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Saddle points of potential-energy surfaces for symmetric triatomic molecules determined by an algebraic approach

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The conditions satisfied by saddle points of the analytical potential-energy surfaces of the triatomic molecule are derived from the algebraic approach. The conditions cause the potential parameter α, introduced in a previous paper [J. Chem. Phys. **111**, 4466 (1999)], to be imaginary. The criterion is applied to the triatomic molecules H_2O and O_3.

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I. INTRODUCTION

In recent years, it has been shown that the algebraic approach is a useful method of treating molecular problems. Some comprehensive reviews of the algebraic approach have recently been published [1–3].

Since Iachello, Levine, and others have successfully treated molecular rovibrational states using the Lie algebraic approach [1,2,9–11], many researchers [4–8] have extended the hybrid algebraic method to treat molecular rovibrational states. On the other hand, some researchers are interested in treating time-dependent problems and statistical problems using the (dynamical) algebraic method [12–15].

As another active method, the analytical potential-energy surfaces of the small polyatomic molecules can be obtained by using the molecular algebraic Hamiltonian, since this algebraic Hamiltonian can reproduce the molecular rovibrational states well. Cooper [16] recently derived diatomic potential functions using algebraic theory. Levine and coworkers [17,18] obtained the potential-energy surfaces of the triatomic molecules using U(2) algebra.

Recently, we obtained the potential-energy surface of the triatomic molecules using U(4) algebra [19], which was successfully applied to triatomic species: H_2O, H_2S, SO_2, etc. [19,20]. We previously proposed a new transformation about the bond angle, in which the parameter α appears. The parameter α reflects some properties of potential-energy surfaces, for example, saddle points. The primary purpose of this paper is to show the relation between the saddle points of potential-energy surfaces for triatomic molecules and the parameter α, since the saddle points are one of the important features of potential-energy surfaces.

The paper is structured as follows. In Sec. II we briefly review the algebraic theory appropriate to triatomic potential-energy surfaces. The solutions of stationary equations are also presented in this section. The saddle points and their existing conditions are presented in Sec. III. In Sec. IV we present the relation between the conditions of the saddle points and the parameter α. Samples H_2O and O_3 are shown in Sec. V. Section VI provides our conclusions.

II. THE SOLUTIONS OF STATIONARY POINTS OF POTENTIAL-ENERGY SURFACES

In this section we first begin by reviewing briefly the algebraic theory of triatomic molecular potential-energy surfaces, and then we give the solutions of stationary points of the potential-energy surfaces.

A. Potential-energy surfaces

The dynamical symmetric subgroup chain may be written as

$$U_1(4)\otimes U_2(4)\supset\left\{\begin{matrix}O_1(4)\otimes O_2(4)\\ U_{12}(4)\end{matrix}\right\}\supset O_{12}(4)\supset O_{12}(3)\supset O_{12}(2), \tag{1}$$

where $O_{12}(3)$ and $O_{12}(2)$ describe the molecular rotation. Then the Hamiltonian of the triatomic molecules is expanded in terms of the Casimir operators of subgroups in the group chain [1,19]

$$H=A_1C_1+A_2C_2+A_{12}C_{12}^{(1)}+A'_{12}C_{12}^{(2)}+\lambda M_{12}+\cdots, \tag{2}$$

where A_1, A_2, A_{12}, A'_{12}, λ, are the expansion coefficients, and they can be determined from spectroscopic data. C_1 and C_2 are the Casimir operators of groups $O_1(4)$ and $O_2(4)$, respectively. $C_{12}^{(1)}$, $C_{12}^{(2)}$ are two Casimir operators of $O_{12}(4)$, and M_{12} is the Majorana operator [1].

