Analysis of Potential Energy Surfaces

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The concept of a potential energy surface (PES) is one of the most important in chemical physics. It plays a fundamental role in chemical kinetics, spectroscopy, and the study of bulk properties of matter.

A detailed understanding of the mechanism of chemical reactions requires a knowledge of the PES. Chemical reactions and conformational changes correspond to paths of minimum energy on PES's. Valleys or minima represents reactants and products. Intermediates are associated with minima. Activated complexes (transition states) are represented by first-order saddle points (*1*). Theoretical study of reaction paths and transition states is of great importance because in most cases the regions of the PES that are not close to stable structures are not accessible to experimental methods.

In general a PES is not available analytically and must be evaluated numerically point by point by quantum chemical methods. Thus the construction of a PES is a formidable task that requires the evaluation of an energy grid containing n^v points, where v is the number of variables on which the energy depends and n is the number of values of each variable required to characterize the PES (*2, 3*).

To reduce the dimensionality of this problem one could choose one or two degrees of freedom as independent variables keeping the remaining ones constant or, better, optimizing them for each value of the independent variables (*4*). This approach, however, is still very expensive and takes the risk of failing to include the transition state. Sometimes function fitting techniques are used to generate an analytic function representing the reduced PES, which is then analyzed (*5*).

Another approach would consider all the degrees of freedom of the system trying to locate only certain chemically interesting points of the PES: minima and saddle points. Minima are easily located by current optimization techniques. Localization of saddle points is usually a difficult task and constitutes the main problem in applying the transition-state theory to chemical reactions (*6, 7*). The potential energy and its derivatives must be evaluated in all the steps required for locating the desired points by using both analytic and numerical techniques.

The purpose of this paper is to propose as an exercise in chemical physics such an analysis of PES's. First we will work on an analytic expression proposed as a model PES. In the second place, we will locate and analyze the transition state on the LEPS (*8*) PES for the H_3 system using a combination of analytic and numerical derivatives.

Mathematical Features of Stable Conformations and Transition States on a PES

Let us consider a molecule composed of N atoms with coordinates q_i. The position of the nuclei are defined by $3N$ independent coordinates. If three coordinates specify the orientation of the molecule as a solid body (two coordinates for linear molecules) and three coordinates specify the center of mass, the potential energy is a function of $3N - 6$ ($3N - 5$ for linear molecules) variables:

$$E(q_1, q_2, \ldots, q_n) = \langle\psi|\hat{H}|\psi\rangle \quad (1)$$

where $n = 3N - 6$ (or $3N - 5$) and where ψ and $\hat{H}$ are the wave function and the Hamiltonian of the molecule. Equation 1 defines an energy surface (an energy hypersurface when $n > 2$).

Minima (reactants, products, intermediates) and saddle points (transition states) are stationary points on the PES and are characterized by zero gradient: $\mathbf{g}(q_1, \ldots, q_n) = 0$, i.e.

$$\mathbf{g}_i = \frac{\partial E}{\partial q_i} = 0$$

for all $i = 1, 2, \ldots, n$. We can further determine the nature of these stationary points in terms of the Hessian matrix, $H(q_1, \ldots, q_n)$, of the second derivatives

$$H_{ij} = \frac{\partial^2 E}{\partial q_j \partial q_i}$$

At a minimum $H(q)$ is positive definite (i.e., all the eigenvalues of $H(q)$ are positive) while at a first-order saddle point $H(q)$ is indefinite and has only one negative eigenvalue (*1*). The geometric vector corresponding to the eigenvector associated with this negative eigenvalue is called the transition vector (*9*).

