r_j^2}+V_j\right]\Psi_j=E\Psi_j, \qquad (8)$$

where $r_j = j\Delta r$, $= 0, 1, 2, 3. \ldots. N$.

If $j=1$, boundary condition $\Psi_0=\Psi(0)$ is used. If $j=N-1$, boundary condition $\Psi_N=\Psi(R)=0$ is used. From formula (8) we obtained the following equations

$$-\Psi_2+2\Psi_1+\frac{2\mu}{\hbar^2}(\Delta r)^2V_1\Psi_1 = \frac{2\mu}{\hbar^2}(\Delta r)^2E\Psi_1 \quad j=1, \qquad (9)$$

$$-\Psi_{j+1}+2\Psi_j-\Psi_{j-1}+\frac{2\mu}{\hbar^2}(\Delta r)^2\left[\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r_j^2}+V_j\right]\Psi_j=\frac{2\mu}{\hbar^2}(\Delta r)^2E\Psi_j \quad j=2,3,\cdots,N-2, \qquad (10)$$

$$2\Psi_{N-1}-\Psi_{N-2}+\frac{2\mu}{\hbar^2}(\Delta r)^2\left[\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r_{j-1}^2}+V_{N-1}\right]\Psi_{N-1}=\frac{2\mu}{\hbar^2}(\Delta r)^2E\Psi_{N-1} j=N-1, \qquad (11)$$

Let

$$\beta_k=2+\frac{l(l+1)}{k^2}+\frac{2\mu}{\hbar^2}(\Delta r)^2V_k, \qquad (12)$$

$$\alpha_k=\frac{2\mu}{\hbar^2}(\Delta r)^2. \qquad (13)$$

The corresponding secular equation for formulae (9), (10), (11) is

$$\begin{bmatrix} \beta_1-\alpha_1E & -1 & 0 & \cdots & 0 & 0 \\ -1 & \beta_2-\alpha_2E & -1 & \cdots & 0 & 0 \\ 0 & -1 & \beta_3-\alpha_3E & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & \beta_{N-2}-\alpha_{N-2}E & -1 \\ 0 & 0 & 0 & \cdots & -1 & \beta_{N-1}\alpha_{n-1}E \end{bmatrix}=0, \qquad (14)$$

This $(N-1)(N-1)$ matrix in equation (14) is a symmetrical triple diagonal matrix; it can be represented by two one- dimensional arrays. As N and R become large enough, the matrix provides energy eigenvalues.

Ⅳ Computed result and discussion

Pure vibrational and vibrational- rotational energy eigenvalues of molecule $^7Li_2$ in $A^1\Sigma_u^+$ state were computed; the computing results are shown in table 1 and table 2, respectively. Pure vibrational and vibrational- rotational energy eigenvalues of molecule $^7Li_2$ in $X^1\Sigma_g^+$ state were also computed. The computed results are compared with Ley- Koo's results, as shown in Table 3- Table 6. As Ley- Koo did, in computing R is 31.74 × 10^{-8}cm, when the diatomic molecule is in the two states, the unit of energy is as Morse and Ley- koo did[1-2]. Other Parameters in formula (3) are taken as the same as Ley- Koo did in computing[1-2]. Table 1 and table 2 show how pure vibrational eigenvalues and vibrational- rotational eigenvalues change as N is increased, respectively. From these two tables we can see that the computed results by this method are stable and converging. When N= 4000, the computed result is converging in the sixth digit. Numbers in top rows in Table 3 - Table 6 show that the difference between computed results and Ley- Koo' s results begin from the fifth or sixth digit, when N is 4000.

Ⅴ Conclusion

Pure vibrational and vibrational- rotational energy of the diatomic molecular can be computed by the difference method in region ($0< r< \infty$). Because the matrix of secular equations in computing is a symmetrical triple diagonal matrix, in fact, the computing process only needs putting two one - dimensional arrays, the square matrix does not need computing. Therefore, this method is simple, it saves computer memory, minimizes computing work , and it can also get good results. On the other hand, in computing by the difference method, there is no need for overlapping limited eigenfuctions of the free- particle subject to the same boundary condition to overlap to form approximate wave functions, so it decreases truncation error that is brought about by limited functions. At the same time it further decreases the amount of computing work.

Table 1 Pure vibrational energy eigenvalues E_v for $^7Li_2$ in the $A^1\Sigma_u^+$ state(l = 0, R= 31.74× 10^{-8}cm, D= 8940cm^{-1}= 34.997 ħω, r_e = 3.10821, a= 0.616× 10^{-8}cm)

N	E_0	E_1	E_2	E_3	E_4
600	– 34.50127280	– 33.52488919	– 32.57126053	– 31.63988222	– 30.73026321
800	– 34.50026330	– 33.51993621	– 32.55861024	– 31.61596855	– 30.69170139
1000	– 34.49979699	– 33.51765417	– 32.55279914	– 31.60501986	– 30.67410903
1200	– 34.49954390	– 33.51641711	– 32.54776029	– 31.59554402	– 30.65891361
1400	– 34.49949136	– 33.51567201	– 32.54776029	– 31.59554402	– 30.65891361
2000	– 34.49917435	– 33.51461905	– 32.54508924	– 31.59052894	– 30.65088347
4000	– 34.49901916	– 33.51386197	– 32.54316833	– 31.58692406	64511532
6000	– 34.49899042	– 33.51372179	– 32.54281278	– 31.58625708	– 30.64404851
8000	– 34.49898036	– 33.51367273	– 32.54268834	– 31.58602366	– 30.64367519
10000	– 34.49897570	– 33.51365001	– 32.54263075	– 31.58591562	– 30.64350240