Using the canonical coordinates $(\mathbf{q}_1,\mathbf{q}_2)$ and momenta $(\mathbf{p}_1,\mathbf{p}_2)$, the potential-energy surface is obtained from the classical limit of the algebraic Hamiltonian (2) [19],

$$\begin{aligned}V(\mathbf{q}_1,\mathbf{q}_2)&=H_{cl}(\mathbf{q}_1,\mathbf{p}_1=0,\mathbf{q}_2,\mathbf{p}_2=0)\\&=(A_1+A_{12})N_1^2(2-\mathbf{q}_1^2)\mathbf{q}_1^2+(A_2+A_{12})\\&\quad\times N_2^2(2-\mathbf{q}_2^2)\mathbf{q}_2^2+2A_{12}N_1N_2[(2-\mathbf{q}_1^2)(2-\mathbf{q}_2^2)]^{1/2}\\&\quad\times\mathbf{q}_1\cdot\mathbf{q}_2+\frac{1}{4}\lambda N_1N_2\{(2-\mathbf{q}_2^2)\mathbf{q}_1^2+(2-\mathbf{q}_1^2)\mathbf{q}_2^2\\&\quad-2[(2-\mathbf{q}_1^2)(2-\mathbf{q}_2^2)]^{1/2}\mathbf{q}_1\cdot\mathbf{q}_2+2(\mathbf{q}_1\times\mathbf{q}_2)^2\}.\end{aligned} \tag{3}$$

The transformations between the canonical coordinates and the molecular coordinates are, as suggested in Ref. [19],

$$q_i^2=e^{-\beta_i(r_i-r_{ie})}\quad(i=1,2), \tag{4}$$

$$\mathbf{a}_1\cdot\mathbf{a}_2=\frac{1}{\cosh\alpha(\phi-\phi_0)},\tag{5}$$

where r_i is the ith bond coordinate, r_{ie} is the equilibrium bond length, β_i is the spectroscopic parameter, $\mathbf{a}_i$ is the unit vector along the vector $\mathbf{q}_i$, ϕ is the bond angle, ϕ_0 is the bond angle at equilibrium position, and α is a parameter. The potential-energy surface of a triatomic molecule $V(q_1,q_2,\phi)$, using Eqs. (4) and (5), may be written as [19]

$$\begin{aligned}V(r_1,r_2,\phi)={}&(A_1+A_{12})N_1^2[2-e^{-\beta_1(r_1-r_{1e})}]e^{-\beta_1(r_1-r_{1e})}+(A_2+A_{12})N_2^2[2-e^{-\beta_2(r_2-r_{2e})}]e^{-\beta_2(r_2-r_{2e})}\\&+2A_{12}N_1N_2\{[2-e^{-\beta_1(r_1-r_{1e})}]e^{-\beta_1(r_1-r_{1e})}[2-e^{-\beta_2(r_2-r_{2e})}]e^{-\beta_2(r_2-r_{2e})}\}^{1/2}\frac{1}{\cosh\alpha(\phi-\phi_0)}\\&+\frac{1}{4}\lambda N_1N_2\Bigg[2e^{-\beta_1(r_1-r_{1e})}+2e^{-\beta_2(r_2-r_{2e})}-2e^{-\beta_1(r_1-r_{1e})-\beta_2(r_2-r_{2e})}\frac{1}{\cosh^2\alpha(\phi-\phi_0)}\\&-2[(2-e^{-\beta_1(r_1-r_{1e})})e^{-\beta_1(r_1-r_{1e})}(2-e^{-\beta_2(r_2-r_{2e})})e^{-\beta_2(r_2-r_{2e})}]^{1/2}\frac{1}{\cosh\alpha(\phi-\phi_0)}\Bigg].\end{aligned}\tag{6}$$

