

Potential energy surface for linear triatomic molecules: An algebraic method

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Recently, we proposed a new transformation between the angle of canonical coordinates and the bond angle to describe the bending motion in Potential Energy Surfaces (PES) of bent triatomic molecules. In this work we extend the transformation to include linear triatomic molecules. Results for the linear triatomic molecule N_2O are reported.

KEY WORDS: potential energy surface, bent triatomic molecules, linear molecules

1. Introduction

In recent years, algebraic approach has been extensively used in chemical physics and molecular physics after Iachello and Levine treated the molecular vibrational problems using Lie algebraic approach [1,2]. Now many researchers use this approach and its hybrid to treat polyatomic vibrations [3–8] and other various problems [9–13].

Recently, we obtained the whole potential energy surfaces of bent triatomic molecules using $U(4)$ algebra by introducing a new transformation between the angle of canonical coordinates and the bond angle [12]. This potential energy surface can be used to describe the stretching motion of two bonds and the bending motions of the bond angle. And this method has successfully used to the bent molecules H_2O , H_2S [12], SO_2 , O_3 [13] etc.

This method is quite general and can be extended to linear triatomic or polyatomic molecules. In this paper it shows how to implement the method in the case of linear molecules. We have chosen as an example the N_2O molecule, but it can be, in principle, applied to any linear triatomic molecules.

This paper is organized as follows. In section 2 the briefly reviews that the algebraic approach applied to potential energy surfaces are given. The transformation between the angle of the position vectors in abstract phase space and the bond angle are given. The expression of parameter α which we introduce a new parameter is presented in section 3. In section 4 we present example N_2O molecule, the dissociation energies, force constants etc. are obtained.

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2. Algebraic theory of Potential Energy Surfaces

It is suitable to describe triatomic molecules using $U(4)$ algebra. In this case triatomic molecules are of dynamical symmetric chain [14]

$$U_1(4) \otimes U_2(4) \supset \left\{ \begin{array}{c} O_1(4) \otimes O_2(4) \\ U_{12}(4) \end{array} \right\} \supset O_{12}(4). \quad (1)$$

Here, $O_{12}(3)$ and $O_{12}(2)$ are throw out since the rotation of triatomic molecules is not considered.

The Hamiltonian of triatomic molecules for the chain (1) is

$$H = A_1 C_1 + A_2 C_2 + A_{12} C_{12}^{(1)} + A'_{12} C_{12}^{(2)} + \lambda M_{12}, \quad (2)$$

where A_1 , A_2 , A_{12} , A'_{12} , and λ are expansion coefficients, and they can be determined by fitting spectroscopic data. C_1 and C_2 are the Casimir operators of $O_1(4)$ and $O_2(4)$, respectively. $C_{12}^{(1)}$ and $C_{12}^{(2)}$ are the two Casimir operators of $O_{12}(4)$, M_{12} is so-called Majorana operator, and it relates to the Casimir operator of $U_{12}(4)$.

It is obvious that the algebraic Hamiltonian (2) has no directly single geometrical meaning, but one can extract potential functions from this algebraic Hamiltonian. One can get the classical limits of algebraic Hamiltonian using “group” coherent state [15] or intensive boson operators approach [16].

The coset space in $U_1(4) \otimes U_2(4)$ algebra is composed of two complex vectors, ξ_1 and ξ_2 . The “group” coherent states read [15]

$$\begin{aligned} |N_1, N_2; \xi_1, \xi_2\rangle &= (N_1! N_2!)^{-1/2} [(1 - \xi_1^* \xi_1)^{1/2} \sigma_1^+ + \xi_1 \pi_1]^{N_1} \\ &\times [(1 - \xi_2^* \xi_2)^{1/2} \sigma_2^+ + \xi_2 \pi_2]^{N_2} |0\rangle. \end{aligned} \quad (3)$$

By introducing canonical coordinates and momenta

$$\xi_1 = (\mathbf{q}_1 + i\mathbf{p}_1)/\sqrt{2}, \quad \xi_1^* = (\mathbf{q}_1 - i\mathbf{p}_1)/\sqrt{2}, \quad (4)$$

$$\xi_2 = (\mathbf{q}_2 + i\mathbf{p}_2)/\sqrt{2}, \quad \xi_2^* = (\mathbf{q}_2 - i\mathbf{p}_2)/\sqrt{2}. \quad (5)$$

The classical Hamiltonian is

$$H_{cl}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{p}_1, \mathbf{p}_2) = \langle N_1, N_2; \xi_1, \xi_2 | H | N_1, N_2; \xi_1, \xi_2 \rangle \quad (6)$$

and the potential energy surfaces are

$$V(\mathbf{q}_1, \mathbf{q}_2) = H_{cl}(\mathbf{p}_1 = 0, \mathbf{p}_2 = 0, \mathbf{q}_1, \mathbf{q}_2). \quad (7)$$

One can, by using equations (3)–(7), obtain the classical limits of every term in equation (2) when $\mathbf{p}_1 = \mathbf{p}_2 = 0$

$$C_i \rightarrow N_i^2 \mathbf{q}_i^2 (2 - \mathbf{q}_i^2), \quad (8)$$

$$\begin{aligned} C_{12}^{(1)} &\rightarrow N_1^2 \mathbf{q}_1^2 (2 - \mathbf{q}_1^2) + N_2^2 \mathbf{q}_2^2 (2 - \mathbf{q}_2^2) \\ &+ 2N_1 N_2 \mathbf{q}_1 \mathbf{q}_2 (2 - \mathbf{q}_1^2)^{1/2} (2 - \mathbf{q}_2^2)^{1/2}, \end{aligned} \quad (9)$$

$$C_{12}^{(2)} \rightarrow 0, \quad (10)$$

$$M_{12} \rightarrow \frac{1}{4}N_1N_2[(2 - \mathbf{q}_1^2)\mathbf{q}_2^2 + (2 - \mathbf{q}_2^2)\mathbf{q}_1^2 - 2(2 - \mathbf{q}_1^2)^{1/2}(2 - \mathbf{q}_2^2)^{1/2}(\mathbf{q}_1 \cdot \mathbf{q}_2) + \mathbf{q}_1^2\mathbf{q}_2^2 - (\mathbf{q}_1 \cdot \mathbf{q}_2)^2]. \quad (11)$$

Hence, the PES can be written, using canonical coordinates, as follows,

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

One can obtain the expression of PES from equation (12) using molecular internal coordinates (r_1, r_2, ϕ) , by introducing an appropriate transformation between the canonical coordinates and the molecular internal coordinates.

The transformation between the bond coordinates r_i and q_i is, as extensively used [12,13,17,18], as follows:

$$q_i^2 = e^{-\beta_i(r_i - r_{ie})} \quad (i = 1, 2). \quad (13)$$

Here we suggest, for the linear triatomic molecule, the transformation between the angle between \mathbf{q}_1 and \mathbf{q}_2 and the bond angle

$$\mathbf{a}_1 \cdot \mathbf{a}_2 = [\cosh \alpha(\phi - \pi)]^{-\alpha^2/|\alpha|^2}, \quad (14)$$

where \mathbf{a}_i is the unit vector along the vector \mathbf{q}_i , ϕ is the bond angle, α is the parameter the calculating formula of which is presented in the next section. By using equations (13) and (14), one can get the explicit expression of PES in the form of the internal molecular coordinates (r_1, r_2, ϕ) .

3. The expression of parameter α

In this section we show how to get the expression of parameter α which we introduce in the transformation (14). The kinetic operator for a triatomic ABC in the internal coordinates can be written as

$$T = -\frac{\hbar^2}{2} \sum_{i,j} G_{ij} \frac{\partial^2}{\partial r_i \partial r_j} \quad (i, j = 1, 2, 3), \quad (15)$$

where r_1 and r_2 are two bond lengths, $r_3 = \phi$ is the bond angle. The matrix G is given by (following Wilson et al. [19]), for linear triatomic molecules,

$$G_{11} = \mu_1 + \mu_2, \quad G_{12} = -\mu_3, \quad G_{13} = 0,$$

$$\begin{aligned}
G_{21} &= G_{12}, & G_{22} &= \mu_2 + \mu_3, & G_{23} &= 0, \\
G_{31} &= G_{13}, & G_{32} &= G_{23}, \\
G_{33} &= \frac{\mu_1}{r_{1e}^2} + \frac{\mu_2}{r_{2e}^2} + \mu_3 \left(\frac{1}{r_{1e}^2} + \frac{1}{r_{2e}^2} + \frac{2}{r_{1e}r_{2e}} \right),
\end{aligned} \tag{16}$$

where $\mu_i = 1/m_i$ ($i = 1, 2, 3$), m_3 is the central atomic mass, m_1 and m_2 are the atomic mass at the two ends. The potential energy for small displacements is

$$V = \frac{1}{2!} \sum_{i,j} k_{ij} S_i S_j, \tag{17}$$

where $S_i = r_i - r_{ie}$. Hence from equations (15)–(17), the Hamiltonian of linear triatomic can be written as

$$H = H_s + H_{ss} + H_{sb} + H_b, \tag{18}$$

where H_s is the stretching Hamiltonian for two bonds, H_{ss} is the coupled Hamiltonian between two bonds, H_{sb} is the coupled Hamiltonian for the stretching and bending vibration, H_b is the bending Hamiltonian. Their explicit expressions are written as follows:

$$H_s = \sum_{i=1}^2 -\frac{\hbar^2}{2} G_{ij} \frac{\partial^2}{\partial S_i^2}, \tag{19}$$

$$H_{ss} = -\hbar^2 G_{12} \frac{\partial^2}{\partial S_1 \partial S_2} + k_{12} S_1 S_2, \tag{20}$$

$$H_{sb} = -\hbar^2 \sum_{i=1}^2 \left[G_{i3} \frac{\partial^2}{\partial S_i \partial S_3} + k_{i3} S_i S_3 \right], \tag{21}$$

$$H_b = -\frac{\hbar^2}{2} G_{33} \frac{\partial^2}{\partial S_3^2} + \frac{1}{2} k_{33} S_3^2. \tag{22}$$

It is obvious that H_b is the Hamiltonian of a harmonic oscillator for variable S_3 , so it is well known that the following relation, after considering the doubly generate of bending motion of linear triatomic molecules, holds:

$$(2\pi c\nu)^2 = 2k_{33} G_{33}, \tag{23}$$

where ν is the bending frequency, and c is the velocity of light. We also can get the force constant k_{33} from equation (12), after considering equations (13) and (14), nearby equilibrium position,

$$f_{33} = \left(-2A_{12} + \frac{3}{2}\lambda \right) N_1 N_2 \alpha^2. \tag{24}$$

Hence from equations (23) and (24), we obtain the expression for α

$$\alpha = \frac{1}{\sqrt{2}} \cdot \frac{2\pi cv}{\sqrt{(-2A_{12} + \frac{3}{2}\lambda)N_1N_2G_{33}}}. \quad (25)$$

So, the parameter α can be determined by the expansion coefficients and the molecular parameters, such as r_{ei} , m_i etc.

4. Application to N₂O

We can apply above equations to the determination of the PES of the linear molecular N₂O.

The expansion coefficients in equation (2) which can be obtained by fitting spectroscopic data, taken from ref. [20], and the parameter α are listed in table 1. For the linear molecules, the work about the properties of parameter α is in progress. Now, the explicit expression of PES, from equations (12)–(14) is given by

$$\begin{aligned} V(r_1, r_2, \phi) = & (A_1 + A_{12})N_1^2[2 - e^{-\beta_1(r_1-r_{1e})}]e^{-\beta_1(r_1-r_{1e})} \\ & + (A_2 + A_{12})N_2^2[2 - e^{-\beta_2(r_2-r_{2e})}]e^{-\beta_2(r_2-r_{2e})} \\ & + 2A_{12}N_1N_2\{[2 - e^{-\beta_1(r_1-r_{1e})}]e^{-\beta_1(r_1-r_{1e})} \\ & \times [2 - e^{-\beta_2(r_2-r_{2e})}]e^{-\beta_2(r_2-r_{2e})}\}^{1/2} \cdot \cos \tilde{\alpha}(\phi - \pi) \\ & + \frac{1}{4}\lambda N_1N_2\{2e^{-\beta_1(r_1-r_{1e})} + 2e^{-\beta_2(r_2-r_{2e})} \\ & - 2e^{-\beta_1(r_1-r_{1e})-\beta_2(r_2-r_{2e})} \cdot \cos^2 \tilde{\alpha}(\phi - \pi) \\ & - 2[(2 - e^{-\beta_1(r_1-r_{1e})})e^{-\beta_1(r_1-r_{1e})}(2 - e^{-\beta_2(r_2-r_{2e})}) \\ & \times e^{-\beta_2(r_2-r_{2e})}]^{1/2} \cdot \cos \tilde{\alpha}(\phi - \pi)\}, \end{aligned} \quad (26)$$

where $\tilde{\alpha} = |\alpha|$.

Table 1
The coefficients of potential energy surface for NO₂*.

N_1	134
N_2	163
A_1 (cm ⁻¹)	-1.7376
A_2 (cm ⁻¹)	-1.5033
A_{12} (cm ⁻¹)	-0.2787
λ (cm ⁻¹)	-0.5105
β_1 (Å ⁻¹)	2.7083
β_2 (Å ⁻¹)	2.7676
r_{e1} (Å)	1.1273
r_{e2} (Å)	1.1815
α	2.6677j

* α and N are dimensionless, 1 = r_{NN} , 2 = r_{NO} .

Table 2
The calculated dissociation energies (eV) and force constants (aJ ; Å; Rad) of the molecule N_2O^\dagger .

	This work	Ref. [22]	Ref. [23]	Ref. [24]
D_e	12.088			
D_{e1}	6.6252			
D_{e2}	3.9572			
k_{11}	18.5647	18.126	18.251	18.653
k_{12}	0.8297	0.96	1.028	0.718
k_{22}	11.74	12.021	11.960	11.693
k_{33}	0.6430	0.683	0.66	0.661
k_{111}	-134.58	-137.969	-133.6	-151.262
k_{112}	-2.247	-2.532	-6.872	-2.584
k_{222}	-89.14	-98.002	-98.830	-94.746
k_{331}	-4.267	-1.691	-1.58	-5.944
K_{233}	-4.36	-1.449	1.537	0.755
k_{1111}	871.65	811.36	691.4	949.184
k_{2222}	598.71	587.169	634.9	571.393
k_{1112}	6.0859	10.111	46.65	-12.017
k_{1122}	-1.1427	0.0797	-3.485	-12.719
k_{1222}	6.3553	17.778	-7.691	-27.299
k_{1133}	18.3963	1.105	1.808	30.755
k_{3312}	11.81	4.041	5.105	4.131
k_{3322}	19.21	2.39	1.491	-18.765

$^\dagger 1 = r_{NN}, 2 = r_{NO}, 3 = \phi$.

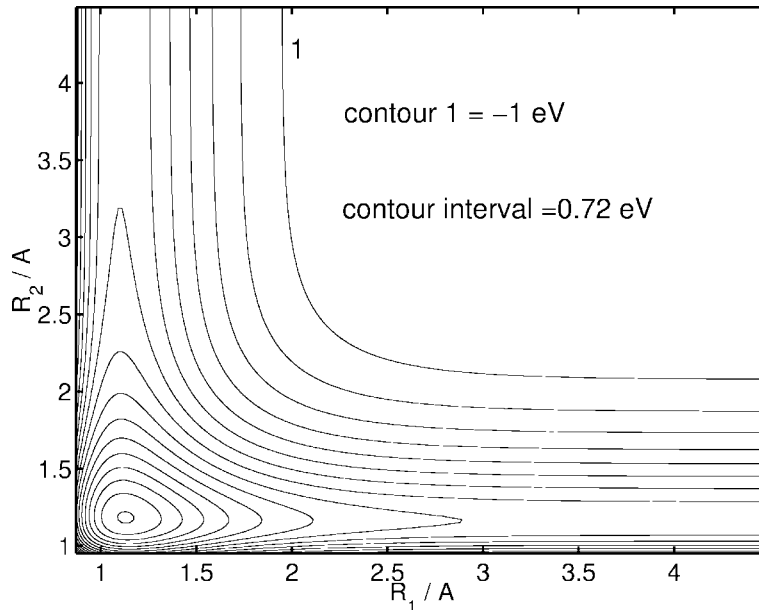


Figure 1. Potential energy surface for N_2O molecule, bond angle is frozen at equilibrium position. Contour 1 = -1 eV. Contours drawn at intervals of 0.72 eV.

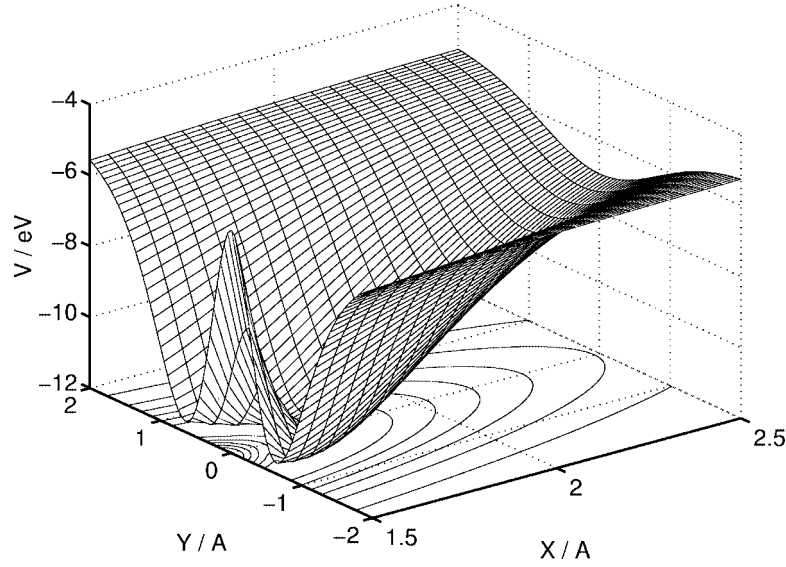


Figure 2. Three-dimensional potential energy surface for motion of the the oxygen atom around the NN fragment.

So, the dissociation energy, D_e , of the molecule and the depth of the i th exit valley, D_{ei} , can be obtained, using equation (26),

$$D_e = -(A_1 + A_{12})N_1^2 - (A_2 + A_{12})N_2^2 - 2A_{12}N_1N_2, \quad (27)$$

$$D_{ei} = -(A_i + A_{12})N_i^2 \quad (i = 1, 2). \quad (28)$$

At the same time, the values of the force constants defined as the derivatives of $V(r_1, r_2, \phi)$ at equilibrium can be obtained:

$$k_{11} = -2(A_1 + A_{12})N_1^2\beta_1^2 - 2A_{12}N_1N_2\beta_1^2 + \frac{1}{2}\lambda N_1N_2\beta_1^2, \quad (29)$$

$$k_{12} = -\frac{1}{2}\lambda N_1N_2\beta_1\beta_2, \quad (30)$$

$$k_{33} = -2A_{12}N_1N_2\alpha^2 + \frac{3}{2}\lambda N_1N_2\alpha^2, \quad (31)$$

$$k_{111} = 6(A_1 + A_{12})N_1^2\beta_1^3 + 6A_{12}N_1N_2\beta_1^3 - \frac{3}{2}\lambda N_1N_2\beta_1^3, \quad (32)$$

$$k_{112} = \frac{1}{2}\lambda N_1N_2\beta_1^2\beta_2, \quad (33)$$

$$k_{133} = -\lambda N_1N_2\beta_1\alpha^2, \quad (34)$$

$$k_{1111} = -14(A_1 + A_{12})N_1^2\beta_1^4 - 20A_{12}N_1N_2\beta_1^4 + 5\lambda N_1N_2\beta_1^4, \quad (35)$$

$$k_{1112} = -\frac{1}{2}\lambda N_1N_2\beta_1^3\beta_2, \quad (36)$$

$$k_{1122} = 2A_{12}N_1N_2\beta_1^2\beta_2^2 - \lambda N_1N_2\beta_1^2\beta_2^2. \quad (37)$$

The calculated values of D_e , D_{ei} and force constants using equations (27)–(37) together with the values of other methods are listed in table 2.

In figure 1 we present the PES contour for N_2O molecule, as the bond angle is frozen at its equilibrium position. Three-dimensional potential energy surface is plotted in figure 2 for the motion of oxygen atom around the N–N bond.

The above tables and figures show that the PES (26) of N_2O reproduce the realistic results. The calculated results are in agreement with other methods.

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