

Limitations of the Murrell–Laidler Theorem

David J. Wales and R. Stephen Berry†

University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW, UK

Counter-examples are found limiting the conditions of validity of a demonstration by Murrell and Laidler concerning saddle points on multidimensional potential surfaces. We show that it is not necessary for the highest energy point on the lowest energy path between two potential minima to be a stationary point of rank 1. Hence, it is possible for a transition state, defined as the highest-energy point on a lowest-energy path, to connect more than two potential wells.

Murrell and Laidler¹ showed that the lowest saddle between two wells on a potential surface can connect only two wells and that any saddle connecting more than two wells must lie at a potential energy higher than some simple saddle. Their demonstration depended upon a Taylor expansion of the energy in normal coordinates, Q_r and Q_s , about a given stationary point, (Q_r^0, Q_s^0) :

$$E(Q_r^0 \pm \delta Q_r, Q_s^0 \pm \delta Q_s) = E(Q_r^0, Q_s^0) + \frac{1}{2} \left(\frac{\partial^2 E}{\partial Q_r^2} \right)_s \delta Q_r^2 + \frac{1}{2} \left(\frac{\partial^2 E}{\partial Q_s^2} \right)_r \delta Q_s^2 + \dots \quad (1)$$

where the second derivatives are evaluated at (Q_r^0, Q_s^0) and the first derivatives vanish, by definition, at a stationary point. Clearly, if the first derivatives vanish and the second derivatives (or curvatures) are both negative then (Q_r^0, Q_s^0) is a local energy maximum, and lower-energy paths must exist which bypass it. This argument implies that the transition state must be of rank 1 (have only one direction of negative curvature) and therefore connect only two minima on the potential surface. This principle is also a tenet of the McIvor–Stanton rules² governing the symmetry of the normal coordinate of the transition state with negative curvature, namely that this must transform as a non-degenerate irreducible representation of the point group.

The Murrell–Laidler theorem itself is correct. However, it is frequently supposed that all real molecules can be expected to satisfy the conditions of the theorem, specifically the condition that the second derivatives of the potential exist and are continuous everywhere including at the saddle point itself. Yet it is not difficult to imagine surfaces with saddles that do connect more than one minimum; at least one, a non-linear triatomic molecule with a linear saddle, is of course realized in nature. We wish to resolve the apparent paradox presented by this conflict between mathematical proof and intuition and observation. We will demonstrate that in several cases, plausible for real potentials but not considered by Murrell and Laidler, a transition state connecting three or more potential wells may indeed exist. In all of our three examples the potentials are continuous; in the first, the first derivatives vanish at the transition state, but one of the second derivatives is not well behaved; in the second, one of the first derivatives is not well defined. The third example is a non-linear triatomic molecule with a linear saddle; all the derivatives exist in this case, and it is the degeneracy of the bending mode of a linear transition state which makes expansion (1) inappropriate. Here we take a transition state to be the point of maximum energy on the lowest-energy, continuous path between two stable configurations (potential

minima), in accord with previous work.³ This definition avoids constraining the derivatives but retains the geometric meaning for continuous, multidimensional functions.

In fact, Murrell and Pratt⁴ have previously alluded to the possibility that three or more valleys may meet at a common transition state. However, they did not pursue this on the assumption that such cubic or higher-order surfaces would not occur for molecular stationary points because there are normally non-zero quadratic terms. For our model surfaces there are indeed non-zero quadratic terms, however, the Taylor series expansion is inappropriate because some of the derivatives are not defined. Collard and Hall⁵ have also discussed the topologies of model surfaces with zero quadratic terms in the Taylor expansion. They analyse some possibilities in terms of catastrophe theory⁶ but point out that such situations are unlikely in molecular systems because they would have to be ‘accidental’.