B. The solutions of stationary points

In this paper, we discuss the saddle points of potential-energy surfaces (6). To reach this goal, we first need to obtain the stationary points of Eq. (6). But it is convenient to start from Eq. (3). At the same time, for mathematical simplicity, we hereby consider the situation where the bond angle is frozen at equilibrium position, that is, $\phi\equiv\phi_0$. Hence, after considering Eq. (5), Eq. (3) reads

$$\begin{aligned}V(q_1,q_2)={}&(A_1+A_{12})N_1^2(2-q_1^2)q_1^2+(A_2+A_{12})N_2^2(2-q_2^2)q_2^2+2A_{12}N_1N_2[(2-q_1^2)(2-q_2^2)]^{1/2}q_1q_2\\&+\frac{1}{4}\lambda N_1N_2\{(2-q_1^2)q_1^2+(2-q_2^2)q_2^2-2[(2-q_1^2)(2-q_2^2)]^{1/2}q_1q_2\}\\\equiv{}&s_1(2-q_1^2)q_1^2+s_2(2-q_2^2)q_2^2+2t\sqrt{(2-q_1^2)q_1^2(2-q_2^2)q_2^2},\end{aligned}\tag{7}$$

where $s_1=(A_1+A_{12})N_1^2+\frac{1}{4}\lambda N_1N_2$, $s_2=(A_2+A_{12})N_2^2+\frac{1}{4}\lambda N_1N_2$, and $2t=2(A_{12}N_1N_2-\frac{1}{4}\lambda N_1N_2)$.

The equations for stationary points are

$$\frac{\partial V}{\partial q_1}=0,\qquad \frac{\partial V}{\partial q_2}=0,\tag{8}$$

with

$$\frac{\partial V}{\partial q_1}=4q_1(1-q_1^2)\left\{s_1+t\frac{(2-q_2^2)q_2^2}{\sqrt{(2-q_2^2)q_2^2(2-q_1^2)q_1^2}}\right\}\tag{9}$$

and

$$\frac{\partial V}{\partial q_2}=4q_2(1-q_2^2)\left\{s_2+t\frac{(2-q_1^2)q_1^2}{\sqrt{(2-q_2^2)q_2^2(2-q_1^2)q_1^2}}\right\}.\tag{10}$$

Four different types of stationary points are obtained.

(a) $\{q_1=0,q_2=0\}$. That is, $\{r_1\to\infty,r_2\to\infty\}$ when transformations (4) are considered. This solution corresponds to the case in which the two bonds are completely broken, i.e., the molecule is dissociated.

(b) $\{q_1=0,q_2=1\}$ and $\{q_1=1,q_2=0\}$. They correspond to $\{r_1\to\infty,r_2\to r_{2e}\}$ and $\{r_1\to r_{1e},r_2\to\infty\}$ after Eq. (4) is considered. The two solutions correspond to the case of one -bond fully extended and the other bond at its equilibrium position.

(c) $\{q_1=1,q_2=1\}$. This solution corresponds to $\{r_1\to r_{1e},r_2\to r_{2e}\}$. It stands that the potential-energy surface reaches the global minimum.

The three cases above are trivial solutions of the equations for stationary points, and they have been discussed in detail in Ref. [19].

(d) $\{q_i^2=1,q_j^2=1\pm\sqrt{1-(t/s_j)^2}\}$, $(i,j=1,2)$. The solutions with the minus sign are the stationary points of potential-energy surfaces.

III. SADDLE POINTS

In Sec. II, we obtained the solutions of stationary points. The solutions of type (d) correspond to saddle points, but they are present only in certain conditions. In this section we will illustrate that the solutions (d) denote the saddle points, and then derive the existing conditions of the saddle points.

The potential-energy surface may be thought of as a function of two variables (q_1,q_2), $V(q_1,q_2)$.

For convenience, we define

$$X=\frac{\partial^2 V}{\partial q_1^2}=4s_1(1-3q_1^2)+4t\sqrt{\frac{(2-q_2^2)q_2^2}{(2-q_1^2)q_1^2}}\left[\frac{q_1^2(q_1^2-3)}{2-q_1^2}\right], \tag{11}$$

$$Y=\frac{\partial^2 V}{\partial q_2^2}=4s_2(1-3q_2^2)+4t\sqrt{\frac{(2-q_1^2)q_1^2}{(2-q_2^2)q_2^2}}\left[\frac{q_2^2(q_2^2-3)}{2-q_2^2}\right], \tag{12}$$

$$Z=\frac{\partial^2 V}{\partial q_1 \partial q_2}=\frac{8t(1-q_1^2)(1-q_2^2)}{\sqrt{(2-q_1^2)(2-q_2^2)}}. \tag{13}$$