Table 2 Vibrational– rotational energy eigenvalues E_v for $^7Li_2$ in the $A^1\Sigma_u^+$ state (l = 1,R= 31.74× 10^{-8}cm, D= 8940cm^{-1}= 34.997ħω, re= 3.10821, a= 0.616$10^{-8}$cm)

N	E_0	E_1	E_2	E_3	E_4
600	– 34.49739918	– 33.52105666	– 32.56746853	– 31.63613021	– 30.72655064
800	– 34.49638976	– 33.51610408	– 32.55481934	– 31.61221866	– 30.68799233
1000	– 34.49592348	– 33.51382224	– 32.54900874	– 31.60127094	– 30.67040157
1200	– 34.49567042	– 33.51258529	– 32.54586335	– 31.59535396	– 30.66090988
1400	– 34.49551788	– 33.51184025	– 32.54397033	– 31.59179595	– 30.65520751
2000	– 34.49530089	– 33.51078738	– 32.54129951	– 31.58678131	– 30.64717810
4000	– 34.49514572	– 33.51003036	– 32.53937877	– 31.58317675	– 30.64141047
6000	– 34.49511698	– 33.50989020	– 32.53902325	– 31.58250982	– 30.64034375
8000	– 34.49510692	– 33.50984114	– 32.53889882	– 31.58227642	30.63997046
10000	– 34.49510226	– 33.50981843	– 32.53884123	– 31.58216839	– 30.63979769

Table 3 Pure vibrational energy eigenvalues E_v for $^7Li_2$ in the A^1 state (l = 0, R= 31.74× 10^{-8}cm, D= 8940cm^{-1}= 34.997 ħω, re= 3.10821× 10^8cm, a = 0.616× $10^8$$cm^{-1}$)

v	Ley– Koo	This work
0	– 34.4987858	– 34.4990191
1	– 33.5130728	– 33.5138619
2	– 32.5416466	– 32.5431683
3	– 31.5845075	– 31.5869240
4	– 30.6416552	– 30.6451153
5	– 29.7130899	– 29.7177286
6	– 28.7988115	– 28.8011314

Table 4 Pure vibrational energy eigenvalues E_v for $^7Li_2$ in the $X^1\Sigma_g^+$ state (l = 0, R= 31.74× 10^{-8}cm, D = 8541cm^{-1} = 24.303 ħω, re = 2.67328 × 10^8cm, a= 0.867× $10^8$$cm^{-1}$)

v	Ley– Koo	This work
0	– 23.8055716	– 23.8068237
1	– 22.8261452	– 22.8280187
2	– 21.8672924	– 21.8700159
3	– 20.9290132	– 20.9327876
4	– 20.0113076	– 20.0163074
5	– 19.1141755	– 19.1205497
6	– 18.2376171	– 18.2454899

Table 5　Vibrational- rotational energy eigenvalues E_v for $^7Li_2$ in the $A^1\Sigma_u^+$ state ($l = 1$, R= 31. 74× 10^{-8} cm, D= 8940cm^{-1}= 34. 997, re= 3. 10821 × 10^{8}cm, a= 0. 616× 10^{8}cm^{-1})

v	Ley- Koo	This work
0	- 34.4949133	- 34.4953008
1	- 33.5092521	- 33.5107873
2	- 32.5378580	- 32.5412995
3	- 31.5807612	- 31.5867813
4	- 30.6379514	- 30.6471781
5	- 29.7094289	- 29.7224365
6	- 28.7951935	- 28.8125045

Table 6　Vibrational- rotational energy eigenvalues E_v for $^7Li_2$ in the $X^1\Sigma_g^+$ state ($l = 1$, R= 31.74× 10^{-8} cm, D= 8541cm^{-1}= 24. 303ħω, re= 2. 67328× 10^{8}cm , a= 0. 867× 10^{8}cm^{-1})

v	Ley- Koo	This work
0	- 23.8027769	- 23.8032385
1	- 22.8234079	- 22.8253050
2	- 21.8646119	- 21.8689086
3	- 20.9263889	- 20.9339409
4	- 20.0087390	- 20.0202967
5	- 19.1116622	- 19.1278750
6	- 18.2351585	- 18.2565781

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差分法计算^7 Li$_2$ 纯振动能级和振- 转能级

衣汉威[1], 张凤东[1], 石爱民[2], 刘淑琴[3], 丁培柱[3]
(1. 长春光学精密机械学院 光学物理系, 吉林 长春 130022;
2. 大连铁道学院 物理系, 辽宁 大连 116028;
3. 吉林大学应用 力学系, 吉林 长春 130026;
4. 吉林大学 原子分子物理所, 吉林 长春 130023)

摘要: 提出了利用差分法计算双原子分子纯振动能级和振- 转能级的具体方法。利用了差分法计算了^{7}Li$_2$ 的能级并且把计算的结果和 Ley- Koo 等人用其他方法计算的结果作了对比, 指出了这种计算方法和其他计算方法不同的是不需要求出相波函数而直接求出能级值, 因此这种计算方法有比较简便的优点, 它可和其他计算方法配合使用更准确地求解双原子分子的振动能级问题。这种计算方法可用于准确确定双原子的解析和数值的势能函数, 进一步可应用在准分子的发光等问题的研究中。

关　键　词: 双原子分子; 振动; 转动; 差分法

作者简介: 衣汉威(1945-), 男, 重庆人, 1969 届吉林大学物理系毕业生, 1981 年吉林大学原子分子所研究生毕业获理学硕士学位, 1986 年赴美国进修一年, 现为长春光机学院光学物理系教师。

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