When $q = \{q_1, \ldots, q_n\}$ is a set of nonorthogonal internal coordinates the eigenvalues and eigenvectors (and hence the transition vector) of $H(q)$ have no precise physical significance (*9*). However, if we choose a set of orthogonal coordinates (in terms of which the kinetic energy is a diagonal quadratic form) it is always possible to transform it by an orthogonal transformation into a new orthogonal set of coordinates $\{Q_1, \ldots, Q_n\}$ in terms of which both the kinetic energy and the Hessian matrix are diagonal (*10*):

$$2T = \dot{Q}_1^2 + \dot{Q}_2^2 + \ldots + \dot{Q}_n^2$$

$$2E = \lambda_1 Q_1^2 + \lambda_2 Q_2^2 + \ldots + \lambda_n Q_n^2$$

In that circumstance, the $\{Q_i\}$ may then be identified with normal coordinates and the eigenvalues of H, λ_i, with the harmonic force constants the frequencies being given by $\nu_i = \sqrt{\lambda_i}/2\pi$. The normal coordinate, which has a negative eigenvalue at the transition state, defines the direction of the reaction coordinate at this point (*11*).

Study of an Analytical Model Surface

Let us now apply the concepts exposed in the previous section to the study of the model potential surface

$$E(q_1, q_2) = (1/2q_2 - \sqrt{3}/2q_1)^4 - 2(1/2q_2 - \sqrt{3}/2q_1)^2 + (1/2q_1 + \sqrt{3}/2q_2)^2 \quad (2)$$

where q_1 and q_2 are a set of coordinates in terms of which we may describe some chemical process. Figure 1 shows a bidimensional representation of this surface (eq 2). A PES qualitatively similar to this one is found, for instance, for the inversion–rotation motion of the amino group in vinylamine (*12*).

Looking for the stationary points of eq 2, let the gradient be zero

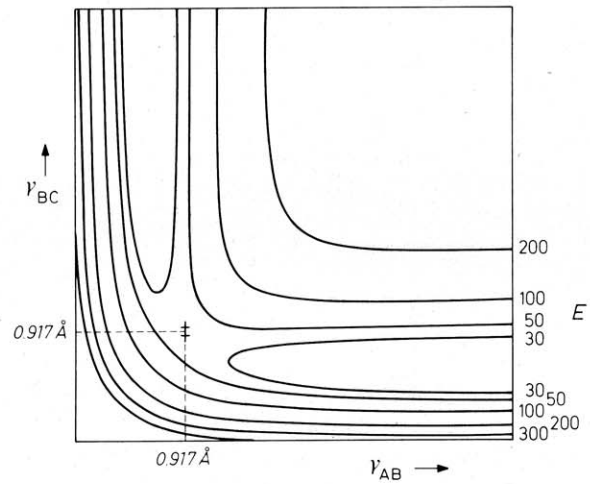

Figure 1. Potential energy contour map for the model PES (*2*). Energy in arbitrary units.

$$\frac{\partial E}{\partial q_1} = -2\sqrt{3}(1/2q_2 - \sqrt{3}/2q_1)^3 + 2\sqrt{3}(1/2q_2 - \sqrt{3}/2q_1) + (1/2q_1 + \sqrt{3}/2q_2) = 0 \quad (3)$$

$$\frac{\partial E}{\partial q_2} = 2(1/2q_2 - \sqrt{3}/2q_1)^3 - 2(1/2q_2 - \sqrt{3}/2q_1) + \sqrt{3}(1/2q_1 + \sqrt{3}/2q_2) = 0 \quad (4)$$

Solving the system of eqs 3 and 4 we find the three stationary points (0, 0), ($\sqrt{3}/2$, $-1/2$) and ($-\sqrt{3}/2$, 1/2).

To determine the nature of these points we will compute and diagonalize the Hessian matrix, H. For both ($\sqrt{3}/2$, $-1/2$) and ($-\sqrt{3}/2$, 1/2) we get from the derivatives of eqs 3 and 4

$$H = \begin{pmatrix} 13/2 & -3\sqrt{3}/2 \\ -3\sqrt{3}/2 & 7/2 \end{pmatrix}$$

which is diagonalized by the orthogonal matrix

$$V = \begin{pmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$$

to give the eigenvalues 2.0 and 8.0. As both eigenvalues are positive, H is positive definite, and the two points analyzed correspond to two minima on the PES (5): reactants and products. For the point (0, 0) we have