As usual, a stationary point (q_{10},q_{20}) at which V is neither maximum nor minimum may be a "saddle point." That is, (q_{10},q_{20}) is a saddle point if [21]

$$\Delta=Z|^2_{(q_{10},q_{20})}-X|_{(q_{10},q_{20})}Y|_{(q_{10},q_{20})}>0. \tag{14}$$

From Eq. (4.59) in Ref. [2], we know that $A_i<0$ $(i=1,2)$ and $|A_{12}|<|A_i|$, so we assume $s_i<0$ $(i=1,2)$ after considering the expression of s_i. Hence we have $s_1s_2>0$. The stationary points of type (d) are $\{q_{10}^2=1,\ q_{20}^2=1-\sqrt{1-(t/s_2)^2}\}$ and $\{q_{20}^2=1,\ q_{10}^2=1-\sqrt{1-(t/s_1)^2}\}$. The stationary points exist, if

$$1-(t/s_1)^2>0 \quad \text{and} \quad 1-(t/s_2)^2>0. \tag{15}$$

So we get $t^2-s_1s_2<0$ from Eq. (15), since $s_1s_2>0$.

We now calculate the values of X, Y, Z at one of the stationary points of type (d), for example, $\{q_{10}^2=1,\ q_{20}^2=1-\sqrt{1-(t/s_2)^2}\}$, i.e.,

$$X|_{(q_{10},q_{20})}=8(t^2-s_1s_2)/s_2, \tag{16}$$

$$Z|_{(q_{10},q_{20})}=0, \tag{17}$$

$$Y|_{(q_{10},q_{20})}=8s_2\frac{(1-q_{20}^2)^2}{2-q_{20}^2}. \tag{18}$$

So,

$$\begin{aligned}\Delta&=Z|^2_{(q_{10},q_{20})}-X|_{(q_{10},q_{20})}Y|_{(q_{10},q_2)}\\&=-8[(t^2-s_1s_2)/s_2]8s_2\frac{(1-q_{20}^2)^2}{2-q_{20}^2}\\&=-64(t^2-s_1s_2)\frac{(1-q_{20}^2)^2q_{20}^2}{t^2/s_2^2}>0,\end{aligned} \tag{19}$$

since $t^2-s_1s_2<0$ [it is obvious that $q_{20}^2>0$, $(1-q_{20}^2)^2>0$, and $t^2/s_2^2>0$]. Therefore, the point $[q_{10}^2=1,q_{20}^2=1-\sqrt{1-(t/s_2)^2}]$ is a saddle point [21].

The same conclusion can be obtained by repeating the above procedure for other points in the solutions of type (d).

IV. THE EXISTING CONDITIONS OF SADDLE POINTS AND THEIR RELATION TO PARAMETER α

In this section the existing conditions of saddle points are presented obviously using fitting parameters in Eq. (6), and then the relation between the conditions and the parameter α is derived.

A. The existing conditions of saddle points

We have shown that the solutions of type (d) are saddle points in Sec. III. In this subsection the existing conditions of saddle points are presented using the coefficients in Eq. (6).

From $s_i<0$, we have

$$\lambda<-\frac{4(A_j+A_{12})N_j}{N_i} \quad (i,j=1,2). \tag{20}$$

For the saddle points $\{q_{i0}^2=1,q_{j0}^2=1-\sqrt{1-(t/s_j)^2}\}$, or, equivalently, $\{q_{i0}^2=1,\ \sqrt{(2-q_{j0}^2)q_{j0}^2}=-t/s_j\}$, we have $t>0$ since $s_j<0$, that is,

$$4A_{12}-\lambda>0. \tag{21}$$

On the other hand, from Eq. (15), one has

$$A_{12}<-A_j\bigg/\left(1+\frac{N_j}{N_i}\right)<-A_j\bigg/\left(\frac{N_i+N_j}{2N_i+N_j}\right). \tag{22}$$

Equations (20), (21), and (22) are the existing conditions of saddle points.