Our first example has four-fold symmetry. Analytically, it has the form

$$f(x, y) = -xy(x^2 - y^2) \frac{(1 - r^2)}{r^2} + \frac{r^8}{10} \\ = -\frac{1}{4} r^2 (1 - r^2) \sin 4\phi + \frac{r^8}{10} \quad (2)$$

which is a bowl (due to the steep second term) with a four-fold wrinkle due to the sinusoidal term. This potential surface is shown in Fig. 1(a), and cross-sections through it in representative directions in the vicinity of the saddle are shown in Fig. 1(b). The first and diagonal second derivatives of $f(x, y)$ are zero at the origin. The second cross derivative is not well behaved in Cartesian coordinates.

Our second example is a Morse function again with a sinusoidal modulation (in fact, $\sin n\phi$ with $n > 2$ could be used in either of these two examples):

$$g(x, y) = \{ [1 - \exp(\ln 2 - r)]^2 - 1 \} \frac{y(3x^2 - y^2)}{r^{3/2}} \\ = \{ [1 - \exp(\ln 2 - r)]^2 - 1 \} \sin 3\phi. \quad (3)$$

This function corresponds to a system that dissociates at large r to an energy of zero, and has three equivalent minima at $r = \ln 2$, where $g = -1$, separated by maxima which also peak at $r = \ln 2$ where $g = 1$. The value of the potential at the origin is zero, which is the smallest lower bound of the maximum energy along any finite path connecting two minima, *i.e.* the energy of the transition state. This surface is shown in Fig. 2(a), and cross-sections of the energy are shown in Fig. 2(b).

Finally, we note that an exception to the Murrell–Laidler argument arises for molecules that have a linear transition state when the reaction path lies along a degenerate bending

† Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, USA.

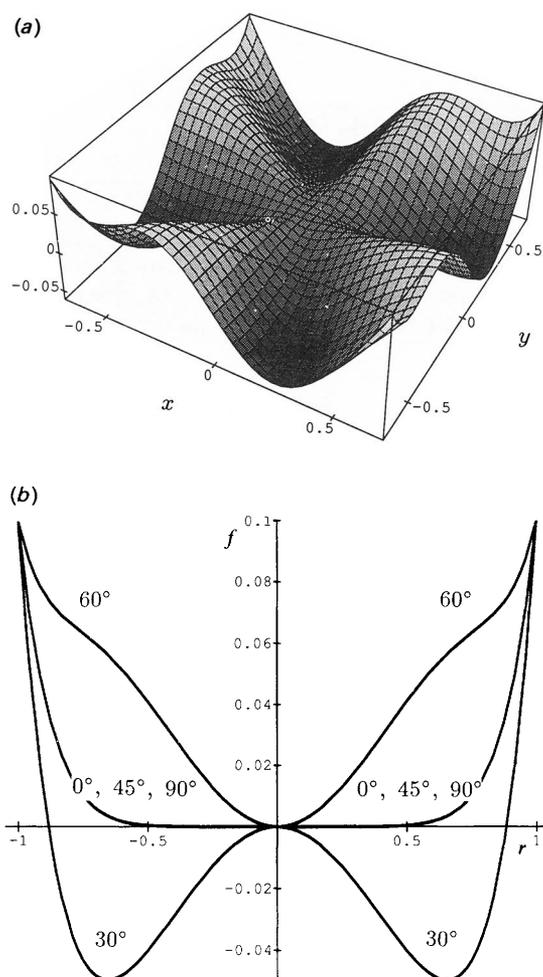


Fig. 1 (a) Surface defined by $f(x, y)$ of eqn. (2) between $-0.7 \leq x, y \leq 0.7$. (b) Sections through the surface at $\phi = 0, 30, 45, 60$ and 90° for $r \leq 1$; 'negative' r values refer to the opposite quadrant