$$H = \begin{pmatrix} -5/2 & 3\sqrt{3}/2 \\ 3\sqrt{3}/2 & 1/2 \end{pmatrix}$$

which is diagonalized by the same orthogonal transformation V giving the eigenvalues 2.0 and -4.0. Therefore, this point corresponds to a saddle point, i.e., to the transition state separating reactants and products. The transition vector is

$$\begin{pmatrix} \sqrt{3}/2 \\ -1/2 \end{pmatrix}$$

If the set of coordinates $\{q_1, q_2\}$ was orthogonal then the transformed set $\{q_1', q_2'\}$

$$\begin{pmatrix} q_1' \\ q_2' \end{pmatrix} = \begin{pmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \begin{pmatrix} q_1 \\ q_2 \end{pmatrix}$$

would be normal coordinates and the transition vector would give the direction of the reaction coordinate at the transition state.

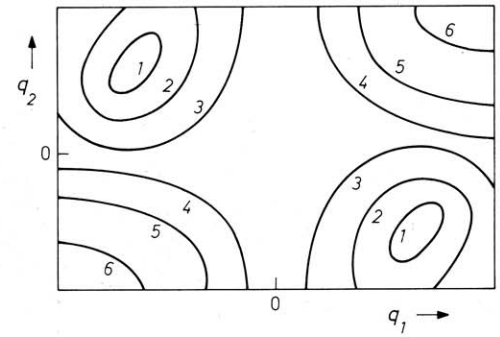

Figure 2. Potential LEPS energy contour map (kJ/mol) for linear H_3 relative to H + H_2 (k = 0.17).

Direct Localization and Identification of the Transition State on the H_3 LEPS Potential Energy Surface

The best known method to search for saddle points is McIver and Komornicki's method (*13*). These authors define a transition state as meeting the following four criteria: (1) it must be a stationary point on the PES, i.e., of zero gradient; (2) the force constant matrix at this point must have one and only one negative eigenvalue; (3) it must be the highest energy point on a continuous line connecting reactants and products; (4) it must be the lowest energy point that satisfies the above three conditions. In practice it is assumed that the lowest energy point found satisfying conditions (1–3) will also satisfy condition (4), which is the most difficult one, provided that chemical intuition is respected. According to condition (1) McIver and Komornicki propose to minimize the norm of the gradient, $\sigma = \Sigma\, g_i^2$ in order to locate the transition state.

As an application of this method we will locate and identify the transition state of the reaction $H_A + H_B - H_C \rightarrow H_A - H_B + H_C$ on the LEPS surface (K = 0.17) for the linear system H_3.

In order to locate the saddle point, we propose to construct a program for the minimization of the norm of the gradient by means of the Simplex method (*14*). Starting from $r_{AB} = r_{BC} = 0.9$ Å (r_{IJ} is the distance between H_I and H_J) the value $r_{AB} = r_{BC} = 0.917$ Å is reached after 28 iterations. The norm of the gradient, σ, being then on the order of 10^{-5} (kJ/mol Å)^2. This result exactly agrees with Sato's (*8*) and Moss and Coady's data (*18*).

The identification of the transition state according to the criterion (2) above requires constructing and diagonalizing the Hessian matrix H. In order to obtain the normal coordinates and the reaction coordinate from the transition vector, the orthogonal coordinates (x, y) as defined elsewhere (*15*) can be used. The first derivatives of the potential energy may be computed analytically by means of the expressions given in the previous work (*15*). For computation of the second derivatives we propose the method of finite differences (*16*). The Hessian matrix at $r_{AB} = r_{BC} = 0.917$ Å evaluated in this way is (difference between cross-derivatives 8.10^{-4})

$$H(x,y) = \begin{pmatrix} 658.929 & 774.910 \\ 774.910 & -235.861 \end{pmatrix}$$

in kJ/mol Å^2, which is diagonalized through the orthogonal transformation matrix

$$U = \begin{pmatrix} \sqrt{3}/2 & 1/2 \\ 1/2 & -\sqrt{3}/2 \end{pmatrix}$$

to give the eigenvalues 1106.323 and -683.256, again in kJ/mol Å^2. Condition (2) above is then satisfied for $r_{AB} = r_{BC} = 0.917$ Å. Satisfaction of conditions (3) and (4) can be verified "de visu" by observing Figure 2.