Here, we discuss the special case of $\lambda\equiv 0$. In this case, the existing conditions of saddle points read

$$A_{12}>0, \tag{23}$$

$$A_{12}<-A_j\bigg/\left(1+\frac{N_j}{N_i}\right), \tag{24}$$

$$0<-\frac{4(A_j+A_{12})N_j}{N_i}. \tag{25}$$

The relation of Eq. (25) is obviously right since we have indicated that $A_j<0$ and $|A_{12}|<|A_j|$.

From Eqs. (23) and (24), we have

$$0<A_{12}<-A_j\bigg/\left(1+\frac{N_j}{N_i}\right). \tag{26}$$

Now the existing conditions of saddle points go back to previous results [17].

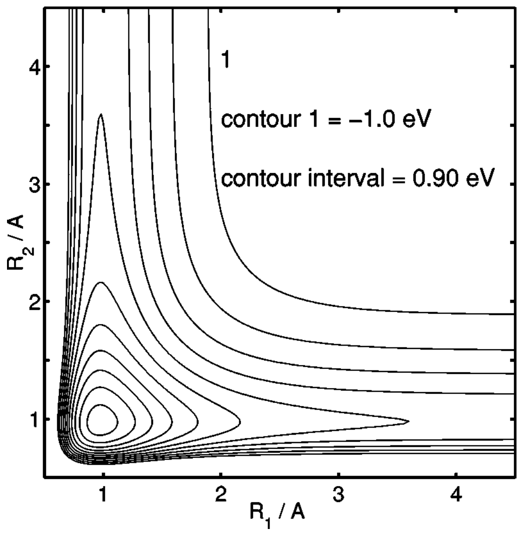

FIG. 1. The PES of H_2O molecule obtained from Eq. (6) with the parameters in Table I. The bond angle is frozen at equilibrium position.

B. The relation between the existing conditions of saddle points and parameter α

In the analytical potential-energy surfaces of triatomic molecules Eq. (6), the calculating formula of the parameter α is given by [19]

$$\alpha=\frac{2\pi c\nu}{N}\sqrt{\frac{m}{(-4A_{12}+3\lambda)\left(1+\frac{2m}{M}\sin^2\frac{\phi_0}{2}\right)}}r_e$$

$$\sim\frac{1}{\sqrt{-4A_{12}+3\lambda}}. \tag{27}$$

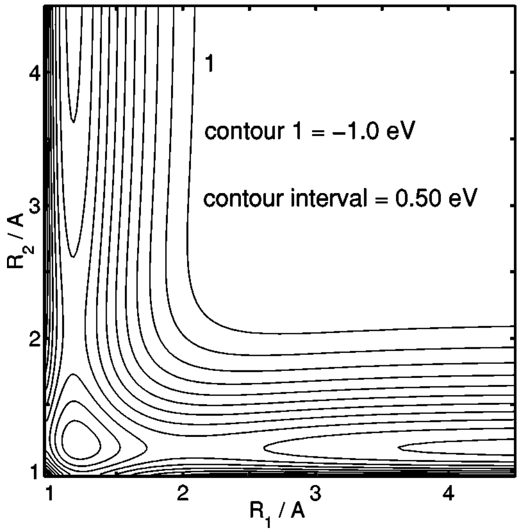

FIG. 2. The PES of O_3 molecule obtained from Eq. (6) with the parameters in Table I. The bond angle is frozen at equilibrium position.

TABLE I. Parameters required in Eq. (6). (For the symmetric triatomic molecules: $r_{1e}=r_{2e}$ is in Å, $\beta_1=\beta_2$ is in Å^{-1}, $N_1=N_2$ is dimensionless, $A_1=A_2$, A_{12}, λ are in cm^{-1}.)

	H_2O	O_3
N_1	42	70
A_1	−18.2219	−11.6522
A_{12}	−2.85	2.9914
λ	1.0571	−3.0782
r_{1e}	0.9706	1.2075
β_1	2.354	2.679
α	1.6694	1.9166I

Using Eqs. (20), (21), and (22), one has

$$\begin{aligned}-4A_{12}+3\lambda&<-4A_{12}-3\left[\frac{4(A_j+A_{12})N_j}{N_i}\right]\\&=-4A_{12}-12A_{12}\frac{N_j}{N_i}-\frac{12N_j}{N_i}A_j\\&=A_{12}\left[-4\left(1+\frac{3N_j}{N_i}\right)\right]-\frac{12N_j}{N_i}A_j\\&<-A_j/\frac{N_i+N_j}{2N_i+N_j}\left[-4\left(1+\frac{3N_j}{N_i}\right)\right]-\frac{12N_j}{N_i}A_j\\&=4A_j\frac{2N_i+N_j}{N_i+N_j}\times\frac{N_i+3N_j}{N_i}-\frac{12N_j}{N_i}A_j\\&=8A_j\frac{N_i+2N_j}{N_i+N_j}<0,\end{aligned} \tag{28}$$

since $N_i>0$ and $A_j<0$.

Hence, the parameter α is imaginary.

TABLE II. The calculated dissociation energies (eV) and force constants (aJ; Å; Rad).

	H_2O		O_3	
	This work	Refs. [24,25]	This work	Refs. [24,26]
D_{ei}	4.39	4.61	5.248	5.115
D_e	10.44	10.2	6.87	6.33
k_{11}	9.39	8.45	6.84	6.16
k_{12}	−0.1026	−0.101	1.075	1.602
k_{33}	0.71	0.697	3.78	2.102
k_{111}	−66.30	−59.4	−54.992	−55
k_{112}	0.242	0.25	−2.879	−2.6
k_{133}	−0.243	−0.23	−2.95	−3.9
k_{1111}	384.49	384.0	230.68	
k_{1133}	−2.79	−1.41	−11.40	
k_{1112}	−0.568		7.713	
k_{1122}	−7.28		45.41	

V. PRACTICAL APPLICATIONS

In this section, the criterion previously introduced is applied to the H_2O and O_3 molecules. The relevance of these two molecules for life processes leads to the importance of experimental and theoretical studies of them. Moreover, the potential-energy surfaces of the water molecule [17,18,22] and of the ozone molecule [17,18,23] have been widely studied using various methods. Recent *ab initio* calculations suggest that there are two equilibrium structures, C_{2v} and D_{3h}, symmetric in the electronic ground state of the ozone molecule [23], called stable open structure and metastable ring structure. The work we are interested in is the stable open structure for the ozone molecule.

In Eq. (6) $A_1 = A_2$ and $N_1 = N_2$ for symmetric triatomic molecules, the contours are plotted in Fig. 1 for H_2O, and Fig. 2 for O_3. The coefficients required in Eq. (6) to produce those plots that can be obtained by fitting spectroscopic data are shown in Table I.

In Table II, we also provide the force constants produced by Eqs. (46)–(54) in Ref. [19], the dissociation energies D_e (for molecule) and D_{ei} (for one bond) produced by Eqs. (33) and (34) of Ref. [19], and those from other calculations. These figures and data are in good agreement with the results produced by other methods [17,18,22–26].

Clearly visible in Fig. 2, as shown in Table I, the parameter α in this case is imaginary ($\alpha = 1.916\,6I$), and the potential-energy surface of the O_3 molecule has saddle points. Conversely, parameter α is real ($\alpha = 1.6694$) for the H_2O molecule and its potential-energy surface has no saddle points, as also indicated by other methods [22,23].

VI. CONCLUSIONS

A simple criterion for the existence of saddle points in triatomic molecular potential-energy surfaces is presented in this paper. That is, the imaginary value of the parameter α indicates the presence of saddle points. Additionally, the coordinates of saddle points are provided.

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