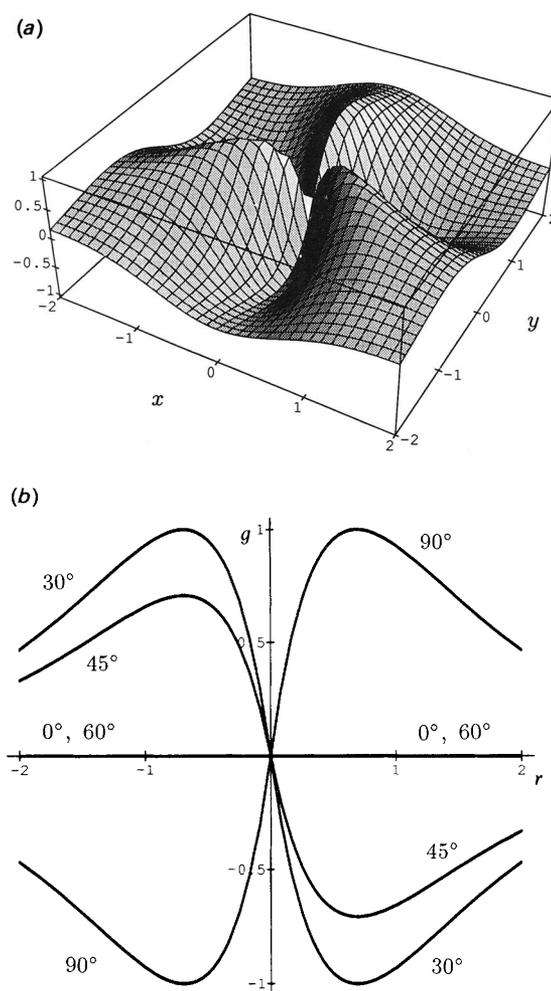


Fig. 2 (a) Surface defined by $g(x, y)$ of eqn. (3) between $-2 \leq x, y \leq 2$. (b) Sections through the surface at $\phi = 0, 30, 45, 60$ and 90° for $r \leq 2$; 'negative' r values refer to the opposite quadrant

coordinate. For example, three atoms bound by a Lennard-Jones potential display such behaviour.⁷ There is one energy minimum on the surface, corresponding to the equilateral triangle, and three permutationally distinct transition states. Each of these has a doubly degenerate negative force constant when the problem is set in three dimensions. Hence they are saddles of rank 2 and also transition states. Here a Taylor expansion of the form given in eqn. (1) is inappropriate because the geometries represented by the displacements δQ_r and δQ_s are equivalent, and there should be only one term of this sort in the expansion. Of course, when the molecule is distorted away from linearity there is no 'extra' internal normal coordinate, and so the Taylor expansion should have $3N - 6$ quadratic terms in both cases.

The Murrell-Laidler argument is certainly correct for systems having well behaved, non-zero second derivatives of the potential energy along the normal coordinate directions at saddle points. However, we may expect to meet occasional oddities such as second-order Jahn-Teller points⁸ or transition states at points of three-fold or higher symmetry. At these points, the effective potential-energy function fails to satisfy the conditions required for the Murrell-Laidler argument to hold. It is therefore possible to find potential surfaces with transition states connecting three or more potential minima. Whether to assign a rank to such singular points is a

semantic rather than a physical argument so we shall not pursue it here.

The authors gratefully acknowledge a NATO Collaborative Research Grant. D.J.W. thanks Lloyd's of London for a Tercentenary Fellowship (1990-91) and the Royal Society for a University Research Fellowship (1991).

References

- 1 J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.*, 1968, **64**, 317.
- 2 J. W. McIver, *Acc. Chem. Res.*, 1974, **7**, 72; R. E. Stanton and J. W. McIver, *J. Am. Chem. Soc.*, 1975, **97**, 3632.
- 3 J. N. Murrell, in *Quantum Theory of Chemical Reactions*, ed. R. Daudel, A. Pullman, L. Salem and A. Veillard, Reidel, Dordrecht, 1979, vol. 1, p. 161.
- 4 J. N. Murrell and G. L. Pratt, *Trans. Faraday Soc.*, 1969, **66**, 1680.
- 5 K. Collard and G. G. Hall, *Int. J. Quant. Chem.*, 1977, **12**, 623.
- 6 R. Thom, *Structural Stability and Morphogenesis*, Benjamin, New York, 1975.
- 7 D. J. Wales, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, in the press.
- 8 See e.g. J. K. Burdett, *Molecular Shapes*, Wiley, New York, 1980, ch. 5.