Working with mass adjusted coordinates we get

$$2T = m(\dot{x}^2 + \dot{y}^2) = \dot{Q}_1^2 + \dot{Q}_2^2$$

$$2E = (xy)H(x,y)\begin{pmatrix} x \\ y \end{pmatrix} = (Q_1 Q_2)\Lambda \begin{matrix} Q_1 \\ Q_2 \end{matrix}$$

where $m = 2/3\ m_H$(m_H mass of a hydrogen atom), Λ is the Hessian matrix $H(x,y)$ in diagonal form

$$\Lambda = U^{-1}1/mH(x,y)U$$

and the normal coordinates (Q_1,Q_2) are given by

$$U\sqrt{m}\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix} = \sqrt{m}\begin{pmatrix} \sqrt{3}/2(r_{AB} + r_{BC} - 2r_0) \\ 1/2(r_{AB} - r_{BC}) \end{pmatrix}$$

r_0 being the equilibrium distance in H_2.

From the eigenvalues of Λ we obtain the vibration frequencies. In Table 1 the values obtained in this way for the symmetrical and asymmetric stretching modes ν_s and ν_a are shown together with other authors' values for comparison. Our results are in much better agreement with Weston's calculations on a LEPS surface than Moss and Coady's results.

For comparison we present in Table 2 the force constants obtained in this work for the normal coordinates

$$\begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} = \begin{pmatrix} 1/\sqrt{3}m & 0 \\ 0 & 1/\sqrt{m} \end{pmatrix}\begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix} = \begin{pmatrix} 1/2(r_{AB} + r_{BC} - 2r_0) \\ 1/2(r_{AB} - r_{BC}) \end{pmatrix} \quad (5)$$

together with other calculations. Again the present results are in good agreement with the other estimations, especially with the results of Weston, who uses a LEPS surface, too.

The geometrical vector (1/2, −1/2) in the $\{r_{AB}, r_{BC}\}$ space corresponding to the normal coordinate with negative eigenvalue defines the reaction coordinate at the transition state. Clearly this reaction coordinate corresponds to the formation of the new molecule H_A–H_B and the separation from it of the H_C atom.

Conclusion

This paper constitutes an introduction to the different methodological strategies in analyzing PES's used in chemical reactivity studies (*7*). The study of an analytical model PES may be presented as a first step for physical chemistry students. The direct localization of the activated complex on the H_3 LEPS PES allows a much deeper insight into the concept of transition state and its relationship with the reaction coordinate. We believe that the procedure presented here for calculating normal coordinates and vibrational properties of an activated complex is conceptually much clearer and more straightforward than the GF matrix approach (*24*) or Johnston's treatment as presented elsewhere (*18*). On the other hand, the simple numerical techniques used in this work yield satisfactory results. Because of this, we propose it as an interesting exercise in physical chemistry.

Table 1. Vibration Frequencies (cm^{-1}) for the Symmetrical and Asymmetric Modes, ν_s and ν_a, for the Linear H_3 Activated Complex (LEPS Surface with k = 0.17)

	ν_s	ν_a
This work	2163	1700 i
Weston (*17*)		
($k \approx 0.18$)	2143	1594 i
($k \approx 0.1475$)	2108	1918 i
Moss and Coady (*18*)	2016	2082 i
Boys and Shavitt (*19*)	1945	1361 i

Table 2. Force Constants Corresponding to the Normal Coordinates (5) for the Linear H_3 Activated Complex (LEPS Surface with k = 0.17)

	k_s	k_a
This work	0.354	−0.0729
Weston (*17*)		
($k \approx 0.18$)	0.351	−0.0656
($k \approx 0.1475$)	0.339	−0.0924
Boys and Shavitt (*19*)	0.288	−0.047
Porter and Karplus (*20*)		
(1)	0.366	−0.134
(2)	0.364	−0.124
Shavitt and Stevens (*21*)	0.331	−0.137
Siegbahn and Liu (*22*)	0.32	−0.058
Yates (*23*)	0.32	−0.